Organic-rich shales from internal Betic basins (SE Spain): potential source rocks analogs for the pre-Messinian Salt play in the western Mediterranean

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Southeastern Spain has a large number of Late Neogene basins with substantial evaporitic deposits that developed under an overall NNW-SSE compressional regime related to the African-European tectonic plates collision. Located in the Betic Cordillera, they can be considered as marginal Mediterranean basins that became gradually isolated during the Tortonian and Early Messinian due to tectonic uplift. Different evaporitic units accumulated in these basins during isolation and, in several cases, evaporitic conditions were associated to episodes of important organic matter accumulation. Results obtained from Late Tortonian to Early Messinian shales collected from boreholes, mines and outcrops in the internal Betic basins of Las Minas de Hellín, Cenajo and Socovos are presented. The organic matter was studied under fluorescence and scanning electron microscopy (SEM), and the main geochemical characteristics defined. They show a relation between organic-rich intervals with high potential of hydrocarbon generation, native sulfur, bio-induced dolomite and evaporitic deposits. These organic-rich shales can be found before, during and after the evaporitic episodes. Results from the present study are compared with those previously obtained in the pre-evaporitic deposits of the Lorca Basin that showed high oil generation potential, a restricted-marine origin of the organic matter and a low degree of maturity. The occurrence of such potential source rocks in several basins points to a broad regional distribution. At a larger scale, in the Mediterranean Basin, organic-rich sediments were deposited before and during the Messinian Salinity Crisis. The studied examples could represent analogs for potential source rocks of the pre-Messinian salt play in the Western Mediterranean.

Evaporitic basins commonly present anoxic or euxinic conditions during their initial stages of evolution. These episodes usually mark a period of isolation and water stratification in the Basin allowing the accumulations of organic rich sediments (Ortí, 2010). During these episodes, an intense sulfate reduction activity of bacterial origin that inhibits the precipitation of gypsum occurs (Neev and Emery, 1967; Friedman, 1972; Busson, 1978).

This study presents results from geochemical analysis of organic-rich shales of Late Tortonian to Early Messinian age. The samples were collected from different basins (Socovos, Las Minas de Hellín, Cenajo) located in the internal part of the Betic Cordillera (SE Spain). The organic matter was characterized and results compared with those previously obtained in the pre-evaporitic deposits of the Lorca Basin (Permanyer et al., 1994).

The study of organic-rich sediments from internal evaporitic basins of the Betic Cordillera can help to better understand the relationships between this type of sediments and evaporites. The initial objective of this study was to compare the depositional environment, source rocks characteristics and hydrocarbon generation potential of contemporaneous sediments from different basins to understand to what extent they might represent a regional event. If a broad regional extension could be inferred for these sedimentary units, they would become of great interest as source rocks analogs to petroleum systems possibly underlying the Messinian evaporites in the Mediterranean.

**GEOLOGICAL SETTING**

The origin of the Betic Cordillera in SE Iberia is related to the Neogene convergence of the Eurasian and African plate boundaries. Two major geological domains can be differentiated in this orogen: the Internal and External Zones. The Internal Zone is located adjacent to the Alborán Sea and mainly consists of metamorphic rocks. The External Zone comprises sediments deposited on the passive margin of Iberia (Fig. 1).
During the Serravallian the Betic Cordillera was in the initial phase of construction, and most of the marine sedimentation occurred in platform and pelagic environments. The region was part of the so-called North-Betic seaway, where extensive mixed clastic and carbonate (calcarenites) sedimentation occurred. During the Early Tortonian the present geodynamic compressive regime (NNW-SSE direction) was established. Since the Late Tortonian, this general compression was accompanied by an isostatic readjustment and general uplift of the Cordillera with an associated radial extension. This process was responsible for the formation of a mosaic of interconnected marine corridors between the Atlantic Ocean and the Mediterranean Sea (Betic seaway) and post-orogenic basins separated by an archipelago of islands (Montenat, 1977; Sanz de Galdeano, 1990; Sanz de Galdeano and Vera, 1992) (Fig. 2). During the Late Tortonian, the basins located in the inner part of the Betic Cordillera (internal basins) were filled with marine sediments. The uplift of the Cordillera caused the progressive (and probably intermittent) disconnection between the different internal basins leading to isolation from the open sea until their continentalization. During this process the Neogene Betic basins recorded two different evaporitic episodes. The first is related to the closure of the Betic seaway during the Late Tortonian causing the restriction and isolation of the internal Betic basins. The second episode corresponds to the Messinian salinity Crisis (MSC) that was consequence of the restriction in the Atlantic inflow into the Mediterranean Basin between approximately 5.96 and 5.3Ma (Krijgsman, 1999). This evaporitic episode is recorded in the whole Mediterranean Basin. In the Betic Cordillera the MSC only affected a few basins still connected to the Mediterranean during the Messinian: Sorbas, Nijar, San Miguel de Salinas (SE Iberia) and Palma de Mallorca. Organic-rich sediments are associated with the Tortonian Betic evaporitic episode in the basins of Lorca, Las Minas de Hellín, Cenajo and Socovos. In marginal Mediterranean basins the Messinian pre-evaporitic deposits include euxinic shales and sapropels considered excellent potential source rocks in some cases (Roveri et al., 2016).

