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ORIGINAL PAPER

Achim J. Kopf

Global methane emission through mud volcanoes and its past and present impact on the Earth's climate

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Abstract Mud volcanism is an abundant, global phenomenon whereby fluid-rich, low-density sediments extrude both on land and offshore. Methane, which generally exceeds 90 vol% of the gas phase, is emitted at high rates during and after emplacement of the mud domes and is known for its high global warming potential (GWP). This comprehensive estimate of the annual contribution of mud volcano degassing assesses the significance of mud volcanism for the accumulation of greenhouse gases in the atmosphere. A first-order estimate for the earlier, pre-anthropogenic volume of methane released through mud volcanoes further supports their profound effect on the Earth's climate since at least the Paleozoic (570 Ma).

Keywords Mud volcanism · Climate change · Emission · Methane

Introduction

Mud volcanoes occur almost everywhere on Earth and are commonly associated with compressional tectonics at convergent margins (Higgins and Saunders 1974; Barber et al. 1986; Kopf et al. 1998). Their abundance shows a positive correlation with (1) thick, rapidly deposited sediments comprising high clay mineral contents (Yassir 1989), (2) sediment overpressuring due to hydrocarbon formation (Hedberg 1974; Lavrushin et al. 1996), (3) a structural association due to tectonic shortening dehydration (Moore and Vrolijk 1992) and/or earthquake activity (Sondhi 1947), (4) fluid emission such as gas, brines, water from mineral dehydration (Moore and Vrolijk 1992) and gas hydrate dissociation (Milkov 2000), and (5) polymictic assemblages of the surrounding rock present in the ejected argillaceous matrix (Robertson and Scientific Party of ODP Leg 160 1996; Kopf et al. 1998). Hence, they are predominantly aligned around subduction zones and orogenic belts (Fig. 1). Here, sediments suffer tectonic stress and are incorporated into accretionary wedges, which later are imbricated and uplifted in compressional belts. Both pore water and organic matter in the marine sediments may be transported to several kilometers depth, where increasing burial stresses and temperatures cause a decrease in porosity and maturation of organic material (Hedberg 1974). The trapped pore water and forming hydrocarbon gas result in considerable overpressures of the mud at depth, and may liquefy already (partially) consolidated sedimentary rocks (Terzaghi 1947). As a consequence of the resulting density inversion, the mud either slowly ascends through the overburden rock (mud diapirs) or extrudes vigorously (mud volcanoes, diatremes) along zones of structural weakness such as faults and fractures (Brown 1990). The admixture of small amounts of gas has been shown to cause a dramatic increase in extrusion rate, so that blocks of several meters in diameter may be mobilized during mud eruption (Kopf 2002).

The amount of water being expelled with extruding mud has been estimated across the submarine Mediterranean Ridge accretionary complex, an area where mud domes are very common and where constraints from scientific deep-sea drilling exist (Robertson and Scientific Party of ODP Leg 160 1996; Kopf et al. 2001). Here, quantitative flux of pore water has been found to exceed flow rates at the toe of accretionary complexes elsewhere, suggesting that mud volcanism is a highly efficient dewatering mechanism along convergent margins (Kopf et al. 2001). Together with this important backflux of deep-seated waters from the rock into the hydrosphere, radiative gas reaches the Earth's surface.

Quiescent as well as catastrophic emission of gas (predominantly methane) accompanies mud extrusion (Hedberg 1974; Brown 1990; Dimitrov 2002; Kopf 2002). Methane and other greenhouse gases (such as CO_2, CFCs) absorb infrared radiation from the Earth and, hence, trap heat that would otherwise be lost to space

A. J. Kopf (✉)
SCRIPPS Institution of Oceanography,
University of California, San Diego (UCSD),
9500 Gilman Drive, La Jolla, California, 92093-0244, USA
e-mail: akopf@ucsd.edu

