The Messinian Salinity Crisis during the Upper Miocene as a Cause for Generating Giant and Super-Giant Biogenic Gas Fields in the Eastern Mediterranean Basin

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Abstract: The discovery of the Zohr supergiant biogenic gas field in the Nile Cone of Egypt has promoted a new impetus in the exploration of hydrocarbons in the Eastern Mediterranean Basin.

For the last 25 years, exploration and exploitation of hydrocarbon fields in the Eastern Mediterranean basin were aimed at locating reservoirs in sandstone rocks hosting oil and/or pyrolytic/thermogenic natural gas. The latter is derived from the thermal breakdown of oil.

The discovery of the Zohr supergiant biogenic gas field, trapped in limestone/coral reefs and generated in a marine paleo-lagoon environment during the Upper Miocene/Messinian period, has turned the attention for hydrocarbon exploration to similar marine paleolagoons that existed in the desiccated Mediterranean Sea some 6 million years ago. Nine fields, similar to the Zohr marine paleo-lagoon, exist in the Eastern Mediterranean basin.

The existence of these very large biogenic natural gas deposits, along with large thermogenic gas deposits, render the Eastern Mediterranean basin as one of the largest natural gas basins in the world.

Key words: Eastern Mediterranean, Biogenic Gas, Messinian Salinity Crisis

Introduction

For the last 25 years, exploration and exploitation of hydrocarbons in the Eastern Mediterranean basin, Figure 1, was centered in discovering gas fields in sandstone reservoirs which were derived from the thermal breakdown or pyrolysis of oil. The amount already discovered, 2.8 tcm, besides the amount discovered in the Zohr biogenic gas field and the amount of pyrolytic natural gas expected to be discovered in the future, was presented last year at the 6th NMIOTC conference by Foscolos, 2015.

The discovery of the supergiant biogenic gas field, Zohr, Zohr-ENI 2015, Figure 2, with reserves of 0.85 tcm, in the Nile Cone gave a new impetus in the exploration of similar biogenic gas fields encountered in the Eastern Mediterranean basin.

The perspective of Eastern Mediterranean basin to become one of the largest, if not the largest, natural gas basin in the world is herein discussed.

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Figure 1. Major hydrocarbon basins in the Eastern Mediterranean. (Nikolaou, 2016).



Figure 2. Zohr biogenic gas field some 85 kilometers north from where the major hydrocarbon exploration and exploitation takes place in the Nile Cone

Discussion

The successful discovery of the supergiant biogenic gas field, Zohr, in the Nile Cone by the Italian company, ENI, was based on the previous discovery of the PERLA biogenic gas field, located offshore Venezuela, Figure 3, and the largest discovered gas field in South America. This gas field was located near a paleo marine lagoon.



Figure 3. Perla's biogenic gas field location in the Gulf of Venezuela. Perla was discovered by ENI in 2009.

During the last 45 years, a large number of institutions were involved in studying the Messinian Salinity Crisis, Figure 4, which took place some 6 million years ago in the Mediterranean Sea. This work indicated that similar paleo marine lagoons should exist in the Eastern Mediterranean basin and, therefore, similar supergiant biogenic gas fields could be found.

Six million years ago, during late Miocene, the Strait of Gibraltar was closed, converting the Mediterranean Sea as well as the Black Sea and the Caspian Sea into lakes. As time progressed, the seas dried up leaving a large number of paleo marine lakes at the deepest areas of the bottom of the seas, Vasiliev et. al., 2014, Figure 5 and 6, Roveri et, al., 2014, Figure 7, Ryan. 2009, Figure 8. In these paleo marine

lagoons, a very large number of plants had grown for hundreds of thousands of years. As they die out, thousands of tons of organic material were buried and preserved. Subsequently, the organic matter was anaerobically decomposed by methane bacteria yielding vast amounts of methane. The emitted biogenic gas, however, was stored in the adjacent coral reefs. When the Mediterranean Sea, as well as the Black Sea and the Caspian Sea were completely desiccated, the lagoons were covered by gypsum and later on by halite, Figure 4.



Figure 4. Distribution of Messinian evaporites and location of the DSDP-ODP boreholes which recovered Messinian deposits. The location of the main hypersaline anoxic deep basins on top of the Mediterranean Ridge is also shown: A, Atlante. B. Bannock. D, Discovery. K, Kyros. M, Medee. T, Thetis. Ty, Tyro. U, Uran. Roberi et. al., 2014. Modified from Rouchy and Caruso (2006) and Menzi et. al., (2012).

