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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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ABSTRACT

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..

KEYWORDS **Organic-rich sediments. Evaporites. Betic Cordillera. Mediterranean. Tortonian. Messinian. Source rock potential.**

INTRODUCTION

Since the late Tortonian, a NNW-SSE regional compression accompanied by an isostatic readjustment was established in Southeastern Spain. This geodynamic situation produced a general uplift in the Betic Cordillera that was responsible for the formation of a mosaic of interconnected marine corridors between the Atlantic Ocean and the Mediterranean Sea with post-orogenic basins separated by an archipelago of islands. The progressive uplift of the Cordillera caused the disconnection between the different internal basins and their progressive restriction and isolation leading to evaporitic conditions (Ott d'Estevou and Montenat, 1985; Sanz de Galdeano, 1990; Sanz de Galdeano and Vera, 1992).

Evaporitic basins commonly present anoxic or euxínic 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).

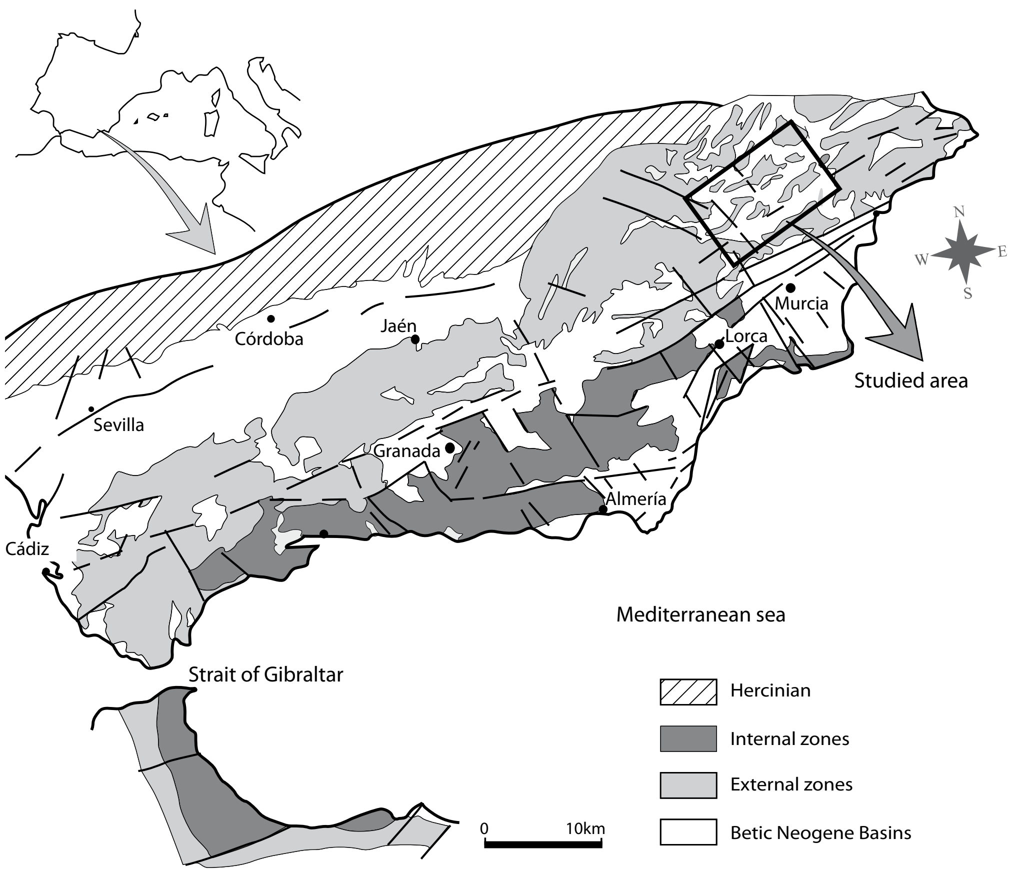

FIGURE 1. Simplified geological map of the Betic Cordillera showing the location of the studied basins.

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

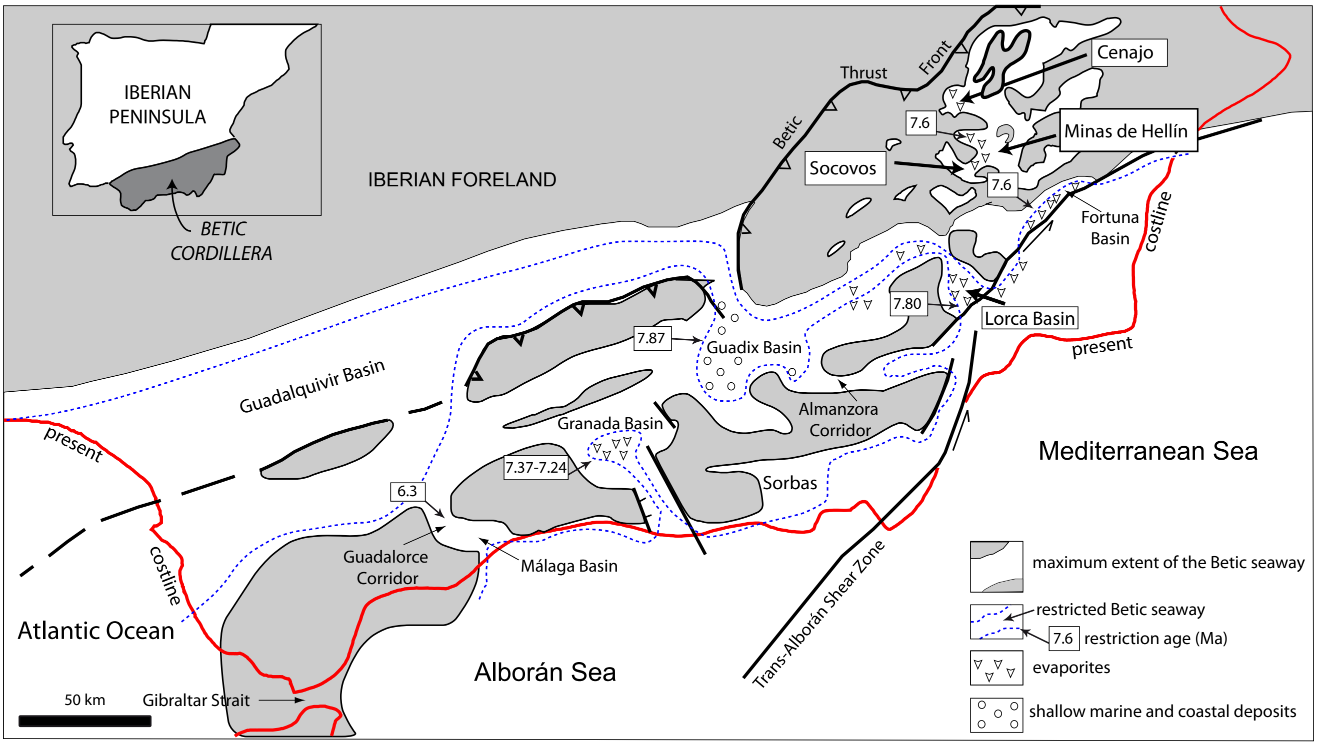

FIGURE 2. Paleogeography of SE Spain during Late Tortonian, with location of the studied basins (adapted from Corbí *et al.*, 2012).

