BIOLOGICAL AND GEOLOGICAL TRAITS OF TERRESTRIAL MUD VOLCANOES – A REVIEW

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Abstract. Mud volcanoes represent related formations, which have structural and functional similarities and can be found on land and in undersea zones. Mud volcanoes are different from other geological forms by their capacity to expell different forms of materia (gas, water and sediment) and the relatively violent kind of performing it. The sizes of mud volcanoes go from very small up to kilometers, shapes go from caldera to cones and they can exhibit from almost inaction to rising columns of fire. The mud consistency also differ, from aqueous to high viscosity, and the emissions can involve high quantities of methane and carbon dioxide. Volcanoes releasing thermogenic methane have the reservoirs at profound depths, while the ones with biogenic gas have the reservoirs no deeper than 2000 m.

This review provides informations regarding genesis and distribution of mud volcanoes, and also the description of morphology and topology of the mud volcano and the adjacent area. The classification types are set out, as well as the phenomenon of mud volcanism. In the end the expelled products are identified, different post-genetic processes being established, thus it can be assessed if the expelled products are of thermogenic or biogenic nature. Microbiological processes within mud volcanoes were also described from anaerobic oxidations, aerobic oxidations to methanogenesis. Both, Archaea and Bacteria are involved in these prcesses. Common patterns were identified for mud volcanoes which harbour a large array of bacterial and archaeal phyla. Mud volcanoes have a consistent share in the natural gass emissions into the atmosphere. They have a global occurance and give us a different way to investigate the Earth's interior, yet are largely unresearched.

Key word: mud volcano, volcanoes eruption, thermogenic methane, biogenic methane.

1. DISTRIBUTION, GENESIS, MORPHOLOGY AND TOPOLOGY OF MUD VOLCANOES

Mud volcanoes are geological features through which argillaceous material is altered and transported from the Earth's interior and expelled onto its surface. The geographical distribution of mud volcanoes is strongly controlled by geological environments in which they occur and the majority of them being localized in areas of recent tectonic activity, particularly in zones of compression [27]. Land mud volcanoes are geologic structures which appear along the edge of Tethys zone. This zone includes the Alpine-Carpathian-Himalayan belt, where the density of land mud volcanoes is maximum [9]. The belt begins in the Mediterranean Sea, passes through Sicily, along Apennine Peninsula, Albania, Romania, Ukraine, the Black Sea, Azerbaijan, Turkmenistan, Pakistan, India, China, and ends in Myanmar. The submarine mud volcanoes can be found in great numbers in the Western region of the Pacific Ocean, where the second belt extends, Sakhalin-Hokkaido-Taiwan-Melanesia-New Zealand. In the Eastern Pacific part there are few mud volcanoes, which can be found only in South Alaska, along the coast of California, and in Peru. The third belt, from the Carribean, comprises the submarine and terrestrial volcanoes from Barbados, Trinidad and Colombia [16]. The maximum density of terrestrial mud volcanoes is associated with the Caspian zone (Azerbaijan). Here some volcanoes can reach record dimensions up to 400 meters in height and 4-5 kilometers in diameter [46, 48, 49]. Other structures have more modest dimensions, as Byandovan volcano with height of 55 meters and diameter of 1.5 km [2].

However, terrestrial volcanoes can not reach the exagerated dimensions of the submarine volcanoes. The submarine volcanoes South-West of Taiwan have a variable diameter, with values between 680 and 4100 m and heights about 345 m [11]. A special case are the mud volcanoes in Mariana Trench, which reach 2 km in height and 25 km in diameter [2].

Mud volcanoes are composed of three main components: mud breccia, water and gas. Depending on local geology and processes at work, the relative quantities and the exact qualitative properties of these components vary. The mud volcanoes comprise related formations, which hold similarities both in structural plane and at functional level and and can be found both on land and in submarine zones. Their occurrence is asociated with the action of three geological factors: the convergent stress which appears after the collision of two or more tectonic plates, exagerated sedimentary deposition on homonymous beds and the vertical migration of the gas-saturated fluid along fractures and breaks. The fundamental geological formation at the basis of each mud volcano is represented by a mud diapir. The genesis process for diapir and mud volcano is identical. In most cases the invocated formations are combined in a single unit. Conventional, the mud volcano is considered a mud diapir which has a fracture above his superficial cone where all subterranean materia discharge named specific structure, emerging upon a mud diapir [10].

The genesis process of mud diapirs is actively debated and numerous hypotheses have been launched, but the majority are based on the geological factors mentiones above, a generalised process can be described. Diapirs emerge at the edges of continental plates or at the level of continental platoes (accretionary prisms, volcanic regions, lagunes) where the rate of sedimentary deposition excels the rate of water discharge from the same sedimentary layer. The quick deposited sediments bring occurence of weak condensed layers, characterised by a high degree of floatability. The incapacity of water flux to pass beyond the sedimentary barrier is caused by the fine particles which compose the sedimentary layer, which usually have a low permeability. Thus, the pressure exerted by the fluid and the preset floatage of the sedimentary layer induces its vertical ascension. Besides the liquid pressure, to the sediments ascension also take part some gases resulting from the kerogen maturation process [25]. On the surface, the process causes topological modifications and formation of common geological structures, dubbed „mounds”, which are nothing else but diapirs. In some cases, the water and gas flux succeeds in passing through the sedimentary barrier via different breaks caused by the inherent dinamics of the diapir or tectonic activity. The places where the gas and water are eliminated are called macro-discharges or mud volcanoes [15].

Mud volcanoes, being structurally related to magmatic volcanoes, give us free rein to use identical terms for their description. Generally, a mud volcano is composed of a *reservoirs* and a *central channel* through which is transported the most part of the matter (Fig. 1). Besides this channel there are smaller channels, named *parasite channels*. The matter is eliminated to the exterior and usual forms a crater. From the excesive exhalation of matter calderas may form. The parasite channels form craters but much smaller, which sometimes are filled with water and form small aquatic basins. The semi-fluid matter saturated with gas, expelled from the deep of the channels bares the name of mud volcano *breccia* or diapiric mixture. This mixture is constituted of three phases: rock, water and gas [15]. Characteristic for a mud volcano is the fact that around the crater grows very few vegetation, thus derives that on a reach around the crater the surface is barren and not compatible with growth of superior organisms [22]. On a variable reach from the crater, the mud supersaturated with water can behave as the quick sands and represents a real danger. Also dangereous are the volcanoes which discharge methane in big quantities, which can easily induce explosions and fires in the presence of air [17].

The topology of a mud volcano vary in time. Thus, the results obtained from interferograms taken by artificial satelites equiped with specialised radars (InSAR) show that the topology of a volcano is not rigid and changes from time to time. These changes are correlated with procese from within the diapir, where the fluid at high pressure redistribuites uneven and creates inflation and deflation zones.

