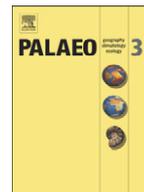




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The Primary Lower Gypsum in the Mediterranean: A new facies interpretation for the first stage of the Messinian salinity crisis

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ABSTRACT

The detailed facies and physical stratigraphic analysis of the Primary Lower Gypsum in the Mediterranean indicates a surprising bed-by-bed correlation at basin-scale (Spain, Italy, Hellenic arc and Cyprus arc), that is tuned to the orbital calibration for the first stage of the Messinian salinity crisis from 5.96 to 5.61 Ma ago. A total of 16, precessionally-controlled, gypsum cycles were deposited rapidly in less than 350 ka, forming sequences up to 300 m thick. The lack of subaerial exposure features and the common facies associations and stacking pattern for sections located thousands of kilometers apart in different geological settings indicates a modest depositional depth, not extremely shallow. Selenite deposition occurred only at the bottom of restricted marginal basins less than 200 m deep, while no gypsum could precipitate in the deeper euxinic Mediterranean portions where only thin and barren shale/dolostone couplets formed. The lowermost selenite beds pass laterally to dolomite-rich limestones interbedded with barren euxinic shales in poorly oxygenated settings, indicating that the gypsum sedimentation was diachronous and did not necessarily mark the onset on the Messinian salinity crisis.

Evaporite facies sequences (EF1 to 8) within individual gypsum beds show small-scale, subaqueous sedimentary cycles that mimic regressive–transgressive cycles: a) initial evaporite precipitation at relatively low supersaturation produced the massive selenite (facies EF3) in a relatively deep setting; b) continuous evaporation and drawdown by oscillating brine level formed the banded selenite (EF4) at the aridity acme of the precessionally-controlled cycle; c) general progressive brine level rise with strong brine flow led to the formation of large selenite supercones branching laterally (supercones in Spain and branching selenite, EF5, in the rest of the Mediterranean); and d) flooding by undersaturated continental water terminated gypsum precipitation with the deposition of argillaceous sediments (EF1, Northern Apennines), and/or limestone (EF2, Sicily and Spain) during the humid phase in the precession climate cycle.

The stacking pattern and selenite facies associations suggest an overall shallowing-upward trend with a basin-wide hydrologic change starting from the 6th cycle (5.84 Ma), which is marked by the appearance of the branching selenite facies (supercones) in Spain and indicates that the brines became current-dominated. The Sr-isotope stratigraphy suggests that in the Northern Apennines the brines were strongly modified by continental waters ($^{87}\text{Sr}/^{86}\text{Sr} = 0.708893$ to 0.708998), and received direct pulses of Atlantic seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70900$ to 0.709024) only in the upper part of the section. In areas away from the mainland, such as Sicily, the continental input was by far less important.

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1. Introduction

The study of huge evaporite deposits, the saline giants, has generated profound controversies in the scientific community. The reason for disagreement among scientists is that great parts of the sequences are buried and it is very difficult to assess their internal

facies relationships. This is mostly because we have no clues to determine water depth in such extreme environments and particularly because no modern analogues for very large and relatively deep deposits are available for comparison. These problems are greatly amplified in the study of the Mediterranean evaporite giant that formed during the late Miocene (Messinian). First, because the data on the Messinian salinity crisis (MSC) were not provided within a reliable stratigraphic framework (Roveri et al., 2008b) and thus different interpretations for the chronology of the depositional phases have been proposed (see Rouchy and Caruso, 2006 and CIESM, 2008

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for a review); second, because of the difficulty in interpreting the very complex array of evaporite facies that are present in the Mediterranean basin (Lugli et al., 2008).

On the other hand, the spectacular lithological cyclicity of this evaporite formation represents a formidable opportunity for the application of astrochronological tuning (Krijgsman et al., 1999) and, if a reliable facies model is provided, then the products of the salinity crisis are certainly suitable for unprecedented very detailed work.

This paper reports the result of our studies on the Messinian Lower Gypsum showing that surprisingly similar facies assemblages and stacking patterns exist across the entire Mediterranean. Our new basin-scale facies reconstruction and correlation carry a particular significance in the light of geochemical stratigraphy and astrochronological tuning of this first phase of the evaporite event that involved the Mediterranean basin in the Messinian.

2. Geological setting, definitions and previous studies of the Lower Gypsum

The Lower Gypsum is part of the Lower Evaporite unit present across the entire Mediterranean area in different geological contexts: wedge top, foreland ramp basins in the Apennine-Maghrebian chain (Piedmont, Emilia-Romagna, Tuscany, Abruzzo, Calabria and Sicily), in pull-apart basins of the Betic Cordillera (Sorbas, Nijar and Vera; Spain) and in minor outcrops of the Hellenic Arc (Zakynthos and Crete Greece), and Cyprus Arc (Fig. 1). The Lower Evaporite unit is separated by the intra-Messinian unconformity from the overlying Upper Evaporite unit and represents the first stage of the Messinian Salinity Crisis that, as a whole, affected the Mediterranean area from 5.96 to 5.33 Ma (Krijgsman et al., 1999).

In the common terminology that is used to associate the Sicilian deposits with the deep Mediterranean sediments, the Lower Evaporite unit comprises the Calcare di Base, the Lower Gypsum and the Salt bodies, that were all considered to be lateral equivalents, respectively as marginal, slope and deep basin deposits (Rouchy and Caruso, 2006).

The Lower Gypsum of Sicily actually consists of two parts: primary evaporitic deposits, the Primary Lower Gypsum (PLG) and a widespread clastic gypsum accumulation, the Resedimented Lower Gypsum (RLG; Manzi et al., 2005 and Roveri et al., 2006) that, as we have discovered, are never associated laterally or vertically. In our recent studies we have shown that all the deposits included in the Lower Evaporite units are not coeval. The Primary Lower Gypsum marks the first step of the salinity crisis, from 5.96 to 5.61 Ma (Roveri et al., 2008b; Fig. 2), whereas the RLG clastic evaporites, and the halite unit, were deposited later, from 5.61 to 5.55 Ma. Moreover, we have already pointed out that the PLG unit shows very particular facies associations that can be distinguished from the ensuing selenite succession of the Upper Gypsum unit that was deposited from 5.53 to 5.33 Ma (Manzi et al., 2009; Roveri et al., 2008b).

In this paper we deal only with the sulfate deposits that originated as primary evaporitic precipitates during the first stage of the salinity crisis, the Primary Lower Gypsum, that are mainly composed of selenite. We use the definition for selenite proposed by Babel (2004), who suggested that primary gypsum crystals larger than 2 mm can be called selenite, although in the literature this definition is usually reserved for relatively large (cm- and dm-tall) and transparent gypsum crystals.

Surprisingly, most of the outcrops of the Italian Primary Lower Gypsum described in the literature are actually, mountain-size blocks translated from their original depositional site by large-scale mass-waste and gliding processes in both wedge top (Vena del Gesso and Ciminna basin) and foredeep (Caltanissetta and Belice basins, Figs. 2 and 3) settings (Roveri et al., 2003; Roveri et al., 2006; Roveri et al., 2008a). Little or no effort has been devoted to the areas where primary Lower Gypsum is in place (Northwest Sicily and on the Hyblean plateau at Licodia Eubea; Figs. 3 and 13). This is because the true nature of these mechanically mobilized deposits has been only assessed recently (Roveri et al., 2003, for the “Vena del Gesso” and Roveri et al., 2006 and Roveri et al., 2008b, for Sicily). Most of the displaced blocks represent the “classical” outcrops that drove the attention of scientists since the beginning of the modern study of

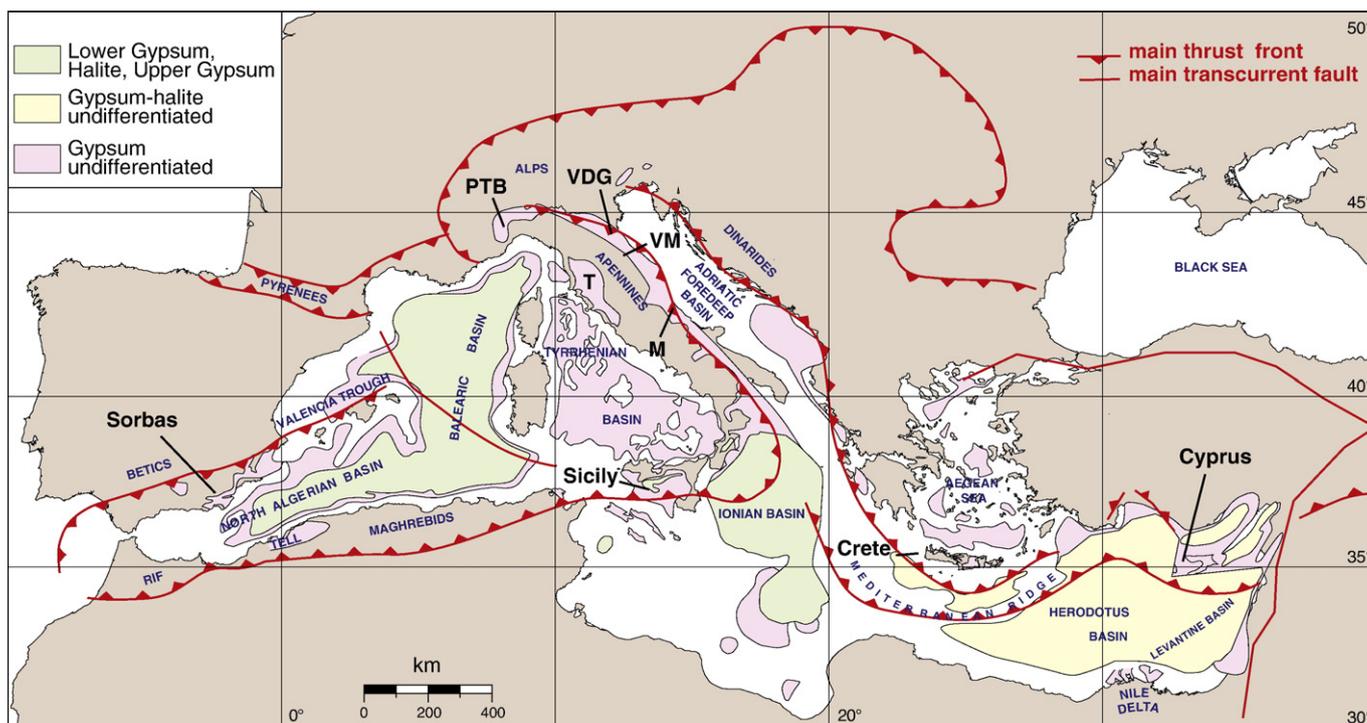


Fig. 1. The Messinian evaporite sediments in the Mediterranean basin. The sulfate deposits consist of Primary Lower Gypsum, Resedimented Lower Gypsum and Upper Gypsum (after Rouchy and Caruso, 2006); M: Maiella; PTB: Piedmont Tertiary Basin; T: Tuscan basins; VdG: Vena del Gesso; VM: Val Marecchia.