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 Hellin 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 $^{40}Ar/^{39}Ar$ 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 Turolian, Messinian (Calvo *et al.,* 1978).

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

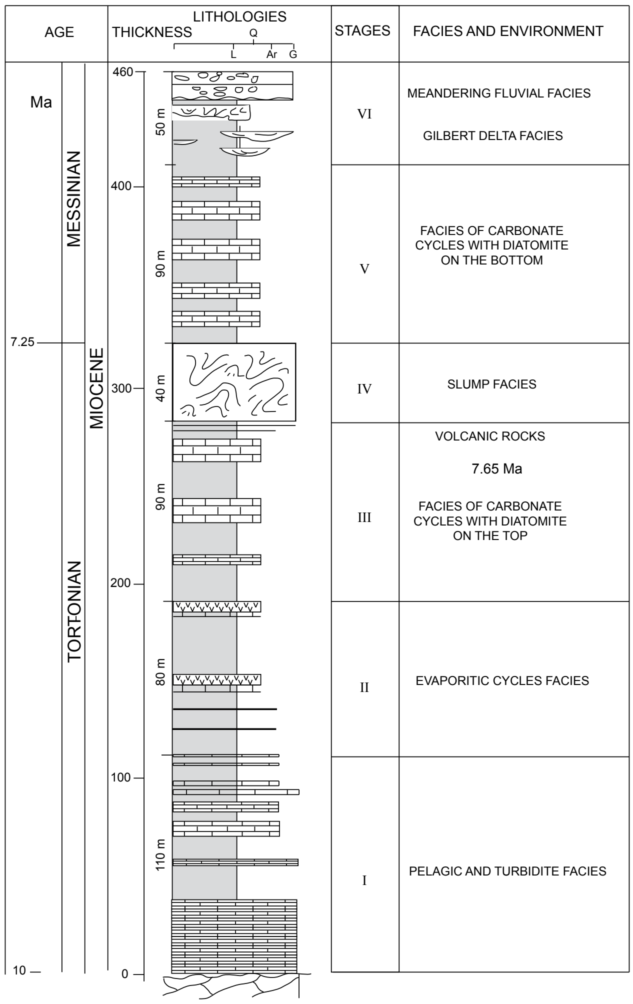

FIGURE 3. General stratigraphic section for the Cenajo and Las Minas de Hellín basins, modified from Elízaga, 1994. The age from volcanic rocks comes from Rosell *et al.,* 2011. Organic-rich shales occur in units II and III.

FIGURE 4. Field picture of the outcrop in the Cenajo Basin. The entire section has a thickness over 460m. The image shows the position of measured sections CMF and ECM with organic-rich shales, a mega slump and the diatomitic unit on the top.

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 CH_2Cl_2, 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. ×

