The Messinian salinity crisis: open problems and possible implications for Mediterranean petroleum systems

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Abstract

A general agreement on what actually happened during the Messinian salinity crisis (MSC) has been reached in the minds of most geologists, but in the deepest settings of the Mediterranean basin the picture is still far from being finalized and several different scenarios for the crisis have been proposed, with different significant implications for hydrocarbon exploration. The currently accepted MSC paradigm - the "shallow-water deep-basin" model - implying high-amplitude sea-level oscillations (>1500 m) of the Mediterranean up to its desiccation, is usually considered as a fact. As a consequence, it is on this model that the implications of MSC events on Mediterranean petroleum systems are commonly based.

Actually, an alternative, deep-water, non-desiccated scenario of the MSC is possible; it i) implies the permanence of a large water body in the Mediterranean throughout the entire Messinian salinity crisis, but with strongly reduced Atlantic connections and ii) envisages a genetic link between Messinian erosion of Mediterranean margins and deep brine development.

In this work we focus on the strong implications for the assessment of petroleum systems of the Mediterranean and adjoining areas (*e.g.*, Black Sea basin) that can be based on such a non-desiccated MSC scenario. In particular, the near-full basin model delivers a more realistic definition of Messinian source rock generation and distribution, as well as of the magnitude of water unloading processes and their effects on hydrocarbon accumulation.

The Messinian salinity crisis of the Mediterranean: the paradigm

The term "Messinian salinity crisis" (MSC) refers to the largest and geologically most-rapid set of high-amplitude environmental changes undergone by the peri-Mediterranean area during the Neogene and possibly the entire Phanerozoic. The sedimentary record of this event involves complex feedbacks between geodynamics, climate and biota, and resulted in a stratigraphy which left an indelible signature in the post-Messinian evolution of the Mediterranean basin, also with important implications for hydrocarbon exploration. Up to now a general agreement on what actually happened during the MSC, particularly in the deepest settings of the Mediterranean basin, is still far from clear; consequently, several different scenarios of the crisis are available (see Roveri *et al.*, 2014a).

This lack of consensus is mainly due to the difficulty in establishing a general, comprehensive, high-resolution stratigraphic framework for the upper Messinian. In fact, in this interval, due to the lack of fossils and for being fully included into the C3r chron, the classical bio-magnetostratigraphic tools cannot be used (Hilgen *et al.*, 2007; Roveri *et al.*, 2014a). Furthermore, most data come from onshore successions, which formed in shallow (0-200 m water depth) or intermediate-depth (200-1000 m water depth) sub-basins, while the deepest Messinian settings, where the largest volume of MSC products accumulated, are buried below the present-day Mediterranean abyssal plains. These deep deposits are virtually unknown, due to the difficulties (both technical and economic) in getting data through scientific drillings or in accessing industry data. Moreover, since onshore and deep offshore Messinian successions are physically disconnected, a synthesis and common view of the MSC remain very difficult to obtain (Roveri *et al.*, 2014a,c; Lofi *et al.*, 2011).

As a consequence, due to the need for additional deep basin data, all the different scenarios so far proposed should be considered as *theories* in need to be proven. However, the "shallow-water deep-basin" (SWDB - Hsü *et al.*, 1973) with its high-amplitude sea-level oscillations (>1500 m) up to its desiccation, is the current MSC paradigm (Roveri & Manzi, 2006; Roveri *et al.*, 2014b). This model is usually considered as a *fact*, with obvious implications in many related fields including hydrocarbon exploration, but such a view could lead to possible misinterpretation.

This model has undergone some modifications through time, all implying that at a certain point the Mediterranean desiccated almost completely and its slopes underwent a phase of subaerial exposure and vigorous erosion related to the rejuvenation of an entire fluvial drainage system (Lofi *et al.*, 2005; Ryan, 2009; Bache *et al.*, 2012). This phase of generalized exposure would have led to the formation of an erosional surface (Messinian erosional surface – MES), which is one of the main stratigraphic features in both onshore and offshore records and a key one for their correlation. The rapid water loading/unloading events would have caused significant pressure release and catastrophic fluid expulsion phenomena (Ryan et al., 1978; Bertoni *et al.*, 2013; Sacleux et al., 2013; Bertoni & Cartwright, 2015) with great impact on pre-existing hydrocarbon migration and preservation.

We think that an alternative scenario, implying the permanence of a large and deep-water body connected with the Atlantic Ocean throughout the MSC (Schmalz, 1969; Roveri *et al.*, 2014b), is not only possible but even more likely. In this paper we also discuss the more general implications of our new scenario for petroleum systems.

An alternative scenario: stratigraphic framework

Our scenario is based on a recently established chronology of the main MSC events mainly built on onshore data (Krijgsman *et al.*, 1999; Hilgen *et al.*, 2007; Manzi *et al*., 2013) , which includes both outcrop and subsurface data. A major consensus has been reached on this stratigraphic framework, which includes three evolutionary stages (Clauzon *et al*., 2006; CIESM, 2008; Roveri *et al.*, 2014a; Fig. 1), each of them characterized by a particular evaporite association recording significant hydrological changes in the Mediterranean basin. The latter are well documented by the $^{87}Sr/^{86}Sr$ Mediterranean curve (Fig. 1), which shows a significant, stepwise detachment from the global ocean curve during the MSC, suggesting a progressive hydrological isolation and/or an increase of the relative proportion of continental waters over the ocean ones (see Flecker *et al.*, 2002; Roveri *et al.*, 2014c). Each one of the three stages of the crisis shows a distinct range of $^{87}Sr/^{86}Sr$ values: >0.708900 for stage 1, between 0.708800 and 0.708900 for stage 2 and <0.708800 for stage 3. In the following section we briefly summarize the main characteristics of each MSC stage.

MSC onset and stage 1 (5.97-5.60 Ma)

The onset of the MSC occurred synchronously at 5.97 Ma (Manzi *et al.*, 2013), *i.e.* well after the base of the Messinian stage (7.246 Ma), following a long phase of progressive reduction of Atlantic connections and consequent restriction of Mediterranean circulation and water column stratification witnessed by the widespread cyclical deposition in deep marine settings of organic and opal-rich sediments (pre-MSC stage; *e.g.*, Tripoli Fm. of Sicily, Hilgen & Krijgsman, 1999).