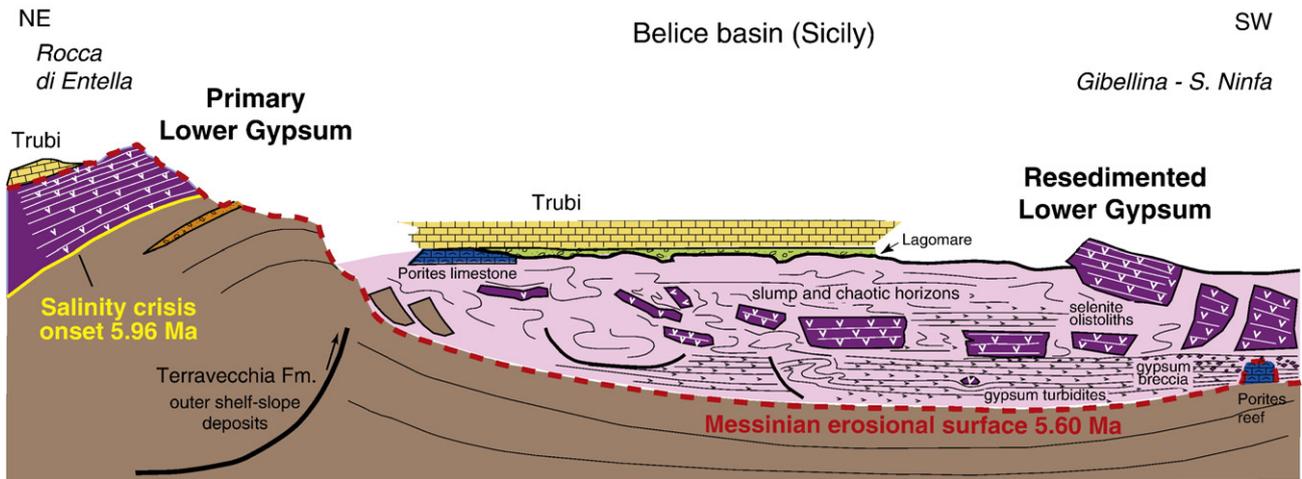


Fig. 2. Schematic geologic cross-section across the Belice basin, Sicily, showing the geometric relationships between the Primary Lower Gypsum and the Resedimented Lower Gypsum (from Roveri et al., 2006). Note the mountain-size blocks of PLG displaced by mass-wasting and gliding processes. The PLG and RLG sequences are sealed by the uppermost Messinian Lagomare sediment and the Pliocene Trubi Fm. The stratigraphy and location of the Rocca di Entella section are given in Fig. 3.

evaporite sedimentology (Hardie and Eugster, 1971; Schreiber and Friedman, 1976; Vai and Ricci Lucchi, 1977). These blocks can be successfully used to describe the facies characteristics of the Primary Lower Gypsum and for correlations, provided that their actual displaced nature is fully taken into account (Fig. 3).

The detailed facies studies of the selenite deposits in the Mediterranean started with the publication of the 1975 and 1976 Messinian

Seminar proceedings, but the only available facies model for the Messinian Lower Gypsum in the Mediterranean was proposed by Vai and Ricci Lucchi (1977). They described the Vena del Gesso succession in the Northern Apennines (Italy; Fig. 4) consisting of 16 cycles. According to their "ideal cycle" each gypsum bed is formed by the vertical repetition of 5 gypsum facies separated by organic-rich shale horizons. The two lowest cycles are thinner and consist of giant

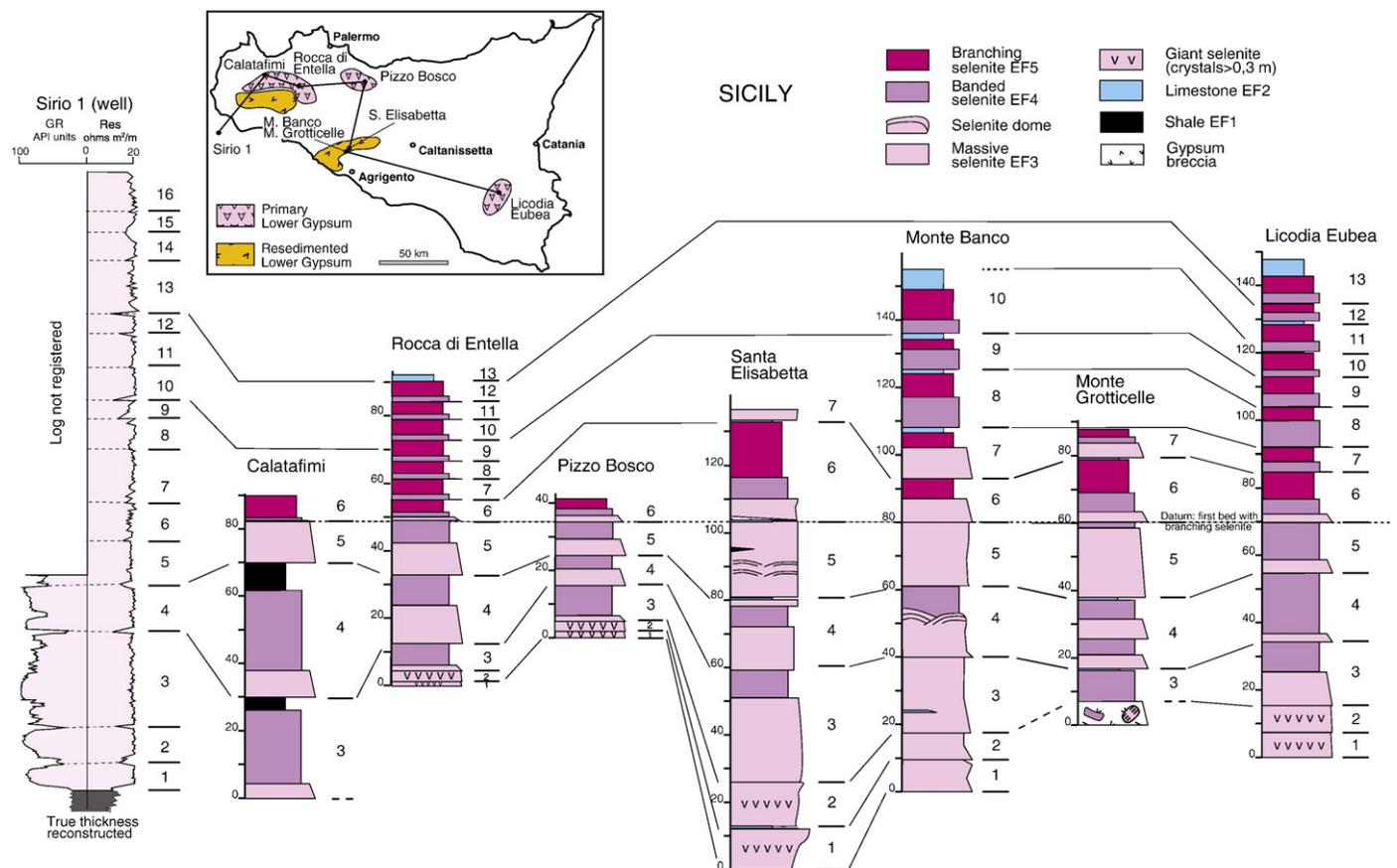


Fig. 3. Correlation of the Primary Lower Gypsum across the Sicilian basins. Note that the Santa Elisabetta, Monte Banco and Monte Grotticelle sections are displaced mountain-size blocks. Logs of well Sirio 1 from Agip (1982).

