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# On the problem of geochemical signatures of mud volcanoes and sediment-hosted hydrothermal systems

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**Abstract.** The present paper is a comparative study of geochemical characteristics of the emissions of the Yuzhno-Sakhalinsky mud volcano and the sediment-hosted hydrothermal systems Salton Sea and Lusi. The comparative analysis was performed using the data on the content of Cl, Br, SO<sub>4</sub>, Li, Na, K, Ca, Mg, B, Ba, Sr, Si, oxygen-18 and deuterium in the discharged fluids, as well as on the content of CO<sub>2</sub>, C<sub>1</sub>-C<sub>5</sub>, carbon-13 in CO<sub>2</sub> and CH<sub>4</sub> in the released gases. It showed the absence of any distinct systematic differences in geochemical parameters between mud volcanoes and sediment-hosted hydrothermal systems. This suggests, inter alia, a need for a detailed geochemical classification of mud volcanoes, which to this day has not been elaborated.

## 1. Introduction

Mud volcanism is a very curious geological phenomenon which is determined by the focused flows of subsurface fluids in the fault zones of the Earth's crust under the influence of abnormally high formation pressure. Along with fundamental questions, studies of mud volcanism typically touch upon a number of significant practical issues: the correlation between mud volcanism and oil-and-gas-bearing capacity, the proportion of mud volcano gases in the global atmospheric budget of greenhouse gases, as well as the possible links between mud volcanism (and the volcano activity) and seismicity. Apart from that, mud volcanism is a natural hazard which needs to be taken into account in implementing engineering projects.

At the present time, there is no clear definition of the term “mud volcano” that would allow us to distinguish between mud volcanoes and other similar natural features. As a rule, geomorphological characteristics are used to make this distinction – a mud volcano is thought of as a large truncated cone-shaped hill comprised of argillaceous deposits. At its summit, there is a funnel-shaped crater with a channel going deep down from which subsurface gases, waters, and mud shales are periodically discharged in large amounts (sometimes with traces of oil film). On the surface of the volcano there are also gryphons and pools – eruptive pathways through which mud, water, and gas are continuously released in relatively small volumes. The definition through morphologies can be applied to a whole range of various objects, which results in subjective interpretations and confusion. Therefore, mud pools and gryphons on the magmatic volcanoes – of the Yellowstone volcano (Wyoming, the USA), the Uzon volcano (Kamchatka, Russia), the Etna volcano (the Island of Sicily, Italy), etc. – can also be classed as mud volcanoes.



In this respect, the issue of fluid systems typification according to their geochemical features is a matter of current interest.

In the study [1] the authors made an attempt to define mud volcanism through the genetic mechanism which determines and controls this natural phenomenon. At the same time, a distinction between mud volcanoes and sediment-hosted hydrothermal systems has been made. It has been suggested that the latter should include, in particular, the fluid system Lusi, which was earlier considered to be a mud volcano. In the study [2] a differentiation of fluid systems into three types has been substantiated – hydrothermal-magmatic, sediment-hydrocarbonic and sediment-hosted hydrothermal systems. It has been suggested that mud volcanoes should belong exclusively to the second type, which implies their difference from sediment-hosted hydrothermal systems despite their superficial resemblance.

The aim of the present study is to analyze the possibility of an unambiguous distinction between mud volcanoes and sediment-hosted hydrothermal systems according to their geochemical characteristics. The analysis was performed as a case-study of three fluid systems: the Yuzhno-Sakhalinsky mud volcano, the Salton Sea and Lusi.

## 2. Materials and methods

The geothermal system Salton Sea (California, the USA) is located in sedimentary basins between the San Andreas Fault and the northern end of the Gulf of California rift [3]. Multiple hydrothermal seeps occur along faults and fault-related folds, where quaternary magmatic intrusions determine a powerful heat flow (up to 600 mW/m<sup>2</sup>). In the south-eastern part of the Salton Sea there is Davis-Schrimpf field, extensively studied in geochemical terms, with a total area of about 22000 m<sup>2</sup>, from the gryphons and pools of which gas, water, and mud are discharged. These gryphons and pools are often associated with mud volcanism manifestations. The overflowing liquid mud is in most cases relatively hot, the temperature in some gryphons and pools reaching 60-70 °C.