The onset of the crisis is not necessarily coincident with the base of the lowermost evaporite bed, as sometimes erroneously envisaged in the literature (see for example Ochoa *et al*., 2015) but by a dramatic decrease of normal marine biota followed by their disappearance (Manzi *et al*., 2007; 2013; 2015). In fact, while the biological record of the onset of the crisis is synchronous throughout the Mediterranean basin and at any depth, the onset of the bottom-grown evaporites of the stage 1 (selenite gypsum of the Primary Lower Gypsum unit - PLG) is diachronous (Roveri et al., 2014a; Manzi et al., 2016). PLG evaporites started to form since 5.97 Ma only in shallow water, semiclosed, silled sub-basins developed along the Mediterranean continental margins (Lugli *et al*., 2010), whereas moving to deeper setting the onset of the PLG is progressively younger (Lugli et al., 2010; Dela Pierre et al., 2011; Roveri et al., 2014a). The water depth limiting the deposition of the bottom-grown gypsum (< 200 m, including areas beyond the shelf break) is suggested by the common occurrence of photosynthetic microorganisms communities trapped within primary gypsum crystals (mainly cyanobacteria; Panieri *et al.*, 2010). MSC onshore records clearly show that in deeper and/or ~~not~~ unsilled sub-basins, evaporite-free deposits accumulated, mainly consisting of organic-rich shales and dolostones barren of normal marine fossils (Manzi et al., 2007; Lugli *et al.*, 2010; Dela Pierre *et al.*, 2011; Ghielmi et al., 2013; Rossi et al., 2015).

Evaporite deposition was modulated by precession-controlled climatic oscillations inducing changes of the Mediterranean hydrological budget (Vai, 1997; Krijgsman *et al.*, 1999; Hilgen *et al.*, 2007). Up to 16 gypsum-shale couplets recording dry-wet precessional cycles formed in stage 1, allowing the end of this phase to be dated at 5.60 Ma (Krijgsman *et al.*, 1999; Roveri *et al.*, 2014a). The lithology of these cycles show an impressive similarity in terms of types of gypsum sedimentary facies, stacking patterns and overall trend, permitting pan-Mediterranean bed-by-bed correlation (Lugli *et al.*, 2010). The gypsum in these beds formed subaqueously; each precessional evaporitic cycle is characterized by a facies sequence recording a progressive increase in brine saturation, followed by a phase of relative dilution (Roveri et al., 2008a); it is worth noting that evidences of subaerial exposure and/or erosion are not observed within these cycles but only at the top of the PLG unit.

This PLG unit may locally consist of less than 16 gypsum cycles, due to the absence of the basal members (replaced by their laterally equivalent evaporite-free deposits; Manzi *et al.*, 2007; Dela Pierre *et al.*, 2011; Gennari *et al.*, 2013) or because of erosion and resedimentation during the subsequent stage 2 (Roveri *et al.*, 2001; 2014; Manzi *et al.*, 2005).

~~Differently to~~ Unlike what is claimed by some authors (e.g., Ochoa et al., 2015), where outcrop observations and complete subsurface data (seismics and boreholes) are available, it has been documented that the PLG evaporites are absent in deep-water and/or unsilled settings during the MSC stage 1 (Manzi et al., 2007; Lugli *et al.*, 2010; Dela Pierre *et al.*, 2011; Ghielmi et al., 2013; Rossi et al., 2015). Two different models have been proposed so far to explain this fact.

Lugli *et al.* (2010) suggest that bottom-grown gypsum only developed in shallow (< 200 m), silled sub-basins acting as bottom brine traps; De Lange & Krijgsman (2010), suggest that a sill is not necessary and that the main controlling factor is the rate of sulphate consumption due to degradation of organic matter which, in deep water below 200 m, would be greater than the supply rate of sulphate, thus hampering gypsum precipitation and preservation. ~~Thus,~~ Both models recognize the absence of primary evaporites of the first stage in deep-water settings and this fact is a fundamental observation for the correlation of deposits from shallow to deep parts of the basin.

Stage 2 (5.60-5.54 Ma)

The second stage of the crisis is characterized by a period of strong erosion of Mediterranean continental margins (MES) and by the concurrent deposition of huge volumes of highly-soluble primary evaporites (halite and K-Mg salts) as well as of resedimented PLG evaporites (i.e. as a clastic facies) in deeper sub-basins (Apennines, Sicily, Calabria, Tuscany, Cyprus). The resulting unit observed in onshore successions has been named Resedimented Lower Gypsum (RLG) and shows very rapid and significant lateral changes in terms of lithology and thickness, which is also related to tectonic activity affecting several Mediterranean areas in this stage. The clastic component of RLG unit mainly consists of gypsum turbidites, giant PLG olistoliths (Roveri *et al.*, 2001, 2008b; Manzi *et al.,* 2005) and microbially-derived brecciated limestones (*i.e.* the Calcare di Base of Sicily; Manzi *et al*., 2011); locally the RLG unit may mainly consist of terrigenous sediments (*i.e.* turbiditic sandstones of the Apennine~~s~~ foreland system depocenters – the Laga p.p. and Fusignano Formations; Roveri *et al.*, 2001; Manzi *et al*., 2005; Rossi *et al.*, 2015). This stage, which is considered the acme of the crisis, encompasses a very short time window, according to cyclostratigraphic considerations based on stage 1 (Roveri & Manzi 2006) and stage 3 cyclic patterns (Manzi *et al*., 2009). Thus the RLG unit would end at 5.54 Ma spanning no more than 60 ka.

Subaerial erosion of stage 1 evaporites (PLG) is commonly observed in onshore successions, suggesting a relative base-level fall whose amplitude, however, cannot be clearly defined (see Lugli *et al*., 2013; 2015; Roveri *et al*., 2014b). Onshore, the MES can be traced downbasin in deeper settings at the base of the RLG unit (Manzi *et al.*, 2005; 2007). It is worth noting that in such settings the deep water equivalent of PLG evaporites do not show evidence of subaerial exposure; in some places these deposits are eroded at the top and only partially preserved, thus suggesting subaqueous erosional processes.