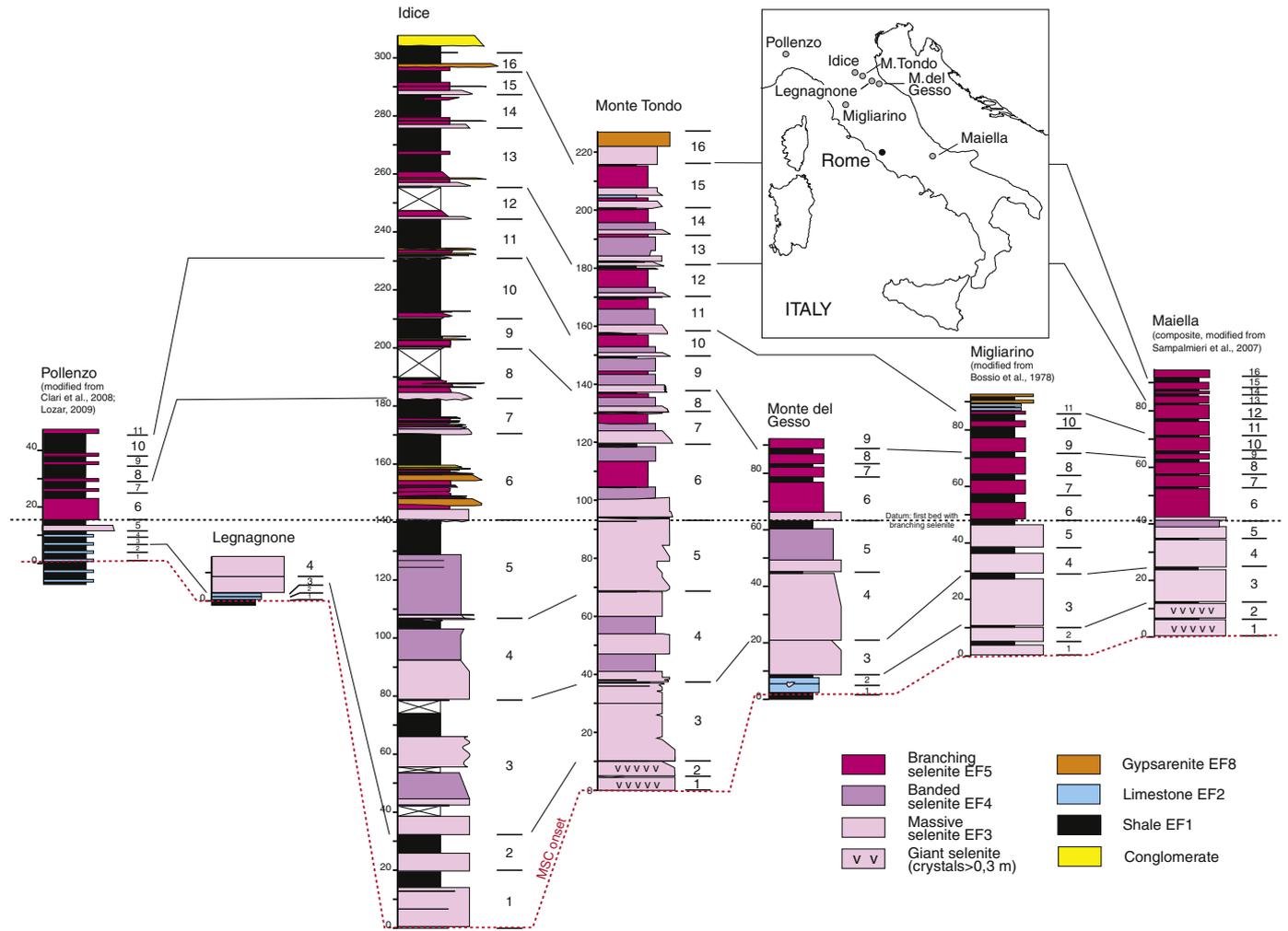


Fig. 4. Correlation of the Primary Lower Gypsum across the Northern and Central Apennines. Some data are from Clari et al. (2008), Lozar (2009), Bossio et al. (1978), and Sampalmieri et al. (2007).

selenite crystals (up to more than 2 m tall). The 3rd, 4th and 5th cycles are made of thick beds (up to 30 m) of vertically-oriented massive selenite grading into banded selenite (F3 and F4 facies, respectively). The upper part of the section (from the 6th to the 15th cycle) consists of thinner beds (average thickness 15 m) with cycles showing a basal massive and banded selenite, followed by nodular and lenticular selenite (F5 of Vai and Ricci Lucchi, 1977). The interpretation of this cyclical facies sequence led to the formulation of the “cannibalistic model” that describes the cyclical depositional regression from shallow (some tens of meters) evaporite deposition to exposure and mechanical reworking of the gypsum. The clastic gypsum was then modified by diagenesis in a sabkha setting (Vai and Ricci Lucchi, 1977).

A revisit of the Vena del Gesso sulfates and a comparison with the other Lower Gypsum basins in the Mediterranean suggest a different interpretation and a new facies model for their deposition. In the following pages we will discuss our new model using a general facies framework modified from Vai and Ricci Lucchi (1977) (Fig. 5).

3. Facies analysis of the Primary Lower Gypsum (PLG)

3.1. Bituminous shale (EF1)

Organic-rich laminated shale layers, generally less than 1 m thick separate the selenite beds in most of the Apennine sections (Figs. 4–6D). Shale partings are generally missing in the Lower Gypsum of Sicily and

Spain, where selenite beds may be separated by thin (less than 1 m) carbonate horizons (see next section), but reach their thickest expression (up to 20 m) in the Idice (Northern Apennines), Calatafimi (Sicily) and Los Yesos (Spain) sections (Figs. 4 and 11). The shale interlayers may contain fish, insects, leaves and twig remains in the Vena del Gesso (Vai and Ricci Lucchi, 1977; Vai, 1988; Carnevale et al., 2008), in Piedmont (Sturani, 1976) and, as we have observed, also in Sicily (Calatafimi). In particular, the shale layer at the top of the 12th cycle in the Vena del Gesso contains fish remains of Carangidae, Atherinidae, Cichlidae, Cyprinodontidae, Gobiidae and Scombridae, suggesting a brackish waterbody, periodically influenced by seawater influx (Carnevale et al., 2008).

The Vena del Gesso shales also contain benthic (*Ammonia*, *Bolivina*, and *Elphidium*) and rare planktonic (small globigerinids) foraminifera (Vai and Ricci Lucchi, 1977).

The presence of shale partings between the selenite beds testifies to the cyclical flooding of the evaporite basin by undersaturated continental waters. These floods carried variable amounts of terrigenous material in suspension, which is greatest in the areas located at the basin margins. The palynology of the shale suggests forested freshwater wetlands (palustrine system) or floodplains, in freshwater swamps, near the mouths of rivers just inland from salt marshes (Bertini, 2006).

The presence of well preserved fish, plant remains, the virtual absence of megabenthos, and the lamination of the shale suggest that

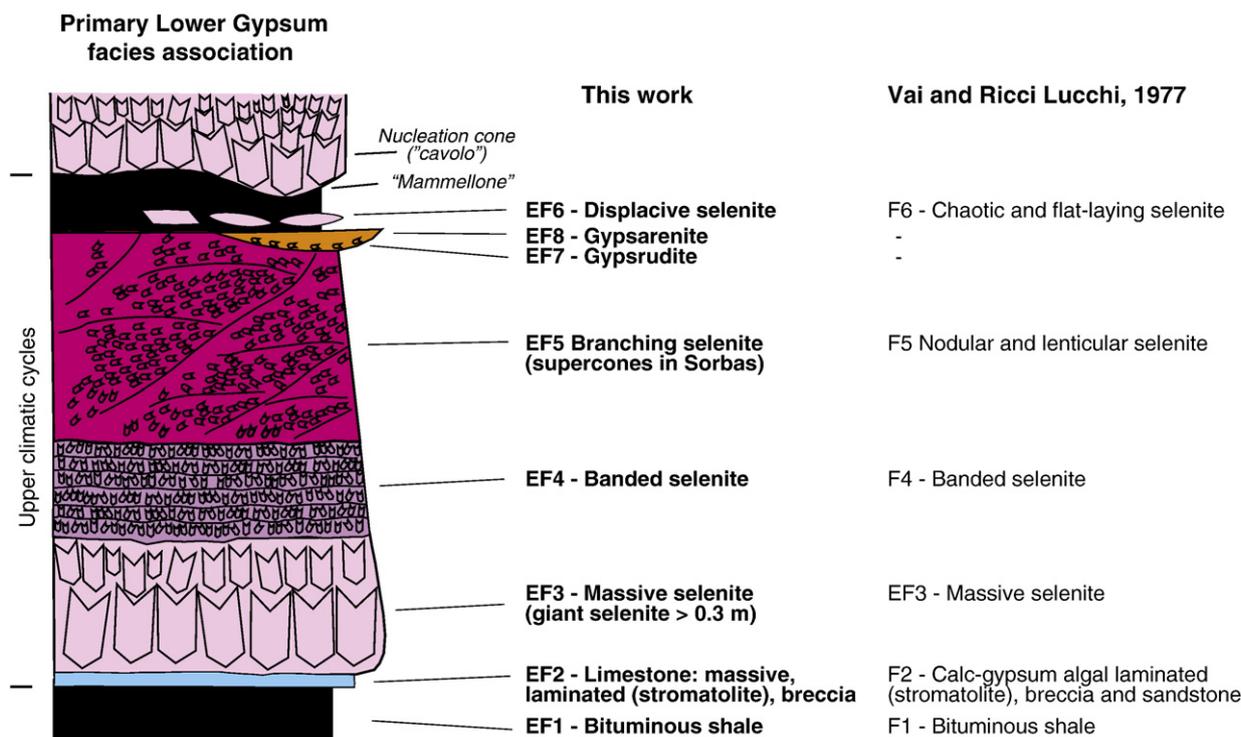


Fig. 5. A typical cycle of the uppermost Vena del Gesso section with the new facies interpretation. This facies description is a revision of the "ideal depositional" cycle of Vai and Ricci Lucchi (1977).

persistent anoxic conditions occurred at the bottom of the basin (Carnevale et al., 2008). Moreover, the abundance of the organic biomarkers gammacerane and isorenieratane indicates that anoxia extended well into the photic zone (Keely et al., 1995; Schaefer et al., 1995; Sinnighe Damsté et al., 1995a,b).

The shale layers represent the expression of the humid periods that were cyclically interrupted by evaporite deposition. As discussed later, the influx of continental water was also recorded by the Sr-isotope composition of the first selenite deposited above the shales formed during the arid periods (Lugli et al., 2007). The cyclical alternance of continental-runoff sediment supply and evaporite is considered to be directly induced by astronomically-driven climatic changes with a precession periodicity (see section on the astronomical tuning).

3.2. Limestone and dolostone (EF2)

Limestone, as thin layers and irregular pockets (less than 1 m), both laminated or massive, may separate the selenite beds (Sicily) or be present at the base of selenite layer atop the shale, or interlayer with the selenite. Most of the carbonate is massive consisting of a calcitic mudstone with variable amounts of dolomite, but laminated limestones also are present (Fig. 6A). These limestones have been reported to contain algal filaments (stromatolitic limestone of Vai and Ricci Lucchi, 1977), but actually consist of cyanobacteria (Panieri et al., 2008, 2010). In Sicily the carbonate content progressively increases upward and massive limestone layers, up to 7 m thick, are present at the top of the succession (Monte Banco and also in the Rocca di Entella section, Fig. 3).

The presence of carbonate indicates the periodic refreshment of the brine that led to sporadic undersaturated conditions with respect to gypsum. In Sicily and Spain the carbonate layers carry a similar significance as do the bituminous shale interlayers (facies EF1) separating the selenite beds. This can be related to a greater distance from the main terrigenous entry points and/or to a larger amount of

carbonate available in the system. The presence of carbonate platforms as in the Sorbas basin during the deposition of the evaporites (Roveri et al., 2009) could have promoted the deposition of limestone (facies EF2), while the close position to the emerged orogens, like in the Northern Apennines, could have favored the deposition of thick shales (facies EF1).

