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The gas hydrate potential of the Eastern Mediterranean basin

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ABSTRACT

Gas hydrate exploration studies have increased substantially since last decade. Gas hydrate reservoirs are commonly found in the marine environment and permafrost. Studies related to natural gas hydrates in the Mediterranean Basin are rare compared to those released on the continental margins of the United States of America, Japan, India, China and Korea. This study provides an evaluation of the gas hydrate potential of the Mediterranean Basin using available literature data such as scientific drilling data (Ocean Drilling Program Leg 160 and Leg 161), sediment data, geothermal data, geochemical data, gas seepage data, mud volcano data etc., It is shown that there is a high producible gas hydrate potential (~ 98.16 standard trillion cubic meter) in the Mediterranean Basin. The Eastern Mediterranean basins have the highest gas hydrate potential due to its high amount of source gas potential and lower geothermal gradient compared to those in the Western Mediterranean.

1. Introduction

Gas hydrate reservoirs are deemed as likely future energy source due to the fact that they can be found amply mostly in permafrost regions and sediments in the oceans, both occupying huge areas of the Earth. According to calculations for hydrate bearing sands globally, there is a great range of global gas hydrate resource between 133 standard trillion cubic meter (tcm) and 8891 tcm (Johnson, 2011). Although through the years, the estimations of gas hydrates have been reduced by the majority of the scientists from their initial findings (Milkov, 2004), it can be stated that even the most pessimistic calculations of total quantity of gas in gas hydrates are much larger than the conventional gas resources (404 tcm) and shale gas (204-456 tcm) (Chong et al., 2016). On the other hand, almost 80% of global natural gas demand is met by conventional sources, with unconventional sources increasing only in recent years. Global energy demand will be ameliorated significantly in the next decades as earth population grows. It has been projected that the global energy consumption will rise by 56% from 524 quadrillion British Thermal Unit (BTU) in 2010 to 820 quadrillion BTU in 2040 (IEA, 2011). Due to its huge potential all over the world, gas hydrates unconventional resources are quite important.

Gas hydrates are crystalline compounds formed from water and suitably-sized gas molecules at high pressure and low temperature conditions. Depending on which gas molecules are present, hydrates form different crystal structures. Cubic structure I (sI), structure II (sII) and hexagonal structure H (sH) are three gas hydrate structures found in nature (Sloan and Koh, 2008). sI hydrate has two types of cavities: a small pentagonal dodecahedral cavity consisting of 12 pentagonal rings of water and a large tetrakaihedral cavity consisting of 12 pentagonal and two hexagonal rings of water. sII hydrate also has two cavity sizes: the pentagonal dodecahedral cavity and the larger hexakaidecahedral cavity consisting of 12 pentagonal

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and four hexagonal rings of water. sH hydrate is composed of 3 small (5^{12}), 2 medium ($4^3 5^6 6^3$) and 1 large cages ($5^{12} 6^8$) (Carroll, 2009). Approximately 46, 136 and 34 water (H_2O) molecules are essential for sI, sII and sH hydrates respectively. Gas hydrates formed by only one type of gas are defined as simple or pure gas hydrates. Simple hydrates of methane (CH_4), ethane (C_2H_6), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and xenon (Xe) are called a sI type of gas hydrate. Moreover, propane (C_3H_8), i-butane (i-C_4H_{10}), nitrogen (N_2), and oxygen (O_2) form the sII type of gas hydrate. Different than sI and sII hydrates, for the formation of sH hydrates, a gas such as CH_4 and other large molecules that have diameters greater than those of isobutane (i-C_4H_{10}), such as isopentane (i-C_5H_{12}) are needed (Carroll, 2009). sI and sII hydrates are common all over the world, while sH hydrates are not common and they were only found in a few regions such as the Gulf of Mexico, Cascadia, and the Caspian Sea (Hester and Brewer, 2009).

Even though gas hydrate reservoirs are examined as contingent energy sources for future, until now there have been only a few short-term production tests and there is no commercial gas production. Gas hydrates are in solid form at reservoir conditions, so conventional oil and gas production techniques cannot be implemented in gas hydrate reservoirs (Chen et al., 2018). Gas hydrate reservoirs are classified in four classes. Class 1 hydrate reservoir has a stable hydrate layer and an underlying free gas zone. Class 2 hydrate reservoir has a stable hydrate layer and an underlying free water zone. Class 3 hydrate reservoir has a stable hydrate layer bounded by permeable or impermeable shale or clay zones. Class 4 hydrate reservoirs are distributed near sea floor with low hydrate saturation and they are not regarded as the productive reservoirs (Worthington, 2010; Moridis et al., 2013). Among these classes, Class 1 hydrates are considered as the most promising gas hydrate reservoirs due to their gas potential in both hydrate section and free gas section. The expected proportions of Class 1, Class 2, Class 3, and Class 4 reservoirs in nature are 14 percentages (%), 5 %, 6 % and 75 % respectively (Yang et al., 2017).

There are four gas production methods for gas hydrate reservoirs: thermal injection, depressurization, chemical injection and CH_4-CO_2 replacement. In thermal injection method, the temperature is accrued with electrical heating, hot fluids injection and microwave heating. The main drawbacks of thermal injection method are the loss of heat in non-hydrate sections, the low injection rates and the expensive cost of thermal injection (Chong et al., 2016). In depressurization method, there is production of free water and or free gas in the pores of gas hydrate reservoirs by using pumps (i.e. electrical submersible pump), hence the reservoir pressure is diminished below hydrate equilibrium pressure and creates the gas hydrate dissociation and the release of gas and water. The drawbacks of depressurization method are sand production, geomechanical risks and slow gas production (Yin et al., 2018). In chemical injection method, chemicals such as methanol, ethylene glycol, brine etc. are used to shift the gas hydrate equilibrium curve leading to gas hydrate dissociation. However, chemical injection method is noxious in marine environments (Xu and Li, 2015). In CH_4-CO_2 method when CO_2 is injected into CH_4 gas hydrate reservoir, CH_4 molecules leave their hydrate cages and CO_2 molecules fill these void cages because of thermodynamic stability difference between CH_4 hydrate and CO_2 hydrate. The low injection rate and low replacement rate are the disadvantages for CH_4-CO_2 method (Kvamme, 2015).

The number of studies related to these gas hydrates in the Mediterranean Sea is low compared to those from the continental margins of the United States of America (USA), Japan, India, China and Korea. This study aims at evaluating the gas hydrate potential of the Mediterranean Basin (especially the Eastern Mediterranean) by using the available literature data such as drilling data, geothermal data, and geochemical data.

2. Gas Hydrate Potential of the Eastern Mediterranean Sea

Recently, there have been many conventional gas reserve discoveries in the Mediterranean Basin most of which are in the Eastern Mediterranean indicating a huge conventional gas potential (Lo, 2017). In order to propose the producible gas hydrate potential of the Eastern Mediterranean Sea, the following criteria should be satisfied:

- Source gas potential (generally biogenic CH_4)
- Migration paths (if source rock and reservoir rock are different, there should be a migration path from source rock to reservoir rock)

- Reservoir rock within gas hydrate stability zone (GHSZ)
- Porous and permeable coarse sands
- Water in porous media

It is essential to study the Eastern Mediterranean Basin literature data to conclude that whether the Eastern Mediterranean Sea has producible gas hydrate potential or not.

2.1. Source Gas Potential in the Eastern Mediterranean Sea

The source gas potential in the Mediterranean Sea was proved with recent conventional gas discoveries. For instance, in the Nile Delta of the Mediterranean Sea, there are 126 gas fields with proven reserves about 1.8 tcm. In the Levantine basin of the eastern Mediterranean, recent gas discoveries have been made. Similarly, it is known that there are potential gas reserves in the south part of Crete and Cyprus (Foscolos et al., 2011). There are widespread gas seepages across the seafloor of the eastern Mediterranean Sea. These extensive gas seepages were mostly observed in mud volcanoes. Mud volcanoes (and/or gas chimneys) are defined as the result of massive mud/fluid expulsion on the seafloor (Praeg et al., 2011). There is a link between mud volcanoes and hydrocarbon occurrences. As the number of mud volcanoes increases, the possibility of hydrocarbon existence increases as well (Kopf, 2002).

Although a few mud volcanoes were detected in the Western Mediterranean Basin, many mud volcanoes were found in the Eastern Mediterranean. According to Milkov (2005), mud volcanoes are important indicators of gas hydrate existence because they show the high source gas potential in the study area. The number of mud volcanoes in the Eastern Mediterranean Sea exceeds 200, which is one of the world's highest abundances of mud volcanoes as seen in figure 1 (Woodside et al., 1998; Kopf, 2002; Charlou et al., 2003; Camerlenghi and Pini, 2009). All of these indicate that there is no problem in the Eastern Mediterranean Sea in terms of source gas potential.