The Yuzhno-Sakhalinsky mud volcano is situated in the southern part of Sakhalin Island and is one of the largest and most active mud volcanoes in the region. The volcano is located in the distribution area of thick (about 3 km) siltstone-argillaceous Upper Cretaceous mass – Bykovsky suite. This suite is thought to be the main source of the solid phase of mud volcano emissions. The volcano orientation coincides with the submeridional Central Sakhalin Fault, which is one of the largest disjunctive dislocations of Sakhalin Island. Along this fault, the W-E oriented Cretaceous deposits pull up to Paleogene-Neogene deposits. It should be emphasized that this natural feature has always been traditionally classed as a mud volcano. It has the form of a large hill comprised (at least, partially) of the products of earlier eruptions. At the volcano summit, there are about 50 gryphons and pools through which liquid mud with gas bubbles is constantly seeping. The liquid mud is cold – its temperature is hardly different from the surrounding air temperature. Powerful eruptions occur intermittently, in which 100-200 thousand m<sup>3</sup> of mud are erupted and new vast mud fields are formed. Such eruptions were documented in 1959, 1979 and 2001. From the personal fieldwork experience of the authors of the present study, the Yuzhno-Sakhalinsky mud volcano is practically identical with the mud volcanoes of Azerbaijan and the Kerch Peninsula.

On 29<sup>th</sup> May 2006, in the Sidoarjo District in the north-western part of Java Island (Indonesia), numerous openings emerged from which gas, water, and mud were seeping [4]. These openings formed a line that extended towards the North-East for over 1 km. Within several days, a large crater formed here, erupting great volumes of boiling mud (the maximum of emissions reached 180 thousand m<sup>3</sup> per day). The temperature of the overflowing liquid mud was as high as 95 °C. This new structure, which was initially regarded as a mud volcano, was given the name Lusi. To this day, over 12 years later, Lusi is still erupting, but with much lesser volumes of emissions. More specifically, in the summer of 2011, Lusi was erupting less

than 10 thousand m<sup>3</sup> of mud per day. According to one theory, the cause of Lusi erupting is the development of the gas field in the vicinity, which is being implemented with serious process non-conformances. Another tentative explanation is that the eruption of Lusi was associated with the earthquake (with a magnitude of 6.3), which occurred on 27<sup>th</sup> May at a distance of 250 km from the volcano. The Lusi fluid system is located in a deep-water back-arc sedimentary basin of North-East Java. The basin is characterized by numerous faults, a high sedimentation rate, organic enrichment of sediments, as well as the presence of a large number of mud volcanoes. The results of recent geochemical and seismic studies suggest that the hydrothermal fluids from the volcanic (magmatic) complex Arjuno-Welirang fuel Lusi through the Watukosek faults system [5, 6]. On these grounds, it was suggested that Lusi should be classes as a sediment-hosted hydrothermal system.

In order to confirm the assumption about the differentiation of various types of fluid systems according to their geochemical properties, a comparative study has been conducted. To this end, the published data on the isotopic and chemical composition of waters and gases from the gryphons and pools of the Salton Sea [3] and Lusi [7, 8] have been used. The sampling from the Yuzhno-Sakhalinsky mud volcano has been performed in various ways on an almost annual basis for the last 15 years. In particular, in July-September 2007, gas-geochemical monitoring [9] was conducted, and in May-September 2015 hydrogeochemical monitoring [10] was carried out. In the present study, the data obtained in the course of the above mentioned monitoring activities were predominantly used and applied to the Yuzhno-Sakhalinsky mud volcano. The comparative analysis was conducted using the generally accepted geochemical diagrams (figures 1–4). In doing so, those geochemical parameters were preferentially selected, the values of which had been obtained for all the three fluid systems in question.

