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13 Mud Volcanoes

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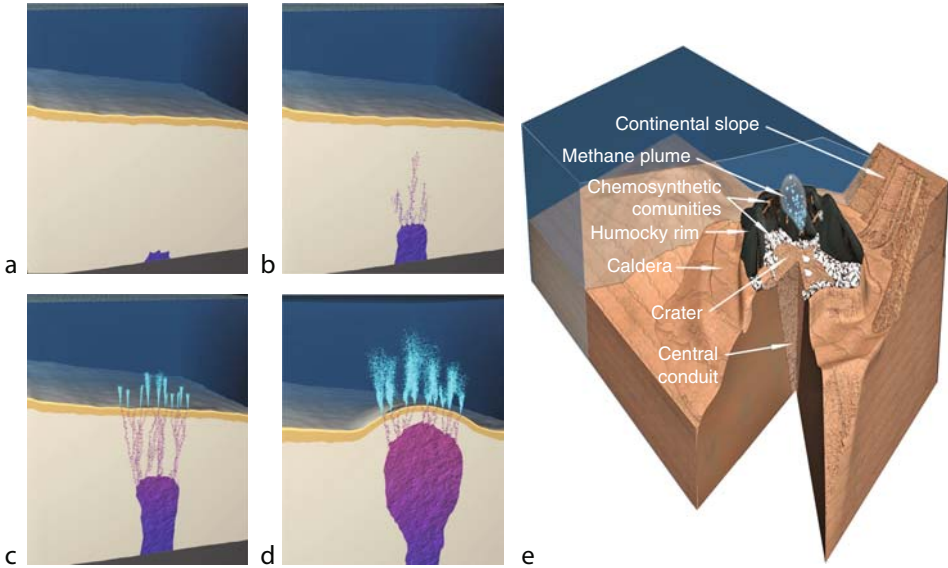
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Abstract: Mud volcanoes are frequently encountered geo-structures at active and passive continental margins. In contrast to magmatic volcanoes, mud volcanoes are marine or terrestrial, topographic elevations built from vertically rising fluidized mud or mud breccia. Commonly, these structures have a crater, hummocky rim and caldera. Mud volcanism is triggered by various geological processes which lead to a high pore fluid pressure at great depth, sediment instabilities and a subsequent discharge of mud, fluids and gases such as hydrocarbons (mostly the greenhouse gas methane). Although global estimates of methane emissions from mud volcanoes vary over two orders of magnitude, mud volcanism could be an important source for atmospheric methane. However, a substantial fraction of the hydrocarbons are retained in the mud volcanoes surface sediments. Here, the upwelled hydrocarbons fuel a variety of free-living and symbiotic, chemosynthetic communities that oxidize these with electron acceptors such as oxygen or sulphate from the water column or the atmosphere. The activity of the chemosynthetic communities is regulated by the availability of either electron donors (hydrocarbons) or acceptors which, in return, is determined by mass transport processes. Most important in this context are the magnitudes of upward advection of electron donors and the influx of electron acceptors due to diffusion and bioirrigation.

1 Introduction

Mud volcanoes are geological structures bearing only little morphological resemblances to magmatic volcanoes. In contrast to true volcanoes which expel magmatic material at plate boundaries and mantle plumes (Schmincke, 2006), mud volcanoes are formed by vigorous mud discharge that is often accompanied by fluid and gas emissions commonly originating from a deep subsurface sedimentary sequence (Brown, 1990; Kopf, 2002; Milkov, 2000). Mud volcanoes have a long tradition of scientific investigation and references were already made in historical documents (e.g., “Naturalis Historia” by Pliny the Elder, first century AD). Nevertheless, the diversity of mud volcano shapes as well geological causes responsible for their formation lead to a variety of definitions and synonymous terms such as mud volcano, mud pie, mud mound and gryphon (among others). Hereafter, a mud volcano is defined as a marine or terrestrial, topographic elevation built from vertically rising fluidised mud or mud breccia (a mud matrix with clasts). Mud volcanism is caused by various geological processes such as tectonic accretion and faulting, rapid burial of sediments due to slope failures (olistostromes) or high sedimentation rates, fluid emissions from mineral dehydration as well as (true) volcanic and earth quake activities (Brown, 1990; Dimitrov, 2002; Kopf et al., 2001, 2002; Mellors et al., 2007; Milkov, 2000). These processes can lead to an abnormally high pore fluid pressure and sediment instabilities and consequently lead to the extrusion of mud, fluids, and gases such as hydrocarbons and carbon dioxide to the sea floor or earth surface (usually through a central conduit; ▶ Fig. 1). A crater or active centre, hummocky rim and surrounding caldera are common features of mud volcanoes. However, the shape of the edifice can range from amorphous mud pies to conical formations and their size varies from a few meters to kilometres in circumference and a few decimetres to hundreds of meters in height. Viscosity and density of the extruded material as well as the duration of eruption events and the development stage of the edifice were identified as major factors determining the shape of mud volcanoes (Lance et al., 1998; Murton and Biggs, 2003; Stewart and Davies, 2006). In general, flat structures are composed of comparably liquid mud matrixes, while high and cone



