The role of geological factors in the formation of H_2S contamination in the Black Sea

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The Black Sea formed within an east-west trending elliptical depression with a surface area of 436,400 km^2, a water volume of 547,000 m^3, and a water depth reaching 2212 m at its lowest point. It is the world's largest (423,000 km^2) meromictic basin, where the deep waters do not mix with the upper layers that receive oxygen from the atmosphere. As a result, over 90% of the deeper Black Sea volume is contaminated by H_2S and is lifeless. There is a trend of increasing H_2S concentration in the seawater with increasing depth. One liter of Black Sea water contains 0.19, 0.83, 2.34, 8.48, and 9.6 mg/l of H_2S at water depths of 150, 200, 300, 1000, and 2000 m, respectively (Zaitsev, 1998). While the trend is obvious, the figures may be adjusted because the upper boundaries of H_2S exposures vary.

At present, the dominant hypothesis is that H_2S in the Black Sea is produced by sulfate-reducing bacteria and archaea. We believe that this opinion is too one-sided, and that H_2S contamination formed in different ways; at least, geological processes are involved in its formation as well. We do not deny the important role of sulfate-reducing bacteria, however, a polygenetic origin of H_2S in the Black Sea must be recognized as well. As such, the main goal of our study is to investigate the contribution of H_2S released from the deep Earth to the anoxic regime of the Black Sea.

The Black Sea was formed in the Mesozoic as a back-arc structure above the northward subducting Tethyan oceanic lithosphere. The basin occurs within the Anatolian sector of the Alpine-Himalayan orogenic system where the northward moving African and Arabian plates collide with the Eurasian plate. As such, the floor of the basin reveals a compressional tectonic regime resulting in active faulting. Tectonic ruptures form weakened zones in the sedimentary cover and act as channels/chimneys/venting sites for upwardly migrating gas (largely methane) emissions through fractures and fissures in the rock and between geological layers (Shnyukov and Ziborov, 2004).

Since 1990, a Ukrainian team of scientists headed by the first author has been studying the Black Sea over the course of numerous expeditions on board the R/Vs "Kiev," "Mikhail Lomonosov," "Akademic Vernadskii," "Professor Vodyanitskii," "Vladimir Parshin," and others during dozens of marine expeditions. One of the main goals of this work was a comprehensive geological-geophysical, hydro-gas-chemical, and biological investigation of gas releasing features in the Black Sea (Shnyukov et al., 2005).

In the course of the survey, at least 4000 high-intensity seeps and about 70 mud volcanoes were discovered and mapped. It was noted that some of them release not only methane but H_2S as well, and in significant quantities. Release of H_2S from the bowels of the Earth was described for the first time by Zelenov (1982) in Matsestinsky County, Caucasus. This was recently confirmed by investigations of the Kerch geological party that discovered uneven concentrations of H_2S within Cretaceous sediments in the area adjacent to Matsesta. A number of aquifers with water enriched by H_2S were discovered in geological sections of Crimea. According to Al'bov (1956), the water enriched with H_2S on the Kerch peninsula, Crimea, is associated with the Lower Neogene, as it was discovered in wells near Pheodosia, Old Crimea, the Belogorsk area (Bogatoe village), Dzhankoi south, and off-shore from Sivash (Gay County). Water enriched with H_2S often forms powerful sulfur-nitrogen springs from the Tavrichesky deposits (Upper Triassic-Lower Jurassic) located in Kuibyshevo village (Aji-

Su), in the Kokkozskaia valley, and Bakhchsarai County, Crimea. Sulfur-sparkling springs are described between Karadag and Sudak (Kizil-Tash), near Perchem-Kai in Sudak. Fetid water was encountered within the well in Alushta.

Almost all geological sequences in Crimea were found on the shelf and continental slope north of the Black Sea. These deposits are not only exposed under water, but are also cut by dozens of deeply incised canyons. In the canyons, discharge of freshwater saturated by H_2S is recorded (Shnyukov et al., 1989). Almost every active mud volcano on the Kerch peninsula is accompanied by a hydrogen sulfide spring. Taking into account that the number of active mud volcanoes on the Kerch peninsula is high (Shnyukov et al., 2010), the number of hydrogen sulfide springs must be high as well. "If the water in most of the hills of the Kerch peninsula can be considered as associated with Neogene and Maikopian deposits, the hills, aerated with carbon dioxide, G.A. Lychagin associates with the sediments from much greater depths, where gas and water rise, probably along tectonic fractures" (Al'bov, 1956).

In our opinion, this assumption should apply to the hydrogen sulfide water to an even greater extent. The depth of mud volcano roots has been traced down to 18 km in Azerbaijan (Mamedov and Guliev, 2003), and 6–9 km on the Taman peninsula (mud volcano Karabetova Gora). Eruptive material from a mud volcano incorporates gas-water flows, and the water can be taken from different horizons, including H_2S water generated at great depths.

The areas most abundant in mud volcanoes include the northern part of the Western Black Sea, Sorokin trough, Tuapsinskaya trough, Shatskiy arch, and the Kerch downfold (the area south of the Kerch peninsula). As of today, the number of known offshore mud volcanoes is close to seventy, and their number continues to increase annually (Shnyukov and Yanko-Hombach, 2010). If the mud volcanoes at the sea bottom are also accompanied by hydrogen sulfide sources, their contribution to contamination of the Black Sea is obvious. Our investigations support this idea. For example, the mud volcano Mitin located on the continental slope of the Kerch peninsula at a water depth of 730 m releases an elevated concentration of H_2S into the bottom water in the form of a dome that reaches 600 m in height (Fig. 1, 2).

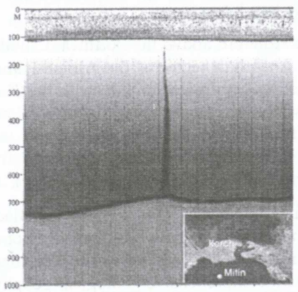

Figure 1. Echo-sound profile across mud volcano "Mitin" [44°37',897" N, 36°01',058" E; depth 730m; height of high intensity seep is about 600 m].

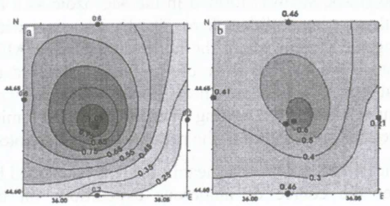

Figure 2. The spatial distribution of concentration gradients of hydrogen sulfide in the area of the volcano "Mitin" a) 5 m from the sea floor, b) 35 m from the sea floor.

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