Active redistribution of the fluid within the diapir appears, usually, before eruption (Akhtarma and Khara-Zira, Azerbaijan volcanoes). But in some cases the variability of topology can not be interpreted as a pre-eruptive procedure but just as a process of rutine which involves the movement of fluid inside volcano (Byandovan, Azerbaijan). Topological changes can be also observed in the post-eruption process. Such modifications were observed during the continuous eruption of the SIRI mud volcano in Indonesia [3]. Initially the study of topological changes was a procedure which tried to predict the activity of magmatic volcanoes. Thus, we can deduce that the mud volcanoes do not resemble magmatic volcanoes only structurally, but have also a deep functional kinship [2].

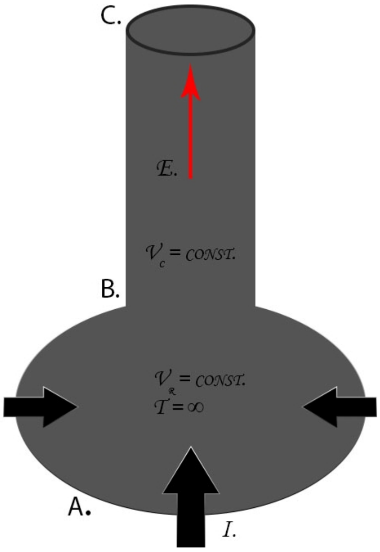

Figure 1. Mud volcano structure (A – Reservoir; B – Conduit; C – Crater Opening; I – Matter influx; E – Mud/Gas Efflux; V_C–Constant conduit volume; V_R– Constant Reservoir Volume; $T\infty$ - Invariable reservoir volume over time) (original).

2. MUD VOLCANOES CLASSIFICATION

a. Mud volcanoes classification according to dimension. There is a classification of mud volcanoes according to their dimensions: gryphons, mud cones and mud volcanoes. Gryphons are up to 3 meters in height, the mud cones are above 3 meters and mud volcanoes above 50 meters [2].

The terms mud volcanoes are misused in most cases. Only the structures with exagerated dimensions are mud volcanoes. The dimensions of the volcanoes are given by the breccia quantity expelled at the surface. According to the viscosity of breccia, the volcano base can have different radii. As well, the pressure of the expelled matter draws its three-dimensional structure. If a volcano eructates often and throws mixture at high pressure, it is obvious that its dimension will be exagerated and its structure can take any form, from the clasical cone to flattened forms or forms imitating a mushroom. Usually, after eruption, breccia, solidifies in a few days. From more eruptions, the multi-layered cone of the volcano is formed [15]. The solid phase of the breccia of a mud volcano consists in different components which vary from zone to zone. For instance, the components of the solid phase in the volcanoes from Taiwan consists mainly in illite, quartz and kaolinite. All these minerals indicate that in the deep layers of the accretionary prisma to which these mud volcanoes belong the process of clay dehydration takes place [9].

b. Mud volcanoes classification according to their activity and morphology. According to these properties, the mud volcanoes classified in three classes:

The first class comprises the *Lokbatan* type volcanoes. These are extremly active and the exhaled gas is often self-incinerated. The eruptions are intermittent and take place at long time lapses. This is due to the long time in which the central channel is filled with dry pieces of mixture. When the channel is clogged by matter, a violent explosion occurs. This type of volcanoes have usually conic abrupt shape and mixture with small viscosity.

The second class comprises *Chikishlyar* type volcanoes. These volcanoes are calm and the volume of gas and fluid is eliminated at a constant rate. They have a specific structure, resambling an flattened dome and are supersaturated with water. The supersaturation is given by the multitude of parasite channels which eliminate water.

The third class of volcanoes is represented by the so-called *Schugin* volcanoes, which represent a hybrid between the first two classes. The eruptive periods are followed by a long inactivity. This type of volcanoes are more outspread. Their three-dimensional structure is extremly diversified. This type of classification is one of the oldest (1964) and one of the most objective ones [15].

3. DINAMICS AND ACTIVITY OF MUD VOLCANOES

The mud volcanoes are different from other geological forms in their capacity to discharge diverse matter and the relatively violent way they perform it. Even though some mud volcanoes discharge mater in a violent way, these crises are intermittent and take place quite rare [15]. For instance, the mud volcano Byandovan, from the Caspian zone, had two eruptions, first in 1932 and then in 1989. Another volcano in the same zone, dubbed Akhtarma-Pashaly, had two eruptions, in 1986 and 2013 [2].

Violent eruptions can be very destructive. Such an eruption took place in Indonesia (LUSI mud volcano). The discharge of matter begun in 2006 and still continues. This violent eruption forced the evacuation of 60000 people and buried in mud an area of about 7 km^2. At the beginning of the eruption, the rate of discharged matter reached about 50 000 m^3/day, in a few months the rate increased, reaching 180000 m^3/day. During the following years, the rate considerably diminished, so that in 2010 the rate of discharged mud took values of 10 000 m^3/day [3]. This event triggered the beginning of researching the study of mud eruptions and a chance to develop the physico-mathematical models, which could explain the change of matter flow and the longevity of eruptive crises.

Mathematical model of activity. Both the behaviour of a mud volcano and the mud flow discharged foremost depends on its internal structure. Mathematical models which try to describe the activity of the volcano can approximate the behaviour, but cannot describe it entirely.

The first issue which challenges the virtual model consists in the oscillating values, which determine the viscosity and the density of the matter. Thus, the fluid of the mud volcano in mathematical models is a Newtonian fluid, with constant viscosity and the density.

The second issue is closely bound to the geometry of the breaks through which the matter passes. In mathematical computations the break consists in a channel with constant volume through which the fluid flows vertically upwards, but in reality matter can also flow horizontally in the breaks. Alike varies the breaks volume along sedimentary layers. In a mathematical model the mud volcano is defined by a variable-sized reservoir, which absorbs an influx (quantity) of matter from the sediments around (the cause of the influx is neglected) and a channel with constant volume through which the matter is drawn out. Two behaviour models have been described, which depend only on the volumetric evolution of reservoir in time.