This carbonate facies interlayered with the gypsum (EF2) should not be confused with other limestones widespread in the Messinian succession in the Mediterranean, these are: a) the thin carbonate layers that may be present at the bottom of the lowermost cycles of the Lower Gypsum but belong to the pre-evaporitic unit (Monticino, Vena del Gesso, Fig. 7; S. Elisabetta, Licodia Eubea in Sicily) or b) the Calcare di Base that, as a whole, is considered a lateral equivalent of the Lower Gypsum by most authors (Rouchy and Caruso, 2006), but in our interpretation formed after the Primary Lower Gypsum (CdB type 3, Roveri et al., 2008a,b,c) or c) the 'sulfiferous' carbonate originated by the bacterial reduction of gypsum (CdB type 1, Manzi et al., in press).

As discussed in the next sections, our observations in the Northern Apennines demonstrate that limestone/dolostone-marl couplets at the top of the pre-evaporitic successions (CdB type 2, Manzi et al., in press) represent the lateral equivalent of the lowermost gypsum cycles in basinal settings. Moving across the selenite basins we can document a continuous transition from massive selenite to nucleation cones (see Section 3.3) or a few isolated gypsum crystals floating within limestone (the so-called gypsified stromatolites of Vai and Ricci Lucchi, 1977), and finally to pure limestone devoid of gypsum (lowermost cycles of the eastern Santerno valley in the Vena del Gesso and the Monte del Gesso section in Val Marecchia, Fig. 4).

3.3. Giant and massive selenite (EF3)

The giant and massive selenite beds consist of twinned gypsum called arrow-head or swallow-tail crystals, with their minor morphological varieties such as "Siva" (wide-angle twins with curved faces;

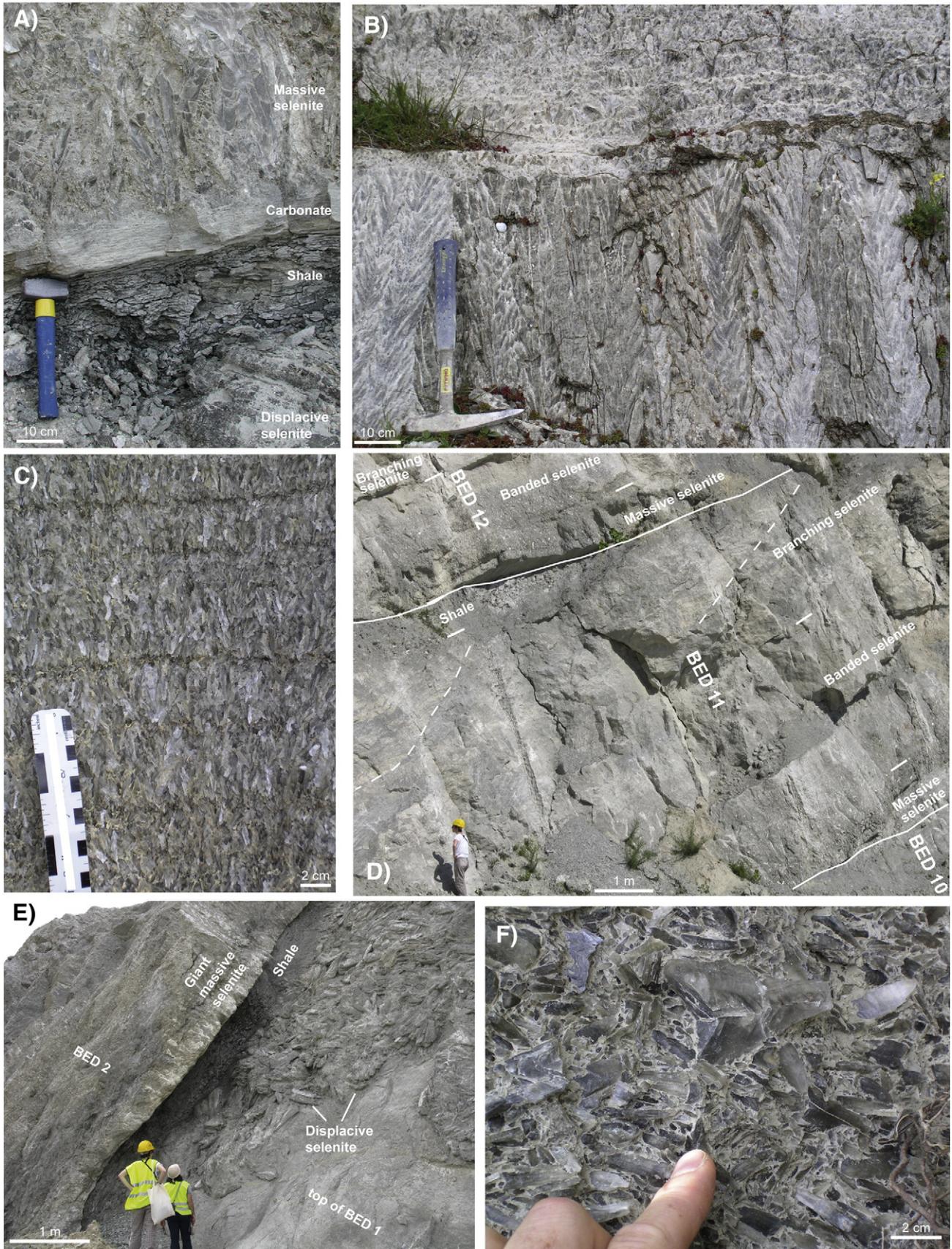


Fig. 6. A) The base of the 3rd bed at the Monte Tondo section of the Vena del Gesso. B) The contact between giant massive selenite (bottom) and banded selenite (top) represent a dissolution surface; note the truncated top of the giant selenite crystals; Rocca di Entella section (Sicily). C) Banded selenite facies at Vita, Belice basin (Sicily) the small selenite crystal layers are separated by thin carbonate veneers. D) The 10th, 11th and 12th beds at the Monte Tondo quarry (Vena del Gesso), note the thin shale layers separating the beds and the curved surfaces outlining the branching selenite clusters. E) The boundary between the 2nd and 3rd beds at the Monte Tondo Quarry (Vena del Gesso); giant lenticular selenite crystals that grew displacively in the lower part of the thin shale layer separating the two beds; in the 2nd bed the size of the giant selenite crystals decreases upward from the bottom. F) Gypsrudite consisting of swallow-tail selenite clasts; the low corrosion of the selenite crystals suggests a minimal transport; Idice section (Vena del Gesso).

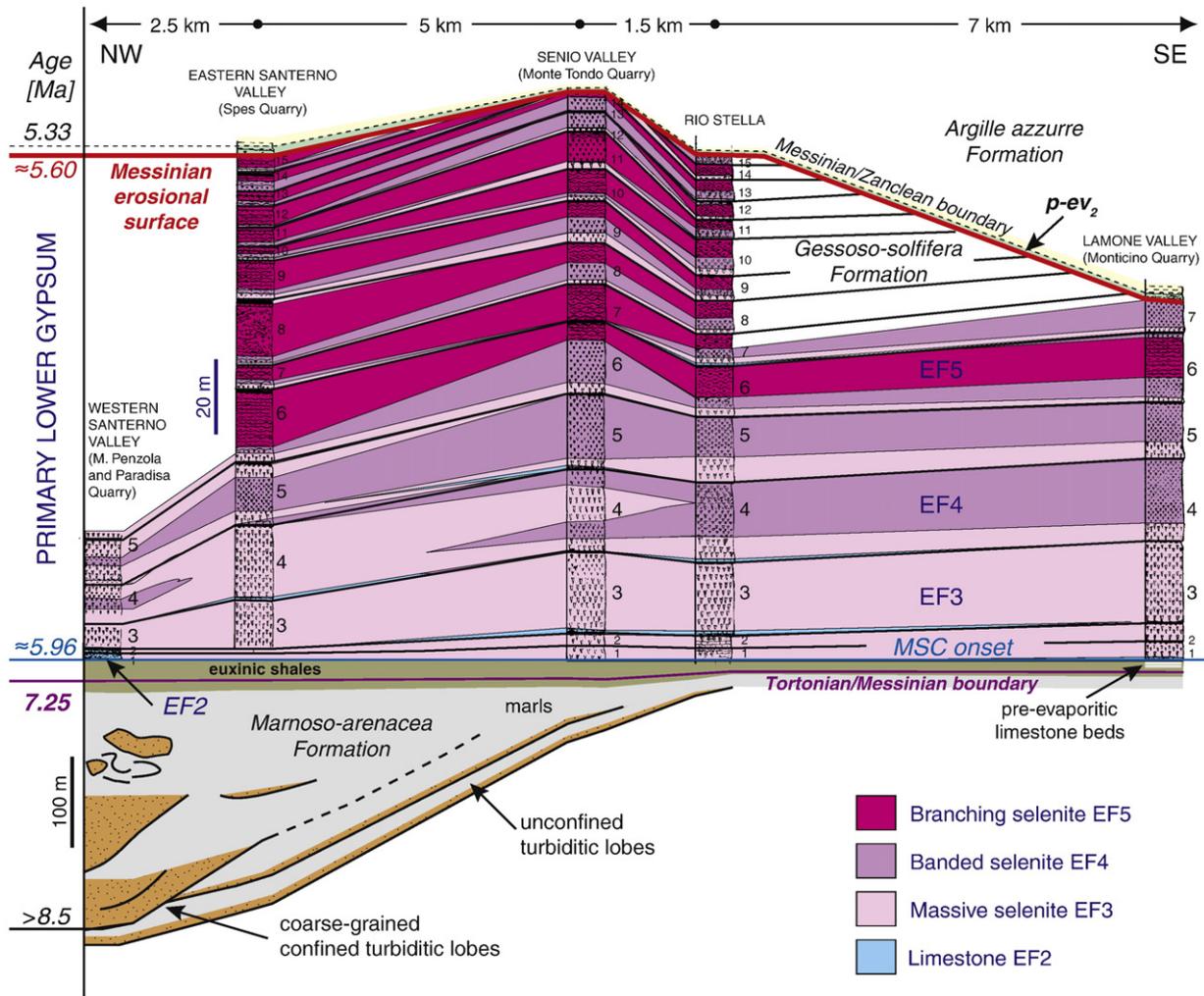


Fig. 7. Gypsum facies variation across the Vena del Gesso basin (Northern Apennines). Sections stratigraphy modified from Vai and Ricci Lucchi (1981).

