Search for hydrogeochemical indicators of the genetic relation between mud volcanism and oil and gas fields

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Abstract. The paper reports the results of a comparative analysis of the chemical and isotope composition ($\delta^{18}$O and $\delta^D$) of mud volcanic waters and formation waters from oil and gas fields. Studies show that the waters discharged by mud volcanoes in most cases are very similar to formation waters. The most characteristic geochemical traits of both waters are elevated concentrations of hydrocarbonate ions, iodine, boron, bromine, and a low content of sulfate ions.

1. Introduction
Mud volcanism is a geological phenomenon associated with the processes of focused discharge of subsurface fluids in fault zones of sedimentary basins. Mud volcanoes are an important element in the transformation of sedimentary deposits – high temperature and pressure induce sediment diagenesis and catagenesis in mud volcanic systems, and drive the maturation of the organic matter contained therein [1]. Transformation of organic matter at high depths can be a major cause of mud volcanoes formation. It is believed that as organic matter matures under clay cap rocks, hydrocarbon gas accumulates there and anomalously high formation pressure forms in mud volcanic chambers. This supposition is largely corroborated by a consistent distribution of mud volcanoes within large oil and gas basins [2]. The possibility of finding industrially exploitable hydrocarbon reserves at mud volcanism occurrences is evidenced by the case of Lokbatan volcano in Azerbaijan. In 1933, a wildcat was drilled at the foot of Lokbatan volcano, discovering an oil and gas field, which is in operation still now [2]. That said, some researchers remark that by far not all oil and gas regions have mud volcanoes. For example, no mud volcanoes have been found in large oil and gas provinces in the Near East, Siberian Platform, Volga-Ural and Timan-Pechora basins [3]. A presumable reason for that is the age and lithological characteristics of the reservoir rock. The oil reservoir rocks for the oil and gas basins with mud volcanoes are Cenozoic (rarely Cretaceous) terrigenous-clay strata. The reservoir rocks in the oil and gas basins lacking mud volcanoes are ancient (Paleozoic and Precambrian) carbonate, terrigenous-carbonate, and evaporate sediments.

Mud volcanoes are natural wells that inform about the processes taking place in the Earth’s interior. Research into the genetic relation between mud volcanoes and oil and gas fields are of high practical importance, as it provides answers for the feasibility of estimating the deep hydrocarbon potential and for the development of new geological prospecting methods. Immediate relation to hydrocarbon fields can be identified through geochemical studies of subsurface fluids discharged by mud volcanoes. Evidence directly pointing to mud volcanoes associated with hydrocarbon fields is oil impurities in...
emissions of mud volcanoes. Not all mud volcanoes in oil and gas regions, however, produce oil seepage [2]. For example, in the South Caspian oil and gas basin, which harbors the largest mud volcanic province worldwide, oil seepage happens only in 40 out of several hundred mud volcanoes. Hence, the absence of oil impurities in the material discharged by a mud volcano is not per se a negative indicator of the region’s hydrocarbon potential.

Another fact in favor of the relation between mud volcanism and the hydrocarbon potential is the geochemical characteristics of gaseous emissions from mud volcanoes. Analysis of worldwide data on the chemical and isotope composition of mud volcanic gases shows mud volcanoes to emit large amounts of hydrocarbon gases, the prevalent one is thermogenic methane [4]. Researchers also point out that many gaseous emissions from mud volcanoes contain carbon dioxide produced through anaerobic biodegradation of petroleum.

The hydrogeological settings are known to significantly affect oil and gas fields, since groundwater always accompanies oil and gas reservoirs [5]. Active participation of groundwater in hydrocarbon synthesis, migration, and destruction processes is the basis for the application of hydrogeochemical indicators for estimate of the hydrocarbon potential. Mud volcanic waters is often similar to formation waters, which is another indicator of a genetic relation between mud volcanoes and oil and gas fields. It is therefore reasonable to inquire whether the geochemical characteristics of the groundwater discharged by mud volcanoes can be used to estimate the hydrocarbon potential of the region?

2. Materials and methods
This paper gives a comparative analysis of the chemical and isotope composition of waters on terrestrial mud volcanoes and formation waters from oil and gas fields made on the basis of published hydrogeochemical data. The study made use of consolidated reports on water composition from over 170 mud volcanoes situated in different parts of the world – Azerbaijan, Georgia, India (Andaman Islands), Italy, China, Russia (Kerch Peninsula, Taman Peninsula, Sakhalin Island), USA (Alaska), Taiwan, Trinidad and Tobago, Turkmenistan, Japan [6–8]. Specific geochemical characteristics of formation waters are highlighted through the cases of several large oil and gas regions of Russia and other countries [9–16].