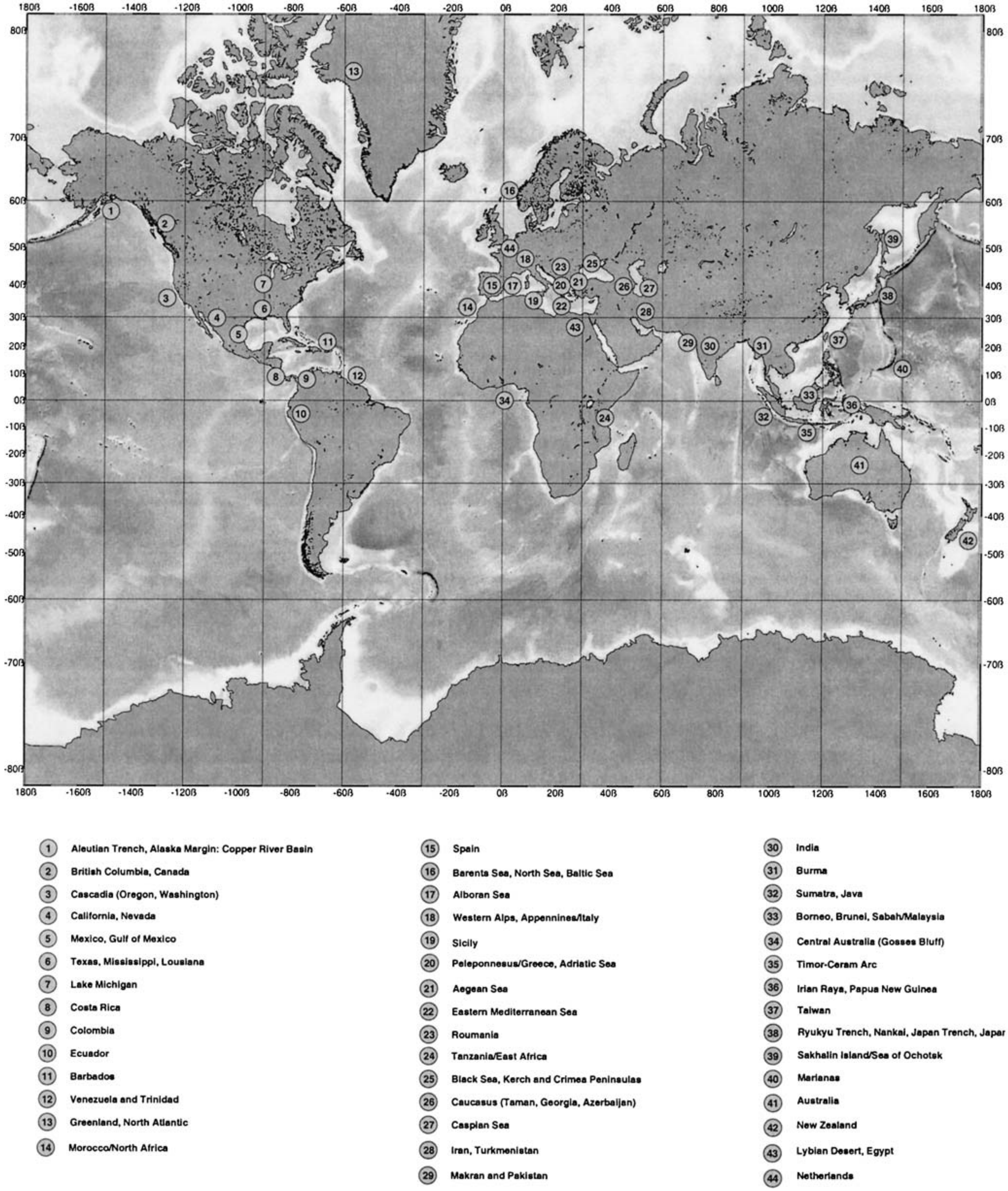

Fig. 1 Map showing global mud volcano occurrences

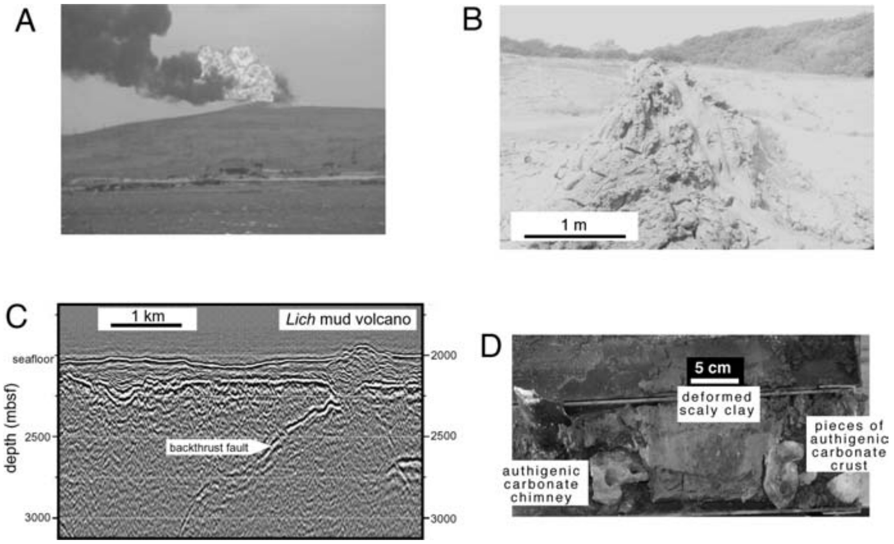

Fig. 2 Examples of typical mud volcanic edifices. **A** Flaming eruption of *Lokhbatan* mud volcano, Azerbaijan. **B** Small onshore mud volcano *Shugo* in the Caucasus, one of the onshore areas where mud volcanoes are most abundant. **C** Seismic reflection profile showing *Lich* mud volcano juxtaposing a backthrust fault on the sea floor of the Mediterranean Ridge accretionary wedge, where first deep scientific drilling into active submarine mud volcanoes took place. **D** Authigenic carbonate crusts and chimneys from *Mound Culebra* mud diapir, offshore Costa Rica. Top of core is seen *right*; penetration was only ~35 cm because of massive carbonate precipitates due to methane venting

(ICPP 2001). Climatologists have predicted that, as a result of increasing concentrations of greenhouse gases in the atmosphere, the Earth's temperature will increase considerably over the next decades, thereby causing changes in local climate, loss of arable land, and a potential increase in sea level. When associated with mud volcanism, self-ignition of emanating methane is an additional societal hazard (Fig. 2A; Bagirov et al. 1996; Bagirov and Lerche 1998).

Scientific rationale, database and method

The first objective of this study is to reliably estimate the amount of methane globally emanating from active mud volcanoes at present. In a second step, these results will be extrapolated back into the past when the relative contribution of mud domes is assumed to be higher (mostly because of the lack of anthropogenic pollution). The tables in this paper show the results from quantitative estimates of methane flux from active mud volcanoes. The quantitative approach is based on an extensive mud volcano compilation (Kopf 2002) as well as recent data on gas discharge (Jakubov et al. 1971; Henry et al. 1996; Hovland et al. 1997; Kopf 1999; Etiope et al. 2002) and episodicity of vigorous mud extrusions (Guliev 1992; Jevanshir 2002; Milkov et al. 2003). When gas emission rates are related to the size and number of mud domes, an annual amount of released methane can be calculated. Such results can then be compared with other sources of radiative gases, such as CH_4 from different origin (Cicerone and Oremland 1988; Hovland et al. 1993; Clayton et al. 1995; Etiope and Klusmann 2002; Judd et al. 2002), or CO_2 emissions from magmatic volcanoes (Williams et al. 1992; Brantley and Koepenick 1995).