Shearman, 1983) or palmate (curved-face twins with a vertical twinning exceptionally developed; Shearman and Orti Cabo, 1976; Schreiber, 1986). One of the most striking characteristics of the selenite beds is that most crystals are vertically oriented with the re-entrant angle of the twins upward (Fig. 6A,B). This peculiar organization of these crystals was first noted by Mottura (1871) and was successfully used to determine the stratal polarity in mining operations in Sicily. The vertical arrangement can be explained by the competition for space of the crystals which favored only the growth of the nuclei that were oriented upward, the only possible free space. All other randomly-oriented crystals stopped to grow against the vertical ones (Fig. 8). As explained in the next chapters locally selenite crystals may grow laterally or even upside-down.

The bottom of each of the selenite beds generally consists of larger gypsum crystals, less than 50 cm in most cases (Fig. 6A), that become smaller, up to a few centimeters, going upsection. Giant selenite crystals, up to 2.5 m tall, are present only in the lowermost two beds, where no other selenite facies associations are present (Fig. 6E). These exclusive characteristics of the first two cycles carry a significant value for stratigraphic correlation and for reconstruction of paleodepth and salinity. The growth of continuous beds of giant selenite crystals suggests that this massive facies represents the maximum brine level in the cyclic evaporite deposition because in order for large size crystals to grow they need to be permanently covered by saturated brines (Bäbel, 2004). The continuous growth of large crystals may also

suggest that the degree of supersaturation was probably the lowest in the earlier phase of the Primary Lower Gypsum deposition, as a few nuclei that grow large are typical of low supersaturation brines (Bäbel, 1999).

Selenite crystals contain the so-called “spaghetti-like” filamentous cyanobacterial fossils (Vai and Ricci Lucchi, 1977; Rouchy and Monty, 1999; Panieri et al., 2008). These represent a very peculiar case of fossilization within gypsum preserving the original material to such an extent that a recent investigation succeeded in extracting what is now the oldest known cyanobacterial DNA ever isolated (Panieri et al., 2010). The closest known relatives of the extracted materials are the representatives of the genus *Geitlerinema* originating from shallow marine, coastal environments. The cyanobacteria filaments are preferentially located into the inclusion-rich triangular core of crystals, but are not present in other portions. The clear area around the core cannot be considered a later diagenetic, displacive overgrowth, as originally suggested by Vai and Ricci Lucchi (1977). Crystallography of gypsum and growth mechanisms suggest that filaments and other particles can be trapped only on the re-entrant angles of the upper portion of the crystal (Fig. 8). The lower portions of vertically-oriented selenite crystals grew only laterally and were not able to trap particles, thus forming clear growth bands around the inclusion-rich dark core. This is also the reason why crystals that grew laterally instead of vertically do not show a dark core, are mostly devoid of trapped filaments and are usually transparent (as described later).

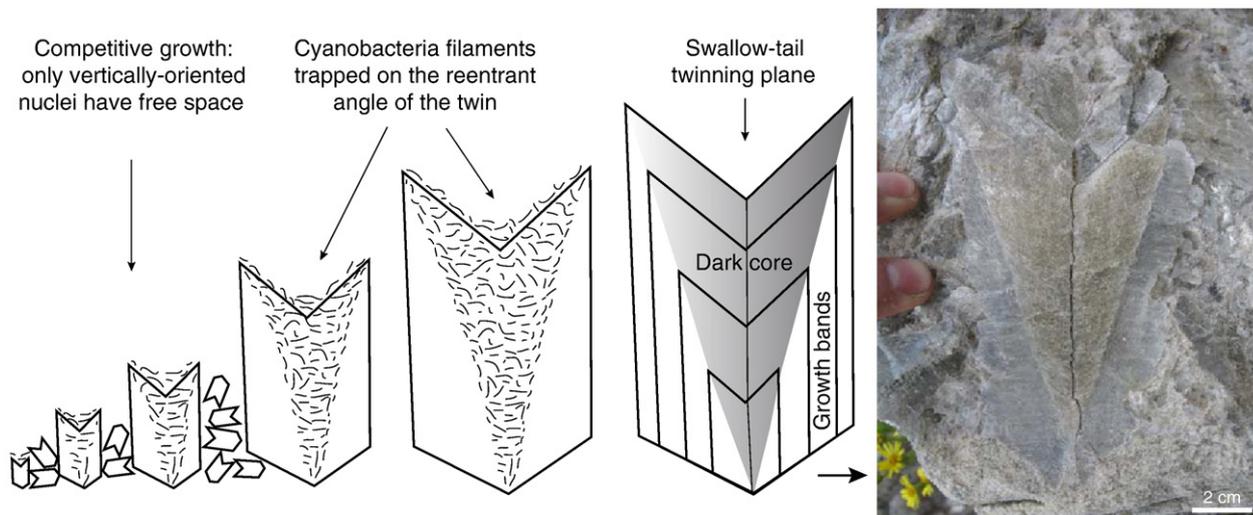


Fig. 8. Diagram showing the competitive growth of selenite determining the typical vertical orientation of the crystals (Mottura's rule) and the trapping mechanism of cyanobacteria filaments on the re-entrant angles of the twins producing the dark triangular core of the swallow-tail crystals.

The vertical competitive growth also produces some typical structures called “nucleation cones” (Dronkert, 1977; Vai and Ricci Lucchi, 1977; Lo Cicero and Catalano, 1978). These consist of conical clusters of crystals that may be present at the base of the selenite beds representing the initial nucleation points that progressively sank into a relatively soft substrate such as mud (both carbonate and clay; Fig. 5). They actually represent load-cast structures that reach a maximum of about 1.5 m across and are called “mammelloni”. Although the basal clusters were sinking in the mud, the relatively rapid competitive growth tends to produce a flat growth surface in the upper part of a bed, which may be further flattened by dissolution intervals during later brine dilution events.

An evolution of these features are the domal structures with a convex-up surface that may appear in the upper part of many beds. They are also generated by the conical clustering of selenite crystals but may grow much larger, up to a few meters across. These domes, also present in the Badenian of Ukraine and Poland (Babel, 2004), are relatively rare in the Lower Gypsum and are observed only in the 4th cycle in Sicily (Monte Banco, Fig. 3). Similar domal structures in Sicily were called “cavoli” by Richter-Bernburg (1973), and, confusingly, “mammelloni” as well by Ogniben (1957), but their descriptions refer to the typical domes appearing on the upper surfaces of the Upper Gypsum unit beds (such as Eraclia Minoa; Manzi et al., 2009).

Pervasive dissolution surfaces may cut through the massive selenite crystals, but are normally devoid of insoluble material (such as carbonate and clay) and the truncated crystals again grew syntaxially across the dissolution surfaces.

The massive aspect of the selenite beds also indicates that the brine concentration did not drop to carbonate saturation, a characteristic that is typical of the banded selenite described in the following section.

3.4. Banded selenite (EF4)

The banded selenite facies (“bedded” selenite of Hardie and Eugster, 1971 and “grass-like” selenite of Richter-Bernburg, 1973; Schreiber et al., 1976) consists of relatively small vertical crystal crusts, less than 10 cm in thickness, that are separated by thin carbonate laminae (a few millimeters thick; Vai and Ricci Lucchi, 1977; Fig. 6B and C).

According to Babel (2007) such features reflect characteristic fluctuations of the pycnocline (*i.e.* the gypsum-saturation interface) that repeatedly stops selenite growth in such a way that no large

crystals may develop (stratified selenite), as opposed to the massive or giant selenite. This is because the formation of carbonate caps the dissolution surface, draping the truncated crystal terminations and stopping their growth. Such crystals may not develop a syntaxial overgrowth and these conditions typically occur during the phase of maximum drawdown in the basin corresponding to the minimum level of saturated brine. For these reasons the banded selenite facies probably mark the acme of the aridity peak in the cyclical deposition of the evaporites (Fig. 9). The considerations already pointed out for the massive selenite also apply for all other aspects of growth of the banded selenite facies.

3.5. Branching selenite (EF5)

This facies has been variously described as “nodular and lenticular selenite” commonly displaying flaser bedding in the Vena del Gesso (Vai and Ricci Lucchi, 1977) or “wavy, needle-like selenite layers” in Sicily (Schreiber et al., 1976 for the Caltanissetta basin; Lo Cicero and Catalano, 1978 for the Cimenna basin) or hemi-radial to radial selenite in Spain (Yesares and Feos sections; Lu, 2006). It consists of clear selenite crystals a few centimeters across with their long axis inclined or oriented horizontally grouped into decimeter-large irregular nodules and lenses separated by thin fine-grained carbonate or gypsum laminae. The clusters are grouped along curved-upward surfaces that are a few meters long (Fig. 10A and B).

These selenite crystals, that do not seem to obey the Mottura's rule, appear only from the 6th cycle onward and were originally considered a clastic deposit (gypsarenite) that was subaerially exposed developing sabkha features, such as anhydrite nodules that were then rehydrated back to form gypsum (Vai and Ricci Lucchi, 1977).

The detailed study of this facies shows neither clastic nor supratidal features because the crystals are devoid of any secondary texture after anhydrite such as cloudy-ameboid texture and anhydrite relicts (Lugli, 2001). The arrangement of the crystals reveals that clusters of selenite grew laterally, grouped in branches projecting outward from an initial nucleation zone into a fine-grained gypsiferous matrix (Fig. 10A and B). The crystals do not show the typical gray core of the vertically-oriented massive and banded selenite because the re-entrant angle of the crystal top was projecting on a side and was not able to trap the microbial mat in such an efficient way as the upward-oriented crystals (see the description in the Giant and Massive Selenite section, Fig. 8).