STUDY AREA

The study area comprises the Las Minas de Hellín, Cenajo, Socovos and Lorca basins, which are part of a cluster of post-orogenic basins that develop in the Betic Cordillera during the Tortonian (Fig. 1). Las Minas de Hellín, Cenajo and Socovos basins are located in the northernmost part of the Betic Cordillera, in the Prebetic zone. These basins have different extensions, ranging from a few km$^2$ (Híjar) to 200km$^2$ (Las Minas) and are typically elongate grabens or half-grabens. The outcropping Neogene sedimentary infill overlie Mesozoic rocks and can reach a thickness over 500m. The Lorca Basin is located 65km

![Figure 2. Paleogeography of SE Spain during Late Tortonian, with location of the studied basins (adapted from Corbí et al., 2012).](image-url)
South of Las Minas de Hellín Basin and is considered to be a pull-apart basin between the Internal and the External zones of the Betic Cordillera. The infilling of the Lorca Basin is over 1500m (Wrobel and Michalzik, 1999), and the transition from marine to non-marine sedimentation is recorded in La Serrata evaporites (Playà et al., 2000; García-Veigas et al., 2015) during the latest Tortonian (Krijgsman, et al., 2000). The studied Las Minas de Hellín, Cenajo and Socovos basins were probably isolated from the sea a little earlier since marine marls of Tortonian age are extensively represented in the Calasparra area (10km SE from Las Minas de Hellín Basin. Though the stratigraphic relation between Las Minas and Calasparra marine sediments is not clear, according to Foucault et al. (1987) these sediments underlie Las Minas de Hellín deposits. The recent discovery of marine evaporites in the nearby Jumilla Basin (20km North) suggest that the marine sedimentation persisted, at least episodically, in this internal basins of the Betic Cordillera until the early Messinian (Rossi et al., 2015). The presence of marine diatoms, forams and the marine isotopic composition of sulfates in gypsum samples from the Las Minas de Hellín Basin also suggest episodic marine incursions that allowed the formation of lagoons (Margalef, 1952, Servant-Vildary et al., 1990; Ortí et al., 2014).

STRATIGRAPHY AND SEDIMENTOLOGY

Despite each basin experienced its own evolutionary trends, a common general lithostratigraphic framework can be used, at list for the Cenajo and Las Minas de Hellín basins (Elizaga, 1994) which were probably connected during the late Miocene. This stratigraphy framework can be divided in 6 stages (Elizaga, 1994) (Fig. 3):

i) Turbidites alternating with fine grained sediments.

ii) Evaporitic cycles with a thickness between 3 and 8m (Ortí et al., 2014) formed by marls, sandstones, carbonates and gypsums. During this stage the native sulfur deposits were developed.

iii) Massive and laminated marls interbedded with carbonates and diatomite to the top. At the end of this stage took place an ultra-potassic volcanic event which allows the dating of the sediments. The last 40Ar/39Ar dating of these volcanic rocks provided by Rosell et al. (2011) gives an age of 7.65±0.09Ma. A Late Tortonian age is also reported from the Lorca Basin (Krijgsman et al., 2000).

iv) Slump dominated interval, interpreted as a seismites succession (Calvo et al., 2014). This interval reach a thickness of 40m (Cenajo Basin) and consist of deformed and resedimented marls, carbonates and diatomites.

v) Cyclic diatomitic unit with a metric alternation of marls and diatomite beds. This indicates an environment with an alternation of relatively wet (diatomite) and dry (marl) episodes. The stable isotopic composition of the carbonates indicates a general trend towards diluted conditions upwards in the section (Bellanca et al., 1989).

vi) Fluvial to deltaic siliciclastic unit with interbedded carbonates. This last stage of the basins infill is characterized by a progressive increase of detrital sedimentation. The age of the top of the overall sequence is known thanks to the finding of micromammals’ fossils attributable to the Late Tuolian, Messinian (Calvo et al., 1978).