■ **Figure 1**

Potential genesis of a gas emitting (marine) mud volcano. (a) High pore fluid pressure leads to the formation of mud breccia at great depth where also gases (mainly methane) are produced. (b) Overpressurised mud breccia and gases migrate along sediment instabilities to the seafloor (c) which is eventually breached (d) and upheaved. (e) Scheme of the Haakon Mosby Mud Volcano. At a “typical” mud volcano, mud and gases are transported through a central conduit and extruded in a crater region. The crater is surrounded by a hummocky rim of displaced sediment material. After an initial outburst and deflation of source material, a caldera (collapse-structure) surrounds the mud volcano. Surface sediments of mud volcanoes can support a wide range of free-living and symbiotic, chemosynthetic organisms which oxidize the upwelled hydrocarbons and hydrogen sulphide with oxidants such as oxygen, nitrate or sulphate from the water column. Giant sulphide oxidizing bacteria forming white mats on the sea floor and symbiotic tube-worms colonizing the sea floor in meadow- or bush-like aggregations are prominent examples of chemosynthetic communities, which are visible for the naked eye. a-d Source: ARCHIMEDIX, e Sabine Lüdeling, MedienIngenieure Bremen.

shaped edifices are build of successively, superimposed flows of more viscous material. Mud volcanoes may thus erupt in regular or irregular time intervals or emit mud, fluids and gases continuously. In addition, they may also become inactive when the source of gas expansion and fluid flow stops (Planke et al., 2003) but also new structures evolve such as the terrestrial LUSI mud volcano in 2006 (Mazzini et al., 2007). Three types of mud volcano activity are distinguished (Dimitrov, 2003 and references therein):

- (1) Lokbatan-type: This type of mud volcanisms was named after the Lokbatan mud volcano, Azerbaijan. Lokbatan type mud volcanoes are characterized by violent outbreaks and long phases of dormancy.
- (2) Chikishlyar-type: Calm, relatively weak and continuous venting of gas, water and mud are typical for this type of mud volcano.

- (3) Shugin-type: This type of mud volcanism is transitional between the other types, characterized by long periods of weak activity interrupted by eruptive events. Dimitrov (2003) suggested that this type of mud volcanism is the most common.

This distinction is based on terrestrial mud volcanism, which has been investigated for a comparably long time. In some cases, also historical documents can be used to infer the mode of activity (Aliyev et al., 2002). In contrast, most oceanic mud volcanoes were discovered and investigated in the last decade, when appropriate high-resolution geophysical tools became available to science which can resolve a few m of difference in height above or below ground. However, from the bathymetry it cannot be resolved what activity-type a particular mud volcano may represent. Eruptive events could be separated by extremely long periods of dormancy. In addition to the temporal heterogeneity of activity, visual investigation of mud volcanoes by towed video cameras, submersibles or remotely operating vehicles showed that marine mud volcanism is also spatially diverse (Niemann et al., 2006b; Sauter et al., 2006). In general, a mud volcano has an active centre above a central conduit which is usually marked by steep temperature gradients, and seepage rates decrease towards the periphery. However, the active centre may not always be the geographical centre and the activity may not follow a concentric arrangement. Our knowledge about mud volcanoes in general and specific structures in particular is therefore very sketchy.