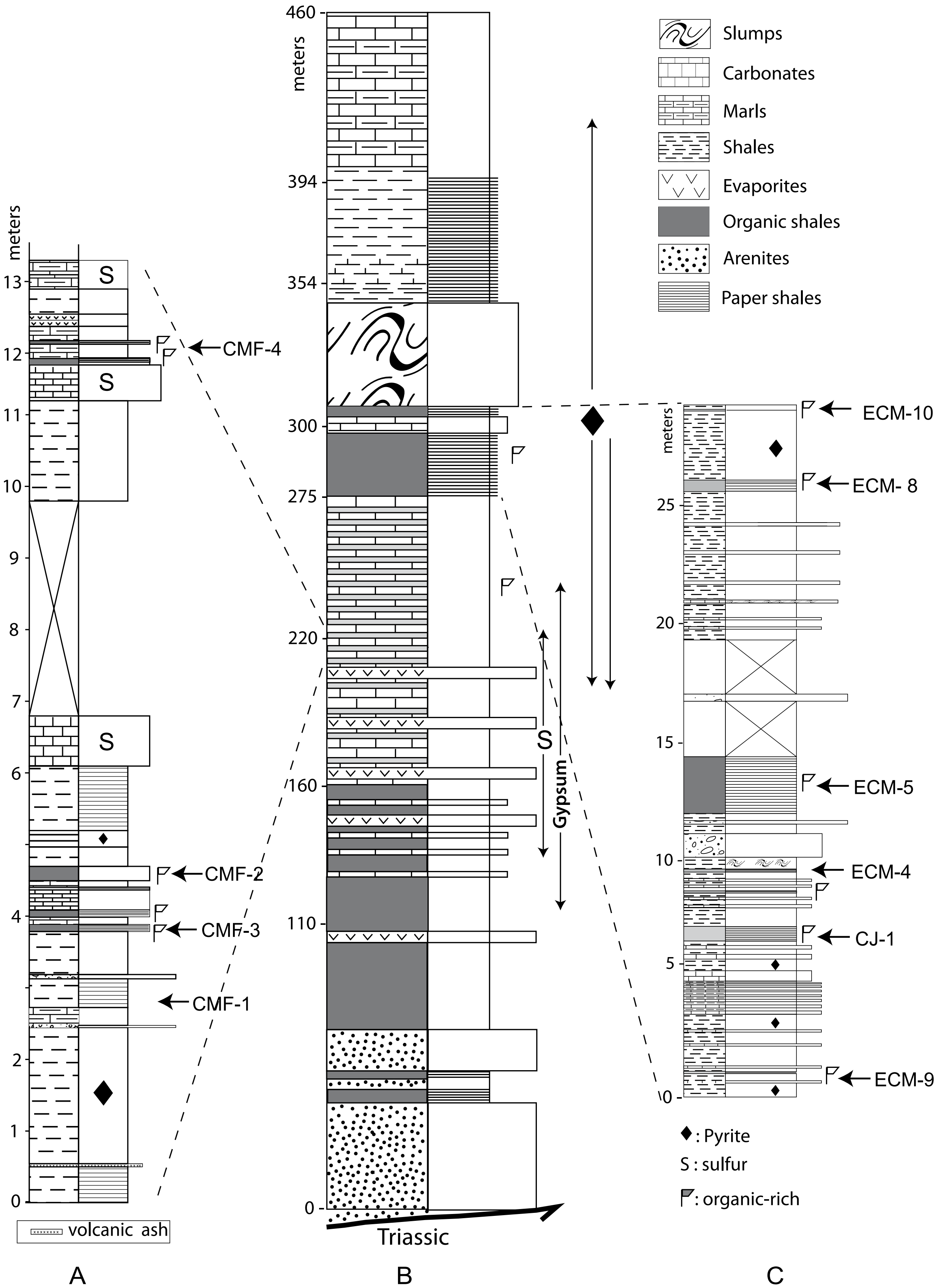

FIGURE 5. The Cenajo Basin field sections. A and C) indicating position of the studied samples. B) General section modified from Elizaga (1994).

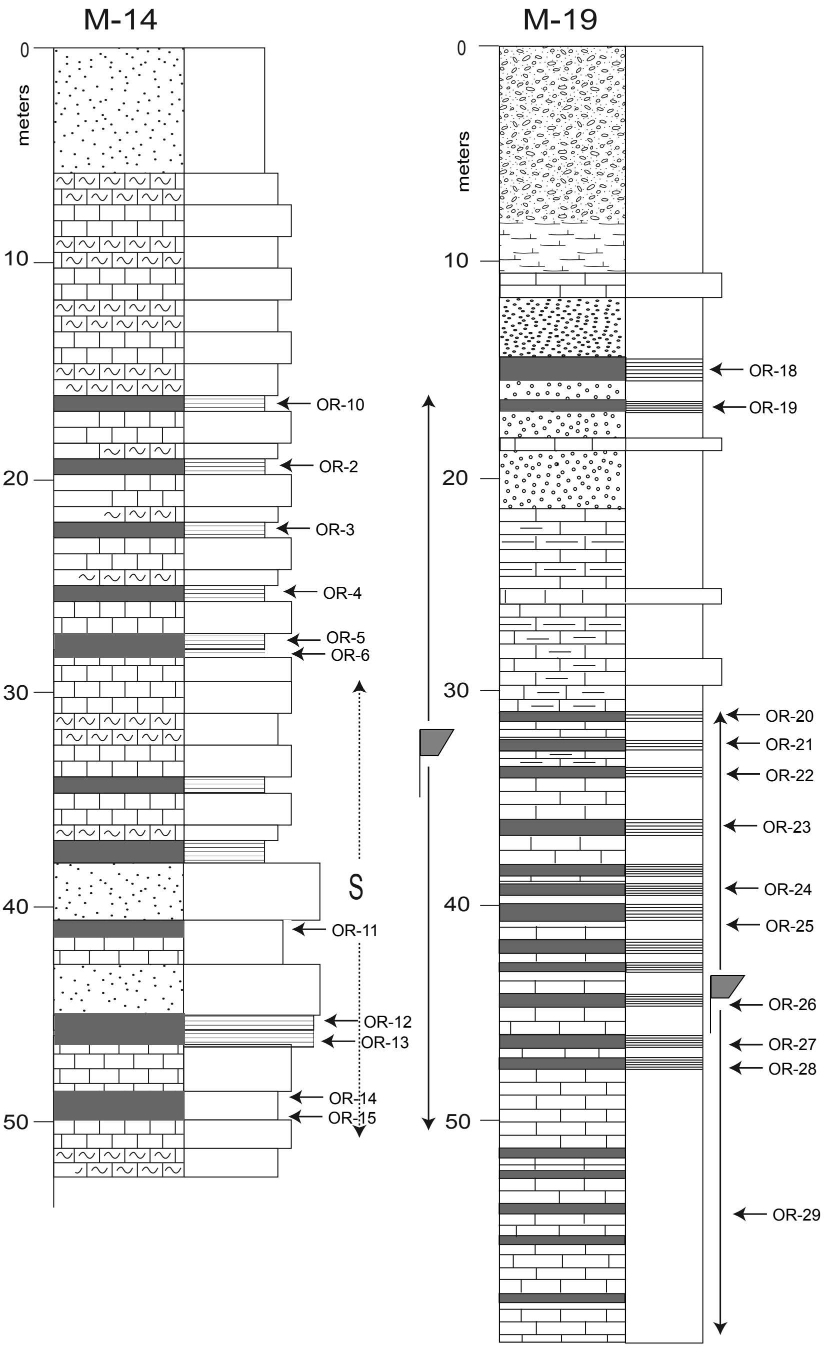

FIGURE 6. M-14 and M-19 wells from Las Minas de Hellín Basin. See Figure 5 for legend interpretation.

0.1µm film). GC conditions were using a splitless injector at 280ºC, and helium was used as a carrier gas with a constant flow rate of 1ml/min. The oven temperature was programmed to run from an initial temperature of 40ºC (held for 1min) to a final temperature of 300ºC at 2ºC/min, and then held at 300ºC for 60min. The mass spectrometer was operated in full scan electron impact mode (electron input energy, 40eV; source temperature, 200ºC) and the data were analyzed with Shimadzu software.