Table 1 Number of onshore and offshore features separated by size. Data from Kopf (2002)

Size of feature	Diameter (m)	On land (*n*)	Offshore (*n*)
Small	<100	125	490
Mid-size	100–1,000	291	329
Large	>1,000	240	235

The mud volcano database for this study consists of 258 references published over a period of two centuries, with more or less detailed field data being presented (Kopf 2002). The total of >1,700 individual features known to date have been separated into the continental and marine realm (Table 1). The two groups have further been subdivided using mud volcano size, as generally the amount of gas flux is linked to the geometry of the dome (Jakubov et al. 1971; Kopf 1999). For each of the three categories (small, mid-size, and large; see Table 1), minimum and maximum gas flux rates have been averaged using all the literature data available (e.g., Jakubov et al. 1971; Guliev 1992; Henry et al. 1996; Hovland et al. 1997; Kopf 1999; Dimitrov 2002; Etiope et al. 2002; Jevanshir 2002; Milkov et al. 2003). As some of these rates seem to be affected by temporal fluctuations and unusual excursions [e.g., influx of warm water dissociating gas hydrates; Henry et al. (1996)], such data were omitted even for the least conservative (=maximum) average rates (Tables 2a, 2b, 2c). The majority of the flux estimates have been taken from studies in the two areas which are arguably the best studied and have the highest

Table 2a Mud volcano gas flux rates: quiescence (Q)

	Gas flux rate (m^3 $year^{-1}$)	Literature source data
On land (small)	5 (min.)	Etiope et al. (2002)
	3,413 (max.)	Etiope et al. (2002)
On land (mid-size)	8,750	
	20,000	
	1,000	Jakubov et al. (1971)
	800	Hovland et al. (1997)
	6000	Jakubov et al. (1971)
Total on land (mid-size)	36,550	
Average of on-land mid-size features	7,310	
Offshore (mid-size)	3,000,000	Henry et al. (1996)
	100,000	Kopf (1999)
	10,000	Kopf (1999)
Total offshore	3,110,000	
Average of offshore	1,036,667	

Table 2c Extrapolated estimates of average flux (m^3 $year^{-1}$) for this study

Size of feature	Minimum flux[a]	Maximum flux[a]
Quiescence Q:		
on land		
Small	100	1,000
Mid-size	10,000	10,000
Large	100,000	1,000,000
offshore		
Small	100	1,000
Mid-size	10,000	100,000
Large	1,000,000	1,000,000
Eruptions E:		
on land		
Small	30,000	500,000,000
Mid-size	30,000	500,000,000
Large	30,000	500,000,000

[a] Eruptive flux used for onshore and offshore mud features

mud volcano abundance: the Caucasus region on land and the submarine Mediterranean Ridge accretionary wedge, both situated in southeast Europe. Mud extrusion here is most likely accentuated by the progressive collision of the African with the Eurasian continental plate (Kopf et al. 1998, 2001). A typical mud volcano edifice of both study areas is given in Fig. 2B and C. Active fluid flow is attested by the soupy mud extruding from the small cone (Fig. 2B) and from the polarity inversion along the fault trace cross-cutting the accretionary prism on the seismic profile (Fig. 2B), respectively. Gas emission has been constrained from in-situ measurements and submersible surveys (Henry et al. 1996; Aloisi et al. 2000). The average flux rates used for this study, together with the relevant references, are listed in Tables 2a, 2b, 2c. Flux data can be divided into background emission during periods of quiescence, and high flux rates during violent mud volcano eruptions. For either group, minimum and maximum values have been calculated from the literature data accessible (Tables 2a, 2b, 2c). Some of the methane emanating from marine mud domes may be precipitated at the sediment–water interface, forming authigenic crusts and nodules (Fig. 2D; concerning the fate of methane emissions see Discussion below).