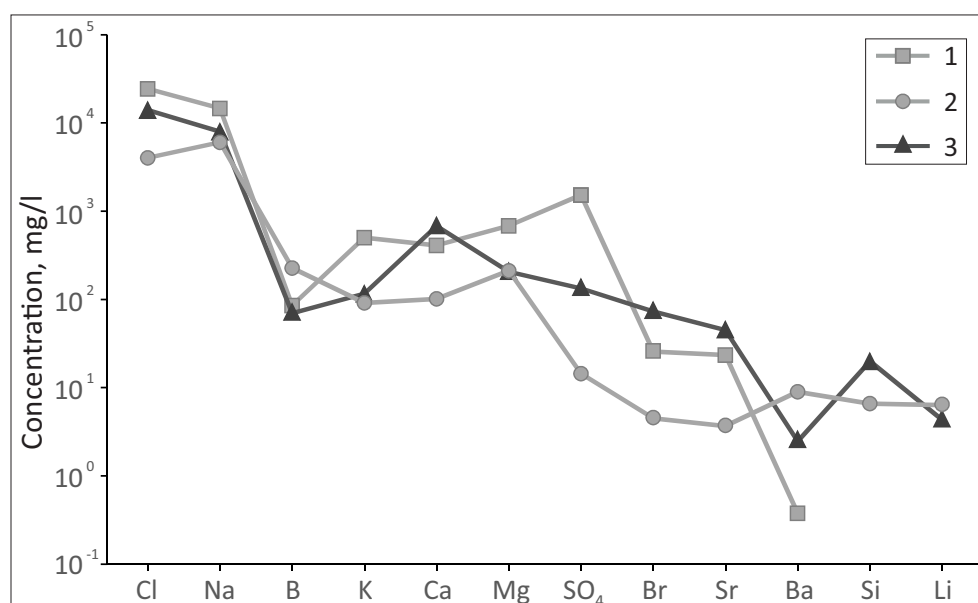
### 3. Results and discussion

The typification of the fluid systems in the study [2] was performed on the basis of two main criteria – the regional geological conditions and the geochemical peculiarities of the emissions. The magmatic-hydrothermal systems exist in locations of active volcanism, characterized by high values of the heat flow. These systems are heated by magmatic intrusions, erupt and discharge hot matter. The adjacent strata are volcanogenic. In the gas emissions, CO<sub>2</sub> prevails – its source being the thermometamorphism of carbonates or mantle degasification. The CH<sub>4</sub> concentration is less than 1.5 vol. %. CH<sub>4</sub> is abiotic, i.e. formed as a result of high-temperature chemical reactions without the direct involvement of organic matter. Sediment-hydrocarbonic systems exist in regions with thick sedimentary deposits which are rich in organic matter. These regions are characterized by a high sedimentation rate, which facilitates the emergence of zones with higher than normal lithostatic pressure. The values of the heat flow are under 100 mW/m<sup>2</sup>. In the gas emissions, CH<sub>4</sub> prevails, which has microbial and/or thermogenic origin. CO<sub>2</sub> also has thermogenic origin, its concentration being under 10 vol. %.

Sediment-hosted hydrothermal systems are hybrid (transitional) fluid systems, where volcanic and sedimentary domains interreact, which leads to the formation of mixtures of inorganic and organic gases. These systems can be found in tectonically active sedimentary basins, disrupted by magmatic intrusions. The thickness of sedimentary deposits is not particularly high here (normally from 1 to 2 km). The heat flow values predominantly vary in the range between 80 and 160 mW/m<sup>2</sup>. In the gas emissions, the mantle or metamorphic CO<sub>2</sub> prevails, its concentration exceeding 50 vol. %. CH<sub>4</sub>, as a rule, has thermogenic origin. Its concentration is no less than 1-2 vol. % and may reach 30-40 vol. %. The Salton Sea and Lusi are both classed as sediment-hosted hydrothermal systems.

The analysis of the study [2] reveals that there is no clear distinction between fluid systems of different types, and therefore this question requires further consideration. It is logical to anticipate differences not only in CO<sub>2</sub> and CH<sub>4</sub> concentrations, as well as in the content of