These models operate with two concepts: amplitude and period. The amplitude represents the volume of matter eliminated to exterior, while the period represents the time lapse between two major eruptions.

a. The first mathematical model describes a mud volcano with a reservoir which decreases its volume in time. The flow of matter eliminated by this volcano will vary in time. Thus, the amplitude will diminish in time, which means that the volume of discharged matter will decrease in time. The decrease in discharged matter is primarily caused by the surface of the reservoir, which changes its values with the decrease of reservoir in volume. The volume being smaller, surface minifies and limits the big inflow of foreign matter in the reservoir. In turn, the small inflow of foreign matter will negatively affect the speed values of the matter and the value of the mud flow discharged. But the period will stay the same, meaning a single thing, that the volume of matter discharged during eruptions will decrease in time, but the proper eruptions will occur intermittent, the crises will be separated by the same time span (Fig. 2).

b. The second mathematical model implies the existance of a reservoir with volume constant in time (Fig. 2). When such a volcano erupts the period and amplitude are constant. The reservoir of such a mud volcano does not sustain any surface change, so the pressure inside will be constant, thus both the values of amplitude and period will remain stable on a long time span [50].

The described models are usefull as regards forcasting the behaviour of a wide spectrum of mud

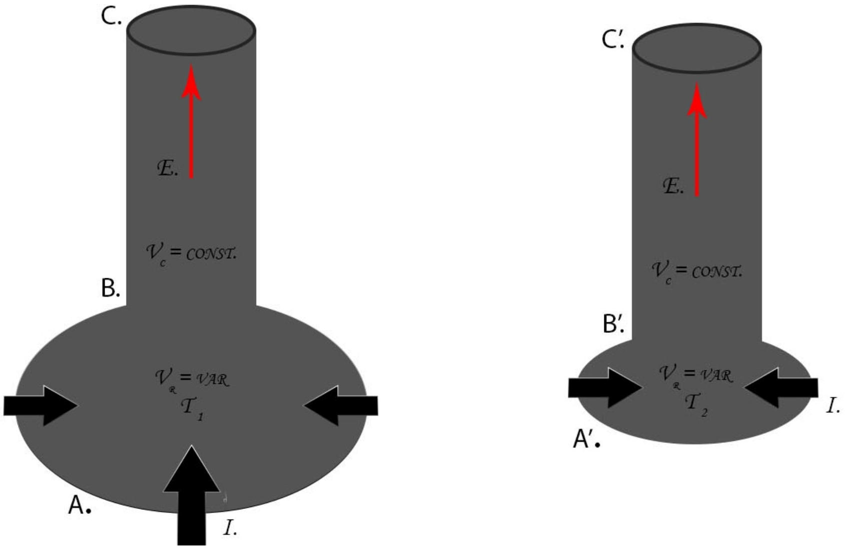

Figure 2. Schematic of two possible mud volcano activity (A, A' – Reservoir; B, B' – Conduit; C, C' – Crater Opening; I – Matter influx; E – Mud/Gas Efflux; V_C– Constant conduit volume; V_R– Variable Reservoir Volume; T_1 and T_2 – Distinct consecutive moments in time (t, t+1 respectively) (original).

volcanoes. Thus, the SIRI volcano from Indonesia falls into the volcano category with a reservoir diminishing in time. This naturally explains the decreasing rates of discharged mud eliminated by this volcano along the years [3].

Top activity and tectonic movements. The causes bringing violent explosions of mud volcanoes are not clear yet, but it is assumed that there is a connection between the eruption af a mud volcano and an earthquake. Along history it was observed that the volcanoes amplify their activity after strong earthquakes. The first link between these phenomenons was observed by Plinius in 91 AD. He wrote that, after a strong earthquake, he saw high fire columns, which could be seen form 10 km. Nowadays it is thought that those columns were caused by the eruption of Montegibbio mud volcano. Most of the times the correlation can not be easily sensed.

Some volcanoes even after a strong earthquake no not show activity, even if the magnitude of the earthquake reaches high values and the epicenter is near. This strange behaviour can be explained just if we introduce the liquefaction concepts and the critical pressure of the mud volcano. Each volcano has a specific pressure at reservoir level. The eruption can be labeld as a direct consequence of reaching the critical pressure in the reservoir. On turn, the earthquake does not have the capacity to induce eruption directly. It operates indirectly and cumulatively, gradually increasing the pressure in the reservoir after the liquefaction process. The liquefaction, although it is characteristic to mud volcanoes, can be applied in a restricted manner to the mud volcanoes. It represents a process of thinning the sediments, which appears after a tectonic stress. Thus, the earthquake induces the liquefaction of sediments at reservoir level, the pressure in the reservoir gradually reaches the critical value which triggers the eruption [5].

4. PRODUCTS EXPELLED BY MUD VOLCANO

A mud volcano can be qualified as a discharge of multiphasic matter. According to the exhaled gas quantity, topology and the associated discharged matter, two categories of seepages were classified: Mini-seepages – formations which do not modify the topology of the surrounding terrain and constantly discharges gas. Macro-seepages are represented by variable structures, which modify the topology of the surroundings. Macro-seepages can be classified according to more parameters. One of the classifications is based on the product emitted by macro-seepages, so that there are three distinct branches of macro seepages: mud volcanoes, water seepages and dry seepages. Mud volcanoes, usually, discharge three phases– gas, water and sediment. The water seepages discharge just water and gas. Such seepages can be found in zones with groundwaters. The dry seepages eliminate just gas [17, 22].

Fluid phase. The origin of the mineralisated fluid discharged from the mud volcanoes has a distinct importance regarding a qualitative characterisation. There are two hypotheses regarding the origin of the fluid. One of them rate that the fuid discharged belongs to the network of groundwaters around the volcano. The second theory assume the existance of a particular hydrological network which is separated by the groundwaters present in the mud volcano zone. Most probably, the fluid belongs both to the deep groundwater and shallow groundwater. For example, in Pineto mud volcano, the fluid from the volcano has hydrochemical characteristics different from the water samples taken from the surrounding aria. The fluid from the volcano is a mixture between the salty fluid originating from the sedimentary inferior layers and groundwaters in the superficial layers. Thus, the eliminated fluid cannot be referable to the hydrologic network which surrounds the mud volcano [36].

Gas phase. The gas produced in the inferior layers is eliminated outside through breaks according to Darcy's law. All the gas in a volcano moves within a pressure and permeability gradient. This movement is named advection and manifest in two ways. One phase advection, when the gas moves through dry breaks, and two phases advection, when the gas replaces water in breaks. Diffusion is another movement mode, but usually this phenomenon pertain to the gas migration on small distances [17].

The gas phase of mud volcanoes is composed by a large spectrum of organic and anorganic substances. The organic constituent has its origins in the inferior sedimentary layers (schist, clay) or in the so called parent rocks. Rarely, the organic component, is given by the products of the methanogen microorganisms metabolism [15]. Generally, the gas phase is formed by methane (CH_4), carbon dioxide (CO_2) and air (oxigen-nitrogen-argon). In most cases, the methane owns the monopole. In some exceptional cases, CO_2 represents the majority part. This exception can be followed at some of the most active volcanoes in South – West Taiwan (Chou-kou), which discharge in the atmosphere mostly CO_2. Ethane (C_2H_6) and propane (C_3H_8) are exhaled very rare due to post-genetic processes [9].