3. Results and discussion
The most characteristic geochemical features of the groundwater accompanying hydrocarbon fields are elevated total dissolved solids, and Cl–Ca or HCO$_3$–Na type water [5]. Formation waters types here are given in accordance with the classification suggested by V.A. Sulin and used in petroleum hydrogeology. The origin of Cl–Ca-type brines is believed to be associated with the geochemical evolution of sedimentation seawaters. The origin of HCO$_3$–Na-type formation waters, on the other hand, is associated with hydrochemical inversions in the sedimentary column. The causes of such inversions are still being debated. Mud volcanic waters, in turn, chiefly belong to the HCO$_3$–Na type according to Sulin’s classification or, less often, to the Cl–Mg type. The synthesis and analysis of worldwide data on the chemical and isotope composition of the waters on terrestrial mud volcanoes show that the primary original source of mud volcanic waters is sediment-buried seawaters [6, 8].

The genesis of natural waters is often identified relying on their isotope composition. Comparisons and analysis of the isotope parameters mud volcanic waters and formation waters demonstrate that both of them feature a wide variation of $\delta^{18}$O and $\delta^D$ values (fig. 1). In most cases, $\delta^{18}$O and $\delta^D$ values are almost identical for mud volcanic waters and formation waters. Supposedly, the diversity of the isotope composition of mud volcanic waters is largely shaped by a combination of the following processes: mixing of the original sedimentation seawaters with the waters formed through dehydration of clay minerals; dilution by meteoric waters; oxygen-18 isotope exchange with the water-hosting rocks [6]. As a result, most mud volcanic waters are significantly enriched in oxygen-18 and have a lower deuterium content than seawaters. The tendency for formation waters from oil and gas fields is generally similar. Like mud volcanic waters, they exhibit a marked positive oxygen shift (fig. 1). Formation waters enrichment in oxygen-18 is largely due to isotope exchange with the reservoir rock.
[10–12, 14, 16]. Ongoing processes of isotope exchange in the “water–rock” system in reservoir conditions indicate that the subsurface is hydrologically rather closed, which is a good sign for the integrity of oil and gas fields. Formation waters enrichment in oxygen-18 can also be due to the input of dehydration waters. Also, the isotope composition of formation waters is significantly influenced by the input of meteoric waters, which is the reason for a reduction in deuterium concentration in the formation waters. This process usually takes place in early stages of sedimentary basin evolution.

Figure 1. The ratio of δ^{18}O and δD of formation waters in different oil and gas areas: 1 – the Lunnan oilfield, China [11]; 2 – the oilfields in Novosibirsk region, Russia [14]; 3 – the Carabobo oilfield, Venezuela [10]; 4 – oil and gas fields of Eagle Ford Group, Texas, USA [12]; 5 – oilfield of San Joaquin Valley, California, USA [16] and Seawater – 6. GLMW – Global Meteoric Water Line. The dotted line marks the area that corresponds to the ratio of δ^{18}O and δD in mud volcanic waters in different regions [6]. The ellipse marks the area of the most typical δ^{18}O and δD values for mud volcanic waters.

An important geochemical feature of the groundwater associated with oil and gas fields is that it is low content of sulfate ions [5]. For example, SO_4^{2-} concentrations in formation waters of oil and gas fields in the Yenisei-Khatanga trough range from 2 to 98 mg/l, while their total dissolved solids content is 2.2 to 21.1 g/l [13]. The low SO_4^{2-} content in formation waters is a result of sulfate reduction processes involving anaerobic bacteria in the presence of organic matter. Mud volcanic waters also feature low SO_4^{2-} concentrations. They are significantly depleted in SO_4^{2-} compared to seawaters. We estimate the average SO_4^{2-} content in mud volcanic waters to be 20.5 mg/l [8]. Such a low SO_4^{2-} content in mud volcanic waters can be a consequence of anaerobic methane oxidation accompanied by sulfate reduction.

Bacterial sulfate reduction in groundwater rich in organic matter is a reaction that produces CO_2. Dissolution of CO_2 in groundwater, in turn, causes a rise in HCO_3^- concentrations. This is believed to be one of the reasons for elevated HCO_3^- content in formation waters [17]. Rather high HCO_3^- concentrations are found also in mud volcanic waters. According to our estimates, average HCO_3^- content in mud volcanic waters is 2 g/l [8]. Analysis of worldwide data, on the other hand, shows that 20% of samples have HCO_3^- concentrations over 5 g/l, and the maximum HCO_3^- concentration record is 15 g/l. CO_2 input to mud volcanic chambers can come from oil biodegradation, as corroborated by high δ^{13}C–CO_2 values in gaseous emissions from mud volcanoes [4]. It is possible also that mud volcanic waters get enriched in HCO_3^- as a result of anaerobic methane oxidation, since methane is a
dominant component of mud volcanic gases. Besides, mud volcanic chambers can get CO$_2$ from mantle degassing and metamorphic CO$_2$ generated during thermal degradation of carbonates.