The gas released at the seafloor of the Eastern Mediterranean Basin is originated by two mechanisms: biogenic and thermogenic gas generation. In the Eastern Mediterranean Basin, part of the gas plumbing system is related to plate convergence between Africa and Eurasia (Farla, 2006). Gas hydrate dissociation may be related to this geological process. The other mechanism responsible for gas migration that is the sedimentary loading within the Nile Deep Sea fan. Huge amount of gas hydrate dissociations occurred due to the increase in the seafloor temperature of the Mediterranean Sea (Poort et al., 2005). Global warming causes gas hydrate dissociations in the different part of the world (Ruppel and Kessler, 2017). Woodside et al. (1998) proposed that most of the mud volcanoes in the Eastern Mediterranean Sea are

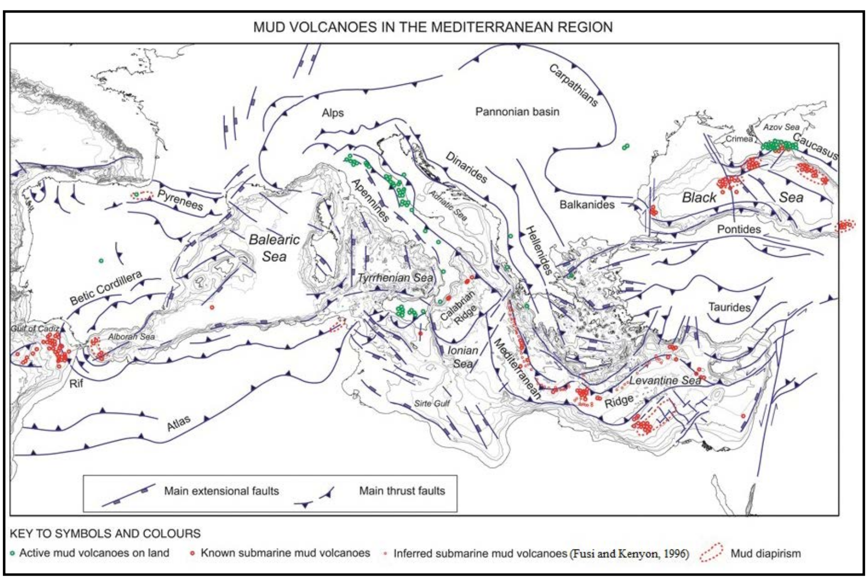

Figure 1- Distribution of mud volcanoes in the Mediterranean region (Camerlenghi and Pini, 2009).

related to tectonic forces and the rest amount is related to gas hydrate dissociation.

Table 1 lists some locations where gas seepages detected in the Eastern Mediterranean Sea (Gontharet et al., 2009; Makovsky et al., 2013; Aloisi et al., 2000; Lykousis et al., 2009; Pape et al., 2010; Werne et al., 2004). As seen in table 1, mostly CH_4 was detected in almost all gas seepages. This is an important sign of biogenic source gas (Charlou et al., 2003). However, there is also thermogenic gas potential in Amsterdam mud volcano (MV) (Anaximander Mountain in the Eastern Mediterranean Sea) in table 1 because gas is composed of 84 % CH_4, 13 % C_2H_6, and 3 % C_3H_8.

While taking gas samples in gas seepage areas in table 1, the core samples were also taken in the seafloor by using gravity corer. Figure 2-a shows the gas hydrate sample collected in Thessaloniki MV (1315 meter (m) below sea level) in the Eastern Mediterranean Sea (Lykousis et al., 2004). Similarly, the gas hydrate was collected from Amsterdam MV (2025 m below sea level) as shown in figure 2-b (Lykousis et al., 2009). Gas hydrate detected in Amsterdam MV is sII hydrate.

In some cores taken from the seafloor of the Eastern Mediterranean Sea, gas hydrate was not found but the sediments were mousy and soupy (Pape et al., 2010). While sampling core samples with the gravity corer, pressure is not preserved so gas hydrate mostly dissociates until it reaches to the sea surface. However, mousy and soupy sediments are also considered as important signs of gas hydrate existence (Merey and Sinayuc, 2016*a*).

Farla (2006) proposed that the amount of CH_4 stored in the Eastern Mediterranean Sea varies from $61x10^9$ cubic meter (m^3) to $490x10^9$ m^3. This indicates huge source gas potential in the Eastern Mediterranean Sea. It is expected that important amount of this source gas is also stored as gas hydrates inside the sediments within gas hydrate stability zone (GHSZ).

2.2. Migration Paths

Conventional petroleum systems are composed of source rock, migration paths, reservoir rock and trap rock (Hunt, 1995). For gas hydrates, source rock and reservoir may coincide. Especially, within the gas hydrate stability zone, source gas may be formed after biogenic processes, so gas migration may not be needed to feed a reservoir. With the necessary pressure and temperature condition, gas hydrates

Table 1- Some gas seepages in the Eastern Mediterranean Sea.

Location	**Sea Depth, m**	**Gas Type**	**Source**
Nile Delta Sea Fan	500 to 3000	Mostly CH_4	Gontharet et al., 2009
Levantine Basin	1100 to 1300	Mostly CH_4	Makovsky et al., 2013
Olimpi Area	1700 to 2000	Mostly CH_4	Aloisi et al., 2000
Thessaloniki MV	1260 to 1320	Mostly CH_4	Lykousis et al., 2009
Amsterdam MV	2025	84 % CH_4, 13 % C_2H_6, 3 % C_3H_8	Pape et al., 2010
Kazan MV	1700	CH_4	Werne et al., 2004

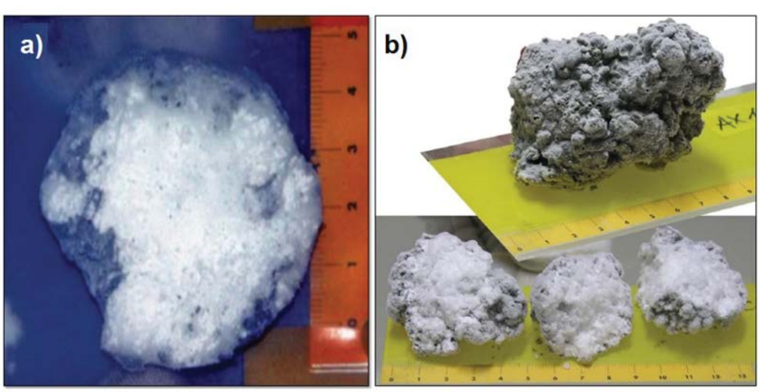

Figure 2- a) Gas hydrate sample in Thessaloniki MV, Eastern Mediterranean (Lykousis et al., 2004) b) Gas hydrate sample in Amsterdam MV (Lykousis et al., 2009)

may form within the source rock. A cap rock is not a must for gas hydrate because gas hydrates are in solid form. However, gas seepages at the seafloor show that there are many migration systems like faults and permeability changes in the Eastern Mediterranean Basin.

2.3. Gas Hydrate Stability Zone (GHSZ)

Gas hydrate stability zone is defined as the interval where gas hydrates form and GHSZ thickness depends on sea depth, sea salinity, geothermal gradient, chemical composition of the gas and the water. Above GHSZ, gas hydrate cannot exist because there is not enough hydrostatic pressure. Below GHSZ, gas hydrate cannot exist as well because temperature raises with depth due to geothermal gradient but hydrostatic pressure is not enough to form gas hydrate (Max and Johnson, 2016).

In order to determine the thickness of GHSZ of the Mediterranean Sea, it is essential to get information about seafloor temperature, geothermal gradient, water depth (pressure), and salinity. The seafloor temperature of the Mediterranean Sea varies from 12.5 Celsius (°C) to 14 °C. The pore water salinity is approximately 3.86 weight % (Praeg et al., 2017). It is known that gas hydrates generally follow hydrostatic pressure and generally they are not over-pressurized as conventional gas reservoirs (Max and Johnson, 2016). The type of gas hydrate affects GHSZ. sII hydrate formed from natural gas mixtures is much more stable than CH_4 (sI) hydrate (Sloan and Koh, 2008) so GHSZ of sII is thicker. Moreover, water depth is an important factor affecting the thickness of GHSZ. As sea depth increases, the thickness of GHSZ increases. Therefore, GHSZ is thinner in sea slopes. For example, Thessaloniki MV is located between 1260 m and 1320 m below sea surface and GHSZ is very thin at this MV. Figure 3 shows the Mediterranean Sea bathymetry. As seen in this figure, the Eastern Mediterranean Sea is deeper than the Western Mediterranean Sea. This also proves the higher possibility of gas hydrate existence in the Eastern Mediterranean Sea compared to the Western Mediterranean Sea.