Origin and emission of methane. Methane is discharged most often by the mud volcano. Methane can be of both thermogenic and biogenic origin. Thus, methane can appear by two distinct processes.

The thermogenic gas represents the result of the kerogen maturation process. Kerogen is a heterogenous matter appeared from thermic degradation of organic substances from the inferior sedimentary layers. The diagenesis and catagenesis processes which occur during more geologic periods initiate reactions which lead to maturation of kerogen. The maturation does not involve only synthesis of aliphatic hydrocarbons with small molecular weight as methane, ethane or propane – compounds which are constantly eliminated by the mud volcanoes. In most cases maturation implies also the geochemical synthesis of polycyclic aromatic compounds and alkanes with big molecular, which likewise have a quota in the diapiric mixture [1, 26, 37].

The biogenic gas results from the enzymatic reactions performed by methanogenic organisms. Thus there are three synthesis pathways for biogenic methane. The first pathway involves reducing carbon dioxide with molecular hydrogen. The second pathway involves methane synthesis from acetate (acetic fermentation) and the third pathway uses for methane synthesis methylated derivatives as methane and dimethyl amine [34]. Within mud volcanoes, first and second pathways are more often occurring. Acetic fermentation, even if exists, has not been observed at mud volcanoes, despite the fact that the majority mass of biogenic methane in the atmosphere is synthesized by acetoclastic pathway. Thus, 75% of the land mud volcanoes eliminate in the atmosphere methane of thermogenic origin, 4% is the biogenic one and 21% mixt [18, 19, 42].

In most mud volcanoes the gas is thermogenic. In order to assess how post-genetic processes affect the molecular composition, statistical methods were developed. Bernard method is mostly used it consists in graphic representation of the interdependence between methane, ethane and propane concentrations (C_1/C_2+C_3) and the value of the stabile carbon isotope in methane ($\delta^{13}C_1$). According to some studies, 75% of mud volcanoes eliminate thermogenic methane, the rest are with biogenic or mix gas. The post-genetic processes can be observed when the results reach values slightly lower or much higher ($\delta^{13}C_1$>-50‰ and C_1/C_2+C_3>500) [45, 47].

Another method for assessing the post-genetic issues consists in forming the Schoell diagram, which takes into consideration the value of the stabile hydrogen and carbon isotope of methane, $\delta^{13}C_1$ and δD_1 respectively. Besides these two methods, the post-genetic impact can be assessed considering the noble gas concentration in the discharge from the crater [9, 17, 18].

The big methane quantity released by the land mud volcanoes actively participate to ingravescence of the greenhouse effect. Thus, the methane emission was carefully studied. It was noticed that gas exhalation does not occur only through the central channel and the associated ones, but also through the so called micro-seepages. Micro-seepages are present on all the surface of the mud volcano and are placed at certain distance from the rest of the channels. These seepages are not accompanied by topological modifications, so they can be studied only with specialised devices. This leads to the idea that gas emissions does not occur only in isolated places, but persists on all the surface of the volcano. The flux of micro-seepages is dependent on the water layer on the surface. Water being impermeable for gas, it participates to modulation of emission on all surface of the volcano. Dependent on the induced water barrier there are two categories of mud volcanoes. The first includes volcanoes covered by water on all the surface. In this case micro-seepages occur only at the extremities of the surface (Pâclele Mici, Romania). The second category is represented by the volcanoes which eliminate small quantities of water, and the micro-seepages are present on all surface (Fierbători and Pâclele Mari, Romania) [22].

5. POST-GENETIC PROCESSES

Mud volcanoes are considered natural refineries, due to methane emission and the incapacity to eliminate into the atmosphere heavier hydrocarbons, as propane and butane. Considering that deep within the sedimentary layers the cracking processes occur chaotically and different hydrocarbons with different molecular weight are obtained, preponderant elimination of an alkane with small molecular weight represents a problem [7]. The difference between the gas in the reservoir and the emitted gas is due to the so called post-genetic processes, which substantially modify the molecular composition of gas [17].

There are five categories of post-genetic processes which can explain the above-mentioned difference.

a. Methane microbial oxidation processes. Anaerobic oxidation is rarely met at land mud volcanoes, but it is common at the submarine ones. A big share of the submarine methane is consumed by different microorganisms through this mechanism. Aerobic oxidation is found much more often at land mud volcanoes, especially in the oxigenated superficial portions of the soil, which do not pass one meter of depth [37, 43].

b. Abiogenic oxidation, involves methane oxidation in the presence of hematite, magnetite or other iron minerals at great depth, where temperature vary between 80˚C and 400˚C.

c. Fractionation by diffusion process – is very slow and does not have a distinguishable effect, because it takes place at very great depths.

d. Molecular fractionation – it is the fundamental process, which explains the molecular difference between the gas in the reservoir and the gas on the surface. Fractionation by advection involves the isolation of methane from other heavy hydrocarbons while the gas ascends in the main and parasite channels. Knowing that the matter discharged from the volcano is composed of three phases, it is logical to assume that the gase phase interacts actively with the other phases. This process is resembling to the chromatographic migration based exclusively on adsorbtion. The gas containing heavy alkans, interracting with water and minerals, becomes lighter, the heavy hydrocarbons being adsorbed by different particles in the inferiour sedimentary layers.

e. Different biodegradation and methanogenesis reactions. These processes are performed by anaerobic microorganisms and are based on the following principle: the alkanes with big molecular weight are initially oxidized to the carbon dioxide in the process of diffusion and advection; afterwards, the carbon dioxide is reduced by the anaerobic microorganisms back to methane. Lately these reactions attract a good deal of attention, because they can affect widely the method of assessing the oil and gas quantity in many basins [17].

The special characteristic assigned to the mud volcanoes is represented by the exhalation of hydrocarbons with small molecular weight. The mud volcanoes indicate the possibility to find natural gas and oil reserves in the vicinity. Hereby, different hydrocarbon basins were found Azerbaijan. The hydrocarbon types eliminated by a mud volcano through the crater and their isotopic particularities can indicate the structure and the depth of the reservoir in that volcano [17]. The volcanoes which eliminate thermogenic methane have reservoirs at great depths. Instead, the volcanoes with biogenic gas have reservoirs at depth no greater than 2000 m [15]. This limit is given by the physiological capacities of the microorganisms. At depths over 2000 meters, the temperature can reach 60˚C - 80˚C [40]. Thus, the existence of microorganisms is compromised by the so-called process of paleo-pasteurisation [28]. The post-genetic process of anaerobic degradation and secondary methanogenesis can help to appreciate the depths of many springs and determine their biogenic origin. This process consists in methane oxidation and further reduction of carbon dioxide.

