



Anomalous Strong Reflections on High Resolution Seismic Data from the Turkish Shelf of the Eastern Black Sea: Possible Indicators of Shallow Hydrogen Sulphide-Rich Gas Hydrate Layers

DERMAN DONDURUR & GÜNAY ÇİFÇİ

Dokuz Eylül University, Institute of Marine Sciences and Technology, Baku Street, No: 100, İnciraltı, TR-35340, İzmir, Turkey
(E-mail: derman.dondurur@deu.edu.tr)

received 21 January 2008; revised typescript received 24 November 2007; accepted 06 May 2008

Abstract: Some strong reflections about 3 to 5 m thick were observed at depths of 25–60 metres below the sea floor using deep-towed, 5 kHz subbottom profiler data in the Turkish shelf and upper slope of the Eastern Black Sea at water depths of 250 to 700 m. Strong reflections of this kind are generally attributed to shallow and localized gas accumulations. We, however, observed that the reflection polarity of these strong reflections was positive, suggesting that they do not correspond to reflections from the upper boundary of a possible gas front. In this study, we evaluate these reflections to determine if they represent hydrogen sulphide-rich shallow gas hydrate layers, which would be an unusual gas hydrate occurrence in a shallow marine environment.

The existence of gas hydrate formations in thermobaric conditions, as in our study area (shallower water depths and relatively higher temperatures), depends completely on the gas composition in the hydrate structure; it is possible for gas hydrates to be stable only if they are formed by a certain amount of hydrogen sulfide together with methane. We closely examined the hydrogen sulphide potential of the area and found that the maximum total hydrogen sulfide concentration in the surficial sediments in the area was, at 5550 ppm, enough to produce hydrogen sulphide-rich gas hydrates.

Using geoaoustic and geochemical data, we propose a conceptual model for the formation of shallow hydrogen sulfide-rich gas hydrates. According to this model, conjectural gas hydrate layers in the area should be formed along the boundary between a sulphate-reducing zone and an underlying carbonate reducing zone, where methane comes into contact with hydrogen sulphide. We also propose that the strongly reflective appearance of these layers on the subbottom profiler data indicates that the hydrate zone consists of a number of gas hydrate sheets with a decreasing thickness towards the seabed, interbedded with non-hydrate-bearing sediments.

Key Words: Black Sea, gas hydrate, hydrogen sulphide, high-resolution acoustic methods

Doğu Karadeniz Türkiye Şelfinde Yüksek Ayrımlı Sismik Kayıtlardaki Anormal Güçlü Yansımalar: Hidrojen Sülfürce Zengin Sığ Gaz Hidrat Tabakalarının Olası Belirteçleri

Özet: Doğu Karadeniz Türkiye şelfi ve üst yamacından alınmış olan derinden çekilen 5 kHz mühendislik sismiği verilerinde, 250–700 m su derinliklerinde, deniz tabanından 25–60 m derinliklerde uzanan 3–5 m kalınlıklarda çok güçlü yansıtıcılar gözlenmiştir. Bu tür güçlü yansımalar, araştırmacılar tarafından genellikle yersel ve sığ gaz birikimleri olarak yorumlanmaktadır. Bununla birlikte, bu çalışmada bu yansımaların polaritelerinin pozitif olduğu gözlenmiş olup, bu durum, bu tür yansımaların olası bir gaz cephesinin üst sınırından alınmayacağı anlamına gelmektedir. Bu çalışmada, bu yansımaların hidrojen sülfürce zengin sığ gaz hidrat tabakalarını yansıtmadığı incelenmiştir.

Çalışma alanının sahip olduğu termobarik koşullar altında (sığ su ve yüksek sıcaklıklarda) gaz hidrat oluşumu ve durağan kalması hidrat yapısının gaz bileşimine bağlıdır ve bileşiminde metan ile birlikte belirli miktarlarda hidrojen sülfür bulunması durumunda olasıdır. Çalışma alanının güçlü yansımaların alındığı kısmında, yüzey tortularındaki toplam sülfür üretimi 5550 ppm'e kadar yükselmekte olup, hidrojen sülfürce zengin sığ gaz hidrat birikimlerinin oluşması için uygun görünmektedir.

Akustik ve jeokimyasal verileri kullanarak, bölgede bu tür hidrojen sülfürce zengin sığ gaz hidrat birikimleri için kavramsal bir oluşum modeli geliştirilmiştir. Bu modele göre, bölgede var olması olası hidrojen sülfürce zengin gaz hidrat birikimleri, metan gazının hidrojen sülfür ile temas haline geldiği sülfat indirgeme zonu ve altta uzanan karbonat indirgeme zonu sınırında oluşmalıdır. Buna ek olarak, bu tabakaların mühendislik sismiği verilerinde çok güçlü yansımalar olarak görülmesi, hidrat zonunun ince gaz hidrat lens veya tabakalarından oluştuğunu, bunların kalınlığının deniz tabanına doğru azaldığını işaret etmektedir.

Anahtar Sözcükler: Karadeniz, gaz hidrat, hidrojen sülfür, yüksek ayrımlı akustik yöntemler

Introduction

Gas hydrates are ice-like crystalline structures of water that contain gas within cavities. They have a pure ice structure with gas in different compositions as a guest molecule (e.g., Kvenvolden & Barnard 1983; Kvenvolden 1993). Although gas hydrates include hydrocarbon gases, such as ethane, propane or butane, and non-hydrocarbon gases, such as CO₂ or H₂S, the guest gas is mainly methane.

Conditions for hydrate formation and retention generally depend on high-pressure and low-temperature regimes in marine sediments. Gas hydrates mainly occur within shallow (<1000 m) sea bottom sediments where the water depth exceeds a few hundred metres to maintain thermobaric stability conditions. However, gas hydrate stability also depends on variations in the geological setting and the chemical composition of the guest gases in the gas hydrate structure (Sloan 1990; Lerche & Bagirov 1998). Pure methane hydrates require higher pressures and lower temperatures for stability than do methane-ethane, methane-propane, methane-CO₂ or methane-H₂S mixtures.

Gas hydrates are important primarily because of the huge amounts of methane stored in the hydrate solid phase: 1 m³ of hydrate contains 164 m³ of gas and 0.8 m³ of water in ideal conditions (Kvenvolden 1993). Therefore, gas hydrates can be considered as a potential energy resource for the future. The release of such amounts of methane into the atmosphere may be an important factor in global warming. Furthermore, the decomposition of the gas hydrates can reduce the shear strength of the sediments and may trigger slope failures on continental margins. As pore spaces and/or interstitial waters are displaced by gas hydrates, they can create an impervious layer which does not permit the gas to migrate upwards; therefore gas hydrate layers can serve as cap rocks allowing gas accumulation below. Gas hydrates may also indicate oil accumulations in deeper sediments, which are considered a potential energy source by the petroleum industry.

Gas hydrates were sampled over some mud volcanoes in central-deep waters of the Black Sea (e.g., Ginsburg *et al.* 1990; Limonov *et al.* 1994; Ivanov *et al.* 1996) and the Sorokhin Trough (e.g., Ivanov & Woodside 1996; Woodside *et al.* 1997). On the seismic records, the main indicator of a gas hydrate accumulation in marginal

sediments is high amplitude reflections known as bottom simulating reflectors (BSR), which is the reflection between gas hydrate-bearing sediments above and often free gas accumulation below. Therefore, BSRs indicate the bottom of gas hydrate accumulations, and because they follow the thermobaric conditions of the subsurface, they mimic the seabed. However, BSRs are not common in the Black Sea and are reported only in a limited area in the northwestern Black Sea (Lüdmann *et al.* 2004; Popescu *et al.* 2006). Apart from these observations in the Black Sea, Woodside *et al.* (2003) have reported the relation between gas hydrates and enigmatic strong reflectors observed on the high-resolution 5 kHz sub-bottom profiler records which were digitally recorded in the Sorokhin Trough, central Black Sea, where gas hydrates were also sampled using a gravity corer. The amplitudes of these strong reflections were over 150% greater than the sea bottom reflection and they were observed at a depth of about 4–7 metres below the sea floor (mbsf), sometimes approaching the seabed. Using synthetic seismic trace generation by forward modelling, Woodside *et al.* (2003) have argued that these strong reflectors represent the top of a shallow gas hydrate layer and have concluded that these gas hydrate layers were formed as alternating thin layers of normal and gas hydrate-bearing sediment. They also proposed that gas hydrate content and the thickness of gas hydrate layer gradually decreased towards the sea floor.

On the Turkish upper slope of the Eastern Black Sea (Figure 1), we observed very similar strong reflections to those observed by Woodside *et al.* (2003) on deep-towed, high resolution 5 kHz MAK sub-bottom profiler data. These strongly reflective layers (SRLs), with a thickness of about 3 to 5 m, lie at a depth of 25–60 mbsf. Although the appearance and acoustic structure of these SRLs is almost completely similar to the enigmatic reflectors observed by Woodside *et al.* (2003) in the Sorokhin Trough, the difference between the SRLs in both areas arises from the water depth; the SRLs in the Sorokhin Trough are located at 1700 m water depth, whereas those in our study area are observed in relatively shallower water depths of about 250 to 700 m. The main purpose of this study is to discuss whether the SRLs observed on the Turkish upper continental slope also represent gas hydrate layers, as in the Sorokhin Trough, and to try and evaluate the possibility of the occurrence of such shallow gas hydrate layers on the Turkish Shelf.

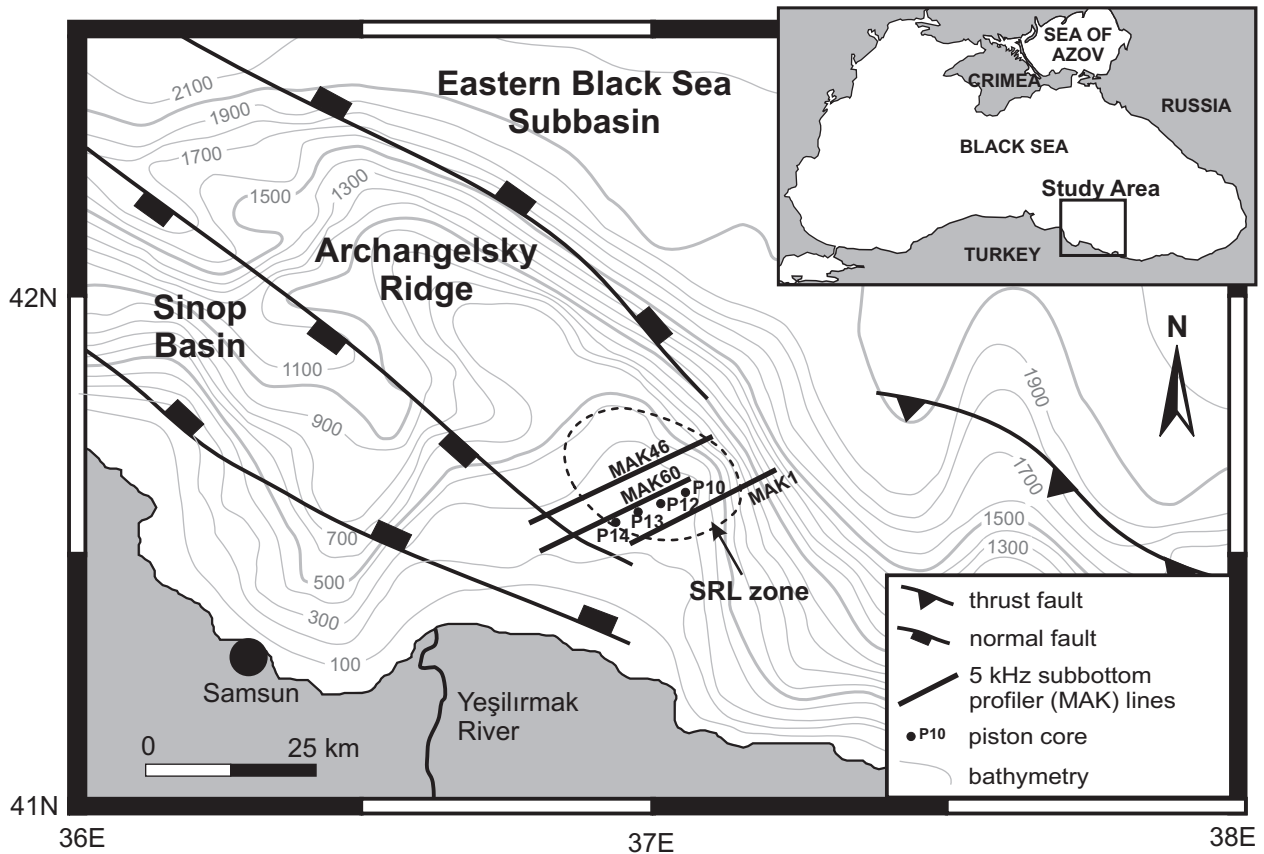


Figure 1. Location map of the study area. Close-up shows the main structural elements of the area superimposed on a bathymetric map with 100 m contour interval. The area outlined by a dashed line represents the strongly reflective layer (SRL) zone. Solid lines represent the locations of 5 kHz subbottom profiler lines and dots represent piston core locations.

The structure and stability conditions of the possible occurrence of shallow gas hydrates in the area are also discussed using acoustic and geochemical data.

Geologic Setting of the Study Area

The Black Sea is a semi-isolated extensional basin surrounded by thrust belts and is considered to be a Mesozoic–Early Cenozoic marginal back-arc basin generated by the northwards subducting Tethys Ocean (e.g., Zonenshain & Le Pichon 1986; Rangin *et al.* 2002). The Black Sea basin comprises western and eastern Black Sea subbasins, which are separated by a regional high, the Mid Black Sea Ridge, which is divided into two parts, the Andrusov Ridge in the north and the Archangelsky Ridge in the south (Figure 1).

The study area is located in the Eastern Black Sea Turkish shelf and slope, north of the central Pontides. It

includes the Sinop Basin and both the northern and southern basin margins of the Archangelsky Ridge (Figure 1). Meredith & Egan (2002) showed that deeper parts of the area are dominated by extensional faults with relatively large slips (about 1.8 s two way travel time, TWTT) generating half-graben structures. The Archangelsky Ridge itself shows no deposition from the end of the Eocene to the Quaternary. Although the thickness of Quaternary sediments on the ridge is about 150 m, it reaches more than 1000 m in the south near the Sinop Basin. The Cretaceous sequence is about 700 m thick on the ridge and is extensively affected by normal fault systems in the deeper parts of the sedimentary sequence, i.e. in the northern and southern flanks of the Archangelsky Ridge (Meredith & Egan 2002). The Sinop Basin is located between the Archangelsky Ridge and the Turkish coastline (Figure 1) and has been affected by late Miocene normal faults along the Turkish margin and the Archangelsky Ridge (Rangin *et al.* 2002).

The shelf break is located at a water depth of about 300 m. The overlying plateau of the Archangelsky Ridge (Figure 1) is also marked by numerous pockmarks between the 180 and 300 m bathymetric contours, indicating extensive gas and/or fluid expulsions. Pockmarks are the depressions that, because of the overpressure conditions in the subsurface, pore fluids or free gas in the pore spaces in the sediments erupt suddenly as an expulsion creating variable-sized collapses on the seabed (Çifçi *et al.* 2003). The continental slope deepens from 300 to 1800 m with a maximum gradient of 14° and becomes progressively steeper as it is traced into deeper water. The slope is characterized by a highly dissected tributary canyon system and the sediments on the slope show slump and gravity flow processes (Dondurur & Çifçi 2007).

In order to investigate shallow lithology of the study area, we used 4 piston cores, P10, P12, P13 and P14 (Figure 2) with recoveries of 4.32 m, 16.2 m, 4.7 m and 4.86 m, respectively. Core P10 showed very soft homogeneous clay with very thin laminations of black clay at the top of the core and very fine shell fragments/coccoliths with gas vacuoles, together with a strong H₂S odour. At greater depth, the core sampled greenish grey clay with laminations and local inclusions of black clay. Core P12 recovered very soft laminated coccoliths; locally small vacuoles and very soft dark olive grey with possibly high sapropel content, some shell fragments at the middle part and very soft olive black friable expansive clay with horizontal expansion cracks at the deeper parts. Core P13 and P14 showed extremely soft laminated (variations in colour) plastic clay, locally

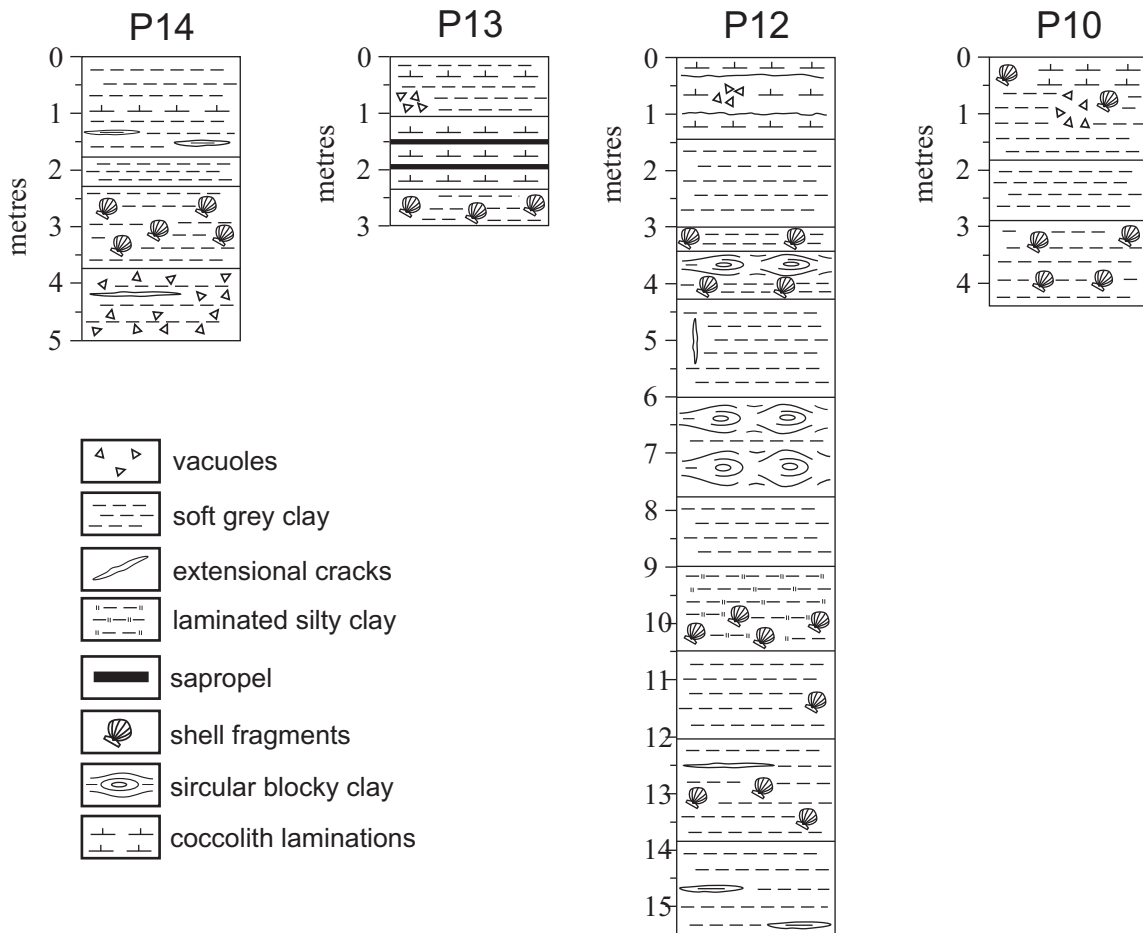


Figure 2. Piston cores P10, P12, P13 and P14 and their core descriptions (see Figure 1 for location). Cores indicate that the sediments in the area mainly consist of laminated silty clay layers, and shell fragments with small vacuoles also exist at deeper parts.

some coccolite laminations and very small vacuoles together with frequent laminations of coccolite and sapropelic layers (Figure 2).

Strongly Reflective Layers in the Upper Continental Slope

The strongly reflective layer (SRL) zone is an elongated area measuring about 15×25 km, which is outlined by a dashed line in Figure 1. The northern boundary of the zone is limited by the 700 m bathymetric contour line and the southern part of the zone corresponds to a pockmarked plateau. The SRLs appear as semi-horizontal continuous horizons and tend to follow seabed topography on 5 kHz sub-bottom profiler sections, with a thickness of about 3 to 5 m at 25–60 mbsf in the shelf and upper side of the continental slope. They can be

traced over an area of several hundred square metres where the seabed relief is relatively smooth. Just below the pockmark structures where feeder channels exist, however, they are often observed as discontinuous strong reflectors a few tens of metres in length.

Figure 3 illustrates a representative 5 kHz sub-bottom profiler section (part of line MAK46) recorded at about 260 m water depth where a number of seabed (P) and buried (BP) pockmarks are present. The SRL is seen at about 30 mbsf and is continuous over distances of about 2200 m. Just below this layer, the sub-bottom profiler section shows acoustically turbid zones (sometimes referred as gas masking or acoustic blanking), attributable to shallow gas accumulations that almost completely absorb the acoustic signal and mask the sedimentary layers. We named this type of gas accumulation in the sediments as acoustic turbidity,

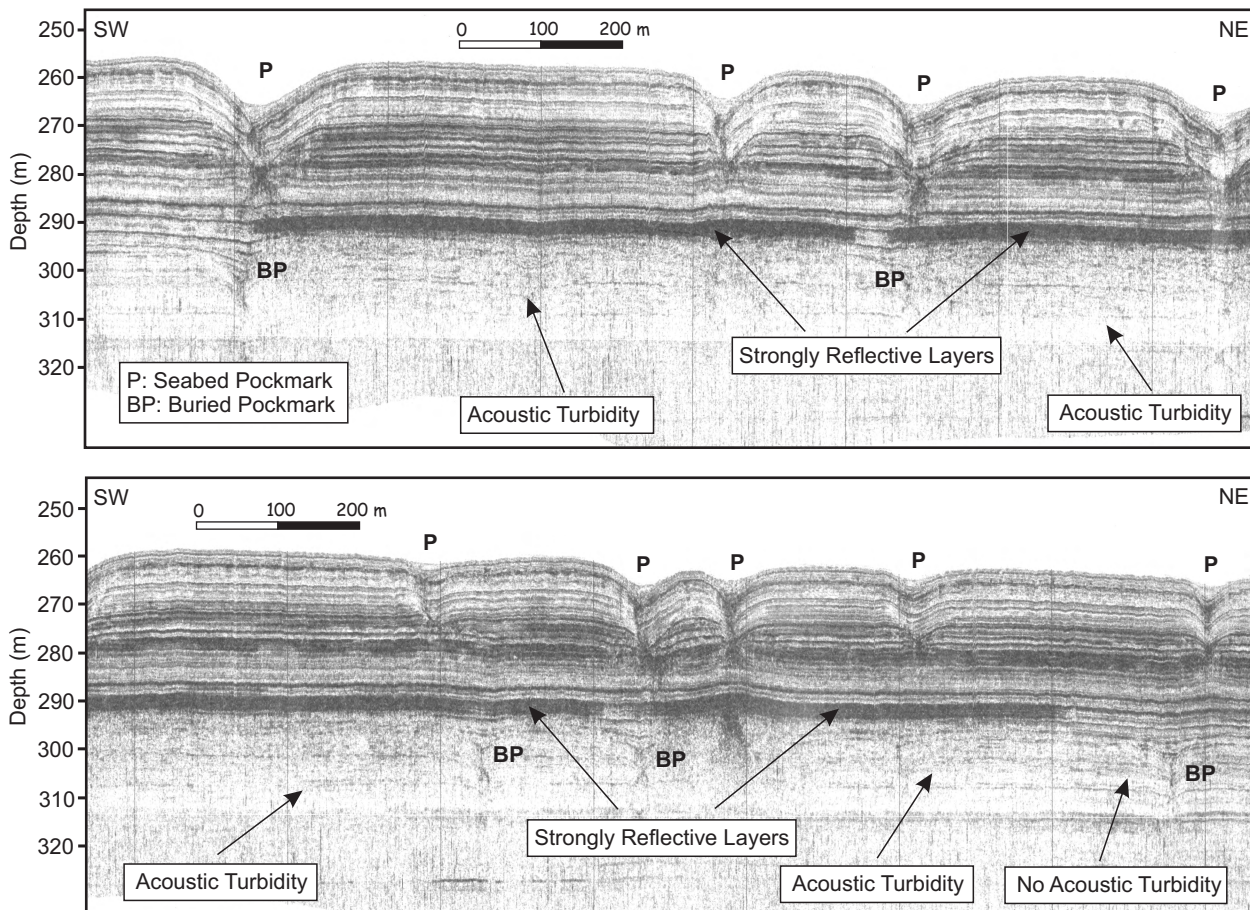


Figure 3. SRL at about 30 mbsf on MAK46 sub-bottom profiler line in the shelf area (see Figure 1 for location). The data in bottom panel is the continuation of the data in upper panel to the NE. P and BP indicates seabed and buried pockmarks, respectively.

following the definition from Garcia-gil *et al.* (2002), who suggested that acoustic turbidity consists of a variable degree of disturbance on the acoustic data. Sometimes it is possible to trace the reflections from normal sediments through the disturbance. Downward continuity of the sediments, as well as buried pockmarks, however, can be observed when the SRL is discontinuous and the acoustic turbidity does not exist. We conclude, therefore, that the SRL in the area acts as a cap rock below which the shallow gas accumulates. The top of SRL appears as a sharp reflecting boundary, whereas, in some places, the bottom boundary appears to have a scattered form, possibly because of the gas front accumulated below the layer.

To the north, the subsurface depth of SRL also increases towards the shelf break. The MAK60 sub-bottom profiler line near the shelf break in Figure 4

shows a discontinuous SRL formed at about 60 mbsf. At this higher sub-bottom depth, one can expect a much lower signal amplitude on 5 kHz sub-bottom profiler data, primarily due to the absorption of the signal and other amplitude losses. The reason for the occurrence of such an anomalously strong reflection in deeper parts in the sediments will be discussed later.

We also examined the polarity of the reflections from SRLs using multichannel seismic data (not shown here), and found that the polarity of these reflections is the same as the polarity of seabed reflection. This implies an increase in velocity, which indicates that this reflection cannot be interpreted as a localized shallow gas front. If this was the case, we would observe a decrease in velocity and hence a polarity reversal would occur.

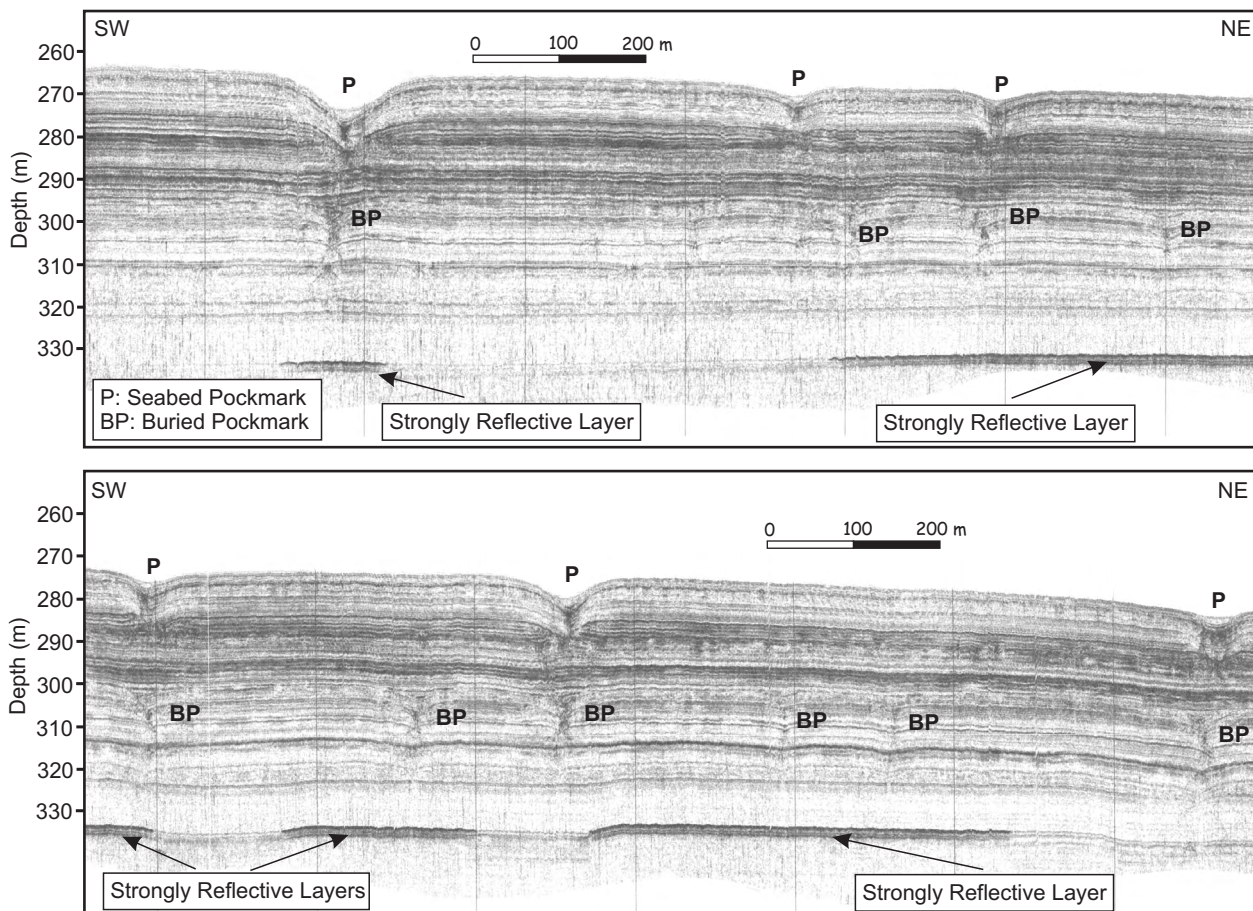


Figure 4. Part of MAK60 sub-bottom profiler line showing SRL near the shelf break (see Figure 1 for location). The data in the bottom panel are the northeasterly continuation of the data in upper panel. P and BP indicates seabed and buried pockmarks, respectively.

Discussion

Similar strong reflections on the high-resolution acoustic data were observed before in the Sorokhin Trough (the Black Sea) and the Mediterranean (Woodside *et al.* 1997), as well as in the Gulf of Cadiz (Baraza & Ercilla 1996), and were interpreted as gas fronts. However, Ivanov *et al.* (1998) suggested that they represent the top of a gas hydrate layer or a 'gas hydrate front'. Using MAK sub-bottom profiler data recorded digitally in the Sorokhin Trough at about 1700 m water depths, Woodside *et al.* (2003) calculated synthetic seismograms and compared them with the real seismic traces on which strong reflections were observed. They concluded that the strong reflections were formed by thin (1.5–2.5 m thick) sequence of alternating acoustic impedance contrasts and represented the upper zone of normal and gas hydrate-bearing sediment. Such a layered model is typical of the upper boundary of the gas hydrate zone, which is formed by a sequence of thin-bedded sediments with no hydrates and sediments containing gas hydrates in the pore spaces. The thickness of gas hydrate layers also gradually decreases towards the seafloor.

The SRLs observed on high-resolution acoustic data in our study area have a very similar appearance to those observed by Woodside *et al.* (2003) in the Sorokhin Trough. The main differences between the two reflections are that the proposed gas hydrate layers in the Sorokhin Trough were formed at shallower subsurface depths (approximately 4–7 m) below the sea floor but in deep water conditions (e.g., 1700 m water depths). We also observed that the reflection polarity of these strong reflections is the same as the polarity of sea floor reflection, suggesting that these reflections do not represent the upper boundary of a possible gas front from a shallow gas accumulation. This positive polarity occurrence is also consistent with the polarity analysis of Woodside *et al.* (2003) for the digital MAK-1 data.

The key question here that we should answer is 'whether or not the SRLs in our study area also represent gas hydrate layers'. The similarity of SRLs in both the Sorokhin Trough and Turkish Shelf areas leads us to tentatively suggest a similar interpretation for the SRLs in the Turkish upper slope of the Eastern Black Sea. However, the difference between the water depths in SRL zones in these areas forces us to evaluate the stability conditions of such shallow gas hydrate layers, since the stability of gas hydrates primarily depends on the

thermobaric conditions. Firstly, the shallow occurrence of such gas hydrate layers needs relatively high amounts of hydrogen sulfide production in the area accompanying the methane to form the gas hydrates, and this stabilizes the hydrate structure even under low pressure and/or high temperature conditions (e.g., Kastner *et al.* 1998; Swart *et al.* 2000).

Methane and Hydrogen Sulfide Productivity of the Region

Rice & Claypool (1981) suggested that the biogenic gas in marine environments is produced by immature organic matter. They also suggested three different chemical zones in marine sediments: (1) aerobic zone, (2) anaerobic sulphate reducing zone and (3) carbonate reducing (or methane production) zone. Hydrogen Sulphide, H₂S, is produced *in situ* by means of the metabolic activity of sulphate-reducing bacteria in the sulphate reducing zone, whereas methane is produced in the underlying carbonate reducing zone. Sulphides in marine sediments exist as insoluble solid metal sulphides or sulphide compounds dissolved in the pore waters. In the presence of oxygen, however, sulphide rapidly oxidizes to sulphate. Therefore, sulphides are widely observed in anoxic waters as well as anoxic seabed sediments such as those in the Black Sea.

Çifçi *et al.* (2002) and Ergün *et al.* (2002) reported extensive shallow gas accumulations at 25–65 mbsf with acoustic blanking effects in the surface sediments of the study area. The gas in the shelf sediments of the Black Sea is mainly biogenic in origin (Hunt & Whelan 1978; Ginsburg *et al.* 1990; Ginsburg & Soloviev 1997). High sedimentation rates (e.g., 30 m/Ma) and at least 0.5% of total organic carbon (TOC) are necessary for biogenic gas generation (Rice & Claypool 1981; Mienert & Posewang 1999). Since the study area is located in the Yeşilirmak River fan, the sedimentation rate in the region is relatively high (more than 30 cm/1000 years; Ross 1977). Therefore, abundant plant debris and organic matter transportation may cause extensive biogenic gas generation (mainly methane) on the shelf and upper slope region. Ergin *et al.* (1996) suggested that the TOC content of Holocene deposits in the southeastern Black Sea ranged from 0.69 to 3.09% and was about 2.60% for the study area, which seems to be sufficient for biogenic methane generation. The acoustic data and core samples presented here also show potential methane

accumulations just below the SRLs as acoustic turbidity zones.

In marine environments, the main sulphide and organic carbon accumulations occur around the continental margins, particularly in deltaic sediments (Lin *et al.* 2002). H₂S is produced in marine sediments by bacterial reduction of dissolved sulphate in the uppermost sediments of the sulphate-reducing zone (Brüchert *et al.* 2003). In this zone, sulphate is rapidly depleted by sulphate-reducing bacteria due to oxidation of organic matter (Fossing *et al.* 2000) and sulphate concentration decreases with depth concomitant with a H₂S concentration increase (Brüchert *et al.* 2003). When sulphate is completely exhausted, methane production takes place in the carbonate-reducing zone below the sulphate-reducing zone (Niewöhner *et al.* 1998; Fossing *et al.* 2000). Since the presence of organic carbon is the primary factor for sulphate reduction and because shelves

and deltaic environments are major sources of organic carbon, the areas where surficial waters and sea-water coalesce, such as river mouths, are considered to be the main sulphide accumulation environments (Lin *et al.* 2002; Wijsman *et al.* 2001). The Black Sea is the largest anoxic basin in the world, having a permanent H₂S reservoir (Codispoti *et al.* 1991), and the large rivers which transport large amounts of dissolved organic matter from deltas to basin environments potentially affect the iron and sulfide cycle in the sediments (Wijsman *et al.* 1999, 2001). Therefore, the mineralization and sulphide levels in the areas of high sediment input such as our study area are expected to be higher than in the deep basin.

Figure 5 shows total sulphide and free H₂S concentrations in seabed sediment samples from the study area, expressed in parts per million (ppm) by weight of total sulphides and hydrogen sulphide in the

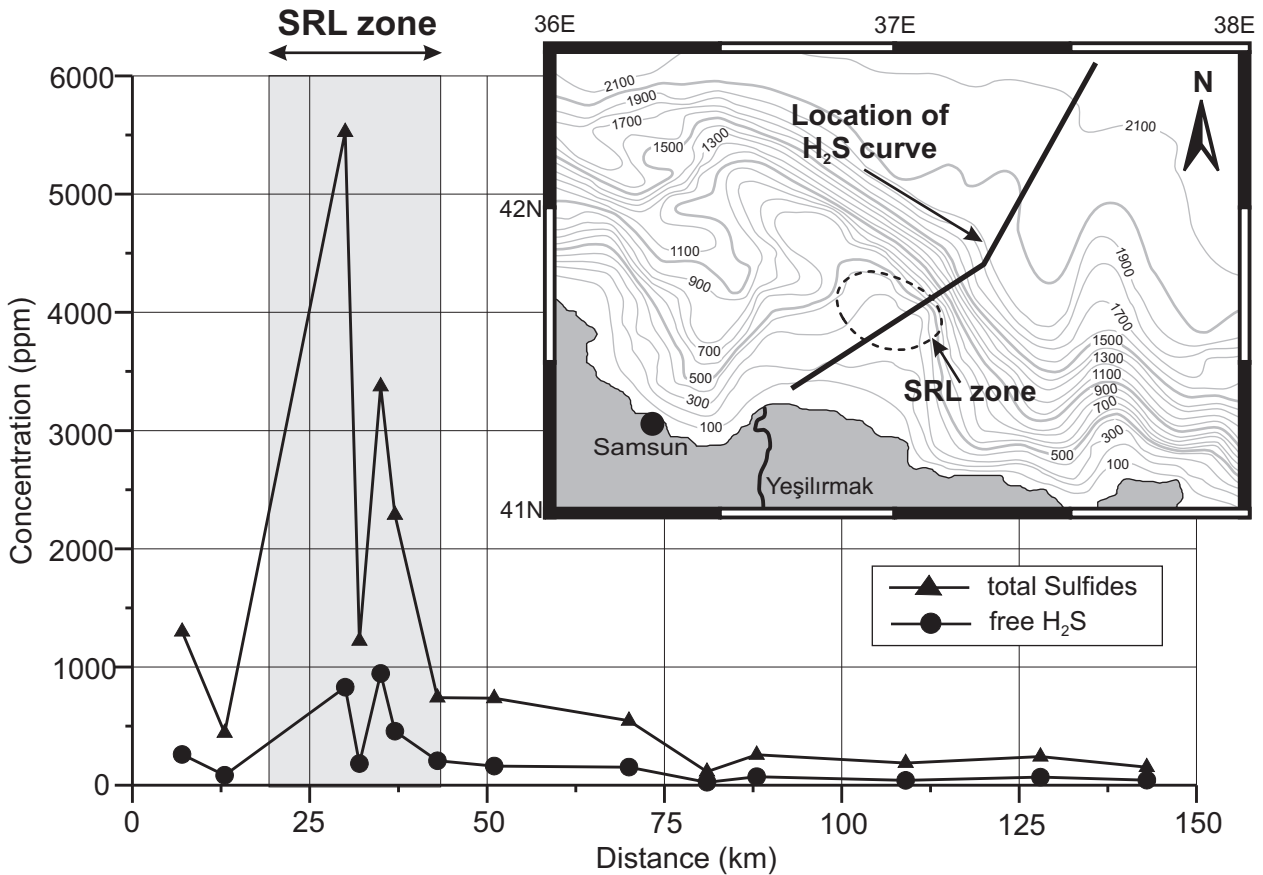


Figure 5. Total sulphide and free H₂S concentrations of surficial sediment samples from shelf to abyssal plain expressed as ppm values. Inset is a bathymetric map showing the location of the curve. The area approximately between 20 and 42 km is the SRL zone.

original sediment sample. The term 'total sulphides' means hydrogen sulphide, together with other water soluble sulphide ions derived from H_2S (HS^- and S^{2-}) and those solid metal sulphides, primarily iron sulphide (FeS), which may exist as components of anoxic seabed sediments. The area approximately between 20 and 42 km in the H_2S concentration curve in Figure 5 is the SRL zone. Within this interval, maximum total sulphide and free H_2S concentrations are 5550 and 945 ppm, respectively. Towards the abyssal plain, the concentrations rapidly decrease downslope to their mean values of 250 and 55 ppm, respectively. The total sulphide concentrations of the area are similar to the concentrations observed in other deltaic environments in the Black Sea. For instance, Wijsman *et al.* (2001) reported total sulphide concentrations more than 6200 ppm in the Danube delta, while Otero *et al.* (2003) observed 9000 ppm total sulphide concentrations in the Gulf of California. Nonetheless, free H_2S concentrations in the study area seem to be slightly higher than other ocean margin regions. For instance, Murray *et al.* (1978) reported 342 ppm off Vancouver Island, Boulegue *et al.* (1982) recorded 167 ppm off Delaware, and Tsunogai *et al.* (2002) noted H_2S concentrations of 510 ppm in the Nankai Trough. Compared to H_2S concentrations in the areas where mixed H_2S -methane hydrates are observed, Swart *et al.* (2000) reported a maximum H_2S concentration of 156.6 ppm off South Australia and Aharon & Fu (2000) reported a maximum concentration of 725 ppm in the Gulf of Mexico.

The sulphide in the pore waters can be analysed as total sulphides, dissolved sulphides or free H_2S . Dissolved sulphide, produced via bacterial sulfate reduction, rapidly reacts with the reactive iron in the sediments to form FeS, which can further react with dissolved sulphide to form pyrite (Tsunogai *et al.* 2002). Therefore, H_2S produced in the sulphate-reducing zone is precipitated more or less immediately as amorphous FeS (Wijsman *et al.* 2001). This may suggest that most of the high total sulphide concentrations produced in the shelf sediments of the study area might be generally result from this FeS precipitation. Lyons (1991) observed approximately 0.7% wt and 0.8% wt FeS concentrations in the Kızılırmak River Delta (central-southern part of the Black Sea) and in the Black Sea outlet of the Bosphorus strait, respectively. Wijsman *et al.* (2001) reported 0.66 wt% FeS concentration in the Danube Delta (northwestern Black Sea), which is a typical value for anoxic Black Sea

deltaic sediments. With regard to FeS, a maximum of 5500 ppm total sulphide concentration in the study area corresponds to a 0.55 wt% FeS concentration and does not seem to be particularly high (Timothy W. Lyons, personal communication 2003). Therefore, it is concluded that the total sulphide concentration in the area can be explained by FeS precipitation. Fe concentrations dissolved in the pore waters in the marginal sediments of the Black Sea are rather limited (e.g., Lyons 1991; Wijsman *et al.* 2001) and it is likely that this limited amount of iron is also rapidly depleted by FeS precipitation. At the same time, sulphate reduction, and hence H_2S production, still continues after FeS is depleted. The lack of iron terminates the production of FeS and can permit elevated free H_2S concentration, which is required for gas hydrate formation in the area.

Sulphate reducing rates, the depth of the sulphate reducing zone, methane and free H_2S concentrations, total sulfides as well as precipitated FeS concentrations can only be properly assessed using geochemical data from Ocean Drilling Projects (ODP). However, a lack of ODP data near the study area limits the above geochemical model because proposed geochemical data was obtained from surficial sediment samples of the study area. Although we do not know the exact geochemical setting down to 25 mbsf, some considerations about the subsurface sediments, such as the depth of the sulphate-reducing zone, were made using seismo-acoustical data.

Stability Conditions for H_2S Rich Hydrates in the Study Area

Pressure and temperature conditions of sedimentary units in which gas hydrates are formed are primary factors controlling hydrate formation and retention in natural environments. The pressure conditions are related to the water depth and subsurface depth of gas hydrate formation, whereas the temperature conditions are mainly controlled by sea-bottom temperature distribution as well as the geothermal gradient in the sedimentary sequence. Because the SRLs in the study area formed at relatively shallow depths in the sediments, the geothermal gradient is omitted in the evaluation of stability conditions.

The temperature distribution in the water column was examined to evaluate the stability conditions. 10 different CTD data were used along a profile and the temperature

values from different depths along the profile were contoured to obtain a cross-sectional temperature distribution of the water column in the study area (Figure 6; Dondurur *et al.* 2001). Figure 6 shows that the sea bottom temperature changes between 8.7 and 8.9 °C for the depth range of 250 to 700 m (about 2500 to 7000 kPa), where the SRLs are observed. Pure methane hydrates usually occur in deeper water areas where low bottom temperatures and high pressures allow the gas hydrate to form. However, adding H₂S to CH₄ decreases the pressure and increases the temperature required for the mixed gas hydrate to be stable. Therefore, if a certain amount of H₂S coexists with the methane, gas hydrate structure can be stable in much shallower depths and higher temperatures (Kastner *et al.* 1998; Swart *et al.* 2000). Figure 7 shows thermobaric stability curves for pure methane hydrates and for H₂S-rich methane hydrates composed of 10, 20 and 30% H₂S

concentrations. For sediments warmer than 10 °C, pure methane hydrates require water depths exceeding 700 m to be stable. The H₂S-rich hydrates (e.g., 10% H₂S and 90% CH₄), however, are stable even at 250 m water depths under the same temperature conditions (Figure 7). The thermobaric conditions for the shallowest SRLs (250 m water depth) in the shelf area are indicated by '●' whereas the thermobaric conditions of the deepest SRLs (700 m water depth in the upper slope) are denoted by '■'. According to the thermobaric conditions of the study area in Figure 7, a minimum 10% of H₂S and a maximum 90% of methane should exist in the hydrate structure for a possible gas hydrate occurrence in shallow water depths (e.g., 250 m). Because H₂S stabilizes the gas hydrate structure in shallow water depths, maximum H₂S concentrations are needed at the shelf area. Due to the increasing pressure, however, lower and lower H₂S concentrations are required from shelf to downslope as

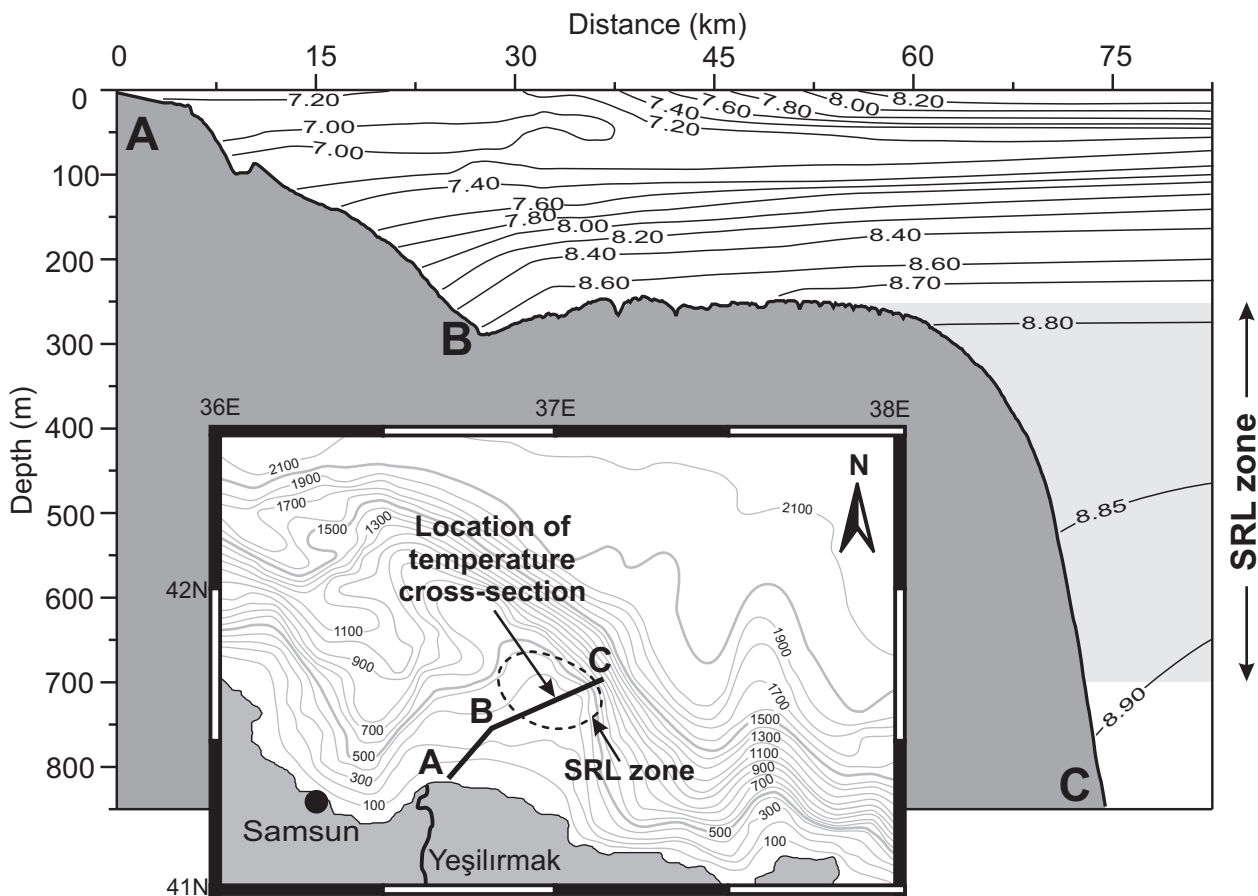


Figure 6. Cross-section showing temperature distribution from shelf to upper slope. The sea-bottom temperature ranges between 8.7 and 8.9 °C in the SRL zone. Inset is a bathymetric map showing the location of the curve.

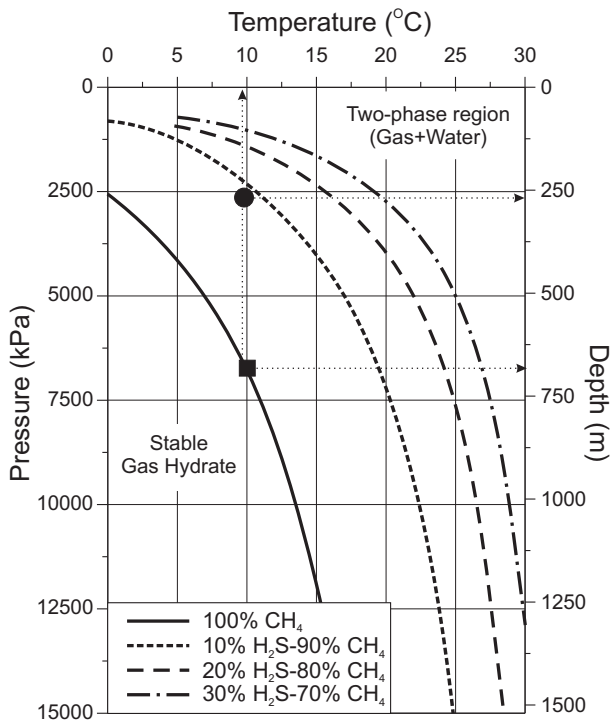


Figure 7. Theoretical gas hydrate stability curves for pure methane hydrates and hydrogen sulphide-rich methane hydrates (for 10, 20 and 30% H_2S compositions) calculated by the CSMHYD program of Sloan (1990). Thermobaric conditions for the conjectural gas hydrate layers for the shallowest and deepest water depths in the study area are indicated by '●' and '■', respectively (see text for details).

the water depth increases. Therefore, we conclude that lower H_2S and higher CH_4 concentrations should exist in the gas hydrate structure formed in deeper waters than those in the shallower shelf area. Total sulphide and free H_2S concentrations in Figure 5 decrease as the water depth increases downslope. This decrease, however, is compensated by a lower H_2S requirement for gas hydrate formation and stability in deeper waters.

Structure of the Conjectural Hydrate Zone

Based on the high resolution seismic data, Okyar & Ediger (1999) indicated that the boundary between the sulphate-reducing and the underlying carbonate-reducing zone in the southeastern Black Sea shelf was at about 35 mbsf. Because almost all the sulphate is depleted via sulphate reduction, H_2S concentration rapidly decreases towards the base of the sulphate-reducing zone and becomes zero in the underlying carbonate-reducing zone (Kastner *et al.*

1998). Furthermore, because methane is bacterially oxidized in the presence of sulphate, methane does not exist in the sulphate-reducing zone (e.g., Borowski *et al.* 1996). Therefore, H_2S concentration rapidly decreases in the carbonate-reducing zone, whereas methane concentration rapidly decreases towards the seabed (into the sulphate-reducing zone). This phenomenon is schematically illustrated in Figure 8a. In particular, sufficient methane flux into the sulphate-reducing zone (e.g., along the fault traces cutting the sulphate-reducing zone) can bring methane into contact with H_2S . That is why H_2S -rich gas hydrates are rare in nature. A geochemical relationship of this type was observed in the Cascadia subduction zone where the observed H_2S concentration at the seabed was >10000 ppm (Kastner *et al.* 1998). This high H_2S concentration then decreases towards the base of the sulphate-reducing zone located at about 20 mbsf, and it rapidly decreases to about 30 ppm at the base of the sulphate-reducing zone.

In the study area, some of the H_2S is precipitated as FeS and, after iron is depleted, the remaining H_2S exists as free and dissolved H_2S in the sulphate-reducing zone while methane is produced in the underlying carbonate-reducing zone. If the SRLs observed in our study area represent gas hydrate layers, they should be formed at the boundary between the sulphate-reducing and carbonate-reducing zones, where methane comes into contact with H_2S (Figure 8b). There is insufficient methane present above, while no H_2S exists below this boundary. Consequently, both sufficient methane and H_2S concentrations required for gas hydrate formation only exist along this boundary.

The formation mechanism of the gas hydrate layers is schematically illustrated in Figure 8b. H_2S is produced in the sulphate-reducing zone down to depths of about 25–60 mbsf. The close-up in Figure 8b shows the structure of the conjectural gas hydrate formation. It is concluded that strongly reflective appearance of gas hydrate layers on the acoustic data indicates that above the gas hydrate zone are several thin gas hydrate sheets or lenses interbedded with non-hydrate-bearing sediments. Individual reflections from consecutive thin gas hydrate layers may interfere with each other because the distances between them are rather small. When this interference is constructive, successive strengthening of the particular reflections can cause the observed anomalously strong reflector appearance on the sub-bottom profiler data.

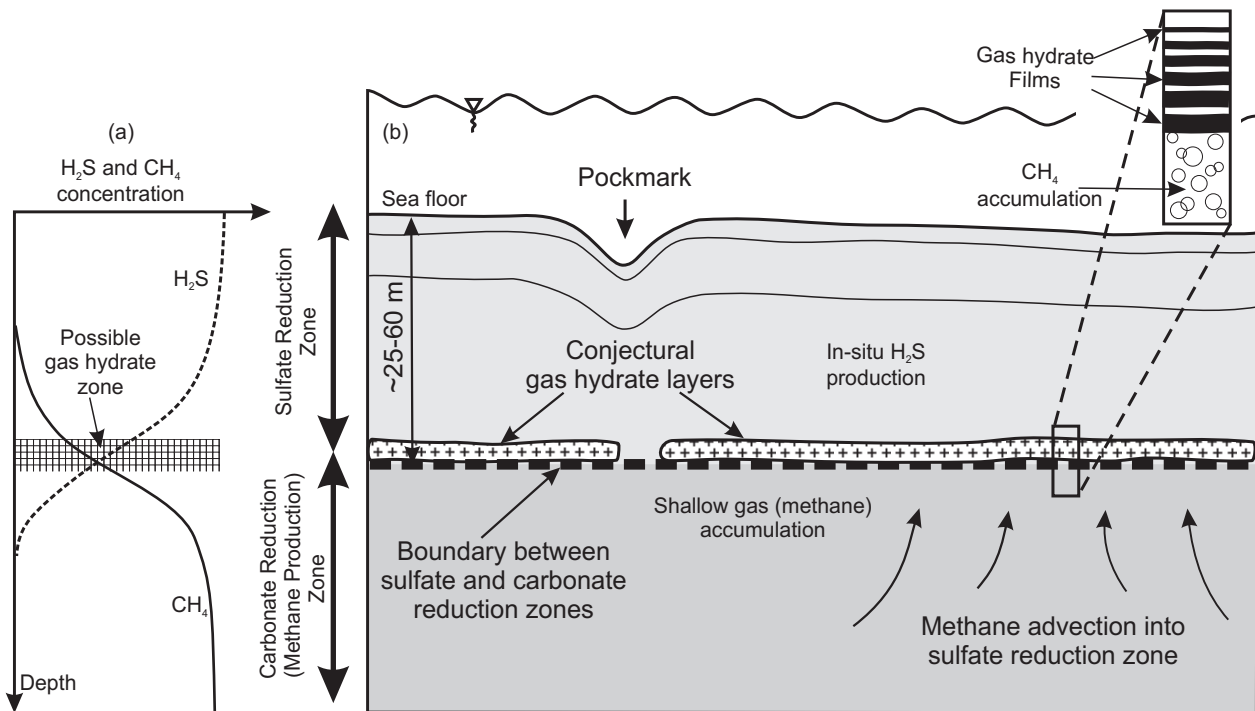


Figure 8. (a) Schematic representation of variations in methane and H₂S concentrations from the seabed to the carbonate-reducing zone (not to scale). (b) Conceptual model for conjectural gas hydrate formations in the area (not to scale). H₂S is produced *in situ* in the sulphate reduction zone down to 25–60 mbsf, while methane is produced in the underlying carbonate-reducing zone (see text for details). The proposed gas hydrate layers consist of a number of hydrate sheets with decreasing thicknesses towards the seabed and are formed along the boundary between the sulphate-reducing and the carbonate-reducing zone, indicated by a heavy dashed line.

Such a sequence can produce a 3- to 5-m-thick strong reflection because of the constructive interference effects of the successive reflections from top and bottom of the gas hydrate sheets even at 60 mbsf, as in Figure 4. Woodside *et al.* (2003) suggested a gradual decrease in the thickness and gas hydrate content of hydrate sheets towards the sea floor. Note that the carbonate-reducing zone in Figure 8b is characterized by acoustic turbidity zones in the acoustic data, indicating potential gas accumulation (e.g., in Figure 3). It is concluded that as pressure forced the methane to move upwards from the carbonate reducing zone, it possibly produced a gas front along the upper boundary of this zone, which is clearly observed on the acoustic data (see Figures 3 & 4).

Depth of SRLs in the study area changes significantly from one seismic line to another (compare Figures 3 and 4). This situation suggests that the thickness of the sulphate reduction zone and hence the depth of carbonate reduction zone increase significantly, especially towards the north (towards the shelf break or continental slope)

as in Figure 4, as expected. Borowski *et al.* (1999) indicated that the thickness of the sulphate reduction zone significantly increases towards the shelf break, so that while it is only a few centimetres thick near the coastlines, it can become more than a hundred metres deep on the shelf break. This observation explains the changes of boundary depths of the sulphide-reduction and carbonate reduction zones in the study area.

Conclusions

Several strong reflections at the subsurface depths of 25–60 mbsf were observed on deep-towed, high resolution sub-bottom profiler data in the Turkish shelf and upper slope of the Eastern Black Sea at the water depths of 250 to 700 m. Using acoustic and geochemical data, the possibility of these reflections indicating H₂S-rich shallow gas hydrate layers are discussed and a conceptual model for such gas hydrate formation is suggested. According to this model, the conjectural gas hydrate layers in the area

should be formed along the boundary between the sulphate-reducing and carbonate-reducing zones, where methane comes into contact with H₂S. In addition, the strongly reflective appearance of these layers on the sub-bottom profiler data indicates that the upper side of the hydrate zone consists of a number of gas hydrate sheets with a decreasing thickness towards the seabed, interbedded with hydrate-free sediments.

Although we do not know the percentages of methane and H₂S of the gas mixture in the proposed hydrate zone, according to the thermobaric conditions of shallowest SRLs in the shelf area, a minimum of 10% of H₂S and maximum 90% of methane should exist in the conjectural hydrate structure.

The main weakness with the suggested model is that it is based on important assumptions, such as the existence of a certain amount of H₂S and methane in deeper sediments as well as the depth of the sulphate-reducing zone in the study area. The model proposed here is based on acoustic and geochemical data, and further investigations are necessary to evaluate the composition and structure of observed SRLs in the area. The main contribution will come from ground-truthing data such as

shallow offshore drilling results and/or deep sediment sampling, which, together with the digital acoustic dataset, can allow us to perform some acoustic modelling attempts.

Acknowledgements

The authors extend their thanks to Dr. Timothy W. Lyons for his helpful comments and discussion on the hydrogen sulphide production and iron sulphide precipitation in the region. We thank Dr. Ana Garcia-Garcia from University of California, Santa Cruz and Dr. John Woodside from Free University of Amsterdam for their helpful comments on the earlier version of this paper. We also thank Dr. Bedri Alpar and Dr. Stuart Egan for their helpful and constructive comments. This research was supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) grant (Project Code: 100Y078), State Planning Organisation of Turkey (DPT) grant (Project Code: 2003K120360) and by Dokuz Eylül University Research Foundation grants (Project Codes: 02.KB.FEN.064 and 2005.KB.FEN. 062). John A. Winchester edited English of the final text.

References

- AHARON, P. & FU, B. 2000. Microbial sulfate reduction rates and sulfur and oxygen isotope fractionations at oil and gas seeps in deepwater Gulf of Mexico. *Geochimica et Cosmochimica Acta* **64**, 233–246.
- BARAZA, J. & ERCILLA, G. 1996. Gas-charged sediments and large pockmark-like features on the Gulf of Cadiz slope (SW Spain). *Marine and Petroleum Geology* **13**, 253–261.
- BOROWSKI, W.S., PAUL, C.K. & USSLER, W. 1996. Marine pore-water sulfate profiles indicate in situ methane flux from underlying gashydrate. *Geology* **24**, 655–658.
- BOROWSKI, W.S., PAUL, C.K. & USSLER, W. 1999. Global and local variations of interstitial sulfate gradients deep-water, continental margin sediments: sensitivity underlying methane and gas hydrates. *Marine Geology* **159**, 131–154.
- BOULEGUE, J., LORD, C.J. & CHURCH, T.M. 1982. Sulfur speciation and associated trace metals (Fe, Cu) in the pore waters of Great Marsh, Delaware. *Geochimica et Cosmochimica Acta* **46**, 453–464.
- BRÜCHERT, V., JØRGENSEN, B., NEUMANN, K., RIECHMANN, D., SCHLÖSSER, M. & SCHULZ, H. 2003. Regulation of bacterial sulfate reduction and hydrogen sulfide fluxes in the central Namibian coastal upwelling zone. *Geochimica et Cosmochimica Acta* **67**, 4505–4518.
- CODISPOTI, L.A., FRIEDERICH, G.E., MURRAY, J.W. & SAKAMOTO, C.M. 1991. Chemical variability in the Black Sea-implications of continuous vertical profiles that penetrated the oxic anoxic interface. *Deep-Sea Research* **38**, 691–710.
- ÇİFÇİ, G., DONDURUR, D. & ERGÜN, M. 2002. Sonar and high resolution seismic studies in the Eastern Black Sea. *Turkish Journal of Earth Sciences* **11**, 61–81.
- ÇİFÇİ, G., DONDURUR, D. & ERGÜN, M. 2003. Deep and shallow structures of large pockmarks in the Turkish Shelf, Eastern Black Sea. *Geo-Marine Letters* **23**, 311–322.
- DONDURUR, D., ÇİFÇİ, G. & ERGÜN, M. 2001. Gas hydrate structures in the Eastern Black Sea Basin. *36th CIESM Congress, Monaco, Abstracts*, p. 21.
- DONDURUR, D. & ÇİFÇİ, G. 2007. Acoustic structure and recent sediment transport processes on the continental slope of Yeşilirmak River fan, Eastern Black Sea. *Marine Geology* **237**, 37–53.
- ERGÜN, M., GAINES, A., GALLETI, G.C., CHIAVARI, G., FABBRI, D. & YÜCESOY-ERYILMAZ, F. 1996. Early diagenesis of organic matter in recent Black Sea sediments: characterization and source assessment. *Applied Geochemistry* **11**, 711–720.
- ERGÜN, M., DONDURUR, D. & ÇİFÇİ, G. 2002. Acoustic evidence for shallow gas accumulations in the sediments of the eastern Black Sea. *Terra Nova* **14**, 313–320.

- FOSSING, H., FERDELMAN, T.G. & BERG, P. 2000. Sulfate reduction and methane oxidation in continental margin sediments influenced by irrigation (South-East Atlantic off Namibia). *Geochimica et Cosmochimica Acta* **64**, 897–910.
- GARCIA-GIL, S., VILAS, F. & GARCIA-GARCIA, A. 2002. Shallow gas features in incised-valley fills (Ria de Vigo, NW Spain): a case study. *Continental Shelf Research* **22**, 2303–2315.
- GINSBURG, G.D., KREMLEV, A.N., GRIGOREV, M.N., LARKIN, G.V., PAVLENKIN, A.D. & SALTYSKOVA, N.A. 1990. Filtrogenic gas hydrates in the Black Sea. *Soviet Geology and Geophysics* **31**, 8–16.
- GINSBURG, G.D. & SOLOVIEV, V.A. 1997. Methane migration within submarine gas-hydrate stability zone under deep-water conditions. *Marine Geology* **137**, 49–57.
- HUNT, J.M. & WHELAN, J.K. 1978. Dissolved gases in Black Sea sediments. In: ROSS, D.A. & NEPROCHNOV, Y.P. (eds), *Initial Reports of the Deep Sea Drilling Project* **42**, 661–665.
- IVANOV, M.K., LIMONOV, A.F. & VAN WEERING, T.C.E. 1996. Comparative characteristics of the Black Sea and Mediterranean Ridge mud volcanoes. *Marine Geology* **132**, 253–271.
- IVANOV, M.K. & WOODSIDE, J.M. 1996. Shallow gas and gas hydrates on the Crimean continental margin, Black Sea. *Gas Hydrates: Relevance to World Margin Stability and Climatic Change Symposium, Gent, Belgium, Abstracts*, p. 46.
- IVANOV, M.K., LIMONOV, A.F. & WOODSIDE, J.M. 1998. Extensive deep fluid flux through the sea floor on the Crimean continental margin (Black Sea). In: HENRIET, J.P. & MIENERT, J. (eds), *Gas Hydrates: Relevance to World Margin Stability and Climate Change*. Geological Society, London, Special Publications **137**, 177–193.
- KASTNER, M., KVENVOLDEN, K.A. & LORENSON, T.D. 1998. Chemistry, isotopic composition and origin of a methane-hydrogen sulfide hydrate at the Cascadia subduction zone. *Earth and Planetary Science Letters* **156**, 173–183.
- KVENVOLDEN, K.A. 1993. Gas hydrates-geological perspective and global change. *Reviews in Geophysics* **31**, 173–187.
- KVENVOLDEN, K.A. & BARNARD, L.A. 1983. Hydrates of natural gas in continental margins. In: WATKINS, J.S. & DRAKE, C.L. (eds), *Studies of Continental Margin Geology*. AAPG Memoir **34**, 631–640.
- LERCHE, I. & BAGIROV, E. 1998. Guide to gas hydrate stability in various geological settings. *Marine and Petroleum Geology* **15**, 427–437.
- LIMONOV, A.F., WOODSIDE, J.M. & IVANOV, M.K. 1994. *Mud Volcanism in the Mediterranean and the Black Seas and Shallow Structure of the Eratosthenes Seamount*. UNESCO Reports in Marine Sciences **64**.
- LIN, S., HUANG, K.M. & CHEN, S.K. 2002. Sulfate reduction and iron sulfide mineral formation in the southern East China Sea continental slope sediment. *Deep-Sea Research* **49**, 1837–1852.
- LÜDMANN, T., WONG, H.K., KONERDING, P., ZILLMER, M., PETERSEN, J. & FLÜH, E. 2004. Heat flow and quantity of methane deduced from a gas hydrate field in the vicinity of the Dnieper Canyon, northwestern Black Sea. *Geo-Marine Letters* **24**, 182–193.
- LYONS, T.W. 1991. Upper Holocene sediments of the Black Sea: Summary of Leg 4 box cores (1988 Black Sea Oceanographic Expedition). In: IZDAR, E. & MURRAY, J.W. (eds), *Black Sea Oceanography*. NATO ASI Series, 401–441.
- MEREDITH, D.J. & EGAN, S.S. 2002. The geological and geodynamic evolution of the eastern Black Sea basin: insights from 2-D and 3-D tectonic modelling. *Tectonophysics* **350**, 157–179.
- MIENERT, J. & POSEWANG, J. 1999. Evidence of shallow- and deep-water gas hydrate destabilizations in North Atlantic polar continental margin sediments. *Geo-Marine Letters* **19**, 143–149.
- MURRAY, J.W., GRUNDMANIS, V. & SMETHIE, W.M. 1978. Interstitial water chemistry in the sediments of Saanich Inlet. *Geochimica et Cosmochimica Acta* **42**, 1011–1026.
- NIWÖHNER, C., HENSEN, C., KASTEN, S. & SCHULZ, H.D. 1998. Deep sulfate reduction completely mediated by anaerobic methane oxidation in sediments of the upwelling area off Namibia. *Geochimica et Cosmochimica Acta* **62**, 455–464.
- OKYAR, M. & EDIGER, V. 1999. Seismic evidence of shallow gas in the sediment on the shelf off Trabzon, Southeastern Black Sea. *Continental Shelf Research* **19**, 575–587.
- OTERO, X.L., HUERTA-DIAZ, M.A. & MACIAS, F. 2003. Influence of a turbidite deposit on the extent of pyritization of iron, manganese and trace metals in sediments from the Guaymas Basin, Gulf of California (Mexico). *Applied Geochemistry* **18**, 1149–1163.
- POPESCU, I., BATIST, M.D., LERICOLAIS, G., NOUZÉ, H., POORT, J., PANIN, N., VERSTEEG, W. & GILLET, H. 2006. Multiple bottom-simulating reflections in the Black Sea: potential proxies of past climate conditions. *Marine Geology* **227**, 163–176.
- RANGIN, C., BADER, A.G., PASCAL, G., ECEVİTOĞLU, B. & GÖRÜR, N. 2002. Deep structure of the Mid Black Sea High (Offshore Turkey) imaged by multi-channel seismic survey (BLACKSIS Cruise). *Marine Geology* **182**, 265–278.
- RICE, D.D. & CLAYPOOL, G.E. 1981. Generation, accumulation and resource potential of biogenic gas. *American Association of Petroleum Geologists Bulletin* **65**, 5–25.
- ROSS, D.A. 1977. The Black Sea and the Sea of Azov. In: NAIRN, A.E.M., KANES, W.H. & STEHLI, F.G. (eds), *The Ocean Basins and Margins*. Plenum Publications, New York, 445–481.
- SLOAN, E.D. 1990. *Clathrate Hydrates of Natural Gases*. CRC Press, Florida.
- SWART, P.K., WORTMANN, U.G., MITTERER, R.M., MALONE, M.J., SMART, P.L., FEARY, D., HINE, A.C. & ODP Leg 182 Scientific Party 2000. Hydrogen sulphide-rich hydrates and saline fluids in the continental margin of South Australia. *Geology* **28**, 1039–1042.
- TSUNOGAI, U., YOSHIDA, N. & GAMO, T. 2002. Carbon isotopic evidence of methane oxidation through sulfate reduction in sediment beneath cold seep vents on the seafloor at Nankai Trough. *Marine Geology* **187**, 145–160.
- WIJSMAN, J.W.M., HERMAN, P.M.J. & GOMOIU, M.T. 1999. Spatial distribution in sediment characteristics and benthic activity on the northwestern Black Sea shelf. *Marine Ecology Progress Series* **181**, 25–39.

- WIJSMAN, J.W.M., MIDDELBURG, J.J., HERMAN, P.M.J., BOTTCHER, M.E. & HEIP, C.H.R. 2001. Sulfur and iron speciation in surface sediments along the northwestern margin of the Black Sea. *Marine Chemistry* **74**, 261–278.
- WOODSIDE, J.M., IVANOV, M.K. & LIMONOV, A.F. 1997. *Neotectonics and Fluid Flow Through Sea Floor Sediments in the Eastern Mediterranean and Black Seas-Parts I and II*. UNESCO Reports in Marine Sciences 48.
- WOODSIDE, J.M., MODIN, D.I. & IVANOV, M.K. 2003. An enigmatic strong reflector on subbottom profiler records from the Black Sea-the top of shallow gas hydrate deposits. *Geo-Marine Letters* **23**, 269–277.
- ZONENSHAIN, L.P. & LE PICHON, X. 1986. Deep basins of the Black Sea and Caspian Sea as remnants of Mesozoic back-arc basins. *Tectonophysics* **123**, 181–211.