Climatic precession cycle

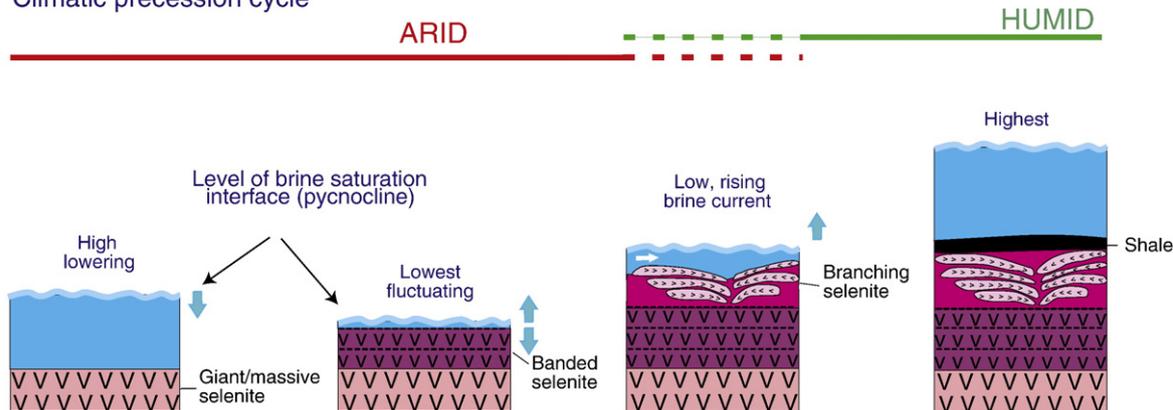


Fig. 9. Growth of the different types of selenite as a function of brine saturation level and precession climatic cycles. Note that branching selenite and supercones grow in the presence of currents and rising pycnocline levels.

The close examination of the “nodular and lenticular” structures reveals that the selenite crystals show the same organization observed in the subaqueous selenite supercone structures described in the Sorbas basin (Spain) by Dronkert (1977, 1985) (Fig. 10E). The supercones consist of clusters of inclined selenite crystals grouped in horizontal branches spreading out from a nucleation zone to form inverted cones (Fig. 10C and D). Here we interpret the “nodular and lenticular” structures as an extreme evolution of Sorbas supercones, that until now were considered a sort of local geological oddity, never observed elsewhere and with no recognized present-day analogue.

In the case where no obvious central conical shape may be recognized, but only the branch terminations against the host matrix are visible, we proposed the use of the term “branching selenite” (EF5) to emphasize the aspect that these crystals grew in organized subaqueous structures. The reason that the conical shape may be difficult to recognize is that cones are widely spaced and very broad so that the nucleation points are not readily visible. Another factor influencing the recognition of the conical growth morphology is that the matrix surrounding the cones may consist mostly of gypsum and the cone structures do not protrude outside the outcrop (Fig. 10A and B) as in the case of the Sorbas basin, where the matrix consists of an easily erodible mudstone and fine-grained gypsum (Fig. 10D and E). We also have evidence that groups of branches may grow without forming conical shapes (Fig. 10A), and this is probably due to the formation of asymmetrical structures growing against strong brine currents. The way in which gypsum crystals may grow inclined toward brine currents has been described in detail by Babel and Bogucki (2007). Curved crystals grown under the influence of a flowing brine are present in the massive selenite of the lower beds, but are sporadic, and thus were probably due to local conditions such as the microtopography of the basin bottom.

The “wavy bedding” and the “flaser structures” described previously in the literature for these deposits are actually irregular branches projecting outward seen from a side and terminating against a fine-grained gypsiferous matrix or juxtaposed to branches belonging to other cone structures. When the branches are particularly flat and isolated they could be mistaken for megaripple structures (such as in the Idice section; Fig. 10A) and/or diagenetic nodules (such as in the Pollenzo section, Piedmont; Fig. 4).

It appears that two conditions must be satisfied to grow superimposed branches forming supercone structures: a relatively strong brine flow to initiate and maintain the horizontal growth of the selenite crystals and a depressed pycnocline that limits the vertical accommodation space and forces the structure to grow only laterally. Moreover, the superimposition of different branches spreading

laterally that are progressively larger going upward to form inverted cones suggests that the pycnocline was rising progressively (Fig. 9).

3.6. Displacive selenite (EF6)

The crystals are mostly lenticular, but a few twinned crystals also have been observed, up to 1 m across, commonly present above selenite beds at the contact with the overlying shale layers. These crystals are common in the Vena del Gesso (Figs. 5 and 6E), but are not present in Sicily and in most of the Spanish outcrop where selenite beds are not separated by shale intercalations.

This facies was described as reworked chaotic and flat-laying selenite crystals (Vai and Ricci Lucchi, 1977). Similar crystals in the Badenian of Poland were interpreted by the growth of isolated gypsum crystals on a muddy substrate assuming that “the crystals grew simultaneously with fallout of clay particles from the water column” (Babel, 1999).

In these crystals we could not find the cyanobacteria filament inclusions shown by Vai and Ricci Lucchi (1977), but only irregular stringers of the host clay. This characteristic and the observation that the crystals are mostly lenticular and not corroded suggest a displacive growth into the lower part of the shale interlayers and not a clastic deposition.

The formation of the crystals apparently occurred during early diagenesis by precipitation from interstitial gypsum-saturated brines that were trapped by shale deposition (facies EF1). The typical horizontal growth (“flat-laying”) of the lenticular crystals is opposed to the vertical growth of the primary selenite twins, as in this case the free space of the displacive growth is only horizontal and not vertical because the shale layers are normally only a few decimeters thick (Fig. 6E).

The occasional incorporation of cyanobacteria filaments in some of the crystals (Vai and Ricci Lucchi, 1977) may be due to displacive growth into carbonate mud layers that are commonly rich in organic remains.

3.7. Gypsarenite (EF7) and gypsrudite (EF8)

Clastic deposits (gypsrudite EF7 and gypsarenites EF8) are present only locally throughout the selenite successions of the Primary Lower Gypsum. They are limited to thin layers in the more marginal successions, such as in the upper half of the Idice section (Fig. 6F) and to the topmost part of the Monte Tondo section (16th cycle; Figs. 4 and 5). In most of the cases the selenite clasts are only slightly corroded suggesting local erosion and deposition as consequences of floods at basin margins.



Fig. 10. A) Branching selenite consisting of clusters of inclined selenite crystals grouped in downward-pointing arms spreading from a nucleation zone, no obvious conical shape is visible; with such flat and downward spreading clusters, the branching selenite may resemble megaripples (Idice section, Vena del Gesso). B) A close up of the previous picture showing the downward termination of the branches against the host matrix consisting of laminated gypsum/carbonate fine-grained sediment. C) Inclined and curved surface marking the termination of selenite branches (left) toward the host fine-grained gypsum, Monte Tondo quarry (Vena del Gesso). D) Selenite crystals arrangement within a branch which grew from the left to the right; crystals became white after an accidental superficial fire (Lugli, 2002); S. Ninfa, Belice basin (Sicily). E) Selenite supercone structures in the Rio de Aguas section of the Sorbas basin (Spain); note that the inverted conical structures grew on top of the banded selenite and are asymmetric, suggesting a brine current from the left to the right; the supercones are draped by a fine-grained gypsum–carbonate deposit (at the top); the branches are made evident by the erosion of the host fine-grained matrix. F) A frontal view of the selenite supercone structures in the Rio de Aguas section, Sorbas basin (Spain). G) Selenite cluster spreading outside the margin of a supercone; note that the growth arrangement of crystals in the cluster is very similar to the branching selenite of panel D); Rio de Aguas section, Sorbas basin (Spain). H) Selenite branches juxtaposed to the host fine-grained gypsum–carbonate matrix surrounding the supercone structures at the Rio de Aguas section, Sorbas basin (Spain).

4. Sr-isotope geochemistry and organic matter

In the peculiar setting of the Mediterranean basin a reliable hydrologic indicator to study the salinity crisis appears to be the Sr-

isotope ratio because it is not influenced by salinity change and evaporation conditions (Flecker et al. 2002). In this paper we focus on a complete Sr-isotope profile across the lower gypsum in the Vena del Gesso (Lugli et al., 2007), in Sicily and Spain according to our new

(1998) in Spain on the basis of the variation in the strontium content of gypsum. Our detailed facies analysis suggests that a striking similarity also exists in stacking pattern, thickness and, most significant, facies assemblages, not only in Italy (Piedmont, Emilia-Romagna, Tuscany, Abruzzo, Calabria, Sicily) but in the entire western Mediterranean (Spain) and in some cases probably also in the Eastern Mediterranean (Zakynthos and Crete).

The general rule across the entire Mediterranean is that the first two cycles commonly are the thinnest (up to a few meters), but show the largest selenite crystals (up to 2.5 m in Sicily; Babel, 2002, cites that 7 m tall crystals were reported in Cyprus, but this information has not been corroborated by our field work). The third to fifth cycles are the thickest and consist of massive and banded selenite. Only starting from the sixth cycle does the branching selenite appear in the sequence and the triplet massive/banded/branching selenite is regularly repeated in all of the succeeding cycles (6th to 15th bed; Figs. 3–5).

Most of the cycles begin with large massive selenite crystals that progressively decrease in size and phase upwards into banded selenite (Fig. 5). The first two beds are made up of only massive selenite, and the cycles starting from the sixth, may contain only branching selenite. In the Sorbas basin selenite supercones appear upsection at the 6th bed, which is the same stratigraphic horizon where the branching selenite is present in the sections across Italy (from the Northern Apennines to Sicily).

This revision of the Messinian stratigraphy reveals that we have a powerful tool to correlate the Primary Lower Gypsum bed-by-bed across the whole Mediterranean (Figs. 3 and 4).

6. A new facies model for the Primary Lower Gypsum

The stacking pattern of the described facies suggests a complete, small-scale, subaqueous sedimentary cycle made up of both increasing and decreasing upward water saturation phases that mimic regressive–transgressive cycles related to small-scale basin water level changes: respectively EF3 facies represents the initial fall, EF4 the lowstand, EF5 the transgression and, finally, EF1 the highstand (Figs. 5 and 9; Roveri et al., 2008c):

- 1) initial evaporite precipitation at relatively low supersaturation produced the massive selenite in a relatively deep setting (large massive selenite, EF3); the crystals were always covered by supersaturated brine (*i.e.*, they were below the pycnocline);
- 2) continuous evaporation and drawdown produced relatively higher and variable supersaturation conditions and growth of sulfate crystals was controlled by oscillating brine level of the pycnocline (banded selenite, EF4);
- 3) a general progressive brine level rise with strong brine flow produced the formation of large supercones branching laterally (branching selenite, EF5);
- 4) flooding by undersaturated water abruptly ended gypsum precipitation with the deposition of argillaceous sediments (EF1, Northern Apennines) and/or limestone (EF2, Sicily and Spain).