Results

The range of emitted methane has been calculated as the product of the number of mud domes of a given size (from Table 1) times the minimum or maximum respective gas flux rate (from Tables 2a, 2b, 2c). These calculations result in minimum and maximum amounts of methane during quiescence (Table 3, top part) and during eruptions (Table 3, bottom part). Eruptions are generally short-lived in nature (hours to days), and occur episodically. The most vigorous of such outbursts uproot trees, ignite methane, and release up to 50,000 m^3 mud and 5 e+8 m^3 gas (where e stands for exponent) (Jevanshir 2002). The most reliable constraints come from historic records of the ~200 onshore mud domes in the Caucasus, and show that during the past two decades, three to five violent eruptions occurred each year. Relating the average four annual eruptions to the total number of domes, each feature erupts every ~50 years. As a consequence, this factor has to be considered when combining estimated methane from extrusive (E) as well as quiescent (Q) periods. For the previous 1 ka (i.e., the time when human influence is considered significant), a total of 1.89–3.65 e+14 g CH_4 (Q_{min} to Q_{max}) and 7.33 e+12 g CH_4 (E_{min}) to 1.22 e+17 g CH_4 (E_{max}) has degassed from mud domes. Combining quiescent and eruptive methane, a total (T) of 1.97 e+14 (T_{min}) to 1.22 e+17 g CH_4 (T_{max}) results. Note that the latter value represents about one third of the anthropogenic methane emission over the same interval. In broad terms, the total amount of methane is derived equally from the onshore and offshore features (Table 3). Even if we assume that none of the methane venting from seafloor mud domes reaches the

Table 2b Mud volcano gas flux rates: eruptions (E)

	Volcano	g CH_4 $year^{-1}$	Date of eruption	Literature source data
On land (mid-size)	Kumani	2.25 e+7	1950	Guliev (1992)
	Touragai	5 e+8	1946	Jevanshir (2002)
	Duvannyi	6.5 e+7	1961	
	Bolshoi Maraza	1.2 e+8	1902	
	Bolshoi Kyanizadag	1.43 e+7	1950	Guliev (1992)

Table 3 Amount of gas emissions (in m^3/year except when noted otherwise)

	Quiescence (Q)		Eruptions (E)	
	Minimum flux	Maximum flux	Minimum flux	Maximum flux
Onshore				
Small: 125	12,500	125,000	3,750,000	6.25 e+10
Mid-size: 291	2,910,000	2,910,000	8,730,000	1.455 e+11
Large: 240	24,000,000	240,000,000	7,200,000	12 e+11
Total	26,922,500	243,035,000	19,680,000	3.28 e+11
Offshore				
Small: 490	49,000	490,000	14,700,000	2.45 e+11
Mid-size: 329	3,290,000	32,900,000	9,870,000	1.645 e+11
Large: 235	235,000,000	235,000,000	7,050,000	1.175 e+11
Total	238,339,000	268,390,000	31,620,000	5.27 e+11
All on/offshore mud volcanoes	265,261,500	511,425,000	51,300,000	8.55 e+11
All on/offshore mud volcanoes (ka)	2.65 e+11[a]	5.11 e+11[a]	1.03 e+10[a]	1.71 e+14[a]
All mud domes (g $year^{-1}$)	1.89 e+11	3.65 e+11	36,640,512,000	6.11 e+14
All mud domes (g ka^{-1})	1.89 e+14	3.65 e+14	7.33 e+12	1.22 e+17

	Minimum	Maximum	Average
Total (T) methane flux from onshore and offshore mud volcanoes (g $year^{-1}$)	1.97 e+11	1.23 e+14	6.15 e+13
Total (T) methane flux from onshore and offshore mud volcanoes (g ka^{-1})	1.97 e+14	1.23 e+17	6.15 e+16
Methane flux from mud volcanoes on land (L) (g $year^{-1}$)	46,602,500	3.28 e+11	1.64 e+11
Methane flux from mud volcanoes on land (L) (g ka^{-1})	4.66 e+10	3.28 e+14	1.64 e+14