6. MICROBIOLOGICAL PROCESSES IN MUD VOLCANOES

Anaerobic oxidation of methane

The post-genetic process of anaerobic degradation and secondary methanogenesis represents, par excellence, a microbiologic process. The first stage, anaerobic degradation, is performed by the so called methanotrophic anaerobic archaea (ANME – anoxic methanotrophs). These Archaea use methane as electron donor and use sulphate and other elements (iron or manganese) as acceptors [43]. They were classified in three groups: ANME-1 (with subgroups a and b), ANME-2 (with subgroups a, b, c, d) and ANME-3 [14].

a. Archaea and microbiological oxidation of diapiric methane

The three groups belong to Euryarchaeota phylum. ANME-1 group has some degree of affinity with methanogen species within Methanomicrobiales and Methanosarcinales orders. The representatives of this group have a bacillus aspect and do not associate in complex structural consortia. ANME-1 were found in different anaerobic habitats – marine sediments, soil or oil leaks. ANME-2 group is affiliated with Methanosarcinales order [14]. ANME-2 cluster includes cosmopolitan species, the group being present in different anaerobic habitats [43]. The representatives of this cluster have cocci appearance and associate in complex structural consortia. ANME-3 group was identified in a low number of habitats (submarine mud volcanoes). The members of the cluster are phylogenetically related with species of Methanococcoides order. ANME-3 group species have appearance and behaviour resembling with the members of ANME-2 cluster [14].

The mechanism by which methanotrophic anaerobic archaea (ANME) oxidises methane to carbon dioxide is not well understood. Thus, methane oxidation represents a delicate and actively debated issue. So far it is not known if the bacteria from ANME groups are capable of an independent oxidation. Two hypotheses arisen in time, sustaining two virtually diametrically opposite ideas. One of the hypotheses asserts that methanotrophic anaerobic archaea (ANME) groups are capable to perform the whole oxidation process. The second hypothesis asserts that ANME clusters do not have the electrochemical capacity and not even the enzyme apparatus to perform the complete oxidation and this is why they collaborate with other bacteria, which take over the secondary products and finally metabolise them [1]. Nevertheless it was proven that archaea from ANME-1 group have the needed baggage of genes, which are responsible for methane oxidation, including mcrA gene, which codifies subunit A of Metil-CoM reductase, the limiting enzyme of methanogenesis [14]. Some Archaea from ANME-2 group were found in different habitats where was possible to isolate syntrophic bacteria, which means that some members of this ANME-2 group are capable of independent oxidation [32, 43]. However, despite some ambiguous proofs, which support the idea of the energy independence of methanotrophic anaerobic archaea, the scientific community unanimously accepted the fact that methane oxidation by methanotrophic anaerobic archaea can not happen without the compulsory presence of desulphating or denitrifying bacteria and that the oxidation process implies a reverse methanogenesis.

In mud volcanoes, both submarine and terrestrial ones, anaerobic oxidation of methane depends on more factors, including the presence of electron acceptors. Depending on this parameter, methanotrophic anaerobic archaea (ANME) population can vary widely. In general, sulphate, nitrate and other metals as iron and manganese are considered electron acceptors. Their concentration vary form one mud volcano to another. Thus, in submarine mud volcanoes the general acceptor is the sulphate dissolved in marine water [1, 12]. In terrestrial mud volcanoes the sulphate concentration is low, and the final acceptor consists in iron or manganese ions [8]. Besides the compounds and the elements which directly participate in the oxidation process, there is an array of heavy chemical elements, which allow us to indirectly detect methane-oxidising archaea in different mud volcanoes. Thereby there is a positive correlation between Archaea presence and elements as arsenic, calcium, vanadium, titanium and strontium. The occurrence of these elements is the consequence of geochemical modifications of the area around the volcano, which arose following the active methane-oxidation process [41].

b. Methane-oxidizing consortium and the sulphate-reducing bacteria

The high sulphate concentration in the blend of the mud volcanoes induces the perpetuating of the existence of desulphating anaerobic bacteria. Both in submarine volcanoes and in terrestrial ones these bacteria are capable to organise syntrophic relations with methane-oxidising archaea. The desulphating bacteria from the mud volcanoes belong to Deltaproteobacteria class and Desulfobacteriaceae family. The most common bacteria belong to DSS group - *Desulfosarcina* and *Desulfococcus* [26]. The bacteria in DSS group can intervene in the syntrophic cooperation with ANME-1 or ANME-2 [1, 43]. ANME-3 make syntrophic relations with Desulfobulbus [14, 32].

Syntrophic relations between desulphating bacteria and ANME are extremely complex and their kinetics is not fully elucidated. The sulphate-dependent oxidation of methane (S-DAMO) starts form two premises: reverse methanogenesis and the final electron acceptor status of the sulphate. Methanotrophic anaerobic archaea (ANME) oxidises CH_4 to CO_2, the product of this reaction being H_2. Molecular hydrogen is taken by desulphating bacteria, with the aim to reduce SO_4^{2-} to S^{2-} (1).

$$CH_4 + SO_4^{2-} \rightarrow HCO_3- + HS^- + H_2O \quad (1)$$

However this mechanism is not satisfactory because the energy produced by this reaction (-16.6 KJ mol-1) is not sufficient even for the existence of one prokaryote individual, the more insufficient for sustaining the syntrophic model [14].

The Archaea species form ANME-2 group are the most abundant. They are affiliated with the methanogens form Methanosarcinales order. Archaea in this group are known for their metabolism mainly based on acetate, while S-DAMO could develop by more complex mechanism, using acetate as intermediary. Two methods which could describe the aceto-dependent mechanism were proposed. The first method consists in CH_4 split and acetate plus H_2 yielding, these products being further consumed by desulphating bacteria. This reaction would provide twice more energy than (1). The second method is dubbed ”Reverse acetoclastic methanogenesis”. It implies the reaction between methane and carbon dioxide, whose product (acetate) will be further consumed by desulphating bacteria [6].