Individual cycles are vertically stacked to form gypsum bodies with an overall aggradational geometry. Taking into account the rapid depositional rate of gypsum deposits, this implies the superimposition of a longer-term shallowing-upward trend on high-frequency evaporite cycles.

7. Depositional setting and depth of the Primary Lower Evaporites

The understanding of the depositional setting of the Lower Evaporite carries an important implication in the long-standing debate on the significance of shallow vs. deep evaporite deposition. These concepts are somewhat controversial because no definitive depth boundary between “shallow” and “deep evaporites” is easily defined

for such extreme depositional settings where other paleobathymetric proxies are not available. To further complicate the issue, studies have focused on very shallow evaporite basins and artificial salt works, but a modern analogue for the deep evaporite settings is not available.

Selenite is considered as the typical product of very shallow evaporite environments at depth ranging from centimeters to a few meters (Schreiber, 1986; Babel, 2004; Babel, 2007) or 10–30 m (Nijar basin, Spain; Lu, 2006). This is based on the comparison with modern artificial and recent (Holocene) natural depositional settings. Another important point corroborating this interpretation is the widespread presence of algal and cyanobacteria filaments within the Messinian selenite, that limits the deposition setting to the photic zone (Schreiber, 1986; Babel, 2004). However, it should be emphasized that only a little is known of the nature and characteristics of the cyanobacteria enclosed in the ancient selenite crystals (Rouchy and Monty, 1999; Panieri et al., 2008; Panieri et al., 2010). On the other hand, despite the extensive literature on modern saline environments population, only shallow water settings have been fully investigated (see Babel, 2004 for a review). Although much is known on the salinity range of modern organisms, we have no information on the maximum depth for the growth of comparable microbial mats. This largely limits our understanding of very complex phenomena, such as the role of floating microbial mats that may possibly sink to greater depth and possibly become incorporated by the bottom-nucleated selenite crystals and also the effect of shadowing by suspended organic matter which would further limit the penetration of light into the brine.

The concept of a water body that is only a few meters or even centimeters in depth clearly cannot apply for the deposition of the Primary Lower Gypsum in the Mediterranean for several reasons:

- a) No karst features are present in any of the sections we have described in detail in Italy and Spain. The only dissolution features that are observed are due to temporary reduction in the CaSO₄ saturation of the brine, but are clearly not related to subaerial exposure; the crystals were always covered by brine, which was episodically diluted sufficiently to become undersaturated. Crystals may have been truncated by dissolution, but no significant pits are present at crystal and bed scale (Fig. 6B). The possible effects of exposure and karstification are not present. The possible, repeated, drawdown of the basin during each cycle never reached such an extent as to expose the already deposited gypsum. The only karst features cutting into the gypsum are associated with the development of the Messinian erosional surface related to an intra-Messinian tectonic phase that occurred well after the sedimentation of the entire succession (Monticino quarry, Marabini and Vai, 1985; Roveri et al., 2008c). No evidence of subaerial exposure during the deposition of any of the 16 gypsum cycles has been observed.
- b) The clear bed-by-bed correlation and facies assemblage continuity is present for sections that are thousands of kilometers apart, in diverse tectonic settings and deposited in a time span of only 340 ka (from 5.960 to 5.61 Ma; Krijgsman et al., 1999; CIESM, 2008; Roveri et al., 2008b) which appears to be incompatible with an extremely shallow depositional setting.

In our opinion such widespread and particular depositional characteristics were achieved only by rapidly filling basins which were possibly already about 100–200 m deep. This is because sulfate minerals may have a very rapid depositional rate, reaching up to 80 m/ka in shallow water (Schreiber and Hsü, 1980) and may largely overcome any subsidence rate. This does not necessarily imply that the brine was as deep as 200 m, because, as shown by Babel (2004) for the saline environment, drawdown may have lowered the brine level of the restricted marginal basins below the average Mediterranean sea level. Brine level would easily rise together with sedimentation and basin infill.

One controlling factor that would limit selenite deposition only to “shallow” depth is the absence of oxygen in “deep” stratified anoxic basins. This condition, in turn, lowers the SO₄ available for gypsum precipitation (Nurmi and Friedman, 1977; Babel, 2004) and/or degradation of organic matter by bacterial sulfate reduction that would promote the formation of dolomite instead of gypsum (De Lange and Krijgsman, 2010).

However, this idea is a general concept and does not provide a maximum depth for selenite deposition which can be universally applied: if the basin was oxygenated down to a depth of less than 200 m, then bottom-nucleated selenite could reasonably form. No direct observations are available in modern settings for such microbial-oxygen-dependent depth of formation of primary gypsum.

These considerations open a new interesting question: what is the nature of the sediments which were deposited in the deeper parts of the Mediterranean during the precipitation of the marginal Primary Lower Gypsum in the first part of the salinity crisis? We know that in the Messinian Mediterranean the limiting condition for gypsum precipitation was achieved in the more open basinal sea, away from the shallow marginal sub-basins. The known examples of Primary Lower Gypsum were deposited only on marginal settings with circulation restricted, to some degree, by structural sills, whereas the adjacent deeper parts, on the contrary, experienced deposition of organic-rich, barren shale and dolostone in Sicily (Serra Pirciata and Falconara sections) and in the Apennine foredeep (Fanantello section; Manzi et al., 2007; Roveri et al., 2008c). This organic-rich unit, which has been proven to be coeval with the Primary Lower Gypsum (Manzi et al., 2007; Gennari et al., 2009) is usually overlain by the RLG deposits through a sharp surface that can be traced upslope into the Messinian erosional surface (Fig. 2; Roveri et al., 2008b).

However, similar stratigraphic relationships also have been recently documented in marginal basins characterized by deposition of PLG evaporites; in the Piedmont Basin a barren unit consisting of up to four carbonate–marl couplets is overlain by the primary gypsum but is younger than 5.96 Ma (Alba sub-basin; Clari et al., 2008; Lozar et al., 2009). The presence of the branching selenite in the local second gypsum bed of this basin indicates that it actually represents the sixth cycle at the Mediterranean scale, suggesting that the underlying barren carbonate–marl unit is the lateral equivalent of the four lowermost gypsum cycles. This correspondence is confirmed by recent biomagneto- and cyclostratigraphic data (Gennari et al., 2009).

A similar situation also appears in the Legnagnone section (Val Marecchia, Northern Apennines) where the first two basal gypsum cycles are missing and are represented by two barren marl–carbonate couplets (Gennari et al., 2009; Fig. 4). An important implication of such observations is that the onset of the MSC is not necessarily recorded by the first gypsum bed; this is true not only for deep settings but even for shallow ones, suggesting the importance of local controlling factors (Fig. 12).

The possible role of structural sills in regulating bottom water saturation in shallow, marginal sub-basins and hence promoting gypsum precipitation during the first MSC stage, has been questioned by De Lange and Krijgsman (2010). Based on the difficulty of accepting the idea of a synchronous onset of evaporite deposition in sub-basins with sills likely having different heights and widths, they suggested an alternative model implying: 1) the saturation up to sulfate values of surface waters throughout the Mediterranean, 2) the dilution of brines moving toward deep basins due to biogeochemical processes leading to the precipitation of dolomite instead of gypsum in deeper settings, and 3) the preservation of gypsum brines only on

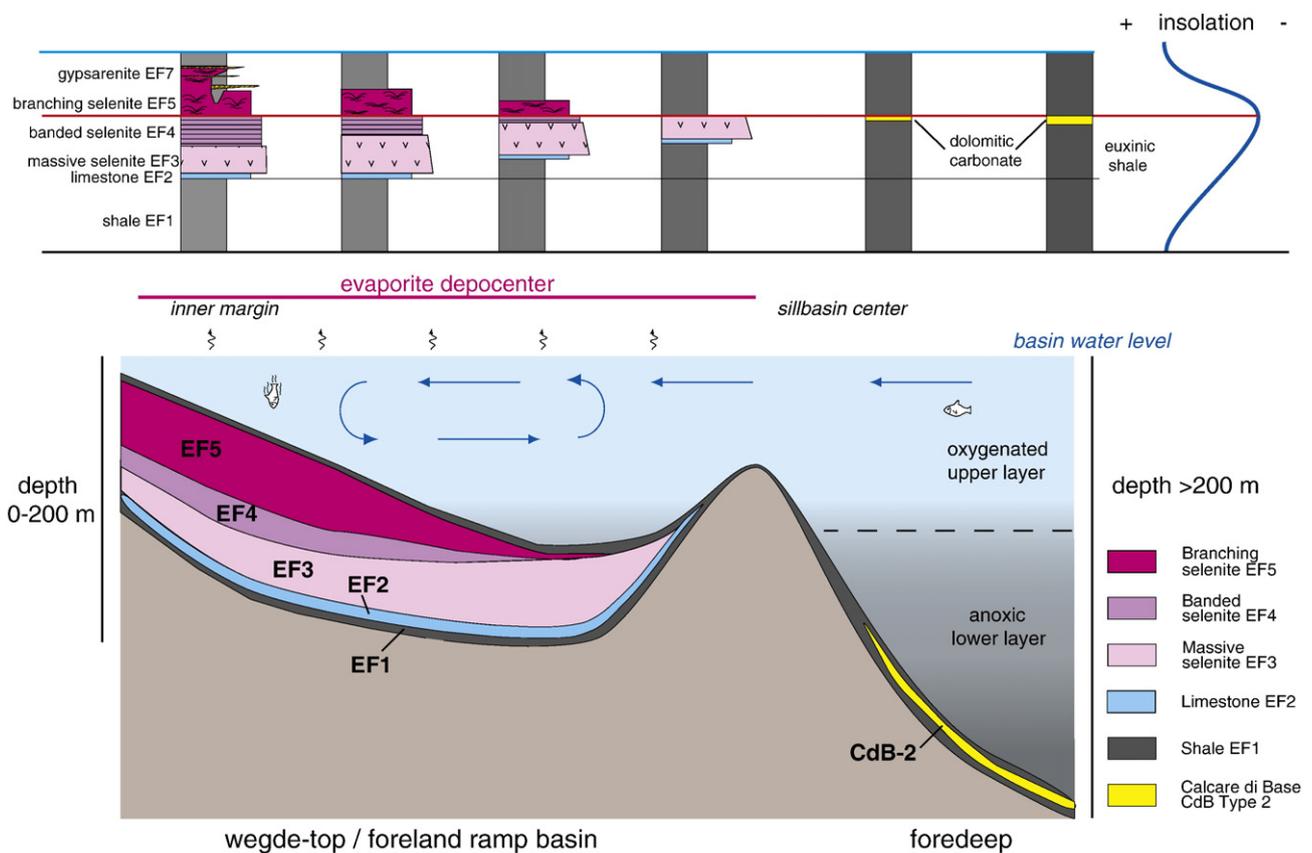


Fig. 12. Diagram showing the vertical selenite arrangement as a function of the climatic precessional cycle and the lateral facies transition from the shallow silled selenite basin to the deeper anoxic carbonate/shale-dominated areas.