Some 5.3 million years ago, the Strait of Gibraltar reopened and water from the Atlantic Sea flowed into the Mediterranean Sea covering the thick layers of salt. Moreover, in the Eastern Mediterranean Basin, two rivers, the proto Nile from Egypt and Kuffra from Libya were adding their sediments. The net result was the capping of all marine paleo lagoons with additional sediments whose thickness was close to 2000 meters. The location of these paleo marine lagoons is shown in Figure 8. Zohr super-giant gas field was discovered near a paleo marine lagoon, Ryan 2009.



Figure 5. HYPERSALINE LAKES. Topo-Europe, Draught in the Miocene of the Black Sea. Presentation at the Instituto de Ciencias de la Terra, Jaume Almeira, Spain. Iuliana Vasiliev, 2014, Barcelona.



Figure 6. Hypersaline Lakes in the Eastern Mediterranean. Topo-Europe, Draught in the Miocene of the Black Sea. Presentation at the Instituto de Ciencias de la Terra, Jaume Almeira, Spain. Iuliana Vasiliev, 2014, Barcelona



Figure 7. Cross section of marine lagoons from Gibraltar to Israel, Roveri et. al. 2014. Marine Geology v. 352 pp. 25-58.



Figure 8. Location of paleo marine lagoons in the Eastern Mediterranean basin, Ryan 2009.

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Figure 9. Occurrence of mud flow volcanoes and hydrocarbon reservoirs in the Nile Cone and Cyprus (Modified from Dupre et al., 2008 and Robertson 1996).



Figure 10. Large anticline on the toe of deep Nile Delta fan with Messinian low-stand delta clastic sand faulted pre-Messinian. Gas Chimneys are highly visible, Montadert and Nikolaides, 2010.

Three marine paleo lagoons have been identified in Cyprus, Ryan 2009. The prospects of having natural gas deposits are quite high since at least four mud flow volcanoes emitting methane are identified, Figure 9, while geophysical data show the routes of escaping gases, Montadert and Nikolaides, 2010, Figure 10. If these three locations have similar amounts of biogenic natural gas as Zohr biogenic natural gas field, Figure 11, then Cyprus biogenic gas reserves, besides the thermogenic gas reserves e.g. Aphrodite field, should be in the order of at least 90 tcf. This amount is by far higher than the natural gas deposits of Azerbaijan, 41 tcf, BP Statistical Review of World Energy 2016, hence the importance of Cyprus as an energy producer.

In offshore southern Crete, there are five paleo-marine lagoon locations having very similar properties as the three marine paleo lagoons encountered offshore Cyprus, Ryan, 2009, Figure 8. The four main reasons for the optimism in locating large natural gas deposits in offshore southern Crete are:

- Converging plates which hosts 20% of the World's Giant Hydrocarbon Fields
- The existence of the Mediterranean Ridge with accretionary prisms.
- Active mud flow volcanoes along with gas hydrates deposits on the floor of the Mediterranean Sea, offshore southern Crete
- Existence of a large number of coral reefs during the Middle to Late Miocene which acted as reservoirs for storing / trapping biogenic methane gas

These are discussed in more detail in the following section.

A. Converging Plates

The geodynamic regime of the Eastern Mediterranean which leads to the evolution of the Mediterranean Ridge is discussed in detail by MacKenzie, 1972, Minster and Jordan, 1978, Le Pichon, 1982, Ryan *et al.*, 1982, Meulenkamp *et al.*, 1988, Jackson, 1994, Oral *et. al.*, 1995, Ten Veen and Mejer, 1998, Cocard *et al.*, 1999, Papazachos, 1999, 2002, McClusky et al., 2000, Knapmayer and Harges, 2000, Huguen *et al.*, 2001, Mountrakis, 2001, Hollenstein *et al.*, 2002, McClusky *et al.*, 2003, Ten Veen and Kleinspehn, 2003, Kreemer and Chamot-Rooke, 2004, Reilinger *et al.*, 2004 and Pavlaki, 2006.

The afore-mentioned scientists have indicated that in the wider area of Crete there is an active geodynamic system that is characterized by the motion of two converging plates: the Eurasian and the African. The Arabian plate moving counterclockwise is pushing westward the Anatolian plate which, in turn, pushes southward the Aegean plate, Figure 12. The interaction of these plates is the prerequisites for hydrocarbon accumulation created from the confluence of reservoirs and source rocks and is a way of getting the oil and gas generated from these source rocks into the reservoirs and trapping them there, (Kanasewich and Havskow, 1978). In converg-



Figure 11. Locations of paleo marine lagoons in the Nile Cone and Cyprus based on data from Hodgson, (SPECTRUM), 2016, Esestime, et. al., 2016, and PGS 2016.