The high average water depth in the Mediterranean Sea favors the a thicker GHSZ. However, the sea floor temperature of the Mediterranean Sea is high (~14°C) relatively to the global ocean (Küçük et al., 2016), and this reduces the thickness of GHSZ. The geothermal gradient in the Mediterranean Basin is highly variable (Merey and Longinos, 2018). In the Western Mediterranean Sea, heat flow varies from 50 to >100°C/kilometer (km). However, the Eastern Mediterranean Sea has a geothermal gradient less than 50°C/km (Eckstein, 1978; Praeg et al., 2011). The reason of very high geothermal gradients in the Western Mediterranean Sea is explained with volcanism activity

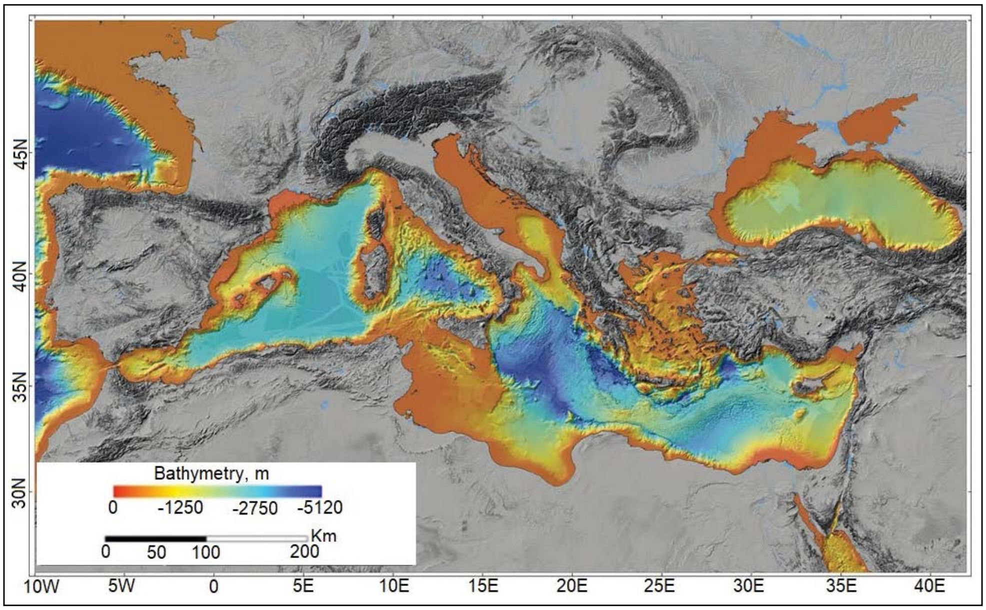

Figure 3- Mediterranean sea bathymetry (Brosolo et al., 2012).

in this area (higher upper mantle temperature below this zone) (Cermak and Rybach, 2012).

Due to its deeper water depth and lower geothermal gradient, the Eastern Mediterranean Sea has thicker GHSZ compared to the Western Mediterranean Sea. Methane gas hydrate stability curve in the conditions of the Mediterranean Sea with an average of 3.86 wt. (weight) % salinity was drawn in figure 4 by using HEP software developed by Merey and Sinayuc (2016*b*). For 500 m-thick methane hydrate stability zone (MHSZ), the temperature in the bottom of MHSZ was calculated as 20°C and 39°C for 12°C/km and 50°C/km geothermal gradients respectively (when seafloor temperature is 14°C and sea depth is 2000 m). For 39°C, methane hydrate equilibrium pressure should be 164.5 mega Pascal (MPa). It is not possible to obtain this pressure in gas hydrates because gas hydrates follow hydrostatic pressure gradients and they are not overpressurized as conventional gas reservoirs (Max and Johnson, 2016). In this example, the hydrostatic pressure at 500 meter below seafloor (mbsf) is 26.5 MPa, which is below 164.5 MPa. For this reason, gas hydrate stability zone in the Western Mediterranean Sea is thin as seen in figure 5. However, in the Eastern Mediterranean Sea, there are locations with 12°C/km geothermal gradient. In these conditions, at 500 mbsf (in the example above), hydrostatic pressure and methane hydrate equilibrium pressure in figure 4 are close to each other (~26.5 MPa) so it is possible to observe 500 m thick-MHSZ in the Eastern Mediterranean Sea.

Furthermore, there are many mud volcanoes and gas seepages in the Eastern Mediterranean Sea and gas hydrate samples were collected in the Eastern Mediterranean Sea (Figure 2). All of these supports the widespread existence of gas hydrates in the Eastern Mediterranean Sea. Kopf (2002), Ocakoğlu (2009) and Praeg et al. (2011) proposed this potential as well.

Table 2 lists some of GHSZ predictions in the Mediterranean Sea (Klauda and Sandler, 2003; Praeg et al., 2017; Wood and Jung, 2008; Praeg et al., 2011; Max and Johnson, 2016). Considering all of these variations over the Mediterranean Sea, Praeg et al. (2011) proposed the GHSZ thickness map of the Mediterranean Sea for methane hydrate in figure 5. As expected according to the outcomes of this study, there are huge amounts of gas seeps in figure 1 in the Eastern Mediterranean Sea. Moreover, the thickness of GHSZ in the Western Mediterranean Sea is less than 150 m. On the other hand, the thickness of GHSZ varies from 175 m to 500 m in the Eastern Mediterranean Sea. When figure 3 and figure 5 are analyzed together,

Table 2- GHSZ Predictions in the Mediterranean Sea.

Source	GHSZ, m
Klauda and Sandler, 2003	100 to 400
Praeg et al., 2007	Average 200
Wood and Jung, 2008	100 to 250
Praeg et al., 2011	200 to 500
Max and Johnson, 2016	Maximum 400

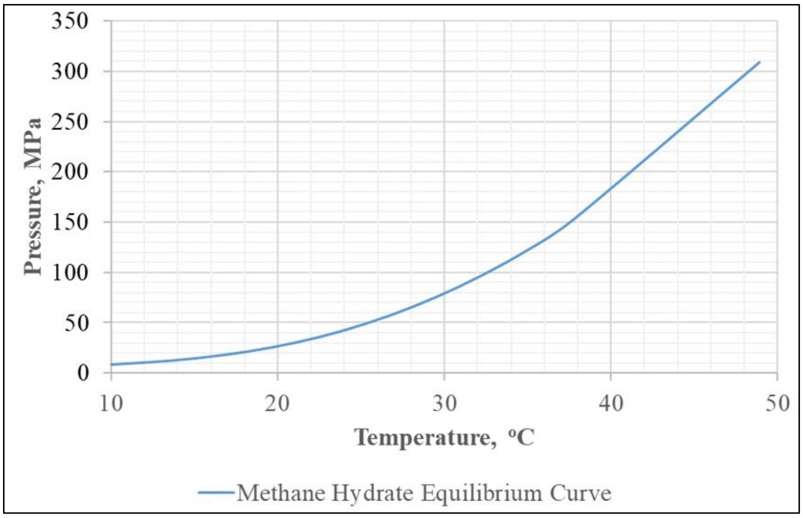

Figure 4- Methane hydrate stability curve in the conditions of the Mediterranean Sea with an average of 3.86 wt. % salinity.

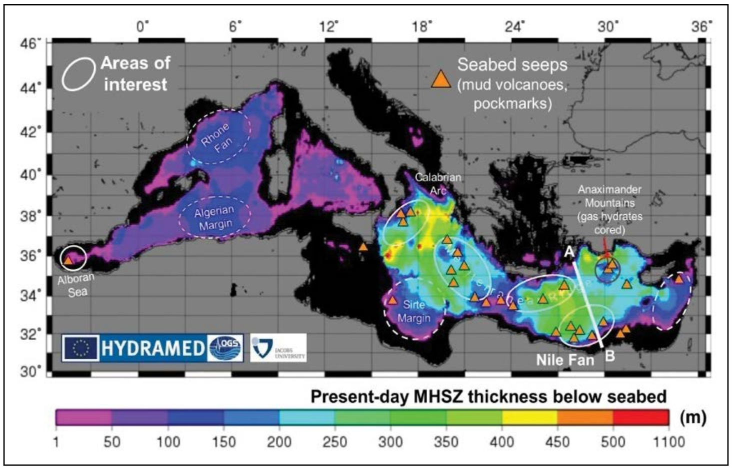

Figure 5- Methane Hydrate Stability (MHSZ) in the Mediterranean Sea; orange triangles indicating the general locations of known seabed gas seeps (Praeg et al., 2011).

it can be concluded that GHSZ strongly depends on water depth because in deeper part of the Eastern Mediterranean Sea, GHSZ is thicker. Furthermore, due to higher geothermal gradient (50-100^{o}C/km) in the Western Mediterranean Sea, GHSZ is thin in this part of the Mediterranean Sea. To summarize, the Eastern Mediterranean Sea has thicker GHSZ and it has a good potential of gas hydrate existence.

2.4. Porous and Permeable Coarse Sands

The type of sediments where gas hydrate deposited is quite important for hydrate morphology in porous media. Generally, the permeability of clays and shales is associated to mud volcanoes. CH_4 formed in this geological environment is forced through the host formation by overpressure and hydrofracturing, forming fracture filling gas hydrates and nodular gas hydrates. These gas hydrates are common in the world but they are not considered as producible gas hydrate because the permeability, porosity and hydrate saturations in these types of gas hydrates are very low.