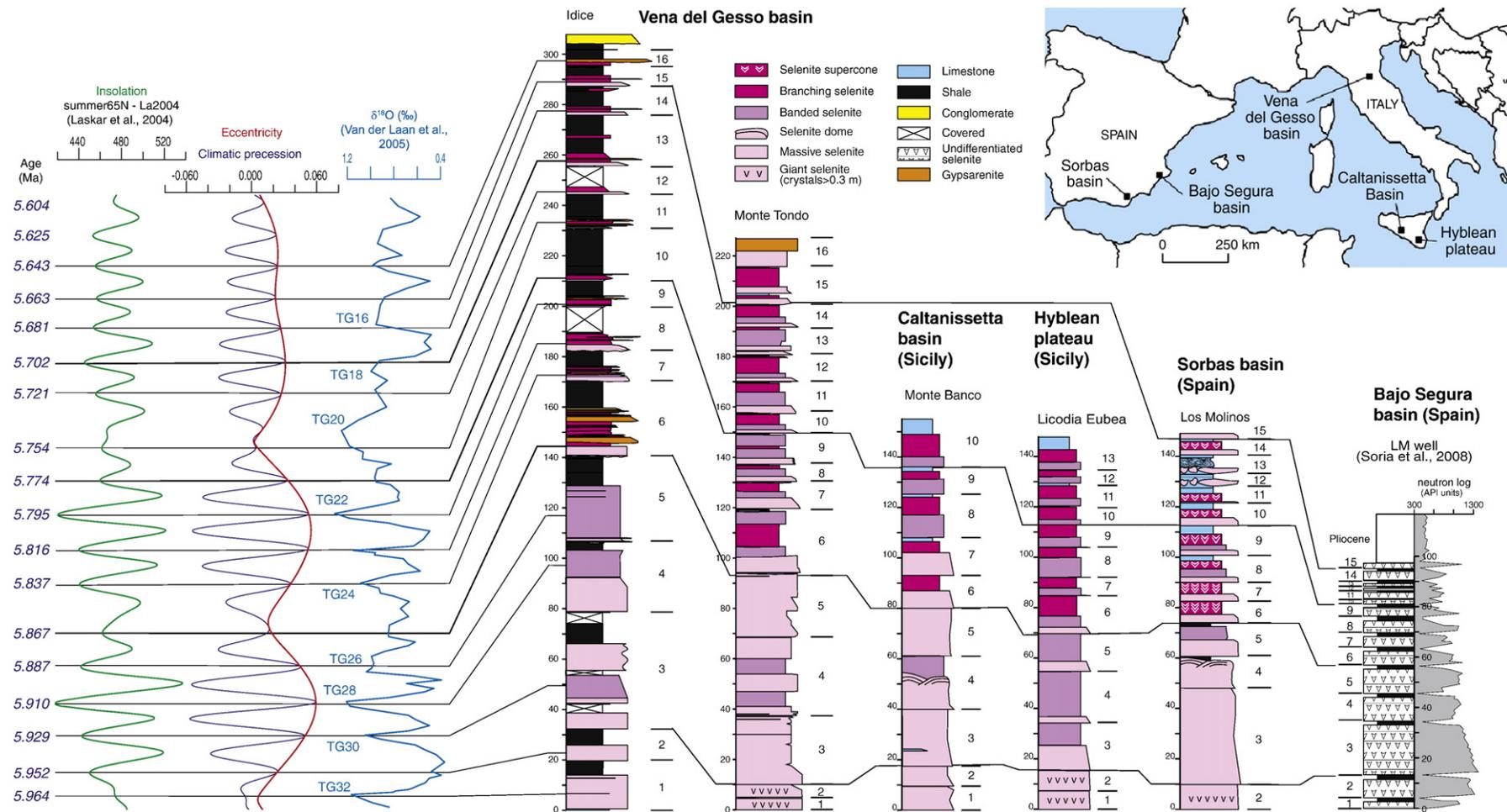


Fig. 13. Refined general correlation and astronomical tuning of the Primary Lower Gypsum across the Mediterranean. The banded selenite represents the aridity peak of the precessional climate cycles, whereas the shale layers were deposited during the humid phase. Note the impressive similarity in facies association and stacking pattern of the sections which are located thousands of kilometers apart in different geological settings. Insolation curve from Laskar et al. (2004); oxygen-isotope curve from Van der Laan et al. (2006) and Bajo Segura stratigraphy from Soria et al. (2008).

shallow, more oxygenated shelves. In their model, no sills are required to favor PLG precipitation. The fact that the only known PLG examples actually come from silled marginal basins is explained by the idea that structural sills have preserved evaporite units from erosion during the development of the Messinian erosional surface (MES) which affected the Mediterranean margins.

However, we observe that: 1) the model seems to imply an evaporitic system dominated by the settling of gypsum cumulates formed at the surface, but this is not the case for the PLG units, that consist of bottom-grown selenite; 2) structural sills bounding PLG basins are always tectonically active structures, whose Messinian movements promoted the partial to complete dismantling of evaporite through gravitational collapse (Roveri et al., 2003; Manzi et al., 2005); 3) in most cases, PLG units are actually giant, collapsed blocks which are not preserved in place (Fig. 2); as a consequence, resedimented evaporites are commonly found in deep basins facing silled marginal shelves; the only significant example of PLG unit preserved in place is the Sorbas basin because of the high and constant subsidence rates of the area throughout the Messinian.

We agree that brines may have formed in a superficial layer throughout the Mediterranean, but our idea is that only in silled, marginal sub-basins could those brines have been trapped, thus permitting concentration at the bottom for selenite growth. The locally observed delay in the onset of evaporite formation in some basins could be explained not only by a combination of factors including bathymetry and the local hydrological balance, but also the sill efficacy.

8. Astronomical tuning of the Lower Gypsum

The spectacular lithological cyclicity of the Primary Lower Gypsum that is expressed by the shale/selenite or carbonate/selenite cycles has been interpreted as controlled by astronomical precession (Krijgsman et al., 1999; Krijgsman and Meijers, 2008). According to this interpretation, evaporite deposition occurred during precession maxima (insolation minima), during relatively dry periods when evaporation exceeded precipitation. Each cycle would thus record a time span of about 21 ka.

If our interpretation model for the deposition of selenite is correct, then we have a new tool to refine the proposed astronomical tuning for the Primary Lower Gypsum. According to this new model, the banded selenite represents the lowest brine level interface (pynocline) and thus is possibly strictly related to insolation minima phases during the acme of the aridity peak in the precessional cycles (Fig. 13).

A refined general correlation scheme across the entire Mediterranean would thus correlate the shale and/or carbonate layers separating the selenite beds with the humid period in the precession climate cycle and the banded selenite facies with the aridity acme (Fig. 9). Given the very high rate of gypsum deposition the time span for selenite formation could have been relatively short, possibly a few thousand years at the peak of the aridity phase of the precessional cycle.

At the larger scale, the close relationships between the stacking pattern of gypsum cycles and the insolation curve are clearly evident, confirming that evaporite precipitation during the salinity crisis was directly controlled by climate oscillations driven by eccentricity-modulated precessional changes. The first gypsum bed was deposited at the 100 ka eccentricity minimum centered at around 5.97 Ma. The thickest gypsum cycles (3rd and 4th) correspond to the 400 ka eccentricity maximum at around 5.90 Ma, while the appearance of the branching selenite facies in the 6th cycle is coincident with the 100 ka eccentricity minimum at 5.84 Ma. The thin cycles from the 11th to the 16th developed in a phase of low eccentricity leading to the 400 ka minimum at 5.6 Ma which marks the end of the PLG deposition and stage 1 of the salinity crisis. This event is probably also related to the glacial peaks TG12 and TG14, but the role of an important tectonic pulse affecting large part of the Mediterranean basin also has to be taken into account (Roveri et al., 2008c; Roveri and Manzi, 2006).

9. Conclusions

The detailed study of the Primary Lower Gypsum in the Mediterranean has provided us with new tools to investigate such elusive sediments in the complex and controversial context of the Messinian salinity crisis. A Mediterranean-scale bed-by-bed correlation by means of facies analysis and physical stratigraphy appears clearly applicable for the first stage of the salinity crisis (5.96 to 5.61 Ma). A refinement of the orbital calibration suggests that each facies change in the sequence can be accurately dated: the banded selenite facies represent the peak of the aridity precessional cycle at insolation minima, whereas the shale and/or carbonate layers separating the gypsum beds correlate with the most humid phase. Each selenite cycle was deposited in a very short time interval, possibly a few thousand years.

The implications of such a large-scale correlation for sequences located thousands of kilometers apart and in different geological contexts are inescapable: the brine depth was probably not so shallow as previously thought, not certainly centimeters nor meters. Selenite deposition occurred only at the bottom of shallow restricted shelfal marginal basins less than 200 m deep at brine depths that were possibly lowered by drawdown. At the same time the deeper Mediterranean portions were euxinic and at such extreme conditions no gypsum could precipitate and only thin shale/dolostone couplets were deposited (CIESM, 2008; Roveri et al., 2008b; De Lange and Krijgsman, 2010). The stacking pattern and facies associations suggest a general shallowing-upward trend with a global change in hydrology starting from the 6th cycle (5.84 Ma ago), when the brines became current-dominated for all the Mediterranean marginal basins. This phase also records direct pulses of Atlantic seawater that entered the selenite basins filled with brines that in some marginal areas were considerably modified by input of continental water.

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