[a] Note that quiescent degassing has been multiplied by 1,000, but eruptive emission has been multiplied by 200 because of episodicity

Table 4a Contribution (absolute and relative) of mud volcanism and other sources to gas emission

Methane emission	g CH_4 $year^{-1}$	Literature data source	Ratio	L_{min}	L_{max}	$L_{average}$
Total global methane	5.4 e+14	Cicerone and Oremland (1988)	Mud volcanoes:total methane	0.00036	0.22685	0.00030
Natural sources	1.8 e+14	Cicerone and Oremland (1988)	Mud volcanoes:natural methane	0.00107	0.68056	0.00091
Anthropogenic sources	3.6 e+14	Cicerone and Oremland (1988)				
CH_4 from coals (min; max)	5 e+13; 1.14 e+14	Clayton et al. (1995)	Mud volcanoes:methane from coal	0.00394	1.07456	0.00328
Amount of anthropogenic methane over the last 1 ka	3.6 e+17	Cicerone and Oremland (1988)				
Years it takes to emanate 3.6 e+17 g CH_4 $year^{-1}$				1,829,375.4	2,938.8	2,193,185.3

atmosphere, 4.66 e+10 (L_{min}) to 3.28 e+14 g CH_4 (L_{max}) is released on land (L; Table 4a).

If compared with recent estimates of other methane sources (Cicerone and Oremland 1988), the mud volcano emissions are found to contribute significantly to the global CH_4 budget (Table 4a and Fig. 3A). The annual emission from all mud domes shows a wide scatter from 0.4% (T_{min}) to 22.7% (T_{max}) of the 5.4 e+14 g CH_4 $year^{-1}$ of all methane sources (Cicerone and Oremland 1988). Even if it is assumed that all methane from submarine features undergoes precipitation to carbonate [Fig. 2D; Trehu et al. (1999)], remains in the water column (Suess et al. 1999), or gets oxidized prior to reaching the seafloor (to CO and CO_2), the onshore emission from mud volcanism alone is approximately on average 0.3% ([L_{min}+L_{max}]/2; Table 4b) of annual CH_4 of all sources compiled by Cicerone and Oremland (1988) (Fig. 3A). Although such a number in the per mil range may appear low, it is clearly not in longer terms. The total anthropogenic methane production over 1 ka is 3.6 e+17 g CH_4 [Table 4a; see Cicerone and Oremland (1988)], but would be met in ~2.2 Ma if only onshore mud volcanoes are considered. This period would be much shorter if all features (i.e., marine and continental mud volcanoes) and the upper range of CH_4 flux rates were considered (Table 4a). Mud volcanic contribution to the overall

Table 4b Comparison CO_2 from igneous volcanoes

CO_2 emission	Minimum (g CO_2 year^{-1})	Maximum (g CO_2 year^{-1})	Literature data source	Ratio	L_{min}	L_{max}	$L_{average}$
Active	–	3.4 e+13	Williams et al. (1992)	Mud volcanoes:active	–	3.60295	0.00483
Passive	2 e+12	3 e+13	Minimum from Brantley and Koepenick (1995); maximum from Williams et al. (1992)	Mud volcanoes:passive	0.09839	4.08334	0.08207
Active + passive	–	6.4 e+13		Mud volcanoes:active+passive	0.00307	1.91407	0.00256
Mid-ocean ridges	–	6.11 e+11	Marty and Tolstikhin (1998)	Mud volcanoes:mid-ocean ridges	3.22018	2,004.55069	2.68601
				Ratio x global warming potential[a]			
				Mud volcanoes:active	–	75.662	0.101
				Mud volcanoes:passive	2.066	85.750	1.724
				Mud volcanoes: active+passive	0.065	40.195	0.054
				Mud volcanoes:mid-ocean ridges	67.624	42,095.565	56.406

[a] Note that CH_4 is 21x more effective than CO_2 as a greenhouse gas