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

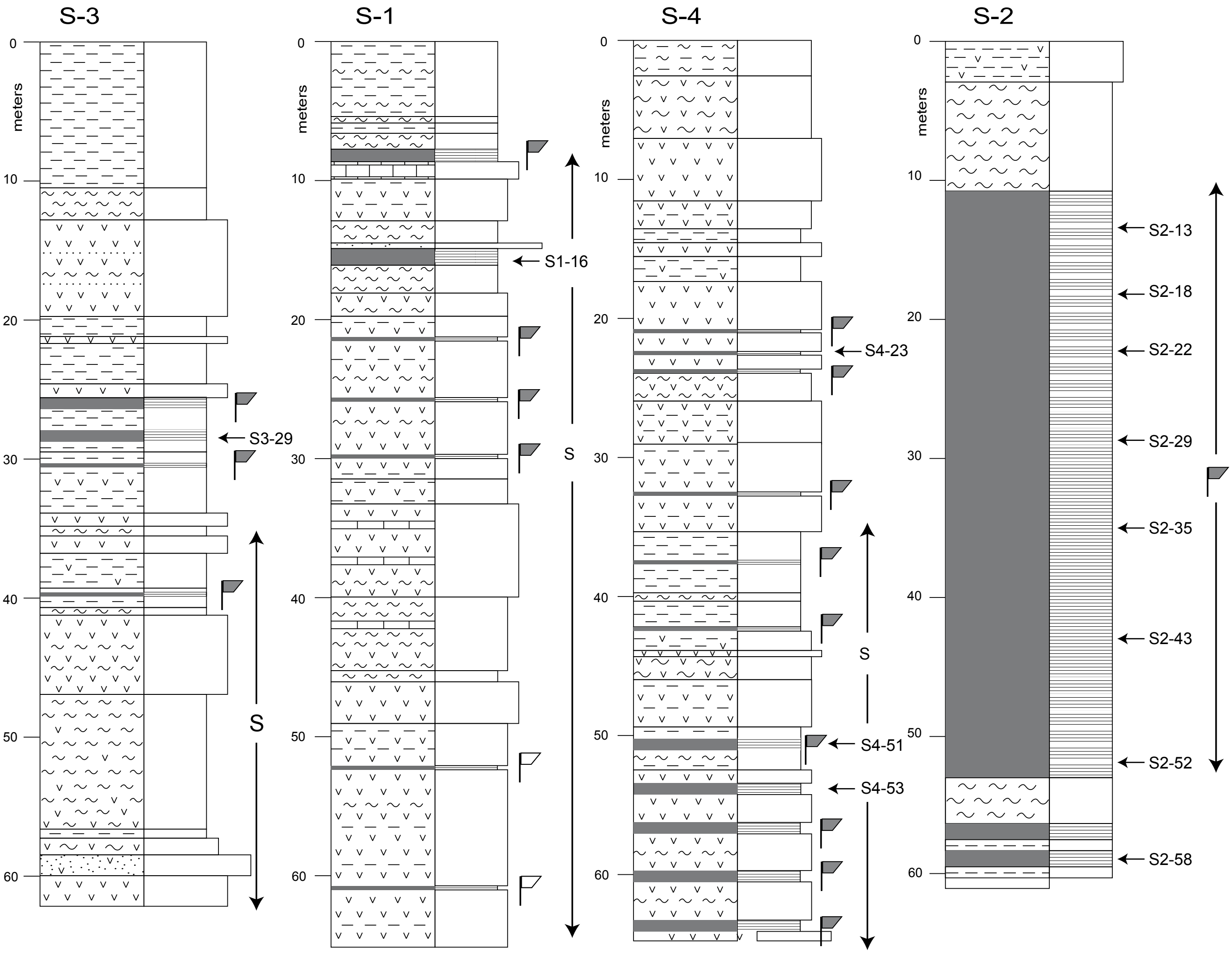

FIGURE 7. Studied wells from the Socovos Basin (modified from ITGE, 1988). Note the increase of organic-shales from S-3 to S2.

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 366º to 420ºC, denoting immaturity. Immaturity is also indicated by the intense greenish-yellowish fluorescence

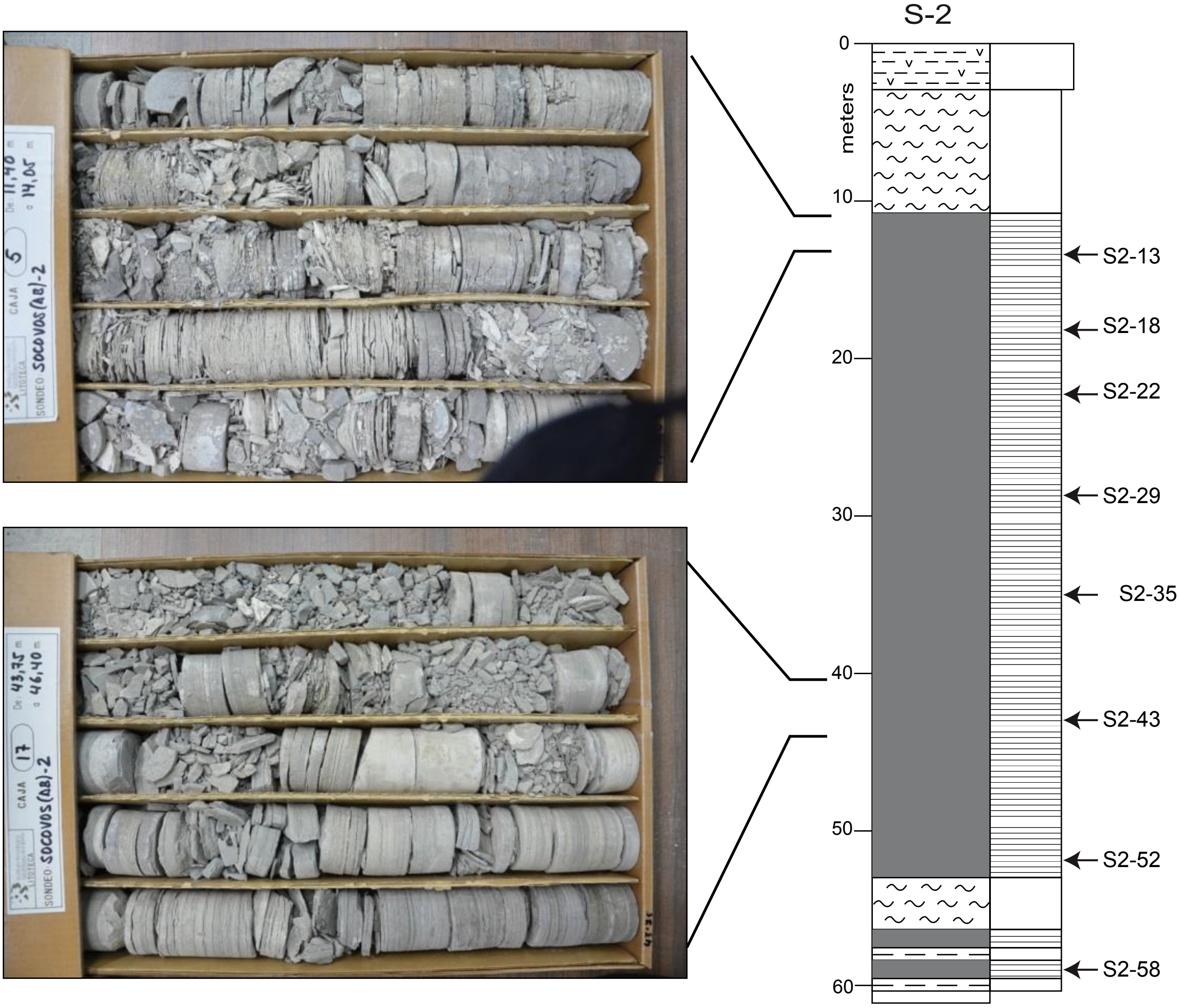

FIGURE 8. Core samples from S-2 borehole from Socovos Basin. Note the fine-laminated paper-shale aspect.