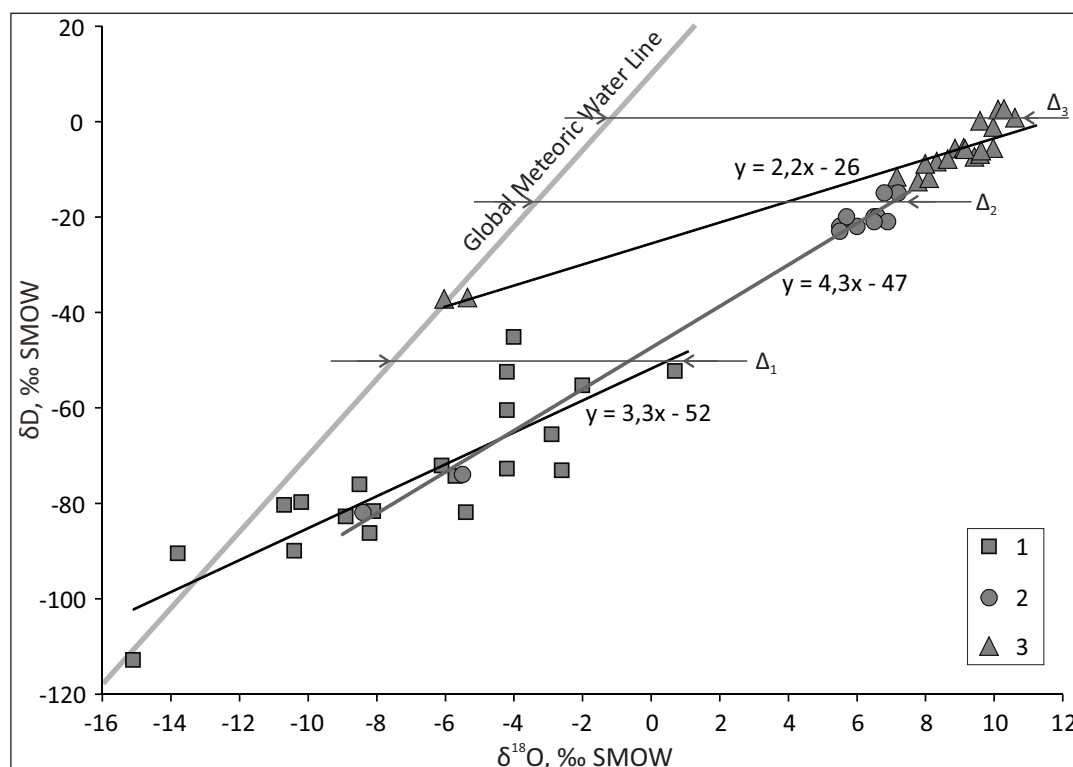
carbon-13 in  $\text{CO}_2$  and  $\text{CH}_4$ , but also in a wider range of geochemical parameters. It also stands to reason to expect the clustering of the analyzed data – isolation (differentiation) of the different types of fluid systems in geochemical diagrams. Meanwhile, the overflowing waters of all the three studied types of fluid systems are very similar in their chemical composition (figure 1). The hydrochemical type of subsurface fluids is characterized by the ratio of basic anion to cation concentrations. Unfortunately, the  $\text{HCO}_3$  concentration was not measured in the studies [3, 7, 8]. This can be implicitly deduced from the Na/Cl ratio. For the Salton Sea and Lusi, the Na/Cl ratio is predominantly in the range between 0.55 and 0.65, which is very close to the analogous ratio for sea water (which is 0.55). For the Yuzhno-Sakhalinsky mud volcano, the Na/Cl ratio is significantly higher (from 1.4 to 1.6), due to the high content of  $\text{HCO}_3$ . The waters from the Salton Sea gryphons and pools are more acidic (pH being in the range between 5.6 and 6.8), than the waters of the Yuzhno-Sakhalinsky mud volcano (pH being from 7.0 to 7.6). The pH values for Lusi are in the range between 6.4 and 7.2. The Ca concentration in the Salton Sea and Lusi waters is on average remarkably higher than in the waters of the Yuzhno-Sakhalinsky mud volcano. However, the content of Ca (as well as Sr) in the subsurface fluids is controlled by the carbonate balance. For the analysis of the carbonate balance, the data on  $\text{HCO}_3$  concentrations are required, which have not been obtained for the Salton Sea or Lusi so far. The Cl/Br ratios in the waters of the Salton Sea, the Yuzhno-Sakhalinsky mud volcano and Lusi are about 950, 800 and 200 respectively.



**Figure 1.** Chemical composition of the studied waters: 1 – gryphons and pools of Salton Sea, 2 – Yuzhno-Sakhalinsky mud volcano, 3 – gryphons and pools of Lusi.

Likewise, the isotopic compositions of the waters discharged by the studied fluid systems do not reveal any systematic differences (figure 2) – though it may appear at first sight that the content of oxygen-18 and deuterium in these waters is rather different. Yet, it is known that the isotopic composition of meteoric waters has latitudinal dependence – at low latitudes the concentration of oxygen-18 is higher, than at high latitudes [11]. The studied fluid systems are located at different latitudes. Therefore, for a proper comparative analysis it is logical to use such a parameter as positive oxygen shift  $\Delta$ , which is the difference between the content of oxygen-18 in the discharged waters and the content of oxygen-18 in the meteoric waters, with

the same deuterium content. The values of oxygen shifts for the waters of the Salton Sea, the Yuzhno-Sakhalinsky mud volcano and Lusi differ insignificantly. The constructed linear trends of the isotopic composition, presumably associated with their dilution with meteoric waters, are specific for each fluid system and do not depend on its type (figure 2).