With current technology, gas production from gas hydrates deposited inside the porous media of coarse sands is possible in terms of feasibility. This is because permeability, porosity and gas hydrate saturations are high in coarse sands (Merey and Sinayuc, 2016*a*; Max and Johnson, 2016). In recent short-term gas production trials from gas hydrates in Canada, USA and Japan, gas hydrates deposited in coarse sands were chosen (Boswell et al., 2017).

According to the outcomes in this study, the Eastern Mediterranean Sea has high amount of source gas potential, migration paths, and thick GHSZ and these are significant indicators of a gas hydrate potential. However, coarse sands within GHSZ in the Eastern Mediterranean Sea should be detected for the producible gas hydrate potential. Max and Johnson (2016) proposed that the presence of coarse sands with high reservoir quality is possible in the Mediterranean Sea because of its Neogene and younger history.

Although geophysical methods are helpful for detecting coarse sands in GHSZ, the drilling data is necessary to detect these coarse sands possibly including gas hydrates. In this study, the open-source drilling and coring data of Ocean Drilling Program (ODP) Leg 160 and Leg 161 in 1995 were investigated in detail. The wells were drilled in the Eastern Mediterranean Sea during ODP Leg 160 program and the wells were drilled in the Western Mediterranean Sea during ODP Leg 161 program (ODP Leg 160, 1995; ODP Leg 161, 1995). Figure 6 shows the locations of the wells drilled during ODP Leg 160 and Leg 161 programs.

The detection of sands in the lithology of the wells drilled during ODP Leg 160 and Leg 161 are shown in table 3 (Emeis et al., 1996; Robertson, 1998*a*; Kopf et al., 1998; Robertson and Kopf, 1998). in the Western Mediterranean Sea, no sand section was detected during the drilling of the sediments up to 199.4 meter below seafloor (mbsf). However, this is

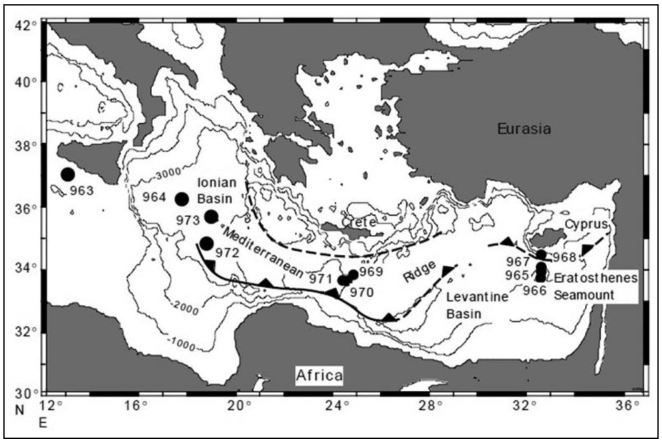

Figure 6- The drilling sites in ODP Leg 160 in the Mediterranean Sea (ODP Leg 160, 1995; ODP Leg 161, 1995).

Table 3- Detection of sands in the lithology of the wells drilled during ODP Leg 160 and Leg 161.

Site Number	Depth, mbsf	Sand	Source
963	199.4	No detected	Emeis et al., 1996
964	112	Limited interval of foraminifer sand	Emeis et al., 1996
965	250.4	Not detected	Emeis et al., 1996
966	350	Relatively rare intervals of crudely stratified coarse carbonate sand	Robertson, 1998*a*
967	600.3	Not detected	Spezzaferri et al., 1998
968	301	Fine sands (up to tens of centimeters thick) (167-301 mbsf)	Robertson, 1998*b*
969	110	Not detected	Emeis et al., 1996
970	200	Poorly consolidated thin- to medium-bedded sands	Kopf et al., 1998
971	200	Thin layers that correspond to relatively sandy	Robertson and Kopf, 1998
972	95.4	Fine sands up to 50 cm in thickness	Robertson and Kopf, 1998
973	150	Interbeds of sands, silts, and nannofossil clays, and a single 14-m-thick interval of sand	Kopf et al., 1998

the data from only one site and the sediments are very heterogeneous. Therefore, with the increase of drilling activities around Site 963 and other sites, there is a possibility to detect coarse sand sections. In Site 964 in the Western Mediterranean Sea, limited interval (centimeter scale) of foraminifer sand was observed. In Site 965 in the Eastern Mediterranean Sea, no sand section was found. However, near Site 965, relatively rare intervals of crudely stratified coarse carbonate sands were detected in Site 966. Even though no sand section was detected in Site 967 in the South of Cyprus, fine sands (up to tens of centimeters thick between 167 and 301 mbsf) were observed in Site 968 in the South of Cyprus. Similarly, poorly consolidated thin- to medium-bedded sands were detected in Site 970 in the South of Crete but near Site 970, sand section was not discovered in Site 969. Near Site 970, thin layers that correspond to relatively sandy sediments were detected in Site 971. In Site 972, fine sands up to 50 cm in thickness were detected but the thickest sand section (14 m) in ODP Leg 160 and Leg 161 was found in Site 973.

The cores recovered from Site 970 and Site 971 were mainly “mousse-like” muddy sediments. It is hard to see gas hydrates in sediments if the core samples are taken to the surface with conventional coring techniques instead of new pressurized coring techniques. However, the appearance of the sediments after conventional coring can be a proxy for the presence of gas hydrates. With gas hydrate dissociation after conventional coring, "soupy" and "mousse-like" sediments are seen as a proxy for the gas hydrate existence (Melgar, 2009; Merey, 2017). Soupy sediments include high amount of water, and high hydrate content might be reason of this when nodular and massive gas hydrate exists. Different from soupy sediments, mousse like sediments are considered to include disseminated gas hydrates in fine sediments (Melgar, 2009). Therefore, the appearance of core samples is one of good indicators of gas hydrates even if they are conventional core samples and these indicators are available in the Mediterranean Sea.

Figure 7 shows the sand % in Site 966, Site 967, Site 969, Site 970 and Site 971. The drilling results of ODP Leg 160 and Leg 161 indicate that there is a potential of coarse sand section within GHSZ. If these sand sections were invaded with source gas, gas hydrate deposition is highly possible inside these coarse sands. Thus, these coarse sand sections in the Mediterranean Sea should be targets for the exploration of producible gas hydrates as in Canada, USA, India, and Japan (Merey and Sinayuc, 2016*a*; Merey and Longinos, 2018)

2.5. Other Indicators

The existence of gas hydrates might be investigated by using different methods. One of them is geophysical method. Bottom-simulating reflections (BSR) are commonly used to detect gas hydrates in marine environment. Above the bottom of GHSZ, gas hydrate is stable but below the bottom of GHSZ, gas hydrate is not stable and gas is available as free gas in the pores of the sediments. Hence, at the bottom of GHSZ, there is a transition from solid phase and gaseous phase of methane. This creates a large acoustic impedance contrast generating a high amplitude reflector called bottom simulating reflector (Thakur and Rajput, 2011) because it mimics sea bottom. Majumdar et al. (2016) proposed that the detection of BSR increases the possibility of gas hydrate detection 2.6 times..

Even though BSRs are widely detected along the world continual margins, only one BSR has been tentatively detected so far in the Mediterranean Sea (Merey and Longinos, 2018). This BSR (Figure 8) is in the Nile Deep Sea Fan in the Eastern Mediterranean Sea (Praeg et al., 2011). The reasons of rare occurrence of BSR in the Mediterranean Sea might be due to (Miles, 1995; Merey and Longinos, 2018):

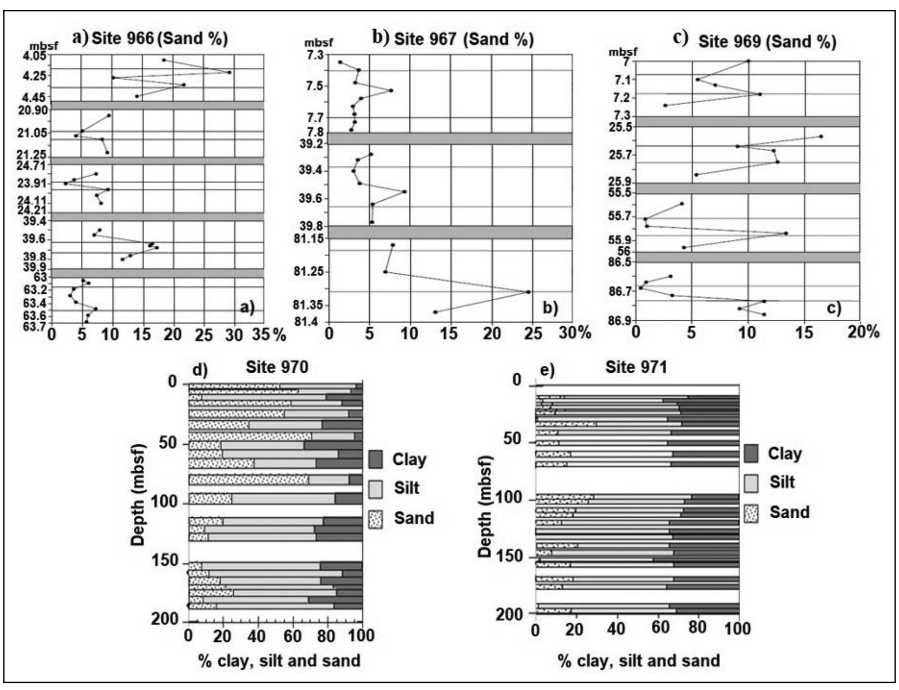

Figure 7- a) Sand % in Site 966 (Robertson, 1998a) b) Sand % in Site 967 (Spezzaferri et al., 1998) c) Sand % in Site 969 (Diester-Haass et al., 1998) d) Clay, Silt and Sand % in Site 970 (Kopf et al. 1998) e) Clay, Silt and Sand % in Site 971 (Robertson and Kopf, 1998).