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} *n*-alkanes 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 ph/*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).

FIGURE 9. The samples collected from an old sulfur mine in the Cenajo Basin (CMM) with a TOC content up to 14 % and S2 up to 100mg HC/g rock. Arrows indicate organic-rich levels interbedded with gypsum.

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-dibenzothiophenes.

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_{33} 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_{16} to n-C_{23}, denoting an algal contribution (Peters and Moldowan, 1993), and the n-C_{23} to n-C_{33} 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).

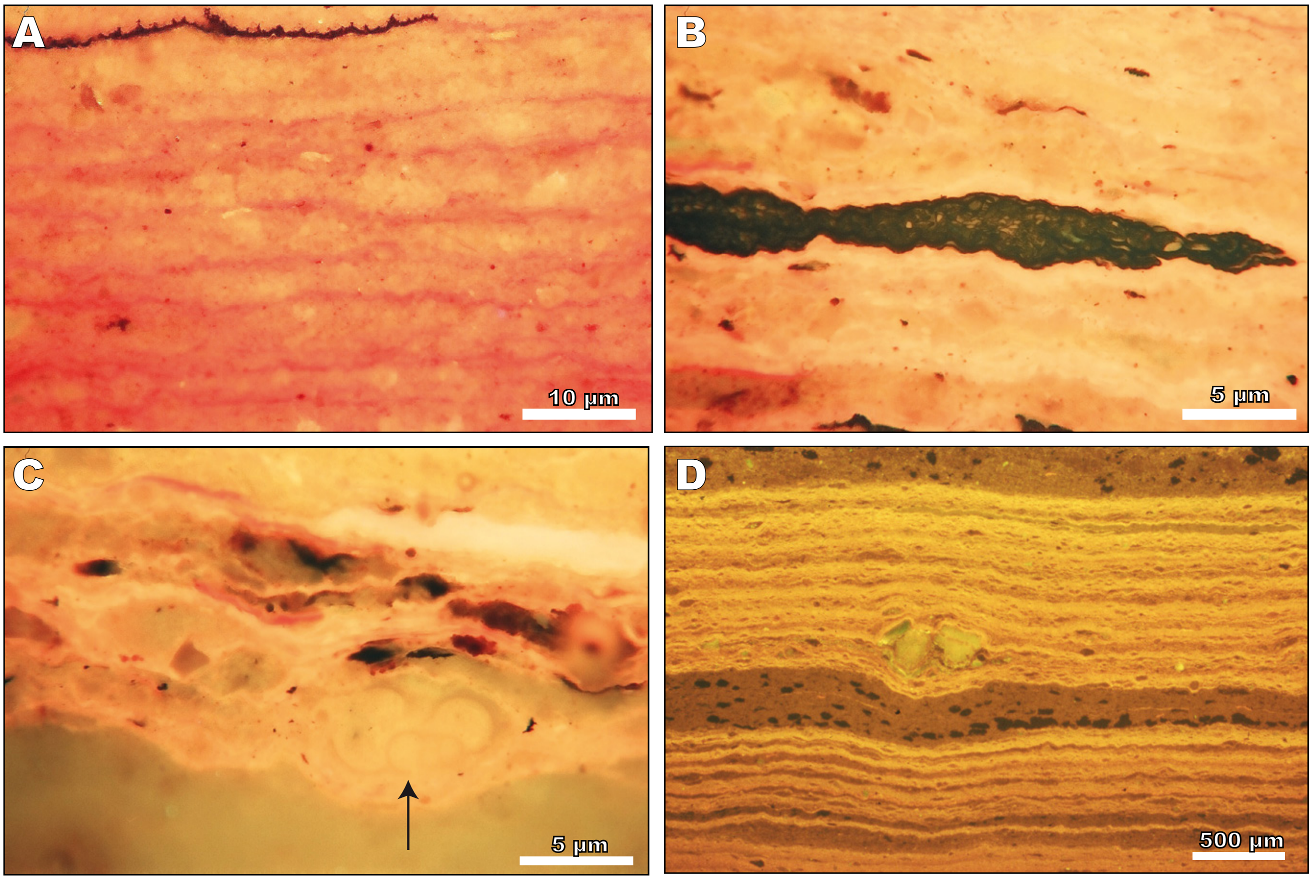

FIGURE 10. A) Finely laminated fluorescent organo-mineral groundmass with intense red or pale greenish-yellow fluorescence; B) sulfur bodies interbedded with organic lamina; C) planktonic foraminifers are identifiable in some samples; D) authigenic quartz crystals wrapped up by alternatively red and/or yellow fluorescence organic matter. Samples A-C are from Las Minas de Hellín; sample D is from Lorca Basin (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 (H_2S) and bicarbonate (HCO_3). The Sulfate Reduction Bacteria (SRB) activity avoids the precipitation of gypsum and generates H_2S which is later oxidized forming sulfur nodules:

$SO_4 + 2CH_2O$ ----------- $2HCO_3 + H_2S$

The presence of pyrite (Fe_2S) associated to the studied organic-rich shales is related to the reaction between the Fe^{++} in solution and the H_2S 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