The organic-rich levels were mainly identified in stages ii and iii (Jorge, 2014).

FIGURE 3. General stratigraphic section for the Cenajo and Las Minas de Hellín basins, modified from Elízaga, 1994. The age from volcanic rocks comes from Rosell et al., 2011. Organic-rich shales occur in units II and III.
SAMPLING AND ANALYTICAL METHODS

Sampling

Samples of organic-rich sediments were collected from outcrops and borehole cores available from the study area. In the Cenajo Basin, two stratigraphic sections were described and identified potential organic-rich intervals sampled (Figs. 4; 5). Well cores were sampled in Las Minas de Hellín basin (wells M-1, M-14, M-15 and M-19, Fig. 6) Socovos Basin (wells S-1, S-2, S-3 and S-4; Figs. 7; 8), and Lorca Basin (well L-3). Six of these cores are stored at the Instituto Geológico y Minero de España (IGME) core repository, and two cores are stored at the Faculty of Geology (Univ. Barcelona). The wells correspond to campaigns of sulfur, diatomite and shale-oil mining exploration conducted by IGME and MINERSA company during the past seventies and eighties (Fig. 8). The stratigraphic position of the samples in Las Minas de Hellín and Cenajo basins corresponds to massive and laminated marls interbedded with carbonate bearing sulfur nodules deposited during stage III that overlies the evaporitic deposits of stage II (Elizaga, 1994; Calvo and Elizaga, 1994; Ortí et al., 2014). The stratigraphy of Socovos Basin is poorly exposed and described based on drilling exploration; the studied samples were collected mainly from cores. The Lorca samples come from the Varied Member of Geel (1979) or Tripoli Member (Rouchy, 1982), this unit is 70m thick and is a transitional unit that overlies the Hondo Marl Formation (basinal marls) and underlies the Serrata evaporites. This member consists of marls, diatomic beds and some gypsum layers that alternate with carbonates bearing native sulfur nodules that were commercially exploited during the past century. According the IGME the average total accumulated thickness of organic-rich shales in the Lorca Basin is 2.25m and extends over an area of 11.55Km x 0.62Km (IGME, 1981, 1982).

Methods

Bulk mineralogy of the organic-rich levels (e.g. Fig. 9) was determined by X-Ray diffraction. The results were interpreted using the program X’Pert HighScore Plus. Fluorescence microscopy was used to study the petrology of organic components. The microscope was equipped with dry and oil-immersion lenses and observations of polished sections were made using a blue-violet light with a wavelength of 395-440nm. In addition, samples were studied using electron microscopes Quanta 200 and Jeol JSM-6510, accompanied by an Energy Disperse Spectrometry (EDS) analysis which allowed the identification of major elements. The samples were coated with gold in order to observe the organic matter.

All samples (n=70) were geochemically analyzed with a Rock Eval II pyrolysis device (RE), equipped with a carbon module. The sulfur content was determined by elemental analysis. Selected samples were powdered and then extracted with CH2Cl2, and extracts were fractioned into saturated and aromatic hydrocarbons, and polar compounds. Gas Chromatography - Mass Spectrometry (GCMS) full scan analyses were carried out on a Shimadzu QP2010 gas chromatograph-mass spectrometer with a DB-5 Agilent Technologies column (60m x 0.25mm i.d. ×
RESULTS

All studied samples consist of a finely-banded organo-mineral matrix displaying intense greenish-yellow and red fluorescence under blue violet reflected light (Fig. 10). The organic matter is optically amorphous. In some cases, authigenic quartz and dolomite crystals grew deforming the laminated material around them (Fig. 11). Pyrite clusters are present, as well as inorganic bodies, which...
have been determined to be sulfur aggregates. Marine planktonic foraminifera has been identified in samples from the Cenajo and Las Minas de Hellín basins and sponge spicules and diatoms are abundant in the Cenajo Basin samples (Fig. 11).