Stage 3 (5.54-5.33 Ma)

The last stage of the MSC is probably the most enigmatic phase. Onshore successions consist of both shallow and relatively deeper water deposits. Sr isotope data (<0.708800) and fossils (mollusks and ostracods) suggest that surface waters underwent a significant dilution with the development of brackish environments throughout the Mediterranean. Deeper successions are usually barren of fossils, thus hampering palaeoenvironmental reconstructions. Despite this general signal of more diluted waters, primary evaporites (sulfates) are formed also in this stage, but only in the southern and easternmost sectors of the Mediterranean (e.g., Sicily, Calabria, Cyprus). These evaporites, named Upper Gypsum (UG) bear some lithologic similarities with stage 1 PLG evaporites, but can be easily distinguished based on their facies characteristics and particularly on their Sr isotope values (Manzi *et al.*, 2009). Like the PLG, the UG unit has a well-developed cyclical pattern induced by precession, which allows its accurate chronostratigraphic calibration. Stage 3 can be subdivided into substages 3.1 and 3.2, based on the sudden increase of terrigenous sediment input at around 5.42 Ma, especially in the northern and western Mediterranean sectors. Substage 3.2 is also characterized by the greatest development and diffusion of the inclusion of Lagomare faunal assemblages, which have been classically considered to derive from the Paratethys (e.g. Orszag-Sperber, 2006; Roveri et al., 2008a). In this low-salinity environment, some evidence of the permanence of the Atlantic connections is given by the occurrence of marine fish (Carnevale *et al*., 2008) and alkenons (Mezger *et al*., 2012). The return to normal marine conditions is sudden and marks the base of the Zanclean at 5.33 Ma, usually interpreted as related to a catastrophic re-opening of the Atlantic connections.

Seismic and well log expression of evaporitic units

When its 16 lithological cycles are largely preserved, the PLG unit may attain a total thickness ranging between 100 and 300 meters (Lugli et al., 2010), typically around 150-200 m in the best outcrops of the Apennines, Sicily and southern Spain. This unit does not have a peculiar seismic facies allowing to distinguish it from the evaporitic units of the other MSC stages, especially where only commercial, low-resolution seismic profiles are available. In this case, it appears as a thin seismic unit consisting of 1-2 parallel, high amplitude reflectors, similar to the RLG and UG units, where the latter are thinner. However, the PLG unit can be well identified in well logs due to its peculiar blocky pattern, as documented in many offshore and onshore boreholes (Roveri et al, 2005; Lugli et al., 2010; Rossi et al., 2015). Where high-resolution seismic profiles are available, PLG evaporites appear as a horizontal bedded unit (BU of Lofi et al., 2011) with a conformable base and an erosional top (e.g. the MES; see Maillard et al., 2014; Driussi et al., 2015); the erosional vs. non-erosional character of the bounding surfaces is probably the most useful criteria for distinguishing it from other evaporite-bearing units (i.e. the suggested equivalents of RLG and UG units, respectively the MU and UU units of Lofi et al., 2011). RLG, in particular, is usually thicker (up to 2 km in the deepest Mediterranean basins) and mainly consisting of halite, thus appearing as an acoustically transparent seismic unit; locally, the RLG unit may include chaotic seismic facies related to slump and/or debris flow deposits. Its base, the MES, is commonly unconformable at margins and becomes conformable in the basin center.

The onshore lesson: clues for shallow to deep correlations

This three-stage Messinian stratigraphic framework is based on the onshore record of the MSC but has a large potential for also being applied to deep offshore successions because of its robust physical stratigraphic architecture, constrained by key surfaces and time lines (*e.g.*, MES, Zanclean base) that can be easily recognized from available seismic and borehole data, allowing a sequence-stratigraphic approach (Roveri *et al*., 2008c; Rossi *et al.*, 2015). The three stages of the model are characterized by distinctive Sr isotope values that can be easily obtained analyzing the evaporite rocks and the fossils from cores or cuttings. A first attempt of suggesting an onshore-offshore correlation has been provided by Roveri *et al.* (2014c; Fig. 2) based on the recognition that onshore successions also include intermediate-depth (up to 1,000 m) depocenters showing continuous subaqueous deposition. These relatively deep settings are the key stratigraphic link between the shallow and the deep basin records.

According to this correlation, a possibility exists that the largest part of the evaporitic deposits lying in the deepest basins could have formed during MSC stage 2. The evaporitic unit in the western Mediterranean and in the Ionian basin is a tripartite seismic unit (the famous "Messinian trilogy"); the three seismic units (LU, Lower Unit; MU, Mobile Unit; UU, Upper Unit; Lofi et al., 2011) have been classically considered to be the offshore equivalent, from the bottom to the top, of the Lower Gypsum (*i.e.* the PLG), of the Sicilian salt and of the Upper Gypsum. In the Levantine Basin the evaporitic unit is not tripartite and only the MU is recognized (Lofi et al., 2011).

Actually the MES, marking the boundary between stages 1 and 2, can be traced downbasin to deep offshore areas, where it corresponds to the basal surface of the deep canyons (Lugli *et al.*, 2013) that possibly continued into the erosional features imaged at the base of the deep Levantine evaporites (Bertoni and Cartwright, 2007). The MES also represents a pervasive erosional surface of the Mediterranean slopes that can be followed in the deeper basins (BES; Lofi et al., 2011) and that progressively smooths out in the basin plain settings becoming a correlative conformity (BS; Lofi et al., 2011) marking the base of the Lower Evaporites (Lower Unit; Lofi *et al.*, 2005; 2011)**.**

Because of these characteristics the MSC stages 1 and 3 would be represented respectively by: i) a thin, evaporite-free layer below the base of the Lower Evaporites; ii) a relatively thin unit, mostly below seismic resolution, composed of shales with minor evaporites laying above the Mobile unit. As for the uppermost evaporites of the MU recovered from the DSDP-ODP cruises, Sr isotopes signature suggest they still belong to the MSC stage 2 (Roveri *et al.,* 2014c),.

An alternative scenario: erosion and deposition in a non-desiccated deep Mediterranean basin

The shallow water-deep basin model (SWDB) is mainly based on: 1) the interpretation of the erosional features of the margins as due to mostly subaerial processes, and 2) the supposed shallow-water to subaerial nature of the deep evaporites. As for the second point, recent studies (Hardie & Lowenstein, 2004; Lugli *et al.*, 2015) have demonstrated that the evaporites at the top of the MU do not show evidence for subaerial exposure and could have precipitated at any water depth. As for the first point, it was possible to document that only the~~ir~~ shallower parts of the onshore successions underwent subaerial erosion during stage 2, while the intermediate-depth depocenters experienced continuous subaqueous deposition throughout the crisis and/or subaqueous erosion mainly by gravity flows and related slope failure processes.

