



## Review article

# Analysis of the Black Sea sediments by evaluating DSDP Leg 42B drilling data for gas hydrate potential



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## ABSTRACT

Many gas seepages, temperature, pressure, salinity, anoxic environment and high source gas potential of the Black Sea indicates that the Black Sea might have huge potentials for biogenic and thermogenic gas hydrates. However, the last important parameter to consider gas hydrate as an energy source is the type of sediments. Coarse marine sands are considered as good hydrate reservoirs because of high porosity and high permeability. Only very limited data is available related to the types of lithology of the Black Sea sediments. Hence, in this study, the literature data (especially the drilling and coring data of DSDP Leg 42B program) about gas seepages, temperature gradient, pressure gradient, salinity, anoxic environment and high source gas potential, and the types of the sediments in the Black Sea were investigated and analyzed. Although gas seepages, temperature gradient, pressure gradient, salinity, anoxic environment and high source gas potential of the Black Sea are appropriate for producible gas hydrate reservoirs, the sediments of the Black Sea appear to be generally fine grained with high clay content. Sandy-silt and silty sand layers in turbidites of the Black Sea might be potential producible hydrate reservoirs but these sediments are fine. As well as turbidites, separate thin sand layers might be potential gas hydrate reservoirs as an energy source in the Black Sea.

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## 1. Introduction

Gas hydrates are ice like crystalline structures formed by water and gas molecules at high pressure and low temperature values. They are defined as nonstoichiometric compounds, which means the ratio of the atoms present in the composition is not a simple integer (Carroll, 2009). Hydration number ( $N_h$ ) determines the

chemical formula.  $N_h$  changes according to the type of gas, pressure, temperature, salinity, and pH (Ye and Liu, 2013). There are mainly three types of hydrate structures: Structure I (sI), Structure II (sII) and Structure H (sH) (Carroll, 2009). Simple (pure) gas hydrates are defined as gas hydrates formed with only one type of gas. Hence, depending on the molecular diameter of gas, different types of gas hydrates are formed at high pressures and low temperatures and hydrate structure changes with the type of gas. Simple hydrates of  $CH_4$ ,  $C_2H_6$ ,  $CO_2$ ,  $H_2S$ , and  $Xe$  are sI type of gas hydrates (Zheng et al., 2015). Moreover,  $C_3H_8$ ,  $i-C_4H_{10}$ ,  $N_2$  and  $O_2$  form sII type of gas hydrates. Different than sI and sII hydrates, for the formation of

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sH hydrates, one help gas such as CH<sub>4</sub> and other large molecules with diameters greater than those of isobutane (i-C<sub>4</sub>), such as i-C<sub>5</sub> are needed. sI and sII hydrates are common in all over the world but sH hydrates are not common and they were only found in a few areas such as the Gulf of Mexico, Cascadia and the Caspian Sea (Hester and Brewer, 2009). Although in nature, CH<sub>4</sub> hydrates are common in both permafrost and ocean (~99% of known hydrate reservoirs are in marine sediments) (Sloan and Koh, 2008), there are also sII gas hydrates formed by natural gas including CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and other impurities (Demirbas, 2010). Even the addition of 1% C<sub>3</sub>H<sub>8</sub> into CH<sub>4</sub> gas molecules causes the formation of sII hydrates at the hydrate equilibrium conditions (Zanjani et al., 2011). It is known that even the most conservative estimates place the amount of gas contained within hydrate deposits at 2–10 times larger than the global estimates of conventional natural gas of 4.4–10<sup>14</sup> standard m<sup>3</sup> (Koh et al., 2012).

As well as all marine environments in the world, the Black Sea has also high gas hydrate potential (Vassilev and Dimitrov, 2000; Vassilev, 2006; Meray and Sinayuc, 2016a). Fig. 1-A shows CH<sub>4</sub> hydrate potential in all the Black Sea sediments (Meray and Sinayuc, 2016a; Korsakov et al., 1989; Klauda and Sandler, 2003; Shi, 2003; Vassilev and Dimitrov, 2003; Krasov and Ciesnik, 1988). However, for gas production from hydrates, the targets are the gas hydrates deposited in coarse sands (Meray and Sinayuc, 2016a; Johnson and Max, 2015). Therefore, Fig. 1-B shows the potential producible gas hydrate deposited in coarse sands in the Black Sea (Vassilev and Dimitrov, 2000; Meray and Sinayuc, 2016a; Krasov and Ciesnik, 1988; Johnson and Max, 2015).

In order to understand the Black Sea gas hydrates, it is necessary to analyze temperature gradient, pressure gradient, gas source and its type, sediments types, salinity, geological and geophysical data of the Black Sea. In this article, it is aimed to clarify many questions related to the Black Sea gas hydrate potential.