2 Hydrocarbon Emissions

The processes leading to mud volcanism on the continents as well as at active and passive continental margins are generally related to fluid and gas flow. Subsurface muds and shales in mud volcano-hosting regions often contain high amounts of methane and other hydrocarbons of thermogenic and/or microbial origin. Consequently, mud flows can be accompanied by vigorous gas expulsions, which may even ignite in contact with the atmosphere in terrestrial systems (Charlou et al., 2003; Kopf, 2002; Milkov, 2000; Somoza et al., 2003). Good examples for violent gas emissions from such structures are the terrestrial Lokbatan and the deep water Haakon Mosby Mud Volcano. During the last outbreak in 2001, a flame of about 400 m height lasted for more than a day above Lokbatan mud volcano (Aliyev et al., 2002; Mukhtarov et al., 2003). At Haakon Mosby, a gigantic methane plume of about 600 m was visible on echosounder systems during several cruises and jets of methane emitted from the sea floor were observed during submersible dives (Sauter et al., 2006; Vogt et al., 1997). The annual methane discharge from Haakon Mosby was estimated with 8–35 Mmol (0.1–0.5 Gg) of which free gas accounted for 60–90% (Niemann et al., 2006b; Sauter et al., 2006). About 650 to 900 terrestrial mud volcanoes are known (Kopf, 2003) but global estimates for marine mud volcanoes range between 800 and 100000 (Dimitrov, 2002, 2003; Kopf, 2003; Milkov, 2000; Milkov et al., 2003). For submarine mud volcanoes, it is often not known if and when these structures emit methane. As a result, global assessments of methane emissions from mud volcanoes vary considerably. Recent estimates suggest that terrestrial and shallow water mud volcanoes contribute between 2.2 and 6 Tg yr⁻¹ of methane to the atmosphere (Dimitrov, 2003; Milkov et al., 2003) and that 27 Tg yr⁻¹ of methane may escape from deep water mud volcanoes (Milkov et al., 2003). Revised estimates of the total methane emission from mud volcanoes range between 35–45 Tg yr⁻¹ (Etiopie and Milkov, 2004), 30–70 Tg yr⁻¹ (Etiopie and Klusman, 2002), and – when using only known structures

and correcting for the size of the edifice – between 0.3 Tg yr^{-1} (Kopf, 2003) and 1.4 Tg yr^{-1} (Kopf, 2002). In comparison to the annual methane emissions to the atmosphere (535 Tg yr^{-1} , Judd et al., 2002), mud volcanism may consequently be a significant source for atmospheric methane.

3 Geochemical Forcing

In surface sediments of mud volcanoes potential electron donors such as hydrocarbons and, after their biological conversion with sulphate, hydrogen sulphide from deeper sediment layers meet electron acceptors such as oxygen, nitrate/nitrite, oxidized metals and sulphate from the water column or the atmosphere. In such redox transition zones, mud volcanoes were found to support a wide range of free-living and symbiotic, chemosynthetic organisms utilizing the subsurface energy sources (also known as “geofuels”; [Fig. 1](#)). Thereby, chemosynthetic organisms reduce the efflux of reduced molecules to the hydro- and atmosphere (See [Chapters on hydrocarbon and sulphur oxidising microbes in Vol. 2 “MICROBIAL UTILIZATION OF HYDROCARBONS, OILS AND LIPIDS”](#) of this edition) (Alain et al., 2006; Jørgensen and Boetius, 2007; Joye et al., 2005; Niemann et al., 2006a, 2006b; Olu et al., 1997; Omoregie et al., (in review)). The most important metabolic pathways are methanotrophy (anaerobic oxidation of methane – AOM, and aerobic oxidation of methane - MOx), anaerobic and aerobic degradation of hydrocarbons, thiotrophy (sulphide oxidation with oxygen or nitrate - SOx) and in some recently discovered systems also iron oxidation. The distribution of chemosynthetic communities strongly depends on the availability of electron donors and acceptors which in return is regulated by physical mass transport processes and biological activities (de Beer et al., 2006; Lösekann et al., 2007; Niemann et al., 2006b). Advection accounts for the majority of upward transport of electron donors from deeper sediment layers, while diffusion and bioirrigation are responsible for most of the influx of electron acceptors from the atmosphere or the water column into the mud volcano sediments ([Table 1](#)).

