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

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

3

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15

16 **Abstract**

17

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

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

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

35

36 **The Messinian salinity crisis of the Mediterranean: the paradigm**

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

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

58 As a consequence, due to the need for additional deep basin data, all the different scenarios so far
59 proposed should be considered as *theories* in need to be proven. However, the “shallow-water deep-
60 basin” (SWDB - Hsü *et al.*, 1973) with its high-amplitude sea-level oscillations (>1500 m) up to its

61 desiccation, is the current MSC paradigm (Roveri & Manzi, 2006; Roveri *et al.*, 2014b). This model
62 is usually considered as a *fact*, with obvious implications in many related fields including
63 hydrocarbon exploration, but such a view could lead to possible misinterpretation.

64 This model has undergone some modifications through time, all implying that at a certain point the
65 Mediterranean desiccated almost completely and its slopes underwent a phase of subaerial exposure
66 and vigorous erosion related to the rejuvenation of an entire fluvial drainage system (Lofi *et al.*,
67 2005; Ryan, 2009; Bache *et al.*, 2012). This phase of generalized exposure would have led to the
68 formation of an erosional surface (Messinian erosional surface – MES), which is one of the main
69 stratigraphic features in both onshore and offshore records and a key one for their correlation. The
70 rapid water loading/unloading events would have caused significant pressure release and
71 catastrophic fluid expulsion phenomena (Ryan *et al.*, 1978; Bertoni *et al.*, 2013; Sacleux *et al.*,
72 2013; Bertoni & Cartwright, 2015) with great impact on pre-existing hydrocarbon migration and
73 preservation.

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

78

79

80 **An alternative scenario: stratigraphic framework**

81 Our scenario is based on a recently established chronology of the main MSC events mainly built on
82 onshore data (Krijgsman *et al.*, 1999; Hilgen *et al.*, 2007; Manzi *et al.*, 2013) , which includes both
83 outcrop and subsurface data. A major consensus has been reached on this stratigraphic framework,
84 which includes three evolutionary stages (Clauzon *et al.*, 2006; CIESM, 2008; Roveri *et al.*, 2014a;
85 Fig. 1), each of them characterized by a particular evaporite association recording significant

86 hydrological changes in the Mediterranean basin. The latter are well documented by the $^{87}\text{Sr}/^{86}\text{Sr}$
87 Mediterranean curve (Fig. 1), which shows a significant, stepwise detachment from the global
88 ocean curve during the MSC, suggesting a progressive hydrological isolation and/or an increase of
89 the relative proportion of continental waters over the ocean ones (see Flecker *et al.*, 2002; Roveri *et*
90 *al.*, 2014c). Each one of the three stages of the crisis shows a distinct range of $^{87}\text{Sr}/^{86}\text{Sr}$ values:
91 >0.708900 for stage 1, between 0.708800 and 0.708900 for stage 2 and <0.708800 for stage 3. In
92 the following section we briefly summarize the main characteristics of each MSC stage.

93

94 **MSC onset and stage 1 (5.97-5.60 Ma)**

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

100 The onset of the crisis is not necessarily coincident with the base of the lowermost evaporite bed, as
101 sometimes erroneously envisaged in the literature (see for example Ochoa *et al.*, 2015) but by a
102 dramatic decrease of normal marine biota followed by their disappearance (Manzi *et al.*, 2007;
103 2013; 2015). In fact, while the biological record of the onset of the crisis is synchronous throughout
104 the Mediterranean basin and at any depth, the onset of the bottom-grown evaporites of the stage 1
105 (selenite gypsum of the Primary Lower Gypsum unit - PLG) is diachronous (Roveri *et al.*, 2014a;
106 Manzi *et al.*, 2016). PLG evaporites started to form since 5.97 Ma only in shallow water,
107 semiclosed, silled sub-basins developed along the Mediterranean continental margins (Lugli *et al.*,
108 2010), whereas moving to deeper setting the onset of the PLG is progressively younger (Lugli *et al.*,
109 2010; Dela Pierre *et al.*, 2011; Roveri *et al.*, 2014a). The water depth limiting the deposition of the
110 bottom-grown gypsum (< 200 m, including areas beyond the shelf break) is suggested by the
111 common occurrence of photosynthetic microorganisms communities trapped within primary

112 gypsum crystals (mainly cyanobacteria; Panieri *et al.*, 2010). MSC onshore records clearly show
113 that in deeper and/or ~~not~~ unsilled sub-basins, evaporite-free deposits accumulated, mainly
114 consisting of organic-rich shales and dolostones barren of normal marine fossils (Manzi *et al.*, 2007;
115 Lugli *et al.*, 2010; Dela Pierre *et al.*, 2011; Ghielmi *et al.*, 2013; Rossi *et al.*, 2015).
116 Evaporite deposition was modulated by precession-controlled climatic oscillations inducing
117 changes of the Mediterranean hydrological budget (Vai, 1997; Krijgsman *et al.*, 1999; Hilgen *et al.*,
118 2007). Up to 16 gypsum-shale couplets recording dry-wet precessional cycles formed in stage 1,
119 allowing the end of this phase to be dated at 5.60 Ma (Krijgsman *et al.*, 1999; Roveri *et al.*, 2014a).
120 The lithology of these cycles show an impressive similarity in terms of types of gypsum
121 sedimentary facies, stacking patterns and overall trend, permitting pan-Mediterranean bed-by-bed
122 correlation (Lugli *et al.*, 2010). The gypsum in these beds formed subaqueously; each precessional
123 evaporitic cycle is characterized by a facies sequence recording a progressive increase in brine
124 saturation, followed by a phase of relative dilution (Roveri *et al.*, 2008a); it is worth noting that
125 evidences of subaerial exposure and/or erosion are not observed within these cycles but only at the
126 top of the PLG unit.

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

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

136 Lugli *et al.* (2010) suggest that bottom-grown gypsum only developed in shallow (< 200 m),
137 silled sub-basins acting as bottom brine traps; De Lange & Krijgsman (2010), suggest that a sill is

138 not necessary and that the main controlling factor is the rate of sulphate consumption due to
139 degradation of organic matter which, in deep water below 200 m, would be greater than the supply
140 rate of sulphate, thus hampering gypsum precipitation and preservation. ~~Thus~~, Both models
141 recognize the absence of primary evaporites of the first stage in deep-water settings and this fact is a
142 fundamental observation for the correlation of deposits from shallow to deep parts of the basin.

143

144

145 **Stage 2 (5.60-5.54 Ma)**

146 The second stage of the crisis is characterized by a period of strong erosion of Mediterranean
147 continental margins (MES) and by the concurrent deposition of huge volumes of highly-soluble
148 primary evaporites (halite and K-Mg salts) as well as of resedimented PLG evaporites (i.e. as a
149 clastic facies) in deeper sub-basins (Apennines, Sicily, Calabria, Tuscany, Cyprus). The resulting
150 unit observed in onshore successions has been named Resedimented Lower Gypsum (RLG) and
151 shows very rapid and significant lateral changes in terms of lithology and thickness, which is also
152 related to tectonic activity affecting several Mediterranean areas in this stage. The clastic
153 component of RLG unit mainly consists of gypsum turbidites, giant PLG olistoliths (Roveri *et al.*,
154 2001, 2008b; Manzi *et al.*, 2005) and microbially-derived brecciated limestones (*i.e.* the Calcare di
155 Base of Sicily; Manzi *et al.*, 2011); locally the RLG unit may mainly consist of terrigenous
156 sediments (*i.e.* turbiditic sandstones of the Apennines foreland system depocenters – the Laga p.p.
157 and Fusignano Formations; Roveri *et al.*, 2001; Manzi *et al.*, 2005; Rossi *et al.*, 2015). This stage,
158 which is considered the acme of the crisis, encompasses a very short time window, according to
159 cyclostratigraphic considerations based on stage 1 (Roveri & Manzi 2006) and stage 3 cyclic
160 patterns (Manzi *et al.*, 2009). Thus the RLG unit would end at 5.54 Ma spanning no more than 60
161 ka.

162 Subaerial erosion of stage 1 evaporites (PLG) is commonly observed in onshore successions,
163 suggesting a relative base-level fall whose amplitude, however, cannot be clearly defined (see Lugli

164 *et al.*, 2013; 2015; Roveri *et al.*, 2014b). Onshore, the MES can be traced downbasin in deeper
165 settings at the base of the RLG unit (Manzi *et al.*, 2005; 2007). It is worth noting that in such
166 settings the deep water equivalent of PLG evaporites do not show evidence of subaerial exposure;
167 in some places these deposits are eroded at the top and only partially preserved, thus suggesting
168 subaqueous erosional processes.

169

170 **Stage 3 (5.54-5.33 Ma)**

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

189 and marks the base of the Zanclean at 5.33 Ma, usually interpreted as related to a catastrophic re-
190 opening of the Atlantic connections.

191 **Seismic and well log expression of evaporitic units**

192 When its 16 lithological cycles are largely preserved, the PLG unit may attain a total thickness
193 ranging between 100 and 300 meters (Lugli et al., 2010), typically around 150-200 m in the best
194 outcrops of the Apennines, Sicily and southern Spain. This unit does not have a peculiar seismic
195 facies allowing to distinguish it from the evaporitic units of the other MSC stages, especially where
196 only commercial, low-resolution seismic profiles are available. In this case, it appears as a thin
197 seismic unit consisting of 1-2 parallel, high amplitude reflectors, similar to the RLG and UG units,
198 where the latter are thinner. However, the PLG unit can be well identified in well logs due to its
199 peculiar blocky pattern, as documented in many offshore and onshore boreholes (Roveri et al, 2005;
200 Lugli et al., 2010; Rossi et al., 2015). Where high-resolution seismic profiles are available, PLG
201 evaporites appear as a horizontal bedded unit (BU of Lofi et al., 2011) with a conformable base and
202 an erosional top (e.g. the MES; see Maillard et al., 2014; Driussi et al., 2015); the erosional vs. non-
203 erosional character of the bounding surfaces is probably the most useful criteria for distinguishing it
204 from other evaporite-bearing units (i.e. the suggested equivalents of RLG and UG units,
205 respectively the MU and UU units of Lofi et al., 2011). RLG, in particular, is usually thicker (up to
206 2 km in the deepest Mediterranean basins) and mainly consisting of halite, thus appearing as an
207 acoustically transparent seismic unit; locally, the RLG unit may include chaotic seismic facies
208 related to slump and/or debris flow deposits. Its base, the MES, is commonly unconformable at
209 margins and becomes conformable in the basin center.

210

211 **The onshore lesson: clues for shallow to deep correlations**

212 This three-stage Messinian stratigraphic framework is based on the onshore record of the MSC but

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

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

230 Actually the MES, marking the boundary between stages 1 and 2, can be traced downbasin to deep
231 offshore areas, where it corresponds to the basal surface of the deep canyons (Lugli *et al.*, 2013)
232 that possibly continued into the erosional features imaged at the base of the deep Levantine
233 evaporites (Bertoni and Cartwright, 2007). The MES also represents a pervasive erosional surface
234 of the Mediterranean slopes that can be followed in the deeper basins (BES; Lofi *et al.*, 2011) and
235 that progressively smooths out in the basin plain settings becoming a correlative conformity (BS;
236 Lofi *et al.*, 2011) marking the base of the Lower Evaporites (Lower Unit; Lofi *et al.*, 2005; 2011).
237 Because of these characteristics the MSC stages 1 and 3 would be represented respectively by: i) a
238 thin, evaporite-free layer below the base of the Lower Evaporites; ii) a relatively thin unit, mostly

239 below seismic resolution, composed of shales with minor evaporites laying above the Mobile unit.
240 As for the uppermost evaporites of the MU recovered from the DSDP-ODP cruises, Sr isotopes
241 signature suggest they still belong to the MSC stage 2 (Roveri *et al.*, 2014c),
242

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

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

253 Starting from these considerations, Roveri *et al.* (2014) suggest a genetic link between the
254 deposition of salt in the deepest basins and the erosion along the basin slopes due to the downslope
255 flow of hypersaline, dense waters which led to the formation of deep-water brines. This process is
256 similar to the present-day cascading of dense shelf waters along the Mediterranean margins (Canals
257 *et al.*, 2006); together with sediment gravity flows (i.e. turbidites and hyperpycnal fluvial floods)
258 these processes work together to shape submarine slopes and to cut gullies and canyons (Roveri *et*
259 *al.*, 2014b). We infer that the Messinian slopes were profoundly reshaped during the MSC, and
260 particularly during stage 2, by forming new erosional features or by rejuvenating pre-existing ones,
261 as documented along both the western (Lofi & Berné, 2008) and eastern (Lugli *et al.*, 2013)
262 Mediterranean margins. However, the MES was not generated exclusively by subaqueous
263 processes, since a moderate relative sea-level fall, ranging in amplitude between 200 m (Roveri *et*

264 al., 2014b) and 550 m (Rossi et al., 2015) also promoted the subaerial exposure and erosion of the
265 basin margins. It follows that the MES is a polygenic erosional surface with both subaerial and
266 subaqueous tracts, mainly developed during the peak of the MSC and commonly superimposed on
267 older features. Stage 2 was then characterized by two high-amplitude glacial episodes (TG12 and
268 TG14; Fig. 1) and by an acceleration of active tectonic processes along the entire Africa-Eurasian
269 margin, as clearly shown by the angular unconformity commonly associated with the MES. Thus, in
270 our opinion, a number of geodynamic and climatic causes acted simultaneously to modify the water
271 and the atmospheric circulation within the Mediterranean during the Messinian. These causes were
272 likely linked to complex feedback mechanisms leading to an extreme amplification of processes
273 still acting today along the Mediterranean margins. The Black Sea slopes are characterized by a
274 widespread erosional surface of Messinian age whose origin has been usually interpreted as related
275 to desiccation, similarly to the Mediterranean (Hsü & Giovanoli, 1979); however, Messinian
276 evaporites are absent in the Black Sea (Tari et al., this volume). As occurs in modern time (Flood et
277 al., 2008), we argue that during Messinian cascading of hypersaline, dense waters, together with
278 sediment gravity flows, could have produced the Black Sea erosional surface as well. But in a
279 different way from the Mediterranean, Black Sea deep brines might not have not reached high
280 saturation values, thus explaining the lack of evaporitic deposits.

281 In our model the Mediterranean was a persistent water body characterized by reduced connections
282 with the Atlantic, and by a hydrological budget controlled by regional climate oscillations and by
283 exchanges with the freshwater reservoir of the Paratethys basin(s) (Krijgsman *et al.*, 2010). This
284 general setting could well explain also the last portion of the salinity crisis, which was considered to
285 be characterized by an empty Mediterranean basin with several isolated freshwater or brackish
286 lakes. According to our model, this phase (MSC stage 3) was instead likely characterized by an
287 overall positive hydrological budget and a high base-level, punctuated by cyclical episodes of
288 relative base level fall (Roveri et al., 2008a; Manzi et al., 2009; Roveri et al., 2014a-c; Rossi et al.,
289 2015). Also in this late stage the Mediterranean was a single, permanent water body, as suggested

290 by the ostracod assemblages (Stoica *et al.*, 2016) and uniform Sr isotope values (Roveri *et al.*,
291 2014a-c).

292
293 **An alternative scenario: implications for hydrocarbon exploration**

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

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

304 ***The Messinian source rocks***

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

311 The source rock potential of MSC deposits has been documented in several areas: the Chelif Basin
312 (Northern Algeria; Arab *et al.*, 2015), the Prinos-Kavala Basin (Northern Aegean; Kiomourtzi *et al.*,
313 2008), the island of Zakynthos and the Hellenic Trench (Greece; Maravelis *et al.*, 2013; 2015), and

314 the Northern Apennines (Manzi et al., 2007). However, a full knowledge of the Messinian source
315 rocks is lacking, mainly due to the difficulty in organizing the available scattered data and
316 observations into a comprehensive and detailed stratigraphic framework.

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

326 Substantially every sample considered in this work is immature ($T_{max} < 435^{\circ}\text{C}$), particularly those
327 collected in exposed successions; however, local and regional-scale geological reconstructions
328 document that in the main depocenters, Messinian organic-rich units may have reached burial
329 depths sufficient for the attainment of thermal maturity.

330 S2-TOC values (Fig. 3b-f) provide an estimate of the petroleum potential, and show that most stage
331 1 and 2 values plot in an overall good potential field. Conversely, MSC Stage 3 is generally
332 characterized by reduced organic carbon content and S2 values.

333 The different kerogen types were defined mainly based on the Hydrogen Index; in Fig. 3e-k we
334 display modified Van Krevelen diagrams for samples with TOC > 0.5 % (note that roughly a 20%
335 of these are not represented because since no S3 data were available). HI values show that organic
336 matter of deep-water pre-MSC sediments and stage 1 range between type II and II-III kerogens
337 (*sensu* Peters and Cassa, 1994); stage 2 organic matter plots between kerogen types II and I;
338 conversely, stage 3 records a progressive shift towards kerogens types III-IV, possibly representing

339 an increased influence of continental input in the latest stage of the MSC (see also the organic
340 matter composition of the Northern Apennines Messinian units in figure 4).

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

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

359

360 *Amplitude of Mediterranean base-level changes*

361 In the scenario of Roveri *et al.* (2014b) the amplitude of base-level changes during the salinity crisis
362 was much less pronounced than usually envisaged; we think that the Mediterranean Sea

363 experienced only a moderate relative base-level fall (Christeleit et al., 2015) and that desiccation, as
364 well as a catastrophic refill (Hsü et al., 1973), did not occur. The lower slopes and the deep-water
365 settings did not undergo subaerial exposure and erosion. It follows that the organic matter in the
366 pre-MSC and in the stage 1 deposits was far better preserved than expected for a complete basin
367 desiccation.

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

377

378 **Conclusions**

379 Far from being a “fact,” as commonly considered, the desiccation model of the Messinian salinity
380 crisis is only one of the several possible scenarios. We suggest that an alternative, deep-water, non-
381 desiccated model for the MSC is not only possible, but also even more likely. This model has
382 several important implications for the assessment of the Mediterranean petroleum systems, as well
383 as of the adjoining area (e.g. Black Sea; Tari et al., this volume). We think that the impact of the
384 model for source rock generation and distribution, as well as for the effects of water unloading for
385 breaching pre-existing hydrocarbon accumulations, should be carefully considered and evaluated.
386 Our new data and a re-consideration of all available data suggests that the pre-salinity crisis

387 sediments and the stage 1 source rock have a greater potential than previously thought. In addition,
388 the stage 2 resedimented deposits may provide an excellent seal especially at deep Mediterranean
389 settings.

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

394

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400 interpretation.

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639 **Figure captions**

640

641

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

645

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

651

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

657

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

661