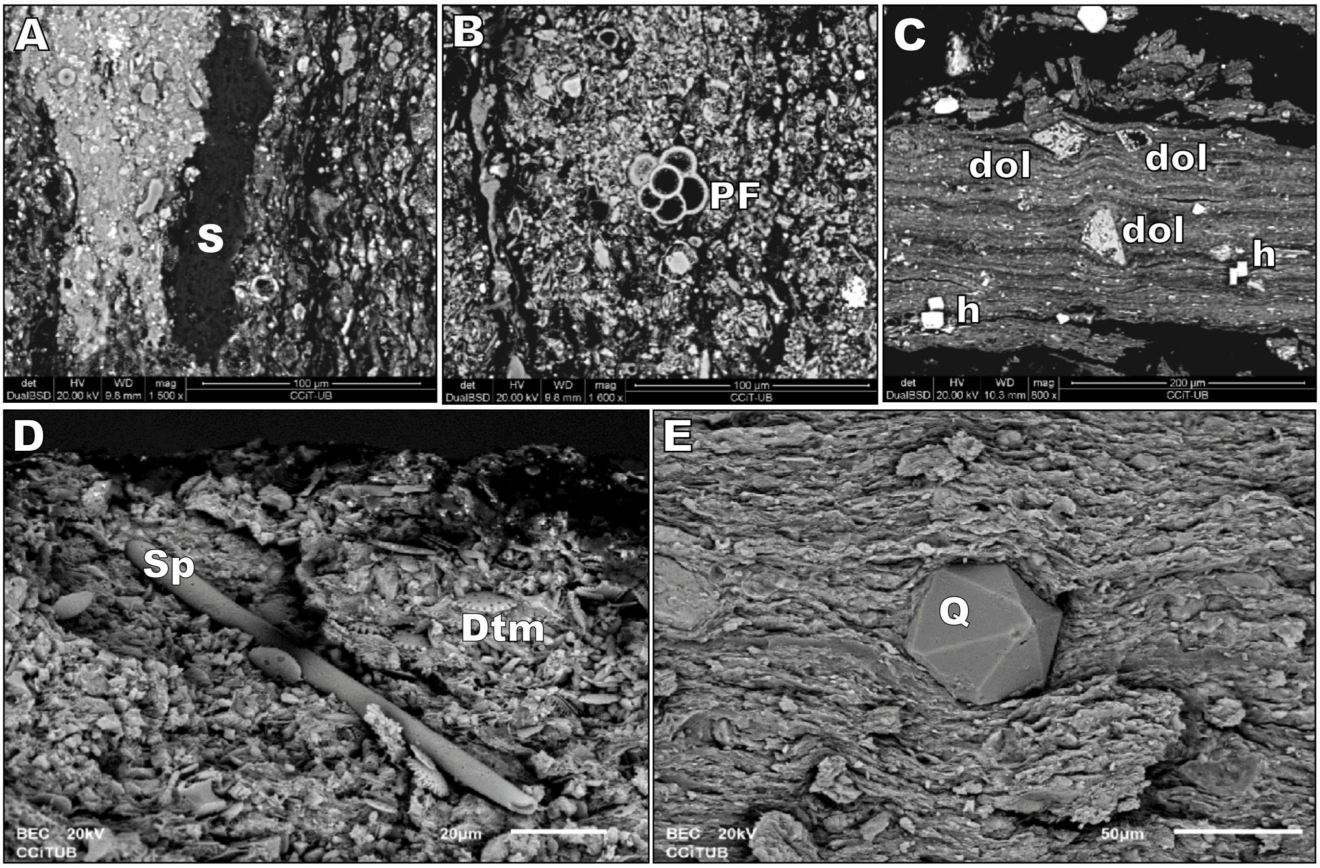

FIGURE 11. Images from Scanning Electron Microscopy. A) sulphur nodule (S) that include organic material; B) planktonic foraminifera (PF); C) laminated organic matter with rhomboidal authigenic dolomite crystals (dol) and diagenetic halite crystals (h) filling porosities; D) sponge spicule (Sp) and abundance of diatoms (Dtm); and E) well-formed authigenic quartz crystal (Q) surrounded by with organic material. A (Cenajo); B, C, D (Las Minas); E (Socovos).

H_2S 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 organo-facies 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

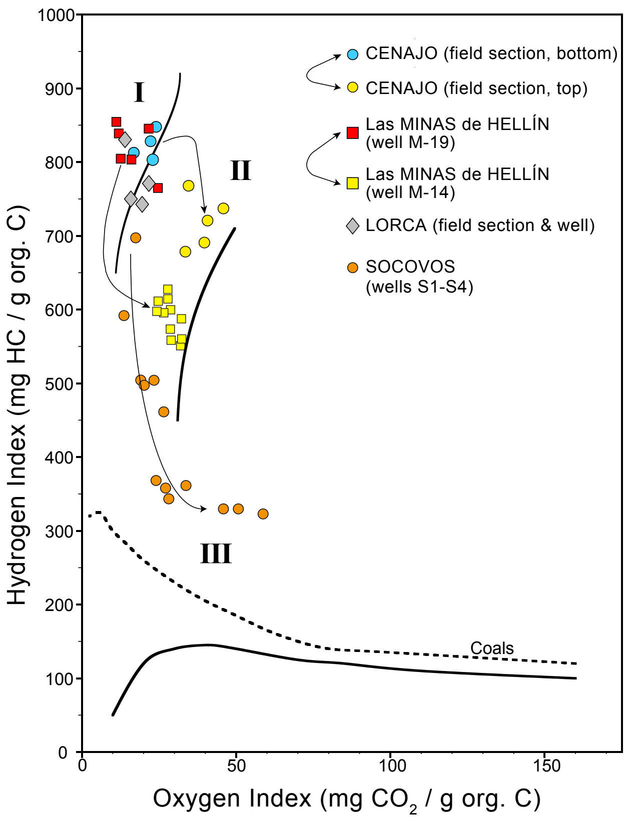

FIGURE 12. HI vs OI diagram showing type of organic matter. Samples from Cenajo (bottom section), Las Minas (well M-19) and Lorca seem to have kerogen type I (lacustrine), whereas the Cenajo (top section) and Las Minas (well M-14) plotted in type II (marine). Samples from Socovos wells range from HI=700 to HI= 350, suggesting an increase in terrestrial input.