Advective transport at mud volcanoes is in the form of mud, fluid and free gas flow (see [section 1](#)). Direct measurements of advection are scarce (Brown et al., 2005; Linke et al., 1994; Mazzini et al., 2007; Sauter et al., 2006). In particular, rates of free gas and mud flow are poorly resolved. Also, the effect of mud and free gas flow on the distribution of chemosynthetic communities is mostly unknown. Fluid flow rates, on the other hand, can be modelled from geochemical porewater gradients and heat flow measurements, which allows for a comparably high temporal and spatial resolution. Recorded values for fluid flow at active mud volcanoes are typically a few centimetres to several metres per year ([Table 1](#)). Except for the spatial and temporal heterogeneity of mud volcano activity, advective pore water transport is a linear process and the advective flux (J_a), i.e., the amount of a pore water solute crossing a given area per time, is determined by the flow velocity (v_a) and the concentration (C) of the solute:

$$J_a = v_a C \quad (1)$$

(Note that C has to be corrected for porosity $-\phi$)

The underlying mechanism of diffusion is Brownian motion (Einstein, 1905), which, for biogeochemical reactions, can be simplified to the heat induced, non-directional movement of atoms/molecules in water. Diffusive transport can be illustrated by assuming two spatially separated entities in sediments or the water column with high and low concentrations of a

■ **Table 1**

Fluid flow velocities (v_a ; in cm yr^{-1}) at selected submarine mud volcanoes

Structure	Location	v_a	Ref.
Haakon Mosby	Barents Sea	40–600*	1,2
Dvurechenski	Black Sea	8–25	3
Capt. Arutyunov	Gulf of Cadiz	10–15	4
Mound 12	East Pacific	10	5
Atalante	West Atlantic	<1–10*	6,7
Kazan	Mediterranean	4	8

Reference: (1) de Beer et al. (2006), (2) Kaul et al. (2006), (3) Aloisi et al. (2004), (4) Hensen et al. (2007), (5) Linke et al. (2005), (6) Henry et al. (1996), (7) Olu et al. (1997), (8) Haese et al. (2006)

*vent-like structures emitting fluids at $>1\text{cm s}^{-1}$ were observed

given solute. The dissolved atoms/molecules will move randomly between both units. But more atoms/molecules will move from the unit of high concentration than from the unit of low concentration. This consequently leads to a net transport to the unit of low concentration until both units are equal in concentration. From this simple example it is apparent that the concentration difference is an important factor determining diffusive flux. The second important factor is the net velocity of the movement. However, in contrast to the linear mode of advective flow, diffusion is random. A diffusing atom/molecule will not move in one direction but, in a simplified manner, forward and backwards. As a result and when considering a large number of atoms/molecules, the mean traveled net distance (L) increases only by the square root of time (t):

$$L = \sqrt{2Dt}; \quad (2)$$

where D , the diffusion coefficient, is a compound specific constant usually expressed in $\text{cm}^2 \text{yr}^{-1}$ (note that D has to be corrected for temperature (T) and ϕ , e.g., Boudreau, 1997). Equation (2) has the very counterintuitive implication that the net velocity of diffusion (v_d) decreases with increasing diffusion distance:

$$v_d = L/t = 2D/L \quad (3)$$

Important electron donors and acceptors at mud volcanoes only need about a ms to travel a distance of 1 μm but already a day for 1 cm and some month for 10 cm (► Table 2)! The diffusive flux (J_d) is hence determined by the concentration difference (δC), the diffusion distance (δx) and D . Assuming steady state conditions, i.e., none of the factors determining the flux changes over the time period of measurement, J_d can be calculated according to Fick's first law of diffusion (Berner, 1980; Boudreau, 1997; Fick, 1855):

$$J_d = D \times \delta C / \delta x \quad (4)$$

For short distances and high concentration differences (i.e., a steep concentration gradient - $\delta C / \delta x$), diffusion is an efficient transport mechanism. Diffusive transport of electron acceptors may thus balance a high advective flux of electron donors from below. However, the redox transition zone in this scenario will be close to the sediment surface where the concentration gradients of the electron acceptors are steep.