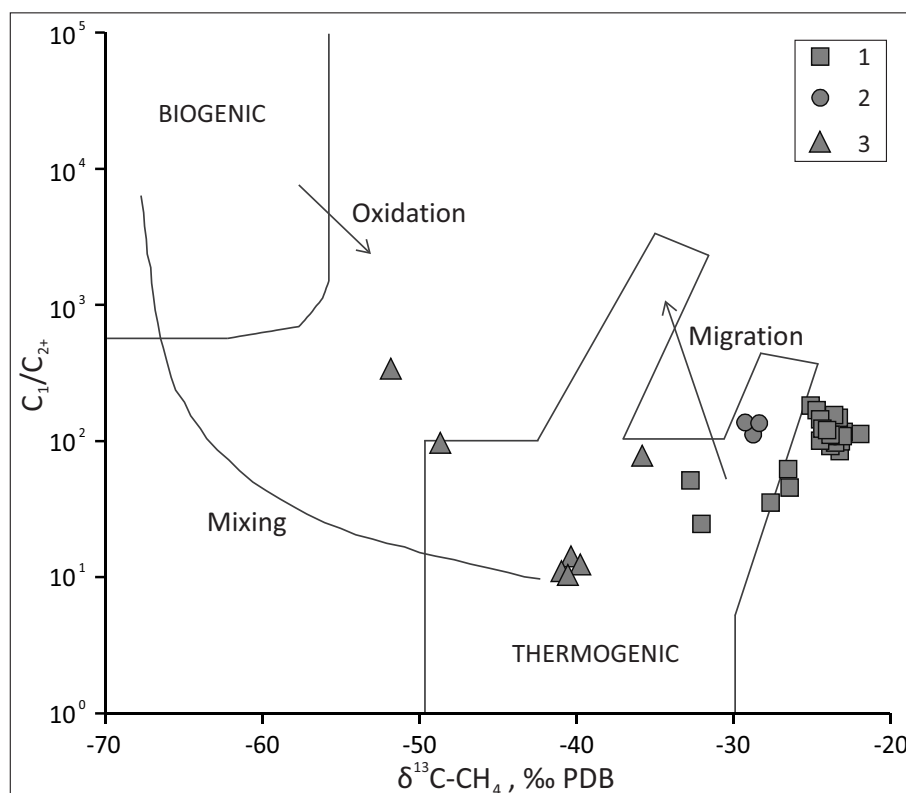


**Figure 2.** Hydrogen and oxygen isotope systematic of the studied waters together with the Global Meteoric Water Line (from [11]): 1 – gryphons and pools of Salton Sea, 2 – Yuzhno-Sakhalinsky mud volcano, 3 – gryphons and pools of Lusi.  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$  – positive oxygen isotope shift for Salton Sea, Yuzhno-Sakhalinsky mud volcano and Lusi, respectively.

The gas genetic diagram (Bernard plot) uses two parameters: the content of carbon-13 in  $\text{CH}_4$  and the ratio of  $\text{CH}_4$  concentration to the sum of the concentrations of its heavy homologues [12]. As is clear from this diagram, the gas samples from the studied fluid systems form a rather extensive and homogeneous cloud of dots – mainly in the gas field of thermogenic origin (figure 3). In other words, the fluid systems of different types are not differentiated in the Bernard diagram.

The degree of the fractionation of carbon isotopes in the system  $\text{CO}_2\text{--CH}_4$  depends on the temperature conditions of the generation of these gases. This temperature dependence of the isotope fractionation coefficient is the basis for isotopic geothermometers. Using the formulas from the study [13] we have calculated the temperatures for the isotopic equilibrium in the system  $\text{CO}_2\text{--CH}_4$ . The calculations show that all the three fluid systems have similar temperatures of gas generation – predominantly in the range between 250 and 400 °C (figure 4).

The gas emissions of the studied fluid systems are also similar in the isotopic composition of He. The  $^3\text{He}/^4\text{He}$  ratio in the Salton Sea gases is  $(6.1\text{--}6.6)\text{R}/\text{R}_a$ , in Lusi gases it is  $(2.8\text{--}6.5)\text{R}/\text{R}_a$ . For the Yuzhno-Sakhalinsky mud volcano only one measured value of the  $^3\text{He}/^4\text{He}$  ratio is known, it equaled  $2.3\text{R}/\text{R}_a$  [14]. Such high values are indicative of an infusion of mantle fluids in the gas emissions.