Starting from these considerations, Roveri et al. (2014) suggest a genetic link between the deposition of salt in the deepest basins and the erosion along the basin slopes due to the downslope flow of hypersaline, dense waters which led to the formation of deep-water brines. This process is similar to the present-day cascading of dense shelf waters along the Mediterranean margins (Canals *et al*., 2006); together with sediment gravity flows (i.e. turbidites and hyperpycnal fluvial floods) these processes work together to shape submarine slopes and to cut gullies and canyons (Roveri *et al*., 2014b). We infer that the Messinian slopes were profoundly reshaped during the MSC, and particularly during stage 2, by forming new erosional features or by rejuvenating pre-existing ones, as documented along both the western (Lofi & Berné, 2008) and eastern (Lugli *et al.,* 2013) Mediterranean margins. However, the MES was not generated exclusively by subaqueous processes, since a moderate relative sea-level fall, ranging in amplitude between 200 m (Roveri et al., 2014b) and 550 m (Rossi et al., 2015) also promoted the subaerial exposure and erosion of the basin margins. It follows that the MES is a polygenic erosional surface with both subaerial and subaqueous tracts, mainly developed during the peak of the MSC and commonly superimposed on older features. Stage 2 was then characterized by two high-amplitude glacial episodes (TG12 and TG14; Fig. 1) and by an acceleration of active tectonic processes along the entire Africa-Eurasian margin, as clearly shown by the angular unconformity commonly associated with the MES. Thus, in our opinion, a number of geodynamic and climatic causes acted simultaneously to modify the water and the atmospheric circulation within the Mediterranean during the Messinian. These causes were likely linked to complex feedback mechanisms leading to an extreme amplification of processes still acting today along the Mediterranean margins. The Black Sea slopes are characterized by a widespread erosional surface of Messinian age whose origin has been usually interpreted as related to desiccation, similarly to the Mediterranean (Hsü & Giovanoli, 1979); however, Messinian evaporites are absent in the Black Sea (Tari et al., this volume). As occurs in modern time (Flood et al., 2008), we argue that during Messinian cascading of hypersaline, dense waters, together with sediment gravity flows, could have produced the Black Sea erosional surface as well. But in a different way from the Mediterranean, Black Sea deep brines might not have not reached high saturation values, thus explaining the lack of evaporitic deposits.

In our model the Mediterranean was a persistent water body characterized by reduced connections with the Atlantic, and by a hydrological budget controlled by regional climate oscillations and by exchanges with the freshwater reservoir of the Paratethys basin(s) (Krijgsman *et al.,* 2010). This general setting could well explain also the last portion of the salinity crisis, which was considered to be characterized by an empty Mediterranean basin with several isolated freshwater or brackish lakes. According to our model, this phase (MSC stage 3) was instead likely characterized by an overall positive hydrological budget and a high base-level, punctuated by cyclical episodes of relative base level fall (Roveri et al., 2008a; Manzi et al., 2009; Roveri et al., 2014a-c; Rossi et al., 2015). Also in this late stage the Mediterranean was a single, permanent water body, as suggested by the ostracod assemblages (Stoica *et al.*, 2016) and uniform Sr isotope values (Roveri *et al.*, 2014a-c).

An alternative scenario: implications for hydrocarbon exploration

The Messinian successions are characterized by an extreme lithological variability expressed in a complex stratigraphy which resulted in a diverse array of potential source rocks, reservoirs and seals. For these reasons, besides their own potential as a petroleum system, the Messinian sediments also played a substantial role for the other Mediterranean petroleum systems, especially for the pre-Messinian ones (see Pawlewicz, 2004; Belopolskyi *et al.*, 2012; Al-Belushi *et al.*, 2013; Bertoni *et al.*, 2015). We think that our chronostratigraphic framework and sequence-stratigraphic approach may help to better identify and characterize those potentials in a coherent scenario.

Here we will focus on two elements directly deriving from our model that should be considered for their potential implications for hydrocarbon exploration: the Messinian source rocks and the effects of base-level changes throughout the crisis.

The Messinian source rocks

Source rocks originate from zones of high organic productivity and where organic-rich sediments are deposited in a low-oxygen environment allowing their preservation. During the Messinian the intermediate and deep-water settings were characterized by water stratification throughout the salinity crisis and even before, due to restricted exchanges with the Atlantic, which eventually led to the formation of deep brines; this resulted in the development of conditions favoring the accumulation and preservation of organic-rich deposits.

The source rock potential of MSC deposits has been documented in several areas: the Chelif Basin (Northern Algeria; Arab et al., 2015), the Prinos-Kavala Basin (Northern Aegean; Kiomourtzi et al., 2008), the island of Zakynthos and the Hellenic Trench (Greece; Maravelis et al., 2013; 2015), and the Northern Apennines (Manzi et al., 2007). However, a full knowledge of the Messinian source rocks is lacking, mainly due to the difficulty in organizing the available scattered data and observations into a comprehensive and detailed stratigraphic framework.

In this respect our MSC scenario offers some clues for a better definition of the source rock potential. We show here a first attempt to systematically organize the available data concerning organic matter in order to assess their areal and temporal distribution and characteristics. We collected Rock-Eval Pyrolisis data (Espitalié et al., 1977) from the literature, also including a set of unpublished data, mainly from Northern Italy and Sicily (Fig. 3a). After age re-calibration of the available samples, we plotted the S2-TOC (Fig. 3b-f) and the Hydrogen and Oxygen Index (HI, OI; Fig. 3j-k) values of sediments belonging to the same stage from different areas. The compilation of these organic matter data into our three-stage~~s~~ chronostratigraphic model provides some revealing trends and features (see below).

Substantially every sample considered in this work is immature (Tmax <435°C), particularly those collected in exposed successions; however, local and regional-scale geological reconstructions document that in the main depocenters, Messinian organic-rich units may have reached burial depths sufficient for the attainment of thermal maturity.

S2-TOC values (Fig. 3b-f) provide an estimate of the petroleum potential, and show that most stage 1 and 2 values plot in an overall good potential field. Conversely, MSC Stage 3 is generally characterized by reduced organic carbon content and S2 values.

The different kerogen types were defined mainly based on the Hydrogen Index; in Fig. 3e-k we display modified Van Krevelen diagrams for samples with TOC > 0.5 % (note that roughly ~~a~~ 20% of these are not represented because ~~since~~ no S3 data were available). HI values show that organic matter of deep-water pre-MSC sediments and stage 1 range between type II and II-III kerogens (*sensu* Peters and Cassa, 1994); stage 2 organic matter plots between kerogen types II and I; conversely, stage 3 records a progressive shift towards kerogens types III-IV, possibly representing an increased influence of continental input in the latest stage of the MSC (see also the organic matter composition of the Northern Apennines Messinian units in figure 4).