Recently, two new models which could describe S-DAMO mechanism were proposed. The first model involve the existence of intermediaries as methantiole and co-operation of desulphating bacteria with methanotrophic anaerobic archaea and methanogenic archaea. The mechanism of methylogenesis begins with CH_4 fixation by the Methyl-CoM Reductase of ANME. This fixation gives ANME the sufficient energy both for ATP synthesis and methantiole yielding. Methantiole, on turn, is produced due to fixation CO_2 by methanogenic archaea. Methantiole is further transferred to desulphating bacteria, which metabolize it [34]. The second model suggests S^0 as an intermediary which links ANME metabolism with the one of desulphating bacteria. The first stage of this model begins with methane oxidation with reduction of SO_4^{2-} to S^0. The second stage consists in attaching S^0 to S^{2-}. The products of this reaction are polysulphides. The polysulphide is taken by desulphating bacteria and metabolised to S^{2-} and SO_4^{2-} through enzymes as SAT (sulphate adenylyltransferase) or APR (adenylylsulphate reductase). The resulting sulphides are metabolised by methanotrophic anaerobic archaea (ANME) [7].

c. Sulphide reducing bacteria and oxidation of hydrocarbons with large molecular mass

A special feature of desulphating bacteria is their capacity to anaerobically oxidized alkanes with large molecular mass and aromatic compounds. Thus, not only the inorganic sulphide concentration signals the presence of suphur-reducing bacteria but also the concentration of large molecular mass hydrocarbons. For example, we can name the terrestrial mud volcanoes at Pâclele Mici, Romania, which is located near hydrocarbon basins. The breccia discharged from the seepage at Pâclele Mici contains polyaromatic compounds: pyrene, crisen and phenanthrene. Despite the low sulphide concentration, the sulphur-reducing bacteria are present in this volcano, so there is a positive concentration between their number and the concentration of hydrocarbons with large molecular mass [1]. A similar situation can be observed also at the submarine mud volcanoes from Guyamas basin, where the acceptors concentration constantly oscillates and breccia is made of alkanes with long chains [26].

The process of anaerobic oxidation of aromatic and aliphatic hydrocarbons with large molecular mass is done in most cases by the DSS clad, and unwraps in a few stages. The first stage consists in activating the alkane by fumarate. Further, the reaction of rearrangement and attachment of Coenzyme A to the carboxyl functional group of fumarate takes place. After that, the obtained compound is subjected to a β-oxidation. It is possible that Acetyl-CoA molecules obtained during degradation are oxidised to carbon dioxide by the metabolic pathway reverse Wood-Ljungdahl [26]. DSS clad could also metabolise methane by using the fumarate attachment mechanism. But this model of methane oxidation is unlikely to exist because of the first reaction of this pathway, involving homolithic split of methane, which is an endergonic process [7].

The desulphating bacteria which do not belong to DSS clad, Desulfobacteraceae, Desulfobulbaceae, Synthrophobacteraceae and Desulfurellales families, are also capable to oxidise hydrocarbons [26].

Sulphide-reducing bacteria have a particular importance also in the dispersal of arsenic within the mud volcanoes. Bacteria from *Shewanella* genus reduce sulphide to elementary sulphur, which subside in the inferior layers along with arsenic [31].

d. Nitrite and nitrate-dependent oxidation of methane

Nitrite and nitrate-dependent oxidation of methane (N-DAMO) can be performed due to the syntrophic relation between ANME and two species of microorganisms, *Candidatus Methylomirabilis oxyfera* and *Methanoperidens nitroreducens*.

Methylomirabilis oxyfera is an anaerobic species within the candidatus phylum *NC10*. The mechanism of N-DAMO activity mediated by this bacteria comes down to three reactions. The first reaction consists in reducing nitrite (NO^{2-}) to nitrogen oxide (NO). The second reaction consists in formation of O_2 (molecular oxygen) and N_2 (molecular nitrogen) out of two molecules of nitric oxide (NO). This reaction is an unconventional one, because intracellular O_2 is formed. The third reaction is reduced to taking over the intracellular O_2 and using it in enzyme transformation of CH_4 to CH_3OH via an enzyme - pMMO (Particulate Methane Monooxygenase) [3].

Methanoperidens nitroreducens is an archaea species which is phylogenetically related to ANME-2d group. These species presents the enzyme baggage suitable for methane oxidation (reverse methanogenesis). Besides this particularity, *Methanoperidens nitroducens* has a nitrate reductase in pseudoperiplasm, which mediates reduction of nitrate (NO^3) la nitrite (NO^2). The course of this nitrate-reducing mechanism consists in the different location of these reactions, and so far it is not known how the electrons obtained from methane oxidation reach the pseudoperiplasm [4].

The mechanism and the microorganisms involved in the metal-dependent methane oxidation are presently unknown. However, there is speculation that the model is ubiquitous, mostly in marine sediments rich in manganese Mn) and iron (Fe). This mechanism would be much more efficient than S-DAMO. M-DAMO could produce about -556 kJ mol-1 in case of Mn^{4+} reduction and -270 kJ mol-1 in case of Fe^{3+} reduction [14].

N-DAMO can be tightly linked also to the aerobic nitrification process, which is driven by bacteria with a special metabolism, anammox type. The microorganisms which can support this metabolic pathway belong to Planctomycetales order. They populate all types of environments, from marine sediments to wastewater treatment plants. Anammox bacteria are capable to metabolise nitrite (NO^{2-}) and ammonium ion (NH^{4-}) to nitrate (NO^{3-}) and molecular nitrogen (N_2) [29]. Nitrate (NO^{3-}) can be considered the intermediary ionic species between anammox bacteria and N-DAMO archaea (*Methanoperidens nitroreducens*). In the mud volcanoes the anammox bacteria could (NO^{3-}) to N-DAMO archaea. This metabolic loop would favours both nitrification and methane (CH_4) oxidation [23].

Aerobic oxidation of methane

Aerobic oxidation of methane in the upper sedimentary layers is done by three phylogenetic groups of methanotrophs. The group (Type I) includes aerobic bacteria from class (γ) Proteobacteria, which comprises the following genera: *Methylobacter, Methylomonas, Methylosoma, Methylomicrobium, Methylotermus, Methylohalobius, Methylosarcina* and *Methylosphaera* [35]. The members of this group use the ribulose monophosphate pathway to assimilate carbon [24]. These bacteria inhabit nutrient rich zones [38]. To the group (Type 2) belong to class (α) Proteobacteria and use serine pathway to assimilate carbon. Type II bacteria comprise *Methylocystis, Methylosinus, Methylocaspa* and *Methylocella* genera.

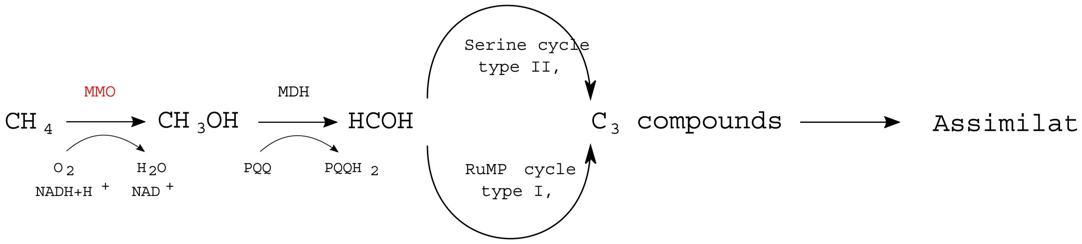

Figure 3. Aerobic oxidation of methane; MMO – Methane Monooxygenase

These genera are more resistant and can survive in saline media or in zones lacking nitrogen due to their capacity to fix atmospheric nitrogen [24, 38]. (Type X) group are capable to assimilate carbon both by serine pathway and by ribulose monophosphate RuMP pathway and are specific to media with high acidity [24].