Mud volcanic waters are characterized by an elevated content of trace elements such as iodine, boron, and bromine. These trace elements in groundwater are direct indicators of the hydrocarbon potential. Groundwater enrichment with iodine is attributed to organic matter transformation in the process of sedimentary rock formation, considering that iodine, being originally a biophilic element, is a constituent of the organic matter in water-hosting rocks. The most significant rise in iodine content in groundwater is believed to happen during the organic matter thermal maturation stage [18]. In content of chlorine and iodine concentrations, waters of mud volcanoes are very similar to formation waters (fig. 2). Iodine concentrations in mud volcanic waters range from 0.02 to 92.5 mg/l. The range of iodine concentrations in formation waters from the oil and gas fields examined in this paper is 0.75 to 81 mg/l.

Analysis of worldwide data shows boron and bromine concentrations in mud volcanic waters to vary widely: from 0.3 to 915 mg/l for boron (75.6 mg/l on average), from 0.1 to 376 mg/l for bromine (44 mg/l on average). Enrichment of mud volcanic waters in these trace elements is often associated with the interaction processes in the “water-rock” system. Namely, high boron content in mud volcanic waters can be explained by smectite transformation into illite, during which large amounts of boron-rich water is discharged into the pore space. The said trace elements in mud volcanic waters can be of biogenic origin, considering that the sedimentation process involves boron and bromine accumulation in the organic matter contained in the sedimentary deposits. The destruction of the organic matter in sedimentary deposits under high temperatures and pressures leads to elevation of bromine and boron concentrations in the groundwater of sedimentary basins [19, 20]. The thermal settings for smectite illitization largely coincide with the temperatures at which hydrocarbons are generated as organic matter is thermally matured. Note that boron and bromine concentrations in formation waters are comparable to those in mud volcanic waters.

Figure 2. The ratio of Cl and I concentrations of mud volcanic waters (1) in different regions [7, 8] and formation waters in different oil and gas areas (2 – the Timan-Pechora oil and gas province, Russia [9, 15]; 3 – the Yenisei-Khatanga regional trough, Russia [13]; 4 – Sakhalin Island, Russia) plotted on a diagram from [18].

The rates of diagenetic and catagenetic processes in sedimentary deposits and the organic matter contained therein are primarily controlled by the thermal conditions, which are directly related to the depth at which these processes are happening. The generation temperatures of mud volcanic waters calculated based on hydrochemical geothermometry can be used as proxies of the bedding depth of the reservoirs that feed mud volcanoes with water. The generation temperatures of mud volcanic waters in different regions of the world, calculated from a geothermometry
dataset (Mg–Li, Na–Li, K–Mg, Na–K), mainly vary from 50 to 110 °C. Judging by the calculated temperatures, mud volcanic chambers are bedded at 1.0 to 3.5 km depths. These are also the depths of the oil and gas generation zone. Let us remark that peak intensities of liquid and gaseous hydrocarbon generation occur at different temperatures (and, hence, at different depths). The principal oil generation zone corresponds to a temperature range of 95 to 175 °C, whereas the main gas generation zone occurs at higher temperatures – 105 to 220 °C [21]. In that case, where the thermal flux is, for example, 60 mW/m², the oil generation zone lies at a depth of 1 to 4.5 km, and the gas generation zone is at 1.7 to 7.5 km depth, i.e. is deeper bedded. Gases emitted from some mud volcanoes were found to contain methane rich in δ13C–CH₄, which is formed in late stages of catagenesis. Hence, mud volcanoes can serve as a source of information on the gas content of deeply buried deposits.

4. Conclusion
Comparative analysis of the chemical and isotope composition of mud volcanic waters and formation waters from oil and gas fields shows them to have similar hydrogeochemical characteristics. In our opinion, the similarity observed between mud volcanic and formation waters is largely due to their shared geological environments – within large sedimentary basins, where groundwater composition is significantly influenced by the processes of hydrostatic compaction of sedimentary deposits, thermal dehydration of clay minerals, organic matter maturation, and interactions in the “water–rock–gas” system. Let us specially emphasize that generation temperatures of mud volcanic waters and depths calculated through hydrochemical geothermometry largely coincide with those of oil and gas generation zones. Thus, the characteristics and patterns of mud volcanic waters and formation waters generation described in this paper suggest that there exists at least a paragenetic relation between mud volcanoes and oil and gas fields.

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