Our results show that the deep-water equivalent of the evaporite deposits of stage 1 have a very good source rock potential, also considering that this unit, where it is preserved below the resedimented evaporite deposits, may have thicknesses in the order of several tens of meters in outcrop (≈ 60 m in the Northern Apennines; Fanantello borehole, Manzi *et al*., 2007), up to 400 meters in the subsurface (Po Plain foredeep basin; Rossi et al., 2015). Furthermore, in the deeper basins, where anhydrite derived from the transformation of clastic gypsum due to lithostatic loading (Manzi *et al.*, 2005; Lugli et al., 2013) may represent an efficient early seal, preventing migration of Messinian hydrocarbons.

In this scenario, the close association in deep settings of the potential source rock (*i.e.* deep water stages 1 and 2 deposits) directly overlain by or interlayered with clastic evaporite deposits may be of great importance for the reconstruction of hydrocarbon migration pathways and for the recognition of potential reservoirs. In this respect it is worth noting that frequently (e.g., Northern Apennines and Sicily), large-scale zones of sulphur mineralization are associated with RLG clastic evaporites. Sulphur formed after bacterial sulphate reduction of Messinian evaporites favored by hydrocarbon migration and leading to the transformation of the parent rock into sulphur-bearing limestone (Dessau et al., 1962; Manzi et al., 2011). Although hydrocarbons involved in these processes may be older sources, the close association of sulphate and organic-rich rocks may point to a Messinian source rock.

Amplitude of Mediterranean base-level changes

In the scenario of Roveri et al. (2014b) the amplitude of base-level changes during the salinity crisis was much less pronounced than usually envisaged; we think that the Mediterranean Sea experienced only a moderate relative base-level fall (Christeleit et al., 2015) and that desiccation, as well as a catastrophic refill (Hsü et al., 1973), did not occur. The lower slopes and the deep-water settings did not undergo subaerial exposure and erosion. It follows that the organic matter in the pre-MSC and in the stage 1 deposits was far better preserved than expected for a complete basin desiccation.

Besides these more obvious aspects, the desiccation scenario implies rapid and massive water loading/unloading in the order of thousands of meters (Ryan et al., 1978; Govers *et al.*, 2009; Sacleaux et al., 2013). These changes and their isostatic effects would cause overpressure and catastrophic fluid expulsions even through the thick Messinian evaporitic unit, that is usually considered an ideal seal (Bertoni & Cartwright, 2015). Another aspect would be the degradation and/or remigrations of pre-existing hydrocarbons (Al-Belushi *et al.*, 2013; Iadanza *et al.*, 2015) with important implications for assessing the overall quality of Mediterranean petroleum systems. In our model, the magnitude of these processes would be considerably lower, translating to a significantly lower exploration risk for pre-Messinian targets (cf. the Black Sea, Tari et al., this volume).

Conclusions

Far from being a "fact," as commonly considered, the desiccation model of the Messinian salinity crisis is only one of the several possible scenarios. We suggest that an alternative, deep-water, non-desiccated model for the MSC is not only possible, but also even more likely. This model has several important implications for the assessment of the Mediterranean petroleum systems, as well as of the adjoining area (e.g. Black Sea; Tari et al., this volume). We think that the impact of the model for source rock generation and distribution, as well as for the effects of water unloading for breaching pre-existing hydrocarbon accumulations, should be carefully considered and evaluated. Our new data and a re-consideration of all available data suggests that the pre-salinity crisis sediments and the stage 1 source rock have a greater potential than previously thought. In addition, the stage 2 resedimented deposits may provide an excellent seal especially at deep Mediterranean settings.

The onshore and offshore perspectives of the MSC will be reconciled only when deep drillings will hopefully reach the pre-salt unit and core data will be made available to the scientific community especially from sediments on the ocean floor of the Mediterranean. This obviously needs a great joint effort between academia and industry.

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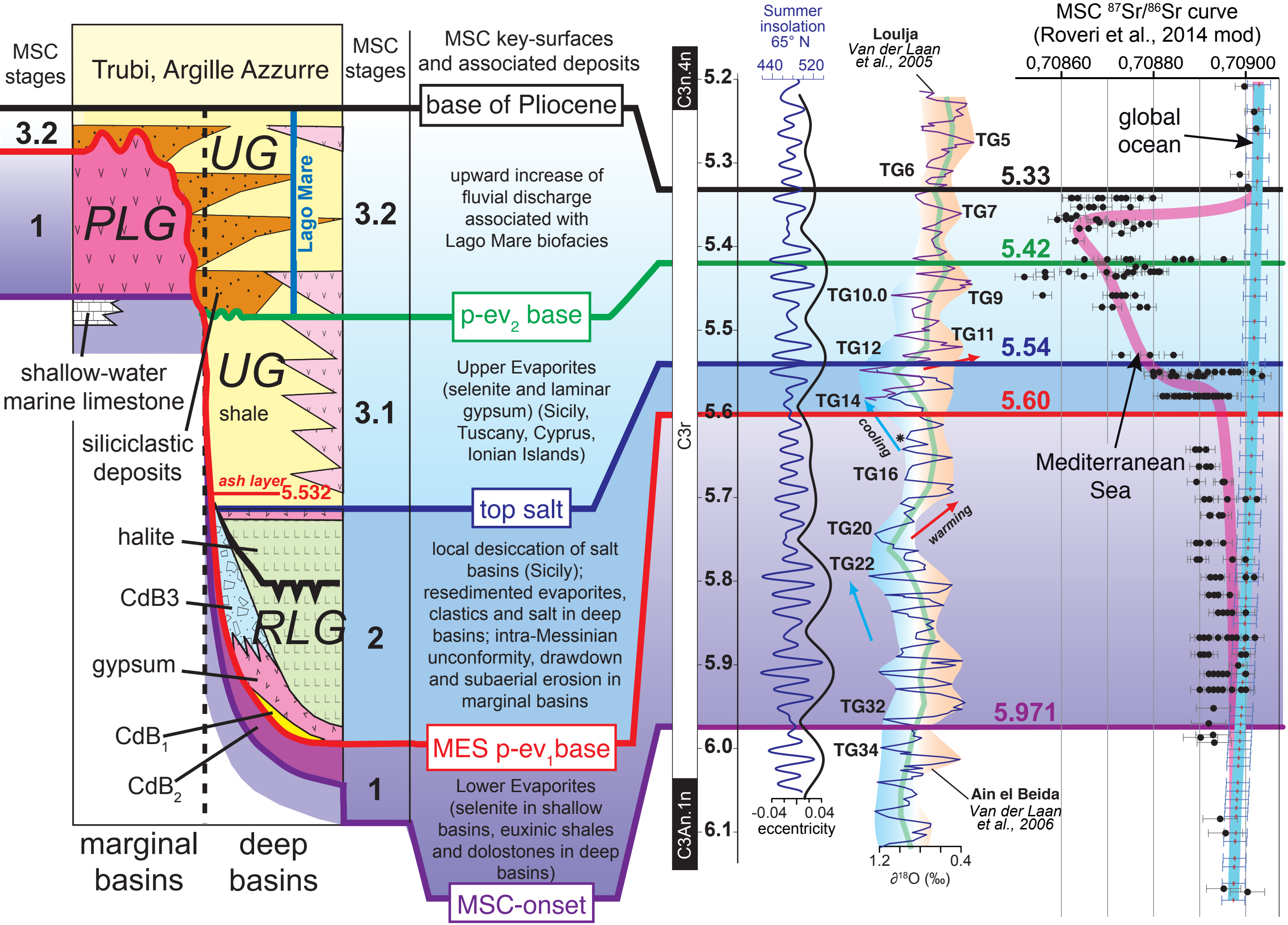
Figure captions