Aerobic oxidation of methane is performed in superficial layers of the mud volcano. The limiting enzyme of this process is *methane monooxygenase*, which oxidate CH_4 to methanol. Methane Monooxygenase (MMO) complex determines the capacity of these bacteria to oxidate methane or other hydrocarbons (Fig. 3). Particulate Methane Monooxygenase (pMMO) is a limiting enzyme and mediates the first stage of aerobic oxidation of methane. Particulate Methane Monooxygenase (pMMO) is a ferment with small specificity [38]. This particularity consolidates the capacity of methanotrophs to oxidate also other hydrocarbons besides methane, as ethane, biphenyl or naphthalene. The product of the relation mediated by MMO is methanol, which is further oxidised to formaldehyde, which on its turn is further metabolised in the assimilation pathways of carbon specific to each phylogenetic group [4].

Methanogensis

Methanogens are classified into five Archaea orders: Methanosarcinales, Methanobacteriales, Methanomicrobiales, Methanococcales and Methanopyrales. The methanogenic archaea can produce methane by three distinct pathways: hydrogenotrophic, methylotrophic and acetoclastic. Out of the three listed orders, the most adapted is Methanosarcinales order, which is capable to synthetize methane by all the three pathways. The other orders are considered obligate hydrogenotrophs [19].

Methanogenesis is mediated by specific Archaea from Euryarchaeota group and implies anaerobic synthesis of CH_4. According to the primary source of energy engaged in the process three methanogenic pathways were defined: hydrogenotrophic (donor - H_2), acetoclastic (donor - CH_3COOH) and methylotrophic (donor – methylated compounds). The first reactions, whose purpose comes down to substrates activation, differs at the two metabolic pathways (acetoclastic and hydrogenotrophic). Acetoclastic archaea at the first activation stage phosphorylates acetate by acetate kinase. The second stage, mediated by phosphotransacetilase, consists in replacing phosphate group with CH_3-CoA. Further, the product of this reaction is used both for providing electrons to the electron transport chain and for providing a methyl group, which is used to methane synthesis [19]. In the case of hydrogenotrophic archaea, CO_2 is activated by the covalent attachment to the carrier molecule methanofuran, attachment catalysed by phormil-MF dehydrogenase. After the activation process, the phormil group in transferred on another carrier molecule, tetrahydromethanopterin (Fig. 4). The resulting compound is initially dehydrated, then reduced by a series of oxidoreductases [13]. These oxidoreductases take the electrons from two reducing agents: reduced ferredoxin and reduced F420 coenzyme. The hydrogenotrophic pathway (H_2/CO_2) and the acetoclastic pathway (CH_3COOH) converge at the last two enzyme reactions which metabolise the product which is common for the two pathways CH_3-$H_4M(S)PT$. These reactions include the next ferments:

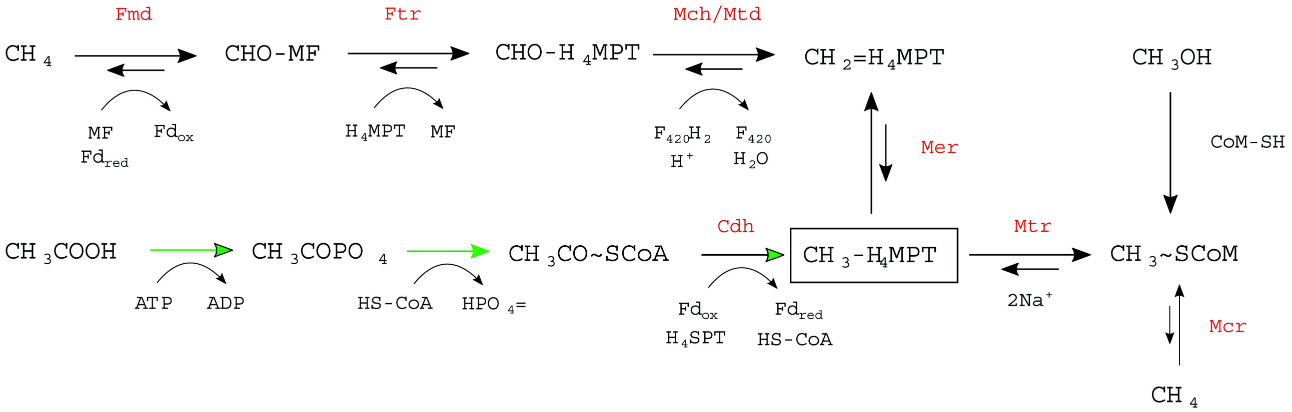

Figure 4. Hydrogenotrophic methanogenesis and ANME (double arrows); Acetoclastic methanogenesis (green arrows); methylotrophic methanogenesis (brown arrows).

CH_3-$H_4M(S)PT$ - coenzyme M methyltransferase and methyl coenzyme M reductase. The mcrA gene which codifies the α subunit of methyl-CoM reductase is ubiquitous used in the phylogenetic analyses of methanogens [19].

The methylotrophic pathway for methane synthesis involves taking compounds as methanol or methylamine under previously activated form CH_3-CoM [13].

Compared to methane-oxidizing bacteria, methanogens do not develop in environments with sulphate, due to the presence of sulphate-reducing bacteria, which have a higher affinity for hydrogen and acetate. But, despite this, there are situations when methanogens and sulphate-reducing bacteria are present in the same environment. This points out the unique capacity of methanogens to use other substrates in different stress conditions. Usually, alternative substrates belong to the compounds having methyl group in their structure. For example, the Archaea species *Methanococcoides* recently found in the Napoli submarine mud volcano, uses as substrate betaine, choline, methanol, dimethylamine and trimethylamine, but can not metabolise H_2/CO_2 and acetate. Methanogen archaea can have syntrophy relations with diverse anaerobic bacteria specialised in fermenting. Thus, fermentative bacteria eliminate protons in the environment, which are further taken by methanogens for hydrogenotrophic synthesis of methane [30].