Organic richness and oil potential have been determined by Rock Eval pyrolysis (Espitalié et al., 1985-86) (Table I). The abundance of organic carbon is very high in all samples from both field and well samples. In general, samples show Total Organic Carbon (TOC) content between 3 and 16%, and oil potential up to 151mg HC/g rock. Samples from the Cenajo and Las Minas de Hellín basins present a high Hydrogen Index (HI) from 650 to 900mg HC/g rock. The values of HI for samples from Las Minas de Hellín basin (well M-14) and those from the upper part of the Cenajo outcrop section indicate a type I kerogen, while HI for samples from the lower part of the Cenajo field section and Las Minas de Hellín Basin (well M-19), indicate a type II kerogen (Fig. 12). In the Socovos Basin, the HI ranges from 700 to less than 350mg/g for the samples from the S-2 and S-4 boreholes. Contents of organic sulfur up to 28% occur in all the basins (Table II), and consequently the kerogen organic types are considered type I-S and II-S, respectively.

All these organic and mineral characteristics are similar in all investigated basins, and in agreement with those obtained for the Lorca Basin, where TOC reaches 22%, oil potential is up to 200mg HC/g of rock, HI is around 800 and sulfur content between 6 and 16% (Permanyer et al., 1994; Benali et al., 1995).

Owing to the absence of terrestrial organic particles, such as vitrinite, the evaluation of maturity was calculated using Tmax values from Rock Eval pyrolysis (e.g. Espitalié et al., 1985-86). All samples show Tmax values from 366° to 420°C, denoting immaturity. Immaturity is also indicated by the intense greenish-yellowish fluorescence.
of the organic matter, whereas red color could be related to the high sulfur content. In fact a negative alteration of the fluorescence has also been observed when samples were exposed for a medium to long time interval under blue-violet light: red color evolving to yellow or yellow-greenish after few minutes (<5 minutes).

Liquid chromatography was performed to obtain the SARA fractions (Saturates, Aromatics, Resines and Asphaltenes). As presented in Table II, resins and asphaltenes are the predominant fraction while saturated and aromatic hydrocarbon fractions represent a minority. The lower abundance of hydrocarbons is in agreement with the low degree of maturity of the samples. In this context, the kerogen cracking is incipient and, consequently, the generation of hydrocarbons is low.

Gas chromatograms of saturated hydrocarbons are shown in Figure 13. Distribution of \( n \)-alkanes mainly shows high odd predominance between \( n-C_{23} \) and \( n-C_{33} \) in all samples. The distribution of \( n \)-alkanes between \( n-C_{19} \) and \( n-C_{23} \) is predominant in the Las Minas de Hellín and Socovos basins. In the Cenajo Basin, \( n \)-alkanes present a more extended homologous series from \( n-C_{16} \) to \( n-C_{23} \). Isoprenoids, like pristane and phytane, show a higher abundance of phytane over pristane (Fig. 13). In the Cenajo, Las Minas de Hellín and Lorca basins the pristane/phytane ratio varies from 0.2 to 0.55, pristane/\( n-C_{17} \) range from 0.31 to 0.78, and \( \phi/n-C_{18} \) between 0.31 and 0.54 (except in Lorca Basin: 8.57) while in the Socovos Basin, the pristane/phytane ratio is 2 (Table III).
Sulfur is present in all studied samples. Values are up to 9% in the Cenajo Basin, 19% in Las Minas de Hellín and 28% in Socovos Basin (Table I). These contents are in the same range of those previously determined in the Lorca Basin (Permanyer et al., 1994). Organic Sulfur Compounds (OSC) were determined by GCMS. Figure 14 (benzothiophenes) shows the main OSC present in the Cenajo, Socovos and Lorca basins. The dominant organic sulfur compounds are dibenzothiophene, methyldibenzothiophenes and C2-alkyl-dibenzo thiophenes.