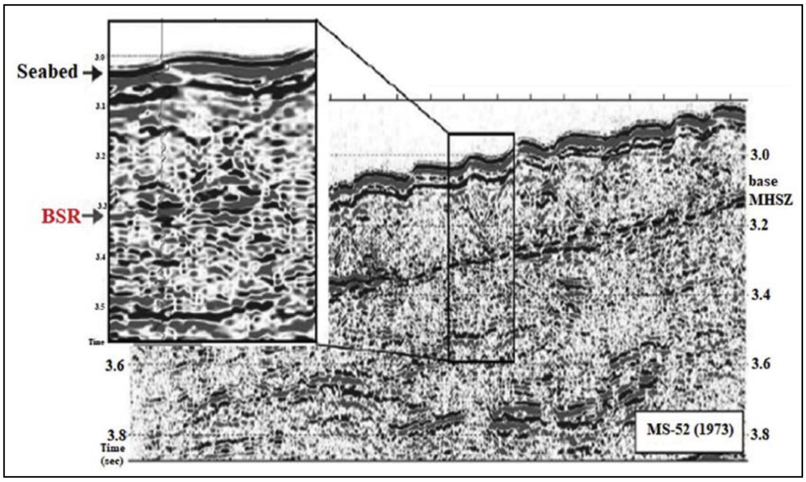

Figure 8- The BSR observed in the central Nile Delta, Eastern Mediterranean Sea (Praeg et al., 2008).

- Less Class 1 hydrate occurrence
- Less shallow geophysical studies

During the drilling of marine sediments, core samples are collected. Chlorine (Cl) content of pore water of cores might be an indicator to determine gas hydrate saturations in cores (Haese et al., 2006; Merey and Sinayuc, 2016*a*). During gas hydrate formation, only pure water is taken to the structure of gas hydrate and salt stays inside the rest of pore water. Although initially Cl content of pore water increases due to gas hydrate formation, it is balanced with the neighbor sediments within geological history. When gas hydrate dissociates and it releases pure water to porous media so Cl content decreases within gas hydrate zones. It is possible to calculate gas hydrate saturation in porous media by using Cl content in porous media and average Cl trend content. In Site 970, Cl content decreased near Milano MV and this is an important indicator of gas hydrate existence (Kopf et al., 1998). Furthermore, Cl content reduction in pore water was observed in Kazan MV and Amsterdam MV in Anaximander Mountain of the Eastern Mediterranean Sea. However, it was proposed that there is an another reason of Cl content reduction, which is due to clay mineral diagenesis (Haese et al., 2006).

3. Gas in-Place in the Potential Mediterranean Sea Gas Hydrates

Since the consideration of gas hydrates as energy resources, they have been many gas-in place calculations in gas hydrates in the world. Although small variations in parameters change gas-in place amount enormously, these calculations are essential to show the gas potential in the study area. It is not enough to calculate gas potential in gas hydrates deposited in all sediments because it is considered that feasible gas production is possible from gas hydrates deposited in coarse sands with current technology. For this reason, in this study, gas amount in producible gas hydrate was also calculated for the Mediterranean Sea and the Eastern Mediterranean Sea.

In order to make gas-in place calculations from the potential Mediterranean Sea gas hydrates, the following parameters were obtained from the literature for this study: Porosity, gas type, average gas hydrate saturation, seafloor temperature, geothermal gradient, sea depth, sea salinity, sediment salinity, pressure gradient, and GHSZ thickness

Equation 1 and Equation 2 are commonly used to calculate CH_4-in place in gas hydrate reservoirs (GIP) (Boswell and Collett, 2011);

$$\mathrm{GIP} = \varphi \times \mathrm{h} \times \mathrm{A} \times \mathrm{EF} \times \mathrm{CR} \times S_h \quad (1)$$

$$\mathrm{EF} = \frac{\mathrm{MW}_{CH_4}}{\mathrm{MW}_{CH_4} + \mathrm{N_H}\mathrm{MW}_{H_2O}} \times \frac{\mathrm{V_H}\rho_\mathrm{H}}{\rho_{CH_4}} \quad (2)$$

where;

φ:	porosity, fraction
h:	thickness of hydrate zone, m
A:	cross-sectional area of hydrate zone, m^2
CR:	cavity fill ratio of CH_4
EF:	Expansion factor of CH_4 in hydrate to surface standard conditions, ratio

S_h: gas hydrate saturation, fraction
$MWCH_4$: Molecular weight of CH_4, g/mol
ρ_H: CH_4 hydrate density, kg/m^3
MWH_2O: Molecular Weight of H_2O, g/mol
N_H: Hydration Number of CH_4 hydrate
ρ_{CH_4}: CH_4 gas density at standard conditions (0.717935 kg/m^3 at 0°C and 1 atm)
V_H: unit hydrate volume (1 m^3)

In the literature, there are two GIP calculations in the Mediterranean Sea (Klauda and Sandler, 2003; Bruneton et al., 2012). In these studies, rough estimations were made. According to Klauda and Sandler (2003), 590 tcm CH_4 is deposited inside the potential Mediterranean Sea gas hydrates. Bruneton et al. (2012) estimated producible CH_4 from CH_4 hydrates in the Mediterranean Sea as 51 tcm. Compared to these two estimations, a detailed literature review in Mediterranean Sea was made for the purpose of this study and table 4 was obtained. Table 4 includes the necessary parameters for Equation 1 and Equation 2. By using the core data and porosity log data in ODP Leg 160 and 161 (ODP Leg 160, 1995; ODP Leg 161, 1995), largest, most likely and lowest porosity values were found for the Mediterranean Sea sediments within MHSZ. As discussed earlier, the thickness of MHSZ varies depending on geothermal gradient, sea salinity and bathymetry. HEP software developed by Merey and Sinayuc (2016b) was used to estimate MHSZ at different geothermal gradient (Eckstein, 1978), sea salinity (Praeg et al., 2011) and bathymetry (Brosolo et al., 2012). Then, the range in MHSZ in the Mediterranean Sea in table 4 was obtained. CH_4 was obtained from the core samples recovered in ODP Leg 160 and Leg 161 (ODP Leg 160, 1995; ODP Leg 161, 1995). From the amount of CH_4 recovered from the cores, the range of gas hydrate saturations (S_h) in table 4 was found. For these estimations, expansion factors estimated with HEP were used.

By using the parameters in table 4, Monte Carlo simulations were made with Equation 1 and Equation 2 to calculate CH_4 stored in CH_4 hydrates deposited in all sediments of the Mediterranean Sea and the Eastern Mediterranean Sea. It is known that the surface of area of the Mediterranean Sea is 2.5 million km^2 and the surface area of the Eastern Mediterranean Sea is 1.65 million km^2 (Simav et al., 2008). The gas hydrate area of the Eastern Mediterranean Sea is shown in table 4 as well. According to the calculations in this study, it was estimated that the potential Mediterranean Sea gas hydrates deposited in all types of sediments (shales, clays, silt, sands, etc.) includes 623.466 tcm (median) (varying from 11.505 tcm to 2091.560 tcm) of CH_4 as shown in table 5. In the Eastern Mediterranean Sea, the amount of CH_4 deposited in gas hydrates deposited in all types of sediments is 552.3 tcm (median) (ranging from 9.96 tcm to 1954 tcm) as seen in table 5. Table 5 indicates the minimum GIP and maximum GIP. Huge variations are due to the variations in the parameters in table 4. With the increase of exploration and drilling studies, these variations will be decreased and much more exact GIP values will be obtained.

As discussed previously, gas hydrates deposited in coarse sands are targets for feasible gas production from gas hydrates with current technology because of coarse sands' high permeability and high porosity. ODP Leg 160 and ODP Leg 161 data is quite helpful

Table 4- Parameters used for the calculation of the amount of CH_4 in the Mediterranean Sea gas hydrates in all sediments.