7. COMMON PATTERNS OF BIODIVERSITY IN MUD VOLCANOES

Representing structures which retain large quantities of organic compounds, mud volcanoes harbour a large array of bacterial phyla. In the environments contaminated with aliphatic or aromatic hydrocarbons, the common microorganisms belong to Actinobacteria, Firmicutes and Proteobacteria phyla. In the oil tanks with low temperatures the β, λ, γ, ε classes of Proteobacteria phylum are the most commonly encountered, in the mesophilous tanks about 50% of the bacterial diversity is represented by Alphaproteobacteria. Species belonging to Alphaproteobacteria are capable to degrade polycyclic aromatic compounds. In contrast, Gammaproteobacteria includes species which degrade only hydrocarbons with low molecular mass [21]. Epsilonproteobacteria are easily isolated from environments reach in oil derivatives, but their role in these environments is not clear. As well, it is not known why in the oil contaminated zones can be encountered species from Actinobacteria phylum, which includes, par excellence, aerobic species with metabolism specialised in degradation of cellulose [33]. The species from Firmicutes phylum are capable to degrade a low range of alkanes [26]. Firmicutes species were not observed to have syntrophic relations with methane-oxidizing archaea [20]. Firmicutes species can be found in various mud volcanoes, they point out aerobic or fermentative processes of degradation of organic matter [1].

The post-genetic process of anaerobic oxidation and secondary methanogenesis in a mud volcano is a process which necessitate presence of both the syntrophic relation between methane-oxidizing archaea and sulphate-reducing bacteria and the presence of methanogenic archaea. The relations between these microorganisms are tight and the whole resulted process can not be treated from the perspective of a reductionistic attitude. The quantity and diversity of these microorganisms can oscillate from a mud volcano to another, depending on a range of parameters. Most often, this set of parameters comes down to few ones, the most essential ones: the origin of the mud volcano and the physical-chemical conditions around it. In order to point out the correlation between these parameters and the amount of microorganisms it is useful to list and analyse some mud volcanoes.

Pâclele Mici nature reserve from Eastern Romania comprises the highest number of mud volcanoes in Europe. Compared with the majority of terrestrial mud volcanoes, the breccia expelled by the volcanoes from Pâclele Mici contains not only methane but also alkanes and aromatic substances with high molecular mass. The big quantity of such compounds can be ascribed to the hydrocarbon sources nearby. The differences also appear at the analyses of the concentrations of inorganic substances. Thus, the sulphate concentration in this mud volcano is quite high, ranging between 1.5mM – 2mM. The concentration is higher than the values obtained in most of the terrestrial volcanoes, but is not comparable with the ones detectable in marine mud volcanoes [1]. The high sulphate concentration can be a consequence of the geological past of that area. The water in this volcano has a high salinity, which imply the existence of marine sediments. By moving along pressure gradient, underground water passes through these sediments, increasing both salinity and sulphate concentration. Thus, the presence of hydrocarbons and sulphate represents a precondition for the presence of sulphur-reducing bacteria, which can take here the status of a native species. Along with the appearance of sulphur-reducing bacteria, the presence of methane-oxidising Archaea is indisputable. Considering the decrease of the sulphate concentration in the upper sedimentary layers, sulphur-reducing bacteria and methanogens can reach here accidentally, during eruptive crises. The same situation can also be followed in the Salse di Nirano mud volcano from Italy, where the sulphate concentration is higher in the lower sedimentary layers. Thus, methane-oxidating archaea form large biofilms at depth and at the surface only small fragments of these formations reach [43]. At Pâclele Mici methanogens are present in the superior layers. The identified methanogenic archaea belong to Methanomicrobiales order. These isolated species synthesise methane on hydrogenotrophic H_2/CO_2 and acetoclastic pathways. The hydrogenotrophic synthesis pathway is also justified by the presence of bacteria from Firmicutes phylum, fermentative bacteria which degrade organic matter and eliminate protons, which are further used by methanogenic archaea as substrate [1].

Mud volcanoes from Pâclele Mici can be considered a hybrid form between a terrestrial volcano and a maritime one. Therefore the diversity of microorganisms is, par excellence, attributed to its maritime origin. In some cases it is not the origin having the decisive role in consolidating the biodiversity but the physico-chemical environment around the volcano. As an example the stratification of microorganisms within the terrestrial mud volcano Shin-Yan-Ny-Hu, from South-Western Taiwan, can be discussed. This volcano is characterised by an unusual sulphate gradient. The sulphate concentration decreases with depths. At the surface, the sulphate concentration vary around 0.8-4.1 mM, but at a depth of 10 cm the concentration reaches empty values. The phenomenon can be followed due to the sulphureous minerals (pyrite and greigite) which exist around the crater. Pyrite and greigite are oxidised by different abiotic factors. Thus, the superficial layers of the volcano are saturated with sulphate, which allow the appearance of sulphur-reducing bacteria and methane-oxidating Archaea. The niche covered by sulphur-oxidating bacteria and ANME is limited to only 10 cm depth. Deeper than 10 cm methanogenic Archaea from Methanomicrobiales order appear. But methanogens can be also found in the 10 cm niche. Here we prevailingly find *Methanolobus* genus, which can cohabit with sulphur-reducing bacteria, because its methanogenesis is of methylotroph nature and the needed substrate is obtained following the fermentation of osmoprotectants - glycerol [12].

At the terrestrial mud volcanoes, where there are not present neither marine sediments, nor sulphurous minerals at the surface, the process of methane-oxidating by archaea becomes problematical. But there is an alternative, using iron and manganese as electron acceptors. By way of illustration, breccia from Lei-Gong-Huo volcano in Eastern Taiwan has a very low sulphate concentration. But aerobic oxidation of methane and sulphur-reducing bacteria are present. In this case sulphur-reducing bacteria do not belong to Desulfosarcina/Desulfococcus group, but belong to a group specialised in reduction of Fe(II) and Mn(II) – Desulforomonas/Pelobacter group. This group can establish syntrophic realtions with many archaea from ANME2 group. Bacteria able to perform reduction of metals were also found in mud volcanoes from China, for example *Desulfuromusa ferrireducens*, anaerobic bacterium performing reduction of Fe(III) [44]. As in Shin-Yan-Ny-Hu volcano, the microorganisms from Lei-Gong-Huo volcano were divided on distinct niches. Oxidation of methane is present as far as 7 cm depths, methanogenesis at 9-27 cm and oxidation again at 29 cm. Methanogenesis in this volcano has its particularities, taking into consideration the high salinity, archaea will synthesise hydrogenotrophic methane, due to fermentative bacteria and the osmoprotectants found in plenty (choline or glycerol) [8].

CONCLUSIONS

This work provides an overview of the genesis and distribution, morphology and topology of mud volcanoes based on a selection of literature. Mud volcanoes differentiate through the capacity to discharge materia in various forms (gas, water and sediment) and the relatively violent manner of performing it. Along their activity fluids and solids are commonly seeping in craters while during the dormant stages are visible the different structures: gryphons, mud cones and mud volcanoes. Based on post-genetic activities and expelled products is possible to determined if these products are thermogenic or biogenic in origin.

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