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

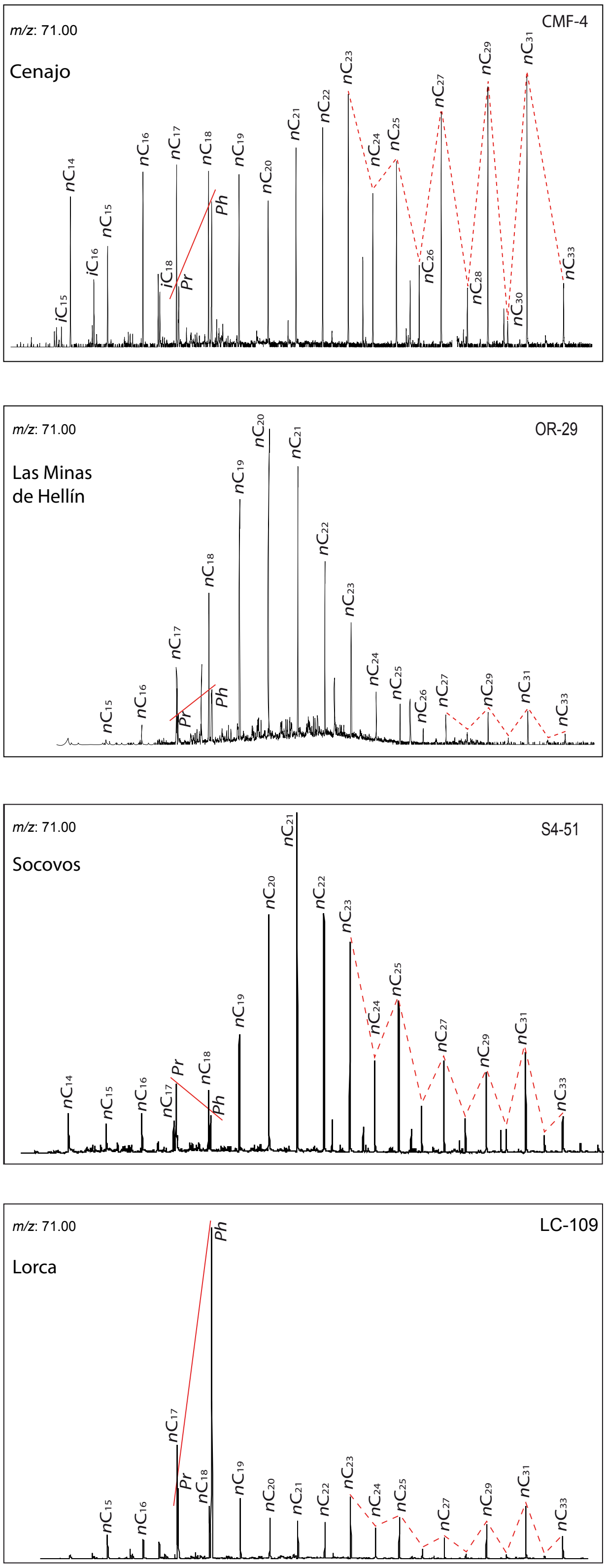

FIGURE 13. Gas chromatograms of representative samples from studied basins. Note the relation between pristane (Pr) and phytane (Ph), and distribution of n-alkanes (n-Cx) from n-C_{23} to n-C_{33}.

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 were 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.

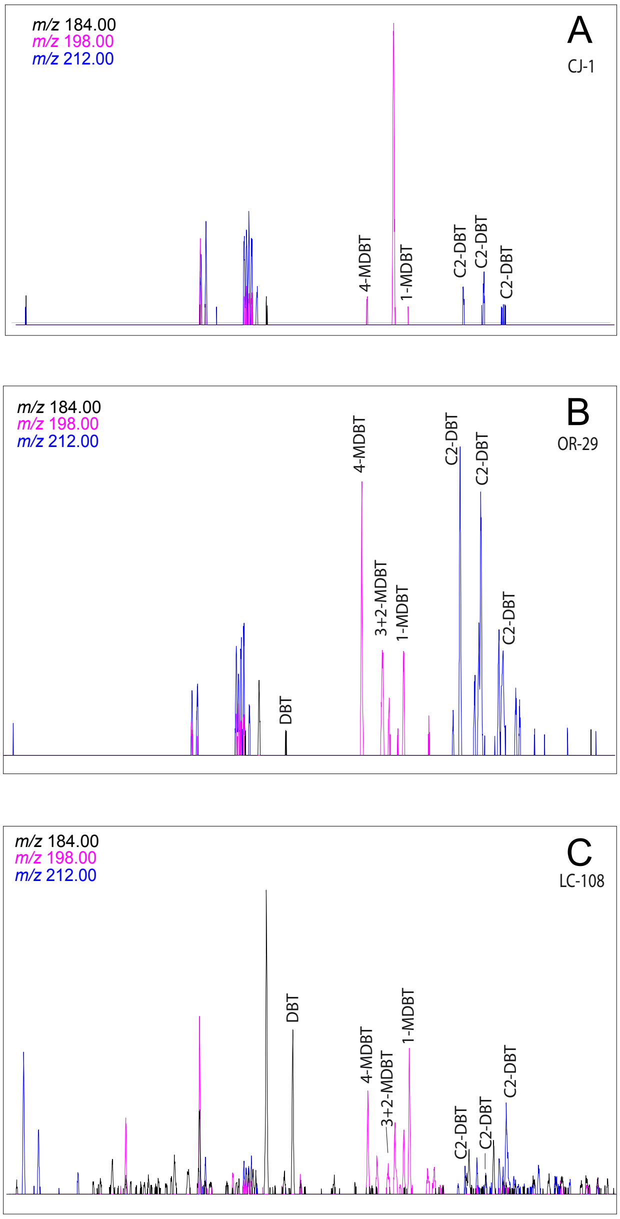

FIGURE 14. Mass fragmentograms (ions 184, 198 and 212) of aromatic fraction showing abundance of sulfur compounds. A, B, C are selected samples from the Cenajo, Las Minas de Hellín and Lorca basins, respectively. DBT: dibenzothiophenes, MDBT: methyl-dibenzothiophenes, C2-DBT: alkyl-dibenzothiophene.