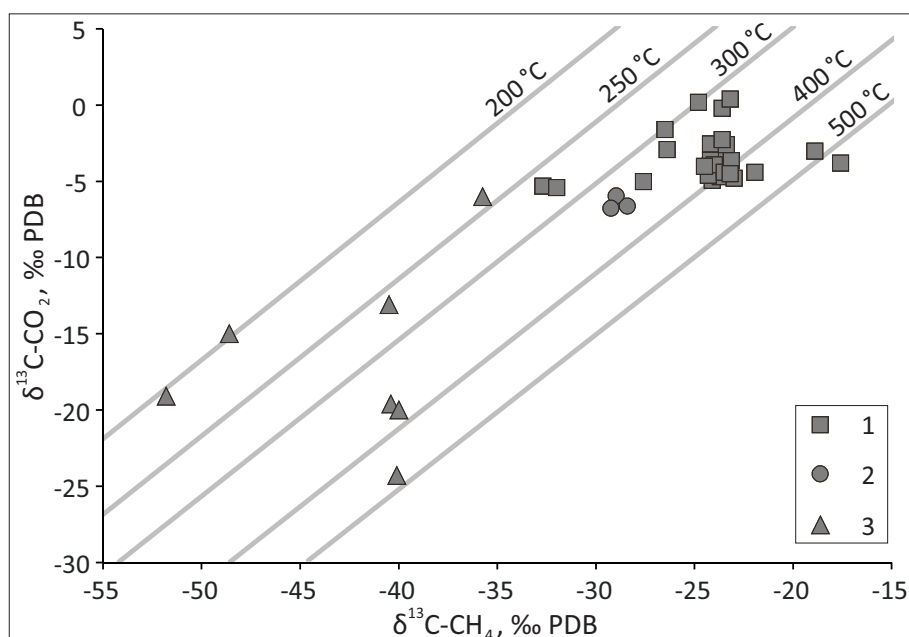


**Figure 3.** Methane carbon isotope vs. hydrocarbons molecular composition diagram (Bernard plot; from [12]) for the studied gases: 1 – gryphons and pools of Salton Sea, 2 – Yuzhno-Sakhalinsky mud volcano, 3 – gryphons and pools of Lusi.

#### 4. Conclusion

The comparative study of the isotopic and chemical composition of the liquid and solid phases of the Yuzhno-Sakhalinsky mud volcano emissions and the sediment-hosted hydrothermal systems Salton Sea and Lusi suggests that these fluid systems have similar geochemical features. This implies two possible interpretations of the results of the present study. The first variant suggests that the Yuzhno-Sakhalinsky mud volcano is also a sediment-hosted hydrothermal system. The second variant presupposes that the existing principles of differentiation between mud volcanoes and sediment-hosted hydrothermal systems are not particularly relevant, and the criteria for their distinction are too ambiguous.

The authors of the present study are inclined to support the second variant of interpretation. We believe that the term “mud volcano” should not only describe the characteristics of the discharged matter, but it should also refer to the way of its delivery from the Earth’s interior onto the surface. A particular cyclicity is normally characteristic of a volcano – violent eruptions are superseded by periods of relative quiescence. Based on the entirety of all features – the occurrence of burst-like eruptions, the low temperature of the discharged mud, the volcano morphology, the material composition of the emissions typical of mud volcanoes, etc. – we have grounds to believe that the Yuzhno-Sakhalinsky mud volcano can be classed as such, that is precisely as a mud volcano. Some mud volcanoes can be slightly different from each other. However, different mud volcanoes have much more common features than differences. In our view, the mere fact that in some mud volcanoes there is a subsurface fluid flow does not disqualify these fluid systems from being referred to as mud volcanoes. This only constitutes a good reason



**Figure 4.** Carbon isotope composition in CH<sub>4</sub> and CO<sub>2</sub> for the studied gases: 1 – gryphons and pools of Salton Sea, 2 – Yuzhno-Sakhalinsky mud volcano, 3 – gryphons and pools of Lusi. Grey lines show isotope equilibrium in system CO<sub>2</sub>–CH<sub>4</sub> (according to [13]).

to elaborate an updated classification of mud volcanoes, which has so far been neglected. For the most part, the classifications proposed before were only based on morphological features. There have been attempts to classify mud volcanoes according to their geochemical properties, but these studies were conducted on the basis of highly limited sampling.

### Acknowledgments

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