## 2. The Black Sea

The Black Sea is an inland sedimentary basin, located between the latitudes of 41°–46°N and longitudes of 28°–41.5°E with an area of 423,000 km<sup>2</sup>, a volume of 547,000 km<sup>3</sup> and a maximum water depth of 2200 m (Murray, 1991). It has a connection to the Sea of Azov by the Kerch Strait in the north, while it is connected to the Mediterranean Sea with the Bosphorus Strait through the Sea of Marmara in the south. In the Black Sea, continental shelves are very narrow along the eastern and southern margins, the continental

slope shelf break is generally abrupt with water depth increasing up to 2212 m as shown in Fig. 2 (Vassilev, 2006; Ross et al., 1974). The Black Sea is a deep valley which was filled with unconsolidated and consolidate sediments above basalt and mantle layer. According to Klaucke et al. (Klaucke et al., 2005), the sedimentation rate in the Black Sea is high because the Black Sea is almost a closed sea and many rivers transport sediments with time. The thickness of the sediments in the Black Sea is considered up to 19 km (Nikishin et al., 2003).

The Black Sea was a fresh water lake from 22,000 to 9000 year B.P. After the rise of the sea level, the warm saline water of the Mediterranean Sea flowed through the Black Sea via the Bosphorus. Then, the denser saline water sank to the bottom and less dense water raised to the top and this created halocline in the Black Sea (Deuser, 1974; Neprochnov and Ross, 1978; Meray and Sinayuc, 2016a). This also formed anoxic water body because halocline creates anoxic environment (Deuser, 1974; Neprochnov and Ross, 1978; Kutas et al., 1997). The salinity of the Black sea increases from 1.75% to 2.23% between sea surface and 200 m below sea level. Then, it is almost constant from 200 m below sea level to sea bottom (Railsback, 2010). Similar observations were observed in the study of Stanev et al. (2014).

Average temperature of seafloor in the Black Sea is approximately 9 °C (Klauda and Sandler, 2003; Railsback, 2010; Stanev et al., 2014). The Black Sea has large amounts of organic matters carried by rivers and they are stored because the Black Sea is almost a closed sea. Therefore, during the bacterial sulfur reduction of these organic matters, H<sub>2</sub>S evolves and it is stored in the Black Sea as dissolved gas (Deuser, 1974; Demirbas, 2009; Egorov et al., 2011).

## 3. Evidences of gas hydrate existence in the Black Sea

As many places in the world, the Black Sea also has a huge gas hydrate potential and it is also considered as the world's most isolated sea, the largest anoxic water body on the planet and a unique energy-rich sea (Ergun and Cifci, 1999; Overmann and Manske, 2006). It abundantly contains gas hydrates and H<sub>2</sub>S as CH<sub>4</sub> and hydrogen source, respectively (Demirbas, 2009; Dondurur and Cifci, 2009). CH<sub>4</sub> seepage is extremely intense on the shelf and on the slope of the Black Sea (Kruglyakova et al., 2004; Demirbas, 2009; Sozansky, 1997; Dimitrov, 2002; Heeschen et al., 2011; Xing, 2013; Küçük et al., 2015).

The reason of these gas seepages is that at certain temperature conditions, gas pressure is below hydrate equilibrium curve so

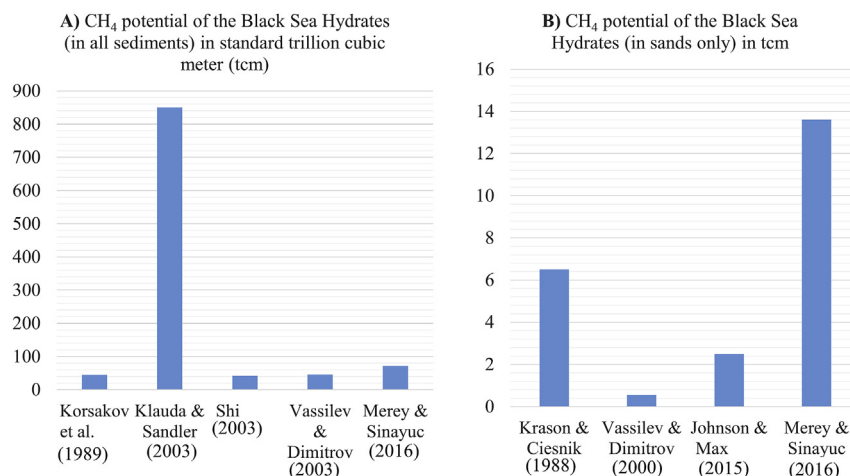


Fig. 1. CH<sub>4</sub> hydrate potential of the Black Sea.

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