	Lowest	Most Likely	Largest	Reference
Porosity, fraction	0.4	0.5	0.7	ODP Leg 160 (1995); ODP Leg 161 (1995)
Average hydrate filling, fraction	0.01	0.1	0.5	ODP Leg 160 (1995); ODP Leg 161 (1995)
MHSZ Thickness, m	100	175	500	Eckstein (1978); Praeg et al., 2011; Brosolo et al., 2012)
Cavity fill ratio calculated with HEP	0.989	0.99	0.994	ODP Leg 160 (1995); ODP Leg 161 (1995)
Expansion Factor with HEP	167.549	167.697	169.206	ODP Leg 160 (1995); ODP Leg 161 (1995)
Hydrate Area, m^2 (Whole Mediterranean Sea)	4.817E+08	2.000E+11	2.151E+11	Bruneton et al. (2012)
Hydrate Area, m^2 (Eastern Mediterranean Sea)	3.315E+08	1.570E+11	1.851E+11	Bruneton et al. (2012)
Sand Fraction %	1	15	35	ODP Leg 160 (1995); ODP Leg 161 (1995)

Table 5- CH_4 potential of the Mediterranean Sea Hydrates.

Source	GIP in the Mediterranean Sea Hydrates, tcm in all sediments	GIP in the Mediterranean Sea Hydrates, tcm in sands	GIP in the Eastern Mediterranean Sea Hydrates, tcm in all sediments	GIP in the Eastern Mediterranean Sea Hydrates, tcm in sands
Klauda and Sandler (2003)	590	-	-	-
Bruneton et al. (2012)	-	51	-	-
This Study	623.466 (11.505-2091.560)	98.160 (1.606-458.868)	552.3 (9.96-1954)	81.2 (1.36-313.8)

to determine average sand contents. In table 4, it was shown that the sand fraction varies from 1 % to 35 % in the Mediterranean Sea. By using Equation 1, Equation 2 and sand content data in table 4, Monte Carlo simulations were run in order to calculate GIP in gas hydrate deposited in the possible sand sections of the Mediterranean Sea and the Eastern Mediterranean Sea. The amount of CH_4 in the Mediterranean Sea hydrates deposited in sands was found as 98.16 tcm (median) (ranging from 1.606 tcm to 458.868 tcm). This amount in the Eastern Mediterranean Sea was estimated by Monte Carlo simulation as 81.2 tcm (median) (varying from 1.36 tcm to 313.8 tcm).

According to GIP estimations in this study, it is shown that the Eastern Mediterranean Sea has a great potential of gas hydrates and producible gas hydrates. In order to evaluate this potential, further geophysical studies, drilling studies, coring studies and well logging studies are requisite.

4. Gas Production Potential from the Eastern Mediterranean Sea Hydrates

Coarse sands have good reservoir properties such as high permeability and high porosity so they are targets for gas hydrate studies in terms of energy. This is because gas hydrates are in solid phase and they decrease intrinsic permeability of the sediments. There should be a huge data (i.e. drilling data, coring data, well log data, seismic data, etc.) to decide on the optimum production method of gas production from gas hydrates (Max and Johnson, 2016; Merey, 2017). Nevertheless, it is necessary to predict possible production methods from gas hydrates in the Mediterranean Sea. According to Boswell et al. (2017), depressurization method is the most widely chosen production method. Generally, chemical injection method is not preferred in marine environment due to their harm to the environment (Xu and Li, 2015). Thermal injection is not feasible when it is applied alone but it is suggested that it might be helpful if it is applied with depressurization method together (Chong et al., 2016). In light of all of these discussions in this study about the Mediterranean Sea, depressurization method might be chosen for gas production from the possible gas hydrates in the Mediterranean Sea. When seafloor temperature is high, this means thin GHSZ. However, the sediments with higher temperature cause the higher gas production with depressurization method due to heat fluxes from the boundaries (Han et al., 2017). The seafloor temperature of the Mediterranean Sea is in the classification of high temperature-seafloor. For this reason, depressurization should be considered as one candidate production method in the Mediterranean Sea.

CH_4-CO_2 replacement method has been considered as a good alternative to depressurization method (Boswell et al., 2017). Basically, especially below 10.3^{o}C, CO_2 hydrate is much more stable compared to CH_4 hydrate so when CO_2 is injected to CH_4 hydrate, there is a replacement between CH_4 and CO_2 molecules. This method was tried in Ignik Sikumi field of Alaska in 2012 but CO_2/N_2 mixture was preferred for better replacement efficiency. After the replacement of CO_2/N_2 and CH_4 in CH_4 hydrate, new mixed hydrate of CO_2-N_2-CH_4 should be stable as well. Figure 9 shows the hydrate equilibrium of different mixed gas hydrates of CO_2-N_2-CH_4 and pressure-temperature data of the Mediterranean Sea sediments. In order to prepare Figure 9, HEP (Hydrate Equilibrium Point Prediction) software of Merey and Sinayuc (2016*b*) was used. Figure 9 indicates that the replacement of CO_2/N_2-CH_4 in CH_4 hydrate is not possible because the seafloor temperature (~14^{o}C) and geothermal gradient of the Mediterranean Sea are high. Even if this replacement occurred, mixed gas hydrate cannot stay in equilibrium in the conditions of the Mediterranean Sea. In this study, it was shown that CO_2/N_2-CH_4 replacement method is not applicable in the Mediterranean Sea. Among four gas hydrate production methods, depressurization with/without wellbore heating is suggested for the Mediterranean Sea gas hydrates.

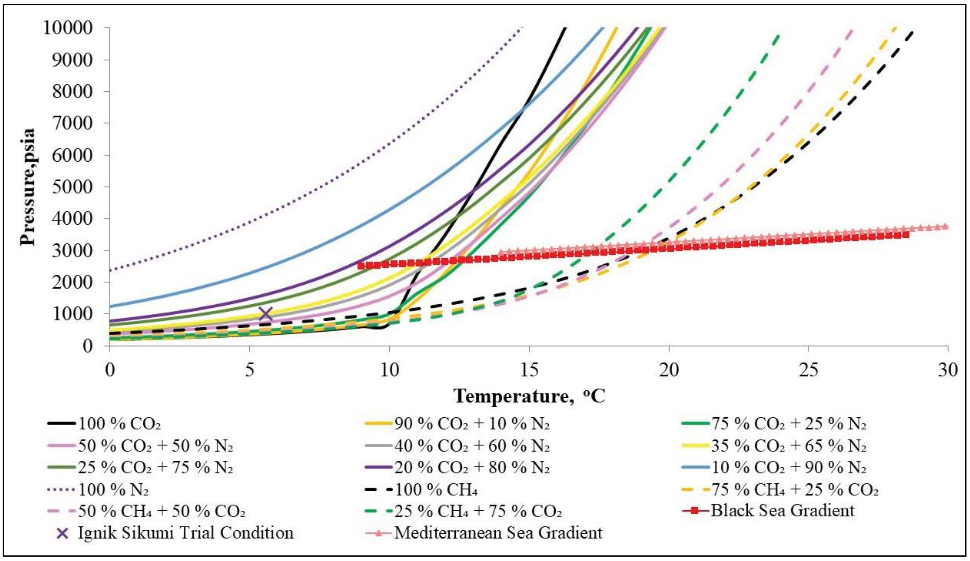

Figure 9- Hydrate equilibrium curves of CO_2, CH_4, N_2 and the pressure and temperature profile of Mediterranean Sea.

5. Conclusions

Gas hydrate reservoirs are considered as near-future energy resources. Although there are many exploration, research and development studies related to gas hydrates in the world, there are not enough studies about the Mediterranean Sea. Initially, it is important to indicate the gas hydrate potential of the Mediterranean Sea. In this study, the following concluding remarks were obtained:

- The Mediterranean Sea has all necessary conditions for the existence of gas hydrates: enough source gas, migration paths, enough thick GHSZ, and water in porous media.
- Source gas potential is higher in the Eastern Mediterranean Sea compared to the Western Mediterranean Sea because most of the gas seepages and mud volcanoes were detected in the Eastern Mediterranean Sea.
- GHSZ in the Eastern Mediterranean Sea is thicker than GHSZ in the Western Mediterranean Sea because sea depth is higher and geothermal gradient is lower in the Eastern Mediterranean Sea.
- According to the analysis of ODP Leg 160 and Leg 161 drilling data, it is concluded that the Mediterranean Sea might include coarse sand sections which might include producible gas hydrates.
- The Mediterranean Sea gas hydrates might include 623.466 tcm of CH_4 in all sediments and 98.16 tcm (median) of CH_4 in coarse sands.
- The Eastern Mediterranean Sea gas hydrates might include 552.3 tcm of CH_4 in all sediments and 81.2 tcm (median) of CH_4 in coarse sands.
- Depressurization method with/without thermal heating production method is suitable for the Mediterranean Sea gas hydrates because the seafloor temperature of the Mediterranean Sea is high and this is advantageous due to the heat transfer from the boundaries during gas production.
- CH_4-CO_2/N_2 replacement production method is not applicable in the conditions of the Mediterranean Sea because of its high seafloor temperature.