Fig. 1. Chronostratigraphy of the Messinian to Early Pliocene in the Mediterranean basin (modified from Roveri *et al.,* 2014a). MSC events are correlated to the oxygen isotope curve of the Atlantic, to the insolation curve and to the Sr isotope curve.

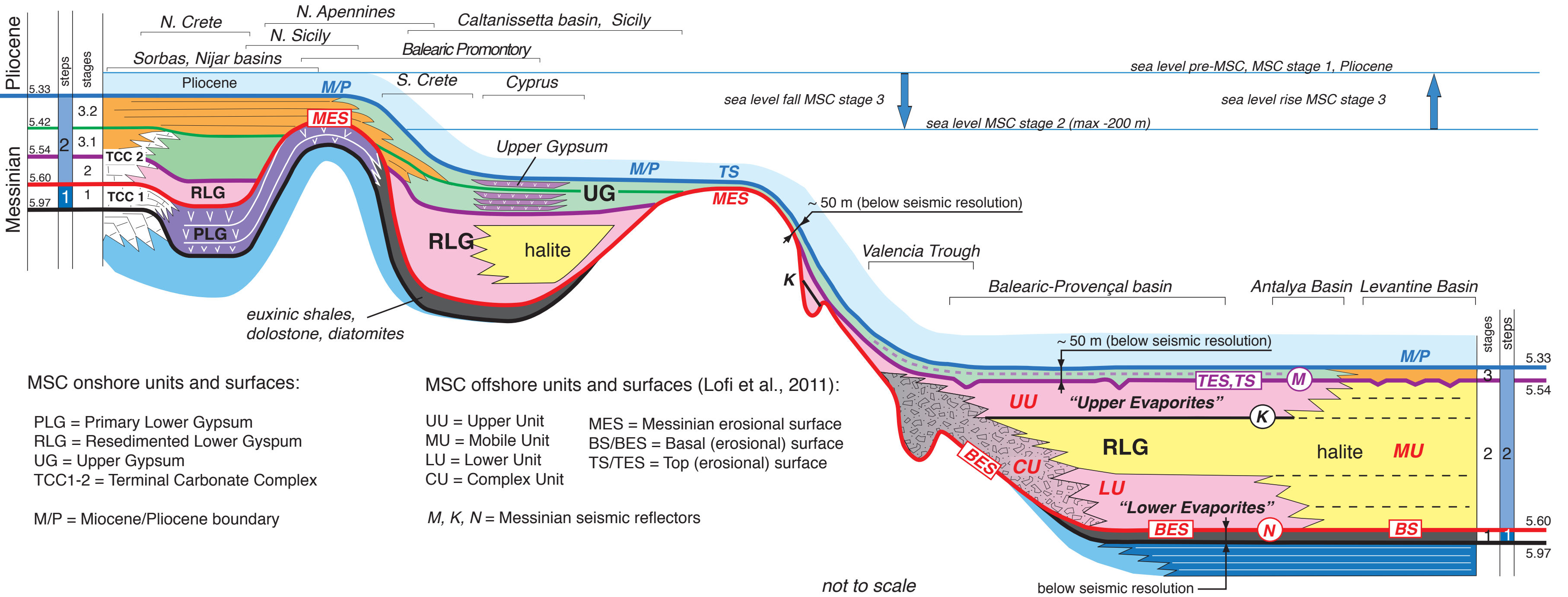
Fig. 2. Stratigraphic model of the Messinian deep basin deposits and their correlation with marginal basin successions (from Roveri *et al*., 2014c). Note that the “Messinian trilogy” of the western basin would actually almost completely belong to stage 2 and correlate with the salt unit (MU) of the eastern basin. Stage 3 deposits in deep basins would be limited to a very thin unit, with thicknesses usually below normal seismic profiles resolution.