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APPENDIX I

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

Basin	Well/Outcrop	Sample	TOC (%)	S1 [mg HC/g rock]	S2 [mg HC/g]	S3	HI [mg HC/g TOC]	OI	Tmax (ºC)	Sulfur
Socovos	S-1	S1-16	5,3	3,7	18,4	1,4	346	26	403	
Socovos	S-2	S2-13	8,0	5,6	41,0	1,8	512	22	418	
Socovos	S-2	S2-18	11,6	10,6	80,4	2,2	695	19	420	
Socovos	S-2	S2-22	2,1	1,1	7,0	1,4	332	64	414	
Socovos	S-2	S2-29	6,1	7,2	28,2	1,6	462	26	395	
Socovos	S-2	S2-35	2,7	0,9	8,8	1,4	332	53	415	
Socovos	S-2	S2-43	9,3	8,8	47,6	1,9	510	20	398	
Socovos	S-2	S2-52	8,2	10,7	42,1	1,5	513	18	392	
Socovos	S-2	S2-58	4,0	1,8	13,8	1,3	349	34	411	
Socovos	S-3	S3-29	3,7	3,5	13,5	0,8	366	23	396	
Socovos	S-4	S4-23	3,8	2,0	12,8	1,0	338	27	413	
Socovos	S-4	S4-51	13,5	10,9	78,7	1,9	581	14	399	27,96
Socovos	S-4	S4-53	1,7	0,4	2,0	0,7	120	38	392	
Cenajo	CMF section	CMF-1	12,7	18,2	103,5	2,2	813	17	387	
Cenajo	CMF section	CMF-2	13,5	17,9	114,2	3,3	847	24	391	
Cenajo	CMF section	CMF-3	14,5	19,3	116,1	3,4	803	23	390	
Cenajo	CMF section	CMF-4	14,2	24,8	94,9	5,6	668	39	417	9,42
Cenajo	ECM section	CJ-1	13,9	9,8	94,4	4,7	679	34	397	
Cenajo	ECM section	CJ-2	13,8	11,1	105,7	4,9	766	35	393	
Cenajo	ECM section	CJ-3	12,2	15,3	97,5	2,7	799	22	405	
Cenajo	ECM section	CJ-4	11,6	8,3	90,3	2,1	779	18	399	
Cenajo	ECM section	ECM-4	2,2	6,6	12,9	1,9	575	83	394	
Cenajo	ECM section	ECM-5	2,6	6,2	15,3	2,3	579	88	413	
Cenajo	ECM section	ECM-8	12,9	20,4	90,3	5,0	700	39	409	
Cenajo	ECM section	ECM-9	12,7	19,1	91,3	5,2	720	41	401	
Cenajo	ECM section	ECM-10	8,7	15,0	64,6	4,1	736	46	418	
Cenajo	ECM section	ECM-11	6,6	9,2	43,2	3,7	654	55	409	
Cenajo	CMM section	CMM-2	13,2	24,8	84,6	5,6	641	42	410	
Cenajo	CMM section	CMM-3	12,1	16,3	87,7	3,9	725	32	390	
Cenajo	CMM section	CMM-4	14,0	24,2	85,2	4,8	609	34	396	
Cenajo	CMM section	CMM-5	11,7	13,8	102,1	3,6	871	30	396	
Las Minas	M-14	OR-2	9.76	16.43	63.69	1.95	652	23	385	
Las Minas	M-14	OR3	10.58	22.49	70.46	2.48	665	23	376	
Las Minas	M-14	OR-4	18.79	17.59	93.89	2.08	499	11	389	
Las Minas	M-14	OR-5	19.35	19.63	101.41	3.4	524	17	389	
Las Minas	M-14	OR-6	17.3	19.7	71.94	2.86	415	16	381	
Las Minas	M-14	OR-10	1,2	1,2	7,4	0,3	598	27	350	
Las Minas	M-14	OR-11	2,1	1,0	10,7	0,8	516	38	415	
Las Minas	M-14	OR-12	4,4	1,8	17,1	1,8	390	41	413	
Las Minas	M-14	OR-14	3,5	3,8	23,1	0,7	665	20	317	
Las Minas	M-14	OR-15	4,8	4,6	32,0	1,1	669	24	353	
Las Minas	M-19	OR-18	3,4	3,3	20,6	1,2	613	37	396	
Las Minas	M-19	OR-19	1,0	0,2	2,2	0,8	223	79	397	
Las Minas	M-19	OR-20	11,4	31,4	71,7	2,8	649	25	373	
Las Minas	M-19	OR-21	10,6	8,0	84,9	1,3	804	13	366	
Las Minas	M-19	OR-22	14,0	7,2	117,5	1,7	838	12	376	
Las Minas	M-19	OR-23	16,8	7,9	143,3	1,9	854	11	370	15,07
Las Minas	M-19	OR-24	10,4	7,0	88,2	2,3	845	22	367	
Las Minas	M-19	OR-25	16,3	9,5	131,2	2,6	803	16	366	17,21
Las Minas	M-19	OR-26	6,2	3,4	40,3	1,4	647	23	383	
Las Minas	M-19	OR-27	3,1	2,5	16,8	1,2	537	38	401	
Las Minas	M-19	OR-28	3,2	1,3	13,5	0,9	420	27	416	
Las Minas	M-19	OR-29	3,5	2,4	18,7	1,0	534	28	401	18,36
Lorca	La Serrata	LC-4	20.36	6.40	151.19	4	743	20	419	
Lorca	La Serrata	LC-73	22.09	16.39	183.45	3.30	830	14	418	
Lorca	La Serrata	LC-104	20	12.83	149.22	3.20	750	16	422	
Lorca	La Serrata	LC-108	19.56	6.34	150.67	4.27	770	22	421	
Lorca	L-3	LC-109	17.81	16.55	119.54	3.20	671	26	409	9

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

Sample	Locality	Sample type	SAT	ARO	RES	ASP	Loss	Sulfur
ECM-10	Cenajo section (upper)	field	2.65	3.14	42.03	31.62	20.56	-
ECM-4	Cenajo section (upper)	field	8.68	8.50	52.31	22.35	8.16	-
CMF-4	Cenajo section (down)	field	4.77	1.16	17.43	60.15	16.50	9.42
CMF-2	Cenajo section (down)	field	0.99	2.62	34.25	35.37	26.86	-
OR-15	Las Minas de Hellín (M14)	well	9.90	13.70	30.81	30.99	14.60	-
OR-23	Las Minas de Hellín (M19)	well	2.5	2.3	4.9	82.30	7.9	15.07
S4-51	Socovos (S-4)	well	6.43	15.51	29.24	22.78	26.04	27.96
S2-13	Socovos (S-2)	well	11.34	6.87	54.16	12.54	15.10	-
LC-109	Lorca	well	2.39	2.41	9.09	81.1	5.01	9

TABLE III. Pristane/Phytane, Pristane/n-C_{17}, phytane/n-C_{18} ratios, and suphur content from selected samples

Sample	Locality	Sample type	Pr/Ph	Pr/*n*-C17	Ph/*n*-C18
ECM-10	Cenajo section (upper)	field	1,37	0,22	0,56
ECM-4	Cenajo section (upper)	field	0,65	0,17	0,18
CMF-4	Cenajo section (down)	field	0,31	0,36	0,86
CMF-2	Cenajo section (down)	field	0,81	0,46	0,34
OR-15	Las Minas de Hellín (M14)	well	2,03	0,21	0,59
OR-23	Las Minas de Hellín (M19)	well	3,65	0,61	0,25
S4-51	Socovos (S-4)	well	1,71	2,07	0,59
S2-13	Socovos (S-2)	well	0,62	0,08	1,58
LC-109	Lorca	well	0,21	0,6	6,29