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Sources of hydrocarbon gases in mud volcanoes from the Sorokin Trough, NE Black Sea, based on molecular and carbon isotopic compositions

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Abstract

Molecular and stable carbon isotope properties of hydrocarbon gases (methane through pentanes and sometimes hexanes) from seven sediment cores collected from five mud volcanoes (MVs) in the Sorokin Trough (NE Black Sea) suggest that these gases are initially derived from the comparable hydrocarbon pools and are likely initial products of non-microbial oil cracking processes. Our results state that dry characteristics of gas and ^{13}C-depleted signatures of methane are result of a high admixture of secondary microbial gas formed due to subsequent microbial anaerobic degradation of redeposited hydrocarbons in the shallow reservoirs. The wet gas components in all MVs and gas hydrates are related to each other. The compositional variations in C_{2+} content appear to result from a complex of secondary processes such oil cracking in the deep subsurface, migration and mixing of resulted gaseous and liquid hydrocarbons, biodegradation of possibly redeposited hydrocarbons forming shallow reservoirs, and additional alterations of hydrocarbon gases in the surface sediments due to currently active microbial processes, such as AOM, C_{2+} consumption, etc. Our data show that the most unaltered gas is in the mud breccia from the Kazakov MV. The gas mixture possibly represents the original properties of the hydrocarbons trapped in the deep subsurface of the Sorokin Trough. Analysis of the hydrocarbon gas data, complemented with published maturity characteristics of organic matter from Maycopian rock clasts and mud breccia matrix implies that the original source of gases is likely to be located below the Maycopian Shale Formation.

Keywords: Hydrocarbon gas; Mud volcanoes; The Sorokin Trough

1. Introduction

Mud volcanoes (MVs) are documented worldwide in both on- and off-shore locations. They reflect the presence of hydrocarbon reservoirs in the deep subsurface. Gas and oil seepage are related phenomena, MVs and gas venting areas commonly occur in petroliferous regions (Guliev and Feizullayev, 1997). The roots of MVs can reach depths of up to 20 km (Shnukov et al., 2005), thus providing key information on the geological history of the area and on the possible hydrocarbon potential (Ivanov et al., 1989, 1998). Comprehensive investigations of numerous on- and off-shore MV provinces have revealed the overwhelming input of hydrocarbon gases (HCGs) in their formation. Eruptions are often manifested in a catastrophic emission of fluids consisting of HCGs (especially methane), hydrogen sulfide, carbon dioxide, petroleum products, water, and a complex mixture of sediments, so-called "mud breccia" (Akhmanov, 1996; Akhmanov and Woodside, 1998; Ivanov et al., 1998). As a rule, a part of HCGs emitted is often thermogenic (i.e. formed by cracking of organic matter in the subsurface resulting from increase in temperature and pressure upon subsurface burial) in

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nature. An alternative origin of HCG is microbial decomposition of organic matter under anoxic conditions during diagenesis. These gases (microbial or biogenic) are dominantly consisted of methane, since significant amounts of heavier HCGs, usually found in thermogenic gas mixtures, so far have never been reported to be formed due to microbial actions. Biogenic and thermal methanes can be readily discriminated by their ^{13}C content (Sackett, 1978; Stahl, 1977; Rice and Claypool, 1981). Methane, formed by microbial methanogens via CO_2 reduction, has the lowest δ^{13}C values, from -60‰ to -110‰, and methane formed by the microbial acetate fermentation is from -50‰ to -65‰ (Whiticar et al., 1986). In contrast, methane formed due to the thermal cracking of humic sourced organic material is ca. -30‰ (Schoell, 1983).

The Black Sea region is well known for the presence of fluid-related structures in shallow to deep-water environments (Ivanov et al., 1989, 1992a, b, 1998; Ginsburg et al., 1990; Limonov et al., 1994; Woodside et al., 1997; Peckmann et al., 2001; Thiel et al., 2001; Kenyon et al., 2002; Michaelis et al., 2002; Blinova et al., 2003; Bohrmann et al., 2003; Krastel et al., 2003; Schmale et al., 2004; Shnukov et al., 2005). Despite an extensive research of the Black Sea during the last decades, there is still an active debate about the possible sources of emitted fluids/HCGs (methane). Reeburgh et al. (1991) suggested that the methane in the Black Sea has dominantly microbial in origin. Michaelis et al. (2002) have also shown that the methane is mainly of biogenic in nature. An extensive overview about fluid fluxes and mud volcanism in the Sorokin Trough was completed by Ivanov et al. (1998). Mazzini et al. (2004) introduced HCG data from the Sorokin Trough suggesting a mix of gasses of biogenic and thermogenic origin. Blinova et al. (2003) reported a study of HCGs from three MVs in the Sorokin Trough and hypothesized a secondary ''biogenic'' origin for the methane, i.e. methane that was formed due to biodegradation of hydrocarbons below the MV.

Indeed, active fluid venting and mud volcanism in the Black Sea (Ivanov et al., 1989, 1992a, b, 1998; Ginsburg et al., 1990; Limonov et al., 1994; Shnukov et al., 2005; Woodside et al., 1997; Peckmann et al., 2001; Thiel et al., 2001; Kenyon et al., 2002; Michaelis et al., 2002; Blinova et al., 2003; Bohrmann et al., 2003; Krastel et al., 2003; Schmale et al., 2004) indicate considerable quantities of hydrocarbons, in particular methane, which are trapped in the sediments, specifically in the form of gas hydrates (Ginsburg and Soloviev, 1997; Soloviev and Ginsburg, 1997; Ivanov et al., 1998; Bouriak and Akhmetzhanov, 1998; Zillmer et al., 2005; Popescu et al., 2006, 2007). Consequently, where such substantial amounts of HCGs are originated from? Blinova et al. (2003) reported δ^{13}C values of methane from gas hydrates between -50‰ and -65‰. This is indicative of mainly microbial origin of methane, kept in the gas hydrate. If this is the case, another question rises regarding active and extensive methane production carried out in the sedimentary subsurface of the Black Sea. To answer these questions, we combined all data on molecular and stable carbon compositions of HCGs from pelagic sediments, mud breccias and gas hydrates collected during two Training-Through-Research (TTR) expeditions, in 1996 (ANAXIPROBE/TTR-6) and in 2001 (TTR-11) in the north-eastern part of the Black Sea, within the Sorokin Trough (Fig. 1). In this paper, we show the molecular and stable carbon isotope properties of methane through pentanes (hexanes) that were defined to reveal the origin/source of HCGs and their eventual subsurface microbial alterations in seven sedimentary

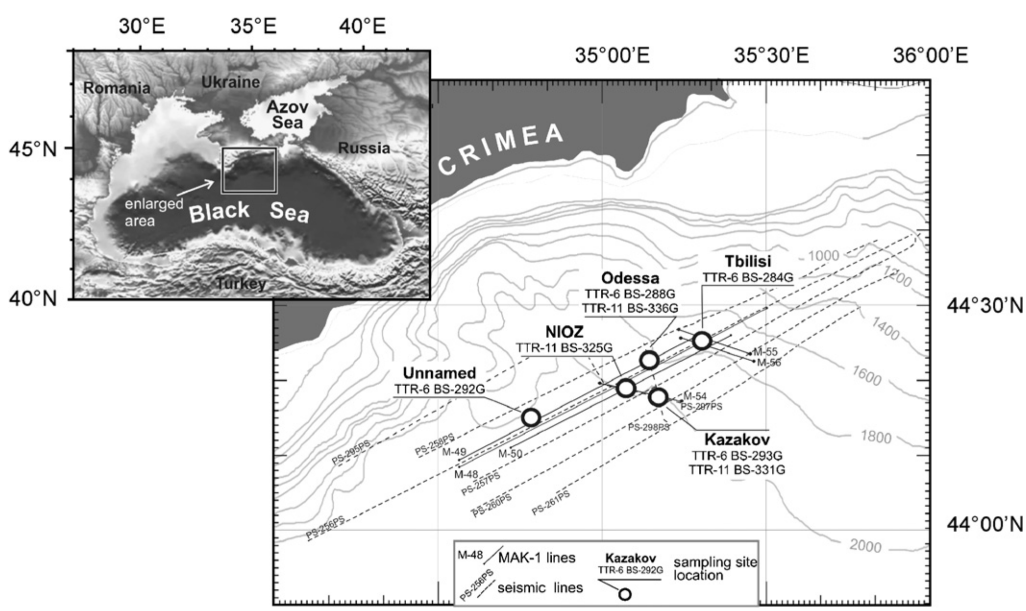

Fig. 1. Location map (modified after Ivanov et al., 1998) of the study area showing sampling sites chosen for the hydrocarbon gas study, seismic and deep-towed side scan sonar MAK-1 lines obtained during the ANAXIPROBE/TTR-6 (1996) and TTR-11 (2001) cruises (Woodside et al., 1997; Kenyon et al., 2002).