■ **Table 2**

Diffusion distance (L) in relation to diffusion time (t) and velocity (v_d) of methane, sulphate and oxygen in sediments at a “typical” submarine mud volcano ($T \sim 3^\circ\text{C}$; $\phi \sim 80\%$)

Methane			Sulphate		Oxygen	
L	t	v_d	t	v_d	t	v_d
1 μm	0.8 ms	40 km yr ⁻¹	1.3 ms	24 km yr ⁻¹	0.7 ms	48 km yr ⁻¹
1 mm	13.2 min	40 m yr ⁻¹	22 min	24 m yr ⁻¹	11 min	48 m yr ⁻¹
1 cm	22 h	4 m yr ⁻¹	36 h	2.4 m yr ⁻¹	18 h	4.8 m yr ⁻¹
10 cm	92 d	0.4 m yr ⁻¹	150 d	0.24 m yr ⁻¹	76 d	0.48 m yr ⁻¹
1 m	25 yr	4 cm yr ⁻¹	41 yr	2.4 cm yr ⁻¹	21 yr	4.8 cm yr ⁻¹
10 m	2.5 kyr	4 mm yr ⁻¹	4.1 kyr	2.4 mm yr ⁻¹	2.1 kyr	4.8 mm yr ⁻¹
100 m	250 kyr	0.4 mm yr ⁻¹	413 kyr	0.24 mm yr ⁻¹	209 kyr	0.48 mm yr ⁻¹
1 km	25 Myr	40 μm yr ⁻¹	41 Myr	24 μm yr ⁻¹	209 Myr	48 μm yr ⁻¹

The transport of electron acceptors due to bioirrigation activities is a known but poorly quantified phenomenon at marine mud volcanoes (Haese et al., 2006; Niemann et al., 2006b) and other types of cold seeps (Cordes et al., 2005; Haese, 2002; Treude et al., 2003). Many mud volcanoes host large populations of chemosynthetic megafauna such as tube worms and bivalves mining for sulphide and methane. Thereby, oxygenated and sulphate rich sea water is flushed through burrows into deeper sediment layers where it becomes available for free living chemosynthetic microbes. Furthermore, some thiotrophic tube worms are known to secrete sulphate actively through posterior body parts to fuel sulphate reduction in the sediment. The flux via bioirrigation (J_b) is solely dependent on the faunal (pumping) activity as well as their extension into the sediment. J_b can be calculated from the concentration differences of non-reactive tracers such as e.g., silica or bromide (Haese, 2002; Haese et al., 2006; Wallmann et al., 1997):

$$J_b = \alpha h(C_0 - C_x) \quad (5)$$

where α is the non-local exchange coefficient (in yr⁻¹, dependent of faunal community composition and density) which has to be modeled from pore water concentration profiles. h is the thickness of the zone in which the transport occurs and C_0 and C_x are the concentrations of the tracer in the bottom water and at depth, respectively. The few estimates available to date indicate that fluid flow due to bioirrigation may be 2 – 3 orders of magnitude higher than the physical transport (Haese et al., 2006; Wallmann et al., 1997).

Because of the different modes and magnitudes of transport, the redox transition zones are found at various depth in mud volcano sediments ranging from the sediment surface to meters below sediment surface. For sediments devoid of burrowing megafauna, the depth is determined by the velocity of upward fluid flow (de Beer et al., 2006).

4 Research Needs

Due to the high spatial and temporal variability of fluid flow at mud volcanoes, and the many questions remaining to the functioning and interaction of geophysical forces as drivers of mud

volcanism, there are still many open questions as to the trigger, sources and change of their activity and longevity. For submarine mud volcanoes an important issue is the relation between gas and fluid flow, heat transport and the formation/dissociation of gas hydrates as well as its consequences for the distribution and activity of faunal communities. One of the best studied mud volcanoes in this regard is the Haakon Mosby Mud Volcano, which has been chosen as a site for long term observation of geophysical and biogeochemical processes of mud volcanism. Specifically for terrestrial mud volcanoes, very little is known about the occurrence, phylogeny, ecology, and activity of chemosynthetic communities.

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