The huge gas hydrate potential of the Eastern Mediterranean Sea should be evaluated with geophysical and exploration studies. With further studies, gas hydrate prospects in the Eastern Mediterranean will be known in detail so better production strategies can be made.

References

Aloisi, G., Pierre, C, Rouchy, J.M., Foucher, J.P., Woodside, J. 2000. Methane-related authigenic carbonates of eastern Mediterranean Sea mud volcanoes and their possible relation to gas hydrate destabilisation. Earth and Planetary Science Letters 184 (2000), 321-338.

Bruneton, A., Konofagos, E., Foscolos, A.E. 2012. Cretan Gas Fields – A new perspective for Greece's hydrocarbon resources. Pytheas Market Focus. https://images.derstandard.at/2013/08/21/greece_crete.pdf. October 21, 2018.

Boswell, R., Collett, T.S. 2011. Current perspectives on gas hydrate resources. Energy & Environmental Science 4, 1206-1215.

Boswell, R., Schoderbek, D., Collett, T.S., Ohtsuki, S., White, M.D., Anderson, B.J. 2017. The Ignik Sikumi Field Experiment, Alaska North Slope: Design, Operations, and Implications for CO_2-CH_4 Exchange in Gas Hydrate Reservoirs. Energy Fuels 31 (1), 140-153.

Brosolo, L., Mascle, J., Loubrieu, B. 2012. Morpho-bathymetry of the Mediterranean Sea. Commission for The Geological Map Of The World. https://ccgm.org/en/catalogue/130-carte-morpho-bathymetrique-de-la-mediterranee-9782917310120.html. September 20, 2018.

Camerlenghi, A., Pini, G.A. 2009. Mud volcanoes, olistostromes and Argille scagliose in the Mediterranean region. Sedimentology 56, 319–365.

Carroll, J. J. 2009. Natural Gas Hydrates: A Guide for Engineers. Gulf Professional Publishing.

Cermak, V., Rybach, L. 2012. Terrestrial Heat Flow in Europe. Springer Science and Business Media, 2012.

Charlou, J.L., Donval, J.P., Zitter T., Roy, N., Jean-Baptiste, P., Foucher, J.P., Woodside, J. 2003. Evidence of methane venting and geochemistry of brines on mud volcanoes of the eastern Mediterranean Sea. Deep-Sea Research I 50 (8), 941-958.

Chen, L., Feng, Y., Kogawa, T., Okajima, J., Komiya, A. 2018. Maruyama. Construction and simulation of reservoir scale layered model for production and utilization of methane hydrate: The case of Nankai Trough Japan. Energy 143 (2018), 128-140.

Chong, Z.R., Hern, S., Yang, B., Babu, P., Linga, P., Li X. 2016. Review of natural gas hydrates as an energy resource: prospects and challenges. Applied Energy 162 (2016), 1633–1652.

Diester-Haass, L., Robert, C., Chamley, H. 1998. Paleoproductivity and Climate Variations during Sapropel Deposition in the Eastern Mediterranean Sea. Robertson, A.H.F., Emeis, K.C., Richter, C., Camerlenghi, A. (Eds.). 1998. Proceedings of the Ocean Drilling Program, Scientific Results 160.

Eckstein, Y. 1978. Review of heat flow data from the eastern mediterranean region. Pageoph 117 (150).

Emeis, K.C., Robertson, A., Richter, C., Fox, P.J., Baldauf, J.,Francis, T.J.G. 1996. Ocean Drilling Program Leg 160 Preliminary Report Mediterranean I. http://www-odp.tamu.edu/publications/prelim/160PREL.PDF/. January 26, 2018.

Farla, R. 2006. Investigation on clathrates localised in the Eastern Mediterranean mud volcanoes. http://geoverse.eu/downloads/clathrates.pdf/. April 10, 2018.

Foscolos, A., Konofagos, E., Bruneton, A. 2011. The Occurrence of Converging Plates, Mud Flow Volcanoes and Accretionary Prism Complexes in the Mediterranean Ridge. Their Relationship to Possible Hydrocarbon Accumulations Offshore Crete. A New Respective for Greece's Oil and Natural Gas Resources. http://www.rieas.gr/images/aoz2.pdf/. August 27, 2017.

Fusi, N., Kenyon, N.H. 1996. Distribution of mud diapirism and other geological structures from longrange sidescan sonar (GLORIA) data, in the Eastern Mediterranean Sea, Mar. Geol., 132, 21-38.

Gontharet, S., Stadnitskaia, A., Bouloubassi, I., Pierre, C., Damsté, J.S. 2009. Palaeo methane-seepage history traced by biomarker patterns in a carbonate crust, Nile deep-sea fan (Eastern Mediterranean Sea). Marine Geology 261 (2009), 105-113.

Haese, R.R., Hensen, C., de Lange, G.J. 2006. Pore water geochemistry of eastern Mediterranean mud volcanoes: Implications for fluid transport and fluid origin. Marine Geology 225 (2006), 191-208.

Han, D., Wang, Z., Song, Y., Zhao, J., Wang, D. 2017. Numerical analysis of depressurization production of natural gas hydrate from different lithology oceanic reservoirs with isotropic and anisotropic permeability. Journal of Natural Gas Science and Engineering 46 (2017), 575-591.

Hester, K. C., Brewer, P. G. 2009. Clathrate Hydrates in Nature. Annual Review of Marine Science 1, 303-327.

Hunt, J. M. 1995. Petroleum Geochemistry and Geology. Freeman.

International Energy Agency (IEA). 2011. World energy outlook special report: are we entering the golden age of gas? 2011, Paris.

Johnson, A.H. 2011. Global resource potential of gas hydrate-a new calculation. 7. International Conference on Gas Hydrates 17-21 July 2011, Edinburgh.

Klauda, J.B., Sandler, S.I. 2003. Predictions of gas hydrate phase equilibria and amounts in natural sediment porous media. Marine and Petroleum Geology 20 (2003), 459-470.

Kopf A. 2002. Significance of mud volcanism. Reviews of Geophysics 40 (2), 1-51.

Kopf, A., Clennell, B., Camerlenghi, A. 1998. Variations in Sediment Physical Properties and Permeability of Mud-Volcano Deposits from Napoli Dome and Adjacent Mud Volcanoes. Robertson, A.H.F., Emeis, K.C., Richter, C., Camerlenghi, A. (Eds.). 1998. 1998 Proceedings of the Ocean Drilling Program, Scientific Results, 160.

Küçük, H.M., Goldberg, D.S., Haines, S.S., Dondurur, D., Guerin, G., Çifçi, G. 2016. Acoustic Investigations of Shallow Gas and Gas Hydrates: Comparison Between the Black Sea and the Gulf of Mexico. Gordon Research Seminars - Natural Gas Hydrate Systems 28 February 28- 4 March 2016, Houston.

Kvamme, B. 2015. Feasibility of simultaneous CO_2 storage and CH_4 production from natural gas hydrate using mixtures of CO_2 and N_2. Canadian Journal of Chemistry 93 (8), 897–905.

Lykousis, V., Alexandri, S., Woodside, J., Nomikou, P., Perissoratis, C., Sakelllariou, D., de Lange, G., Dahlmann, A., Casas, D., Rousakis, G., Ballas, D., Ioakim, C. 2004. New evidence of extensive active mud volcanism in the Anaximander Mountains (Eastern Mediterranean): The "ATHINA"mud volcano. Environmental Geology 46, 1030–1037.

Lykousis, V., Alexandri, S., Woodside, J., de Lange, G., Dahlmann, A., Perissoratis, C., Heeschen, K., Ioakim, C., Sakellariou, D., Nomikou, P., Rousakis, G., Casas, D., Ballas, D., Ercilla, G. 2009. Mud volcanoes and gas hydrates in the Anaximander mountains (Eastern Mediterranean Sea). Marine and Petroleum Geology 6 (6), 854-872.

Lo, C. 2017. Timeline: game-changing gas discoveries in the eastern Mediterranean.https://www.offshore-technology.com/features/timeline-game-changing-gas-discoveries-eastern-mediterranean/. April 7, 2018.

Majumdar, U., Cook, A.E., Shedd, W., Frye, M. 2016. The connection between natural gas hydrate and bottom simulating reflectors. Geophysical Research Letters 43, 7044-7051.

Makovsky, Y., Tibor, G., Herut, B., Waldmann, N.D., Spiro, B., Antler, G., Sivan, O., Ballard, R.D., Coleman, D., Huebscher, C., Avraham, Z.B. 2013. Pervasive Seafloor Gas Flow along the Periphery of the Southeastern Mediterranean. AAPG European Regional Conference 8-10 April 2013, Barcelona.