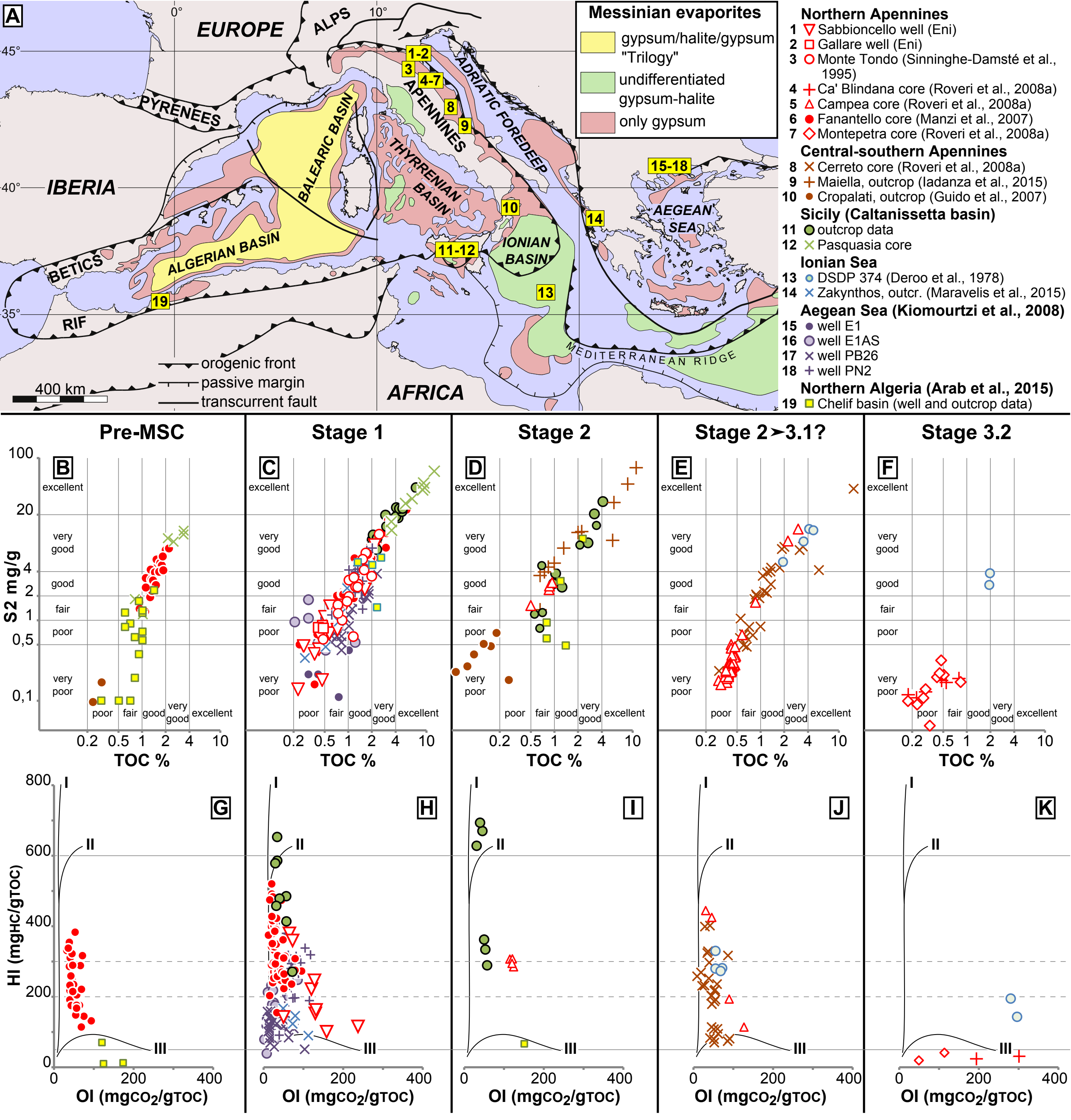
Fig. 3. Source rock potential of Messinian deposits in the different MSC stages. A, map of the central and western Mediterranean showing the provenance of the samples. b-f, S2-TOC plots showing the petroleum potential in particular of pre-MSC and deep stages 1-2 deposits. g-k, modified Van Krevelen diagrams for the different MSC stages. (only including samples with TOC>0,5, and for whom S3 data were available).

Fig. 4. Palynomorph and particulate organic matter distribution in the Messinian successions of the Northern Apennines foreland basin (data from shallow cores). Note the changes in composition in the different MSC stages showing an increase of continental derived organic matter in stage 3.