Figure 12. The geodynamic regime of the wider of Crete and Eastern Mediterranean. The Arabian plate pushes counterclockwise the Anatolian plate which in turn pushes sideways the Aegean plate. The latter overrides the African plate which subducts under the island of Crete creating the orogeny, Pavlaki, 2006



Tectonic sketch of the Eastern Mediterranean (adapted from Barrier, E., Chamot-Rooke, N. and Giordano, G., 2004, Geodynamic Map of the Mediterranean, Commission for The Geological Map of the World, CCGM)

Figure 13. Tectonic sketch of the Eastern Mediterranean showing: A The Mediterranean ridge. B. The abyssal Herodotus basin. Barrier et. al., 2004



Figure 14. Location of mud flow volcanoes along the subduction Zone along with the position of the Aegean Volcanic Arc. Modified after Dimitrov, 2002

ing plates, we usually find large hydrocarbon deposits (Thompson, 1976, Carmalt and St. John, 1986).

B. The existence of the under water Mediterranean Ridge with accretionary prisms

In the Eastern Mediterranean, the compressional forces are also responsible for the formation of an underwater ridge called the Mediterranean Ridge, Figures. 6, 7 and 13. This ridge is forming an accretionary complex whose rate of increase is the fastest in the world (Kopf *et al.*, 2003), Figure 14. The Mediterranean Ridge with its accretionary prisms starts from the western part of the island of Lefkas in the Ionian Sea, bends around the island of Crete and ends roughly south of the island of Kastellorizo following the subduction of the African Plate underneath the Aegean Plate. Underwater ridges with accretionary prisms are also associated with hydrocarbon deposits across the world such as Barbados, Persad 2008, West Timor, Jones et. al., 2011, Andaman Oceanic Island Arc System, Wandrey 2006 and Robinson, 2012. Hence, they are very strong geological indicators that natural gas fields should exist offshore southern Crete.

C. Active mud flow volcanoes along with gas hydrates deposits on the floor of the Mediterranean Sea offshore southern Crete

Numerous mud flow volcanoes exist along the subduction zone between the African Plate and the Aegean Plate, Figure 15. These volcanoes emit methane for hundreds of thousands years which either escapes to the atmosphere or resides at the bottom of the sea in the form of gas hydrates or solid methane, Figures 15 and 16. Mud flow volcanoes emitting methane gases are often associated with hydrocarbon deposits, tectonic subduction zones and orogenic belts¹, Ware and Ichram, 1997.

The area covered by the gas hydrates is close to 200,000 Km^2 and the volume is roughly calculated at 30 trillion m³ (assuming an average thickness of 150 meters), Figure 16. Roughly, 1% of this volume are hydrates, that is 0.30 trillion m³. This value should be multiplied by 170 m³ of natural gas/1m³ of hydrate in order to equate it to the conventional natural gas value (Massari, 2009). This implies that we have the equivalent of 51 trillion m³ of natural gas. The origin of these immense volumes of gas hydrates (equivalent to 328 billion barrels of oil) is attributed either to the thermogenetically breakdown (pyrolysis) of aliphatic components of oil or to the anaerobically breakdown of plant biomass by methanogenic bacteria.

In the eastern portion of the Eastern Mediterranean basin, Figure 1, which includes the Nile Cone, the Levantine basin and offshore Cyprus, thermogenic natural gas fields were discovered in sandstone reservoirs and biogenic natural gas in coral reefs. Henceforth, since the geology of the Eastern Mediterranean basin, which includes offshore southern Crete, is very similar, Robinson 2011, one should expect



Figure 15. Prospective hydrocarbon area offshore southern Crete, Huguen et. al., 2001.



Figure 16. Hydrate thickness at the bottom of the Mediterranean Sea, Praeg et al., 2007.

that the western part of the Eastern Mediterranean basin to have thermogenic as well as biogenic gas fields.

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1. http://en.wikipedia.org/wiki/Mud_volcano#Europe

Gas composition corresponding to (i) biogenic gas, (ii) thermogenic oil-associated gas, (iii) dry post-mature thermogenic gas, and, (iv) gas of mixed biogenic/thermogenic origin have been discussed by Schoell 1983, 1988, Faber *et al.*, 1992, Whiticar, 1994 and Buruss and Laughrey, 2009.

D. Existence of a large number of coral reefs during the Middle to Late Miocene which acted as reservoirs for storing / trapping biogenic methane gas

Coral reefs were ubiquitous in the Mediterranean Sea during mid-Miocene, between 11 Ma and 7 Ma years ago prior to the Messinian Salinity Crisis which was prompted by the closure of the Straits of Gibraltar, Figure 17.