Max, M.D., Johnson, A.H. 2016. Exploration and Production of Oceanic Natural Gas Hydrate: Critical Factors for Commercialization. Springer.

Melgar, E.P. 2009. Sedimentology and Geochemistry of Gas Hydrate-rich Sediments from the Oregon Margin (Ocean Drilling Program Leg 204). PhD Thesis, Universitat de Barcelona 253 p. Barcelona (unpublished).

Merey, S., Sinayuc, C. 2016*a*. Analysis of the Black Sea sediments by evaluating DSDP Leg 42B drilling data for gas hydrate potential. Marine and Petroleum Geology 78 (2016), 151-167.

Merey, S., Sinayuc, C. 2016*b*. New Software That Predicts Hydrate Properties and Its Use in Gas Hydrate Studies. Journal of Chemical & Engineering Data 61 (5), 1930-1951.

Merey, S. 2017. Analysis of the Black Sea Gas Hydrates. PhD Thesis, Middle East Technical University, Department of Petroleum and Natural Gas Engineering 376 p. Ankara (unpublished).

Merey, S., Longinos, S.N. 2018. Numerical simulations of gas production from Class 1 hydrate and Class 3 hydrate in the Nile Delta of the Mediterranean Sea. Journal of Natural Gas Science and Engineering 52(2018), 248-266.

Miles, P.R. 1995. Potential distribution of methane hydrate beneath the European continental margins. Geophysical Research Letters 22(23), 3179-3182.

Milkov, A.V. 2004. Global estimates of hydrate-bound gas in marine sediments: how much is really out there? Earth-Science Reviews 66 (3–4), 183-197.

Milkov, A.V. 2005. Global Distribution of Mud Volcanoes and Their Significance in Petroleum Exploration as a Source of Methane in the Atmosphere and Hydrosphere and as a Geohazard. Martinelli, G., Panahi, B. (Eds.). 2005. Mud Volcanoes, Geodynamics and Seismicity. NATO Science Series (Series IV: Earth and Environmental Series), 51. Springer.

Moridis, G.J., Collett, T.S., Boswell, R., Hancock, S., Rutqvist, J., Santamarina, C., Kneafsey, T., Reagan, M.T., Darvish, M.P., Kowalsky, M., Sloan, E.D., Coh, C. 2013. Gas Hydrates as a Potential Energy Source: State of Knowledge and Challenges. Lee, W.J. (Ed.) Advanced Biofuels and Bioproducts. Springer Science Business Media.

Ocakoğlu, N. 2009. Gas Hydrates and Their Importance: Investigation of Gas Hydrates and Shallow Gas in Seas around Turkey. Istanbul Yerbilimleri Dergisi 22 (1), 29-47.

ODP (Ocean Drilling Program) Leg 160. 1995. Mediterranean Sea I: The Eastern Mediterranean Sites 963-973, 3 March-3 May 1995. http://www-odp.tamu.edu/publications/leg_ndx/160ndex.htm/. April 1, 2018.

ODP (Ocean Drilling Program) Leg 161. 1995. Mediterranean Sea II - The Western Mediterranean Sites 974-979. 3 May-2 July 1995 http://www-odp.tamu.edu/publications/leg_ndx/161ndex.htm/. April 1, 2018.

Pape, T., Kasten, S., Zabel, M., Bahr, A., Abegg, F., Hohnerg, H-J., Bohrmann, G. 2010. Gas hydrates in shallow deposits of the Amsterdam mud volcano, Anaximander Mountains, Northeastern Mediterranean Sea. Geo-Marine Letters 30, 187-206.

Praeg, D., Unnithan, V., Camerlenghi, A. 2007. PROJECT: HYDRAMED. Gas hydrate stability and prospectivity in the Mediterranean Sea. www.dur.ac.uk/ey.go/general_public/AAPG_Newsletter_June.pdf/. 12 February 2018.

Praeg, D., Geletti, R., Mascle, J., Unnithan, V., Harmegnies, F. 2008. Geophysical Exploration for Gas Hydrates in the Mediterranean Sea and a Bottom Simulating Reflection on the Nile Fan. GNGTS 2008 SESSIONE 3.2. pp. 467–469.

Praeg, D., Geletti, R., Wardell, N., Unnithan, V., Mascle, J., Migeon, S., Camerlenghi, A. 2011. The Mediterranean Sea: A Natural Laboratory to Study Gas Hydrate Dynamics? 7.International Conference on Gas Hydrates 17-21 July 2011, Edinburgh.

Praeg, D., Migeon, S., Mascle, J., Unnithan, V., Wardell, N., Geletti, R., Ketzer, J.M. 2017. Geophysical evidence of gas hydrates associated with widespread gas venting on the central Nile Deep-Sea Fan, offshore Egypt. 9. International Conference on Gas Hydrates, June 25-June 30, 2017, Denver.

Poort, J., Vassilev, A., Dimitrov, L. 2005. Did postglacial catastrophic flooding trigger massive changes in the Black Sea gas hydrate reservoir? Terra Nova 17(2), 135–140.

Robertson, A.H.F. 1998*a*. Significance of Lower Pliocene Mass-Flow Deposits for the Timing and Process of Collision of the Eratosthenes Seamount with the Cyprus Active Margin. Robertson, A.H.F., Emeis, K.C., Richter, C., Camerlenghi, A. (Eds.). 1998. 1998 Proceedings of the Ocean Drilling Program, Scientific Results, 160.

Robertson, A.H.F. 1998*b*. Late Miocene Paleoenvironments and Tectonic Setting of the Southern Margin of Cyprus and the Eratosthenes Seamount. Robertson, A.H.F., Emeis, K.C., Richter, C., Camerlenghi, A. (Eds.). 1998. 1998 Proceedings of the Ocean Drilling Program, Scientific Results, 160.

Robertson, AH.F., Kopf, A. 1998. Origin of Clasts and Matrix within the Milano and Napoli Mud Volcanoes, Mediterranean Ridge Accretionary Complex. Robertson, A.H.F., Emeis, K.C., Richter, C., Camerlenghi, A. (Eds.). 1998. 1998 Proceedings of the Ocean Drilling Program, Scientific Results, 160.

Ruppel, C. D., Kessler J. D. 2017. The interaction of climate change and methane hydrates, Rev. Geophys., 55, 126-168.

Simav, M., Yildiz, H., Arslan, E. 2008. Doğu Akdeniz’de Uydu Altimetre Verileri İle Deniz Seviyesi Değişimlerinin Araştırılması. Harita Dergisi 139 (1), 1-31.

Sloan, E. D., Koh, C.A. 2008. Clathrate Hydrates of Natural Gases. CRC Press.

Spezzaferri, S., Cita, M.B., McKenzie, J.A. 1998. The Miocene/Pliocene Boundary in the Eastern Mediterranean: Results from Sites 967 and 9691. Robertson, A.H.F., Emeis, K.-C., Richter, C., and Camerlenghi, A. (Eds.) 1998. 1998 Proceedings of the Ocean Drilling Program, Scientific Results 160.

Thakur, N.K., Rajput, S. 2011. Exploration of Gas Hydrates: Geophysical Techniques. Springer.

Werne, J.P., Haese, J.P., Zitter, T., Aloisi, G., Bouloubassie, I., Heijs, S., Fiala-Medioni, A., Pancost, R.D., Damsté, J.S.S., de Lange, G., Forney, L., Gottschal, J.C., Foucher, J.P., Mascle, J., Woodside, J. 2004. Life at cold seeps: a synthesis of biogeochemical and ecological data from Kazan mud volcano, eastern Mediterranean Sea. Chemical Geology 2050 (3-4), 367-390.

Worthington, P.F. 2010. Petrophysical evaluation of gas-hydrate formations. Petroleum Geoscience 16, 53-66.

Wood, W.T., Jung, W.Y. 2008. Modeling the extent of Earth’s marine methane hydrate cryosphere. 6. International Conference on Gas Hydrates 6-20 July 2008, Vancouver.

Woodside, J.M., Ivanov, M.K., Limonov, A.F. 1998. Shallow gas and gas hydrates in the Anaximander Mountains region, Eastern Mediterranean Sea. Henriet, J.P., Mienert, J. (Eds). 1998. Gas Hydrates: Relevance to World Margin Stability and Climate Change. Geological Society Special Publication 137, 177–193.

Xu, C.G., Li, X. 2015. Research progress on methane production from gas hydrates. RSC Advances 5, 54672–54699.

Yang, Y., He, Y., Zheng, Q. 2017. An analysis of the key safety technologies for natural gas hydrate exploitation. Advances in Geo-Energy Research 1 (2), 100-104.

Yin, Z., Moridis, G., Chong, Z.R., Tan, K., Linga, P. 2018. Numerical Analysis of Experiments on Thermally Induced Dissociation of Methane Hydrates in Porous Media. Industrial & Engineering Chemistry Research 57 (17), 5776-5791.