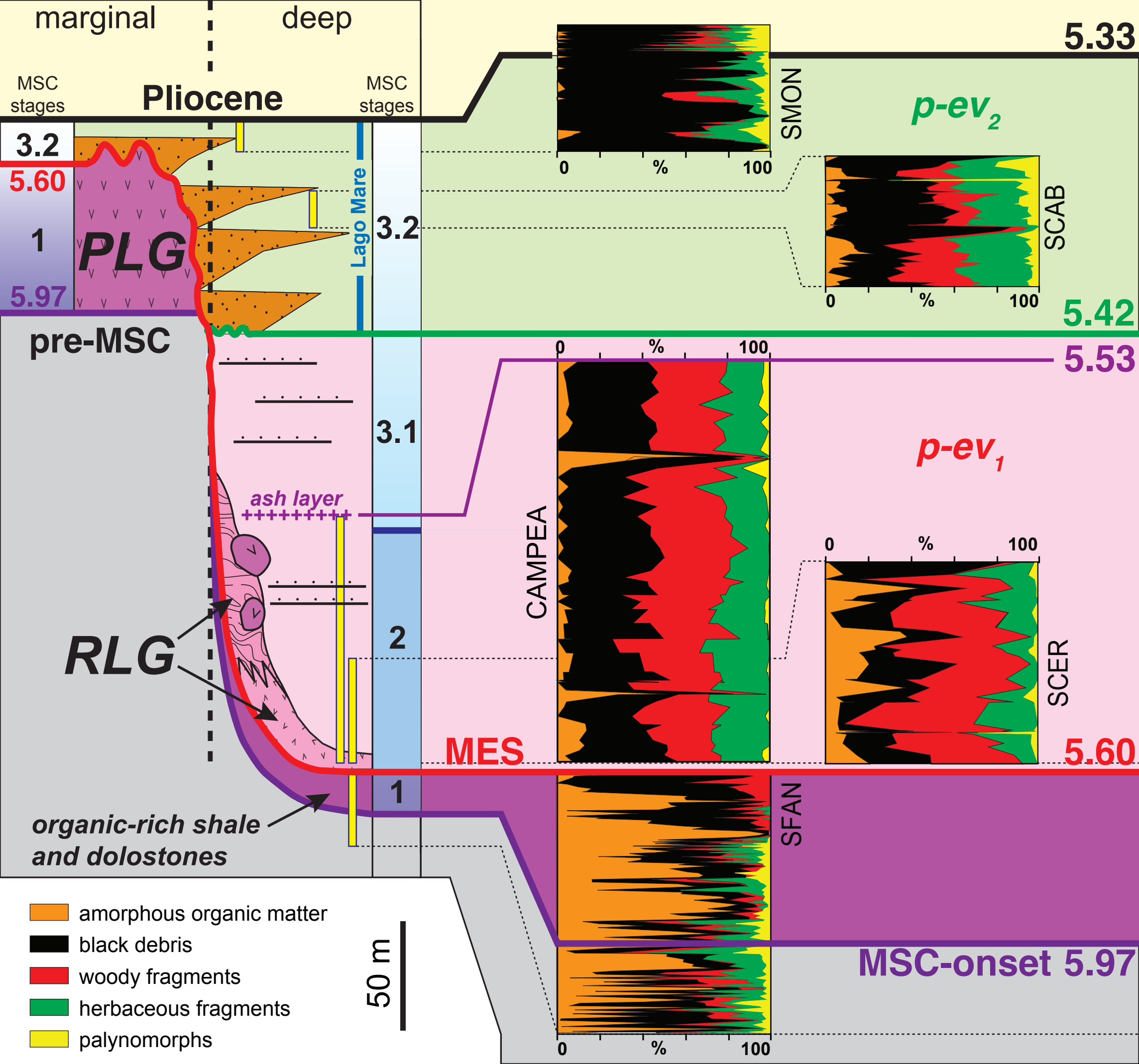


MSC stages
Trubi, Argille Azzurre
MSC stages
MSC key-surfaces and associated deposits
base of Pliocene
3.2
1
PLG
UG
Lago Mare
3.2
upward increase of fluvial discharge associated with Lago Mare biofacies
p-ev2 base
shallow-water marine limestone
UG
shale
3.1
Upper Evaporites (selenite and laminar gypsum) (Sicily, Tuscany, Cyprus, Ionian Islands)
siliciclastic deposits
ash layer 5.532
top salt
halite
CdB3
RLG
2
local desiccation of salt basins (Sicily); resedimented evaporites, clastics and salt in deep basins; intra-Messinian unconformity, drawdown and subaerial erosion in marginal basins
gypsum
CdB1
MES p-ev1 base
CdB2
1
Lower Evaporites (selenite in shallow basins, euxinic shales and dolostones in deep basins)
marginal basins
deep basins
MSC-onset
C3n.4n
C3r
C3An.1n
5.2
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6.0
6.1
Summer insolation 65° N
440 520
-0.04 0.04
eccentricity
Loulja Van der Laan et al., 2005
TG5
TG6
TG7
TG9
TG10.0
TG11
TG12
TG14
cooling
TG16
warming
TG20
TG22
TG32
TG34
Ain el Beida Van der Laan et al., 2006
1.2 0.4
∂18O (‰)
MSC 87Sr/86Sr curve (Roveri et al., 2014 mod)
0,70860 0,70880 0,70900
global ocean
5.33
5.42
5.54
5.60
5.971
Mediterranean Sea


N. Crete
N. Apennines
Caltanissetta basin, Sicily
N. Sicily
Balearic Promontory
Sorbas, Nijar basins
Pliocene
Messinian
steps
stages
5.33
5.42
5.54
5.60
5.97
3.2
3.1
2
1
TCC 2
TCC 1
Pliocene
M/P
MES
S. Crete
Cyprus
sea level pre-MSC, MSC stage 1, Pliocene
sea level fall MSC stage 3
sea level rise MSC stage 3
sea level MSC stage 2 (max -200 m)
Upper Gypsum
UG
M/P
TS
MES
RLG
PLG
RLG
halite
~ 50 m (below seismic resolution)
Valencia Trough
K
euxinic shales, dolostone, diatomites
Balearic-Provençal basin
Antalya Basin
Levantine Basin
~ 50 m (below seismic resolution)
M/P
TES,TS
M
UU
"Upper Evaporites"
K
RLG
halite
MU
BES
CU
LU
"Lower Evaporites"
BES
N
BS
below seismic resolution
not to scale
MSC onshore units and surfaces:
PLG = Primary Lower Gypsum
RLG = Resedimented Lower Gyspum
UG = Upper Gypsum
TCC1-2 = Terminal Carbonate Complex
M/P = Miocene/Pliocene boundary
MSC offshore units and surfaces (Lofi et al., 2011):
UU = Upper Unit
MU = Mobile Unit
LU = Lower Unit
CU = Complex Unit
MES = Messinian erosional surface
BS/BES = Basal (erosional) surface
TS/TES = Top (erosional) surface
M, K, N = Messinian seismic reflectors



A
Messinian evaporites
gypsum/halite/gypsum "Trilogy"
undifferentiated gypsum-halite
only gypsum
EUROPE
ALPS
PYRENEES
IBERIA
BALEARIC BASIN
APENNINES
ADRIATIC FOREDEEP
THYRRENIAN BASIN
ALGERIAN BASIN
BETICS
RIF
IONIAN BASIN
AEGEAN SEA
MEDITERRANEAN RIDGE
AFRICA
orogenic front
passive margin
transcurrent fault
400 km
Northern Apennines
1 Sabbioncello well (Eni)
2 Gallare well (Eni)
3 Monte Tondo (Sinninghe-Damsté et al., 1995)
4 Ca' Blindana core (Roveri et al., 2008a)
5 Campea core (Roveri et al., 2008a)
6 Fanantello core (Manzi et al., 2007)
7 Montepetra core (Roveri et al., 2008a)
Central-southern Apennines
8 Cerreto core (Roveri et al., 2008a)
9 Maiella, outcrop (Iadanza et al., 2015)
10 Cropalati, outcrop (Guido et al., 2007)
Sicily (Caltanissetta basin)
11 outcrop data
12 Pasquasia core
Ionian Sea
13 DSDP 374 (Deroo et al., 1978)
14 Zakynthos, outcr. (Maravelis et al., 2015)
Aegean Sea (Kiomourtzi et al., 2008)
15 well E1
16 well E1AS
17 well PB26
18 well PN2
Northern Algeria (Arab et al., 2015)
19 Chelif basin (well and outcrop data)
Pre-MSC
Stage 1
Stage 2
Stage 2➤3.1?
Stage 3.2
B
C
D
E
F
excellent
very good
good
fair
poor
very poor
S2 mg/g
TOC %
G
H
I
J
K
HI (mgHC/gTOC)
OI (mgCO2/gTOC)



marginal
deep
MSC stages
Pliocene
MSC stages
5.33
SMON
0
%
100
p-ev2
SCAB
5.42
3.2
5.60
1
PLG
5.97
Lago Mare
3.2
pre-MSC
5.53
3.1
CAMPEA
p-ev1
ash layer
SCER
2
RLG
MES
5.60
1
SFAN
organic-rich shale and dolostones
amorphous organic matter
black debris
woody fragments
herbaceous fragments
palynomorphs
50 m
MSC-onset 5.97