Figure 17. Stromatographic column of the Levantine Basin, Esestine et. al., 2016

Coral reefs similar to Zohr biogenic gas field have been discovered in Cyprus, Figure 11. If these reefs have the same amount of biogenic gas as Zohr, then Cyprus's natural gas reserves should be huge. Coral reefs also have been found in Crete, Greece. They are located in the prefecture of Heraklion, Branchert, et. al., 2006, Figure 18 and Vescogni et. al., 2008, Figure 19. Large amounts of biogenic gas are emitted in the southern portion of the Heraklion prefecture, especially in the plains of Messara, Pasadakis et. al., 2009, Panagopoulos et. al., 2011



Figure 18. Late Miocene, 11 million to 7 million years, corral reefs in the Mediterranean Regions, Franseen, et. al., 1996

The Messinian Salinity Crisis (MSC), also referred to as the Messinian Event, and in its latest stage as the Lago Mare event, was a geological event during which the Mediterranean Sea went into a cycle of partly or nearly complete desiccation throughout the latter part of the <u>Messinian</u> age of the Miocene epoch, from 5.96 to 5.33 <u>Ma</u> (million years ago). It ended with the Zanclean flood when the Atlantic Ocean entered and reclaimed the Mediterranean basin, Gauthier, et. al., 1994, Krijgsman, et. al., 1996.

Biogenic methane is attributed to aquatic plants which were thriving for hundred of thousand years in the marine lagoons and marine trenches during the Messinian epoch. Upon their death, plants were decayed and decomposed and subsequently attacked by methane bacteria yielding enormous quantities of biogenic gas. Some of the methane escaped into the air while another portion was stored preceding the Messinian Salinity Crisis, in the coral reefs. Once the Mediterranean Sea had dried completely, the coral reefs were capped by a thick layer of salts whose composition varied from pure gypsum to a mixture of halite and gypsum, Figure 4. Once the Straights of Gibraltar opened, some 5.3 Ma ago, water from the Atlantic Sea along with sediments covered the thick layer of salt. Sediments in the Eastern Mediterranean basin were also received from the Nile river which started to flow at the same time the Straights of Gibraltar opened, some 5,3 Ma years ago.



Figure 19. Corral reefs in the prefecture of Heraklion, Crete, Greece during the Late Miocene, Vescogni, et. al., 2008.

Therefore, to find a biogenic gas field in a coral reef, we have to drill around 5000 meters below sea level since the water depth is 2000 meters, the thickness of sedi-

ments something between 1500 meters and 2000 meters and the thickness of the evaporatic layers, 1500 meters to 2000 meters, The sequence of biogenic gas fields, thermogenic gas fields, gas liquid fields and oil fields are shown in Figure 20, Esestime et. al., 2016. This column shows the prevailing stratigraphy in the Levantine basin. Locations of coral reefs with biogenic gas in the Nile Cone, offshore Cyprus and offshore southern Crete, that is in the Eastern Mediterranean basin are indicated in the map published by Ryan 2009.



Figure 20. Porite corrals from Crete (Greece) open a window into Late Miocene (10 Ma), seasonal and inter- annual climate variability, Branchert, et. al., 2006.

Based upon the work by Hodgson, 2015, the biogenic gas in the eastern part of the Eastern Mediterranean basin, Figure 1, is as follows: Levantine basin at 50 tcf, in Cyprus at 50 tcf while in the Nile Cone the amount discovered by ENI, Zohr gas field, stands at 30 tcf. In the western part of the Eastern Mediterranean basin which is offshore southern Crete, due to geological similarities, Ryan 2009 and Robinson 2011, the amount of biogenic gas is estimated to be at least 100 tcf. Hence, total biogenic natural gas in the Eastern Mediterranean basin, with a probability of over 50%, stands at 230 tcf while the thermogenic natural gas is reported at 572 tcf, Foscolos 2015. These reserves make the Eastern Mediterranean Basin one of the most prominent natural gas basins in the world without counting the huge deposits of gas hydrates.

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Conclusions

- Zohr's biogenic gas discovery has prompted the search for similar biogenic gas fields; something that escaped the attention of many oil companies.
- Based upon the research carried out by a large number of scientists derived from different institutions who were studying the Messinian Salinity Crisis, eight additional locations have been identified in the Eastern Mediterranean basin.
- If the amount of biogenic gas in these additional locations is similar to the amount discovered in the Zohr field located in the Nile Cone, then, by adding the amount of biogenic gas to the expected amount of thermogenic gas, the Eastern Mediterranean basin becomes one of the largest natural gas basins in the world.

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