**INTERPRETATION**

As in the Lorca Basin (Permanyer et al., 1994), the studied organic matter is optically amorphous. This kerogen type most probably originated from bacteria (Largeau et al., 1994) and maybe algae (Largeau et al., 1990a, b; Le Berre, 1992). Distribution of n-alkanes mainly shows predominance of odd members between n-C_{23} and n-C_{35} in all samples. This type of n-alkanes predominance has been related with bacteria input (Johnson and Calder, 1973; Raynaud et al., 1989). It can also occur in algal mats from salt marshes and in recent microbial laminated deposits (Johnson and Calder, 1973; Raynaud et al., 1989; Thomas, 1982; Malinski et al., 1988), as well as in some petroleum source rocks (Raynaud et al., 1989). Some authors have related this bacterial activity with very confined, undisturbed, anoxic and evaporitic environments (Sinninghe Damste et al., 1986; Permanyer et al., 1994). The distribution of n-alkanes between n-C_{19} and n-C_{23} is dominant in the Las Minas de Hellín and Socovos basins suggesting a contribution of cyanobacteria, microalgae and algae. In the Cenajo Basin, n-alkanes present both extended series from n-C_{14} to n-C_{25}, denoting an algal contribution (Peters and Moldowan, 1993), and the n-C_{23} to n-C_{35} odd predominance, related with bacterial contribution.

Isoprenoids, like pristane and phytane, show a strong predominance of phytane over pristane (Fig. 7). In the Cenajo, Las Minas de Hellín and Lorca basins the pristane/phytane values are related with highly anoxic and immature evaporitic environments and have been described previously in the Lorca Basin (ten Haven et al., 1985; Sinninghe Damste et al., 1986; Permanyer et al., 1994). In the Socovos Basin, the pristane/phytane ratio is 2, indicating a less euxinic environment than that of the other basins, and with more siliciclastic input.

The high oil potential linked to the truly amorphous nature of kerogen from the studied samples favors the hypothesis of high bacterial contribution. The recognizable fine lamination observed on thin sections probably represents the small part of resistant polymers of non-bacterial origin, which have persisted through the “selective preservation” process (Permanyer et al., 1994).
In all studied basins, native sulfur is present in the deposits associated to the organic shales in a quantity important enough to be exploited commercially. All sedimentary sulfur ores occurs in evaporitic basins related to hydrocarbons or organic rich deposits (Ortí, 2010; Permanyer et al., 1991), where under anoxic conditions the bacterial reduction of the sulfate ion produced hydrosulfuric acid (H₂S) and bicarbonate (HCO₃⁻). The Sulfate Reduction Bacteria (SRB) activity avoids the precipitation of gypsum and generates H₂S which is later oxidized forming sulfur nodules:

\[
\text{SO}_4^- + 2\text{CH}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}_2\text{S}
\]

The presence of pyrite (Fe₂S) associated to the studied organic-rich shales is related to the reaction between the Fe²⁺ in solution and the H₂S resulting from the previous reaction. Among the carbonates, dolomite seems to be the dominant authigenic mineral (Fig. 8). Massive dolomite deposits has been characterized in Las Minas de Hellín Basin as bio-induced dolomite, and related to sulfate reducing bacteria (Lindtke et al., 2011), then it is reasonable to consider that accumulation of these SRB represents an important contribution to these oil shales.

The values of HI determined for Las Minas de Hellín Basin samples (well M-14) and those from the upper part of the Cenajo field section indicate a type II-S kerogen interpreted to be of marine origin. Whereas HI for samples from the lower part of the Cenajo field section and samples from well M-19 of the Las Minas de Hellín basin, falls within type I-S kerogen interpreted as lacustrine (Espitalié et al., 1985/1986). In the Socovos Basin, the HI ranges from 700 to less than 350 for samples from the S-2 and S-4 boreholes, suggesting kerogen II-S to type III. However no terrestrial input has been observed under the microscope.

In summary the sedimentary environment where these organic-rich shales formed corresponds to a confined, low energy, anoxic and stratified saline system with high productivity and good preservation of organic matter. The organic matter degradation via SRB hampered the gypsum precipitation and produced...
H₂S inducing the formation of different authigenic products: sulfur, pyrite and dolomite. During these anoxic events, the preserved organic matter, mainly of bacterial origin (amorphous), massively accumulated in the basin floor forming organic-rich laminated deposits. Due to insufficient burial, these materials did not reach the maturity level to generate hydrocarbons. These organic rich shales alternate with other sediments (diatomites, carbonates) that formed under different conditions.

The geochemical characteristics and depositional environments deduced from both field observations and chemistry from different basins of similar age suggest a comparable sedimentary evolution, and similar organofacies and source rock potential. Variations can be observed in age and degree of confinement, as marine influence varied from one basin to another in response to eustatic level fluctuation and structural evolution, but the formation of a potential regional source rock of very good potential can reasonably be speculated in some Betic Neogene evaporitic basins.

**COMPARISON WITH MESSINIAN SOURCE ROCKS OF THE MEDITERRANEAN**

At a different scale and age, the presence of organic-rich sediments below evaporites deposited during the Messinian Salinity Crisis (MSC) has been reported in several marginal basins of the Mediterranean. They are described from the Sorbas Basin of southern Spain (Sierro et al., 2001), the Chelif Basin of northern Algeria (Arab et al., 2015), the Caltanissetta Basin in Sicily (Roveri et al., 2008), Piemonte in northern Italy (de la Pierre et al., 2014), Apenines in Italy (Roveri et al., 2014; Manzi et al., 2007; Guido et al., 2007), at ODP site 654 in the Tyrrhenian Sea (Borsetti et al., 1990), the Ionian Basin (Deroo et al., 1978), the Prinos-Kavala Basin in northern Aegean (Kiomourtzi et al., 2008), the island of Zakynthos and the Hellenic Trench in Greece (Maravelis et al., 2013, 2015).

These deposits show that favorable conditions existed for organic matter preservation with a period of restriction and anoxia prior to the deposition of the Messinian evaporites. Some authors even suggest that these anoxic...
conditions and organic matter accumulation could have occurred in deeper areas contemporaneously to the deposition of the initial MSC evaporites (lower evaporites) existing in these marginal basins (de Lange and Krijgsman, 2010).

A recent study (Roveri et al., 2016) reviews the available data of these organic rich sediments, and tries to assess their type and temporal distribution. They show a TOC up to 4% and thermal immaturity with Tmax lower than 435ºC. The authors state that in the main depocenters these sediments could have suffered sufficient burial to reach thermal maturity.

According to Roveri et al., 2016, samples from stages I and II from MSC evaporites shows a good petroleum potential, while values for MSC stage III (Upper Gypsum) is characterized by reduced organic carbon content and low potential. The study defines kerogen types based on the HI and indicate that deep water pre-MSC sediments (stage I) contain kerogens of type II and III while sediments of stage II shows kerogens of type I and II, and sediments of stage III contain type III and IV kerogens (sensu Peters and Cassa, 1994) with greater terrestrial input. The authors conclude that the deep water equivalents of the evaporites deposited during stage I have a very good source rock potential. This unit is overlain by the Resedimented Lower Gypsum (RLG) representing an excellent seal for hydrocarbons. In the Apennines, large areas associated to the RLG have sulfur bearing limestones related to sulfate reduction bacteria activity favored by hydrocarbon migration (Dessau et al., 1962; Manzi et al., 2011). However, thickest deposits of Messinian source rocks should exist below the evaporites deposited in the deep Mediterranean Basin were information is not available.

The TOC and HI from studied samples of the Betic basins are higher than those reported for Messinian samples in the literature. Amorphous organic matter seems to dominate only during pre-MSC sediments. Also organic sulfur compounds (OSC, thiophenes), similar to the ones identified in the studied Betic basins have been described in deposits formed under hypersaline euxinic environments in the Messinian evaporitic basin in the northern Apennines (Sinninghe Damsté et al., 1986; ten Haven et al., 1985). This type of amorphous organic matter and OSC are related to bacterial origin in the Betic basins. Thus, it is reasonable to think that similar euxinic conditions occurred prior to the deposition of MSC evaporites in the deep Mediterranean Basin possibly generating a widely distributed organic matter accumulation.

Since 2009, major gas discoveries have been made in the pre-Messinian salt play offshore Israel (Tamar and Leviathan) and offshore Cyprus (Aphrodite). More than 30tcf of gas appears recoverable (Hodgson, 2012) from sandy deep water turbidite reservoirs of Lower Miocene age intercalated between Miocene and Oligocene shales. At Tamar, there are over 250 meters gross thickness of high quality reservoir with greater than 20 percent porosity and more than 500 millidarcies permeability (Durham, 2013). The 2015 giant Zohr gas discovery in offshore Egypt proved that shallow water carbonates of the margins connected to adjacent Miocene-Oligocene basinal shales could also be effective gas reservoirs. The major part of the gas discovered is of biogenic origin according to operators that also reported that there was a thermogenic contribution at Leviathan (Hodgson, 2012). The source of the biogenic gas is expected to be organic-rich silty layers of Miocene and Oligocene age interbedded with the sandy reservoir. Numerical models suggest that most of the biogenic methane generation ended after the MSC and confirm the probable existence of a deeper thermogenic system (Wygrala et al., 2014; Schneider et al., 2016).

Deposits from marginal Messinian basins are excellent candidates to source biogenic gas systems. They did
not suffer sufficient burial to generate thermogenic hydrocarbons but the presence of similar organic-rich deposits can be suspected in the offshore considering their widespread distribution onshore and homogeneous nature and depositional environment (Roveri, 2016). In the offshore of the Western Mediterranean Basin potential pre Messinian Salt source rocks have suffered a much greater burial and would be covered by up to ~4,000m of sediments (including detrital deposits derived from the Messinian subaerial exposure, Messinian evaporites and the post-Zanclean flood sediments (<5.3Ma)) according to geophysical data (Lofi et al., 2011a, b). The possible existence of both bio- and thermogenic plays below the excellent regional seal constituted by the Messinian Salt provides an exploration challenge in the Western Mediterranean offshore.

CONCLUSIONS

In the SE Spain Betic internal basins of Las Minas de Hellín, Cenajo and Socovos, the organic-rich shales of Upper Tortonian to Early Messinian age constitute an excellent example of immature petroleum source rocks. The sedimentation of these layers occurred before during or after the formation of evaporitic intervals. These source rocks are characterized by a high TOC and sulfur content, and a high oil generation potential. Organic matter is finely laminated and was deposited under euxinic conditions that did not allow bioturbation and at enough water depth to avoid wave disturbance.

During periods of organic matter accumulation, the depositional environment was restricted, sulfate-rich and most probably with water stratification. The organic matter identified is mainly amorphous, similar to that previously described in the Lorca Basin where the bacterial origin dominates. Seemingly, the organic matter is associated with native sulfur that was commercially exploited in the studied basins.

The accumulation of bacterial origin organic matter rich in sulfur associated to stratigraphic units that underlay (Lorca) or overlay (Cenajo, Las Minas de Hellín, Socovos) evaporitic deposits indicates a sedimentary scenario with restricted waters and euxinic environment rich in sulfate reducing bacteria. The presence of native sulfur and bio-induced dolomite associated to these deposits supports the hypothesis of an environment with strong SRB activity that avoids the precipitation of gypsum.

The sedimentary environment that allowed accumulations of amorphous organic matter with high oil potential in the studied Betic basins can be a small scale model for the Mediterranean Basin before and during the MSC.
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FIGURE 14. Mass fragmentograms (ions 184, 198 and 212) of aromatic fraction showing abundance of sulfur compounds. A, B, C are selected samples from the Cenajo, Las Minas de Hellín and Lorca basins, respectively. DBT: dibenzothiophenes, MDBT: methyl-dibenzothiophenes, C2-DBT: alkyl-dibenzothiophene.
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Pre-Messinian organic-rich shales from western Mediterranean region


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## APPENDIX I

### TABLE I. Pyrolysis Rock Eval data and sulfur content of selected samples from studied basins

<table>
<thead>
<tr>
<th>Basin</th>
<th>Well/Outcrop</th>
<th>Sample</th>
<th>TOC (%)</th>
<th>S1 [mg HC/g rock]</th>
<th>S2 [mg HC/g]</th>
<th>S3</th>
<th>HI [mg HC/g TOC]</th>
<th>OI</th>
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Pre-Messinian organic-rich shales from western Mediterranean region
Pre-Messinian organic-rich shales from western Mediterranean region

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**TABLE II.** Extract fractions (SARA) of selected samples. Data are expressed in weight percentages. SAT: saturated hydrocarbons; ARO: aromatic hydrocarbons; RES: resins; ASP: asphaltenes.

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<th>Ph/n-C18</th>
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**TABLE III.** Pristane/Phytane, Pristane/n-C17, phytane/n-C18 ratios, and sulphur content from selected samples.