GEOCHEMICAL CHARACTERISTICS OF HYDROCARBON GASES FROM MUD VOLCANOES OF THE GULF OF CADIZ

E. Bileva, V. Blinova

UNESCO-MSU Center for Marine Geology and Geophysics, Faculty of Geology, Moscow State University, Vorobjevy Gory, Moscow, Russia, fu@geol.msu.ru

The Gulf of Cadiz is an area, characterized by extensive mud volcanism and gas venting processes. The main geochemical objectives of Leg 2 TTR-12 cruise were subsampling of mud volcanic structures and active fluid vents and study of their present activity.

Samples of pelagic sediments, mud volcanic breccia and hydrocarbon gases were collected for geochemical analyses during Leg 2. In general 14 cores were taken and 9 mud volcanoes were studied.

The main objective of this work was geochemical characterization of hydrocarbon gases and mud breccia from 15 mud volcanoes from the Gulf of Cadiz, using the data of TTR-12 cruise and the previous data, obtained in this area during TTR-10 and TTR-11 cruises (V. Blinova, A. Stadnitskaya, 2001).

Concentration and composition of hydrocarbon gas were measured using gas chromatography. Components from methane to pentane, including saturated and unsaturated ones and their isomers were determined.

Using these measurements we can conditionally divide these mud volcanoes into 2 types according to concentration of methane (in general) and its homologues: relatively passive at present days volcanoes and active volcanoes.

The first type is represented by 7 mud volcanoes: Aveiro, Jesus Baraza, Mercator, Tanger, Rabat, TTR and Tasyo. These mud volcanoes are characterized by low concentrations of hydrocarbon gases, which values don't exceed 1 ml/l. Moreover, cores from all of these mud volcanoes consist of pelagic sediments of significant thickness in addition to mud breccia. So due to these facts we can suggest that there were no eruptions from these mud volcanoes for some period.

Gas, sampled from mud breccia from these cores shows the predominance of saturated hydrocarbons over unsaturated ones, while gas samples from pelagic sediments show, that unsaturated hydrocarbons are predominant. These facts imply a presence of active oxidation processes in pelagic sediments and in the upper part of mud breccia.

It is very difficult to indicate the origin (thermogenic or biogenic) of hydrocarbon gases from the cores from mud volcanoes of the first type. However, the ratio of methane to the sum of its homologues for these cores in general does not exceed 100 that imply the thermogenic origin of the gas phase. But because of very low concentrations of hydrocarbons, these measurements are on limit of resolution of this method and we cannot completely trust these values.

Such active volcanoes as Bonjardim, Olenin, Carlos Ribeiro, Ginsburg, Captain Arutyunov, Gemini, Al Idrissi and Fuiza represent the second type of mud volcanoes of the Gulf of Cadiz. All the cores from these mud volcanoes consist mostly of mud breccia, and these cores are characterized by high concentrations of methane, which are measured in n*10 ml/l or higher. Homologues of methane from these cores are also characterized by extremely high concentrations. However the ratio of methane to the sum of its homologues in the area of relatively high concentrations of hydrocarbons for all of these mud volcanoes is different in different cores. According to this fact we can divide structures of this type into two groups:

- with low concentrations of methane homologues, which indicate the predominance of biogenic part of gas. Mud volcanoes Olenin, Al Idrissi, Captain Arutyunov and the bigger crater of Gemini are characterized by such values.

- with high concentrations of methane homologues, that implies the predominance of gas of thermogenic origin. Bonjardim, Carlos Ribeiro, Ginsburg, Fuiza and the smaller crater of

Gemini mud volcano represent this group. Cores from these mud volcanoes consist only of mud breccia and very rarely the presence of insignificant amount of pelagic sediments was observed.

It is very surprising, that two craters of Geminy mud volcano are related to different groups. Most likely, they have the same source of gas, but eruptions through the bigger crater probably took place earlier than through the smaller crater, that can be indicated by the presence of significant part of biogenic gases in gas mixture and the presence of pelagic sediments in the upper part of the core from the bigger crater. Gas from the smaller crater of Gemini mud volcano has not been significantly mixed with biogenic gas from surrounding sediments and its core consists only of mud breccia. Besides we have difference in carbon isotopic measurements of $\delta^{13}C$ of methane. For the bigger crater these values are lower (about -43 ‰), than for the smaller crater (about -37.5 ‰). So we can suggest, that the smaller crater is younger.

Using the same facts, as for the two craters of Gemini mud volcano, we can tell, that the first group is represented by less active mud volcanoes, than the second one.

Gas samples from all of the mud volcanoes of the second type show the predominance of saturated hydrocarbons over unsaturated ones, implying the presence of thermogenic composition part in all of gas mixtures.

All the cores studied in this work show that iso-butanes are predominant over n-butanes, determining the presence of focused gas flow through the sediment.

The values of total organic carbon (TOC) content in all samples are relatively low, varying from 0.22 % up to 0.54 %. It should be noted, that there is no clear correlation between distribution of hydrocarbon gases and TOC content along the cores, which indicates migratory nature of hydrocarbon gases. In all of the examined cores, the uppermost part of the sediments is characterized by low methane concentrations and the rise of methane concentrations is associated with the rise of concentrations of its homologues.

Therefore:

The influence of focused fluid inflow is present in all of the studied cores from 15 mud volcanoes.

According to the concentration of methane all mud volcanoes can be divided into two types: relatively passive at present days and active. Among active mud volcanoes two groups were allocated:

- with significant content of gases with biogenic origin;
- with the predominance of thermogenic hydrocarbons (the most active mud volcanoes).

The hydrocarbon gas from gas-venting sediments in most cases is a mixture of gases with thermogenic and biogenic origin.

Reference:

V. Blinova, A. Stadnitskaya, 2001. Composition and origin of the hydrocarbon gases from the Gulf of Cadiz mud volcanic area. – In: *Geological processes on deep-water European margins – TTR-10 Post-Cruise Conference*. Abstracts, Moscow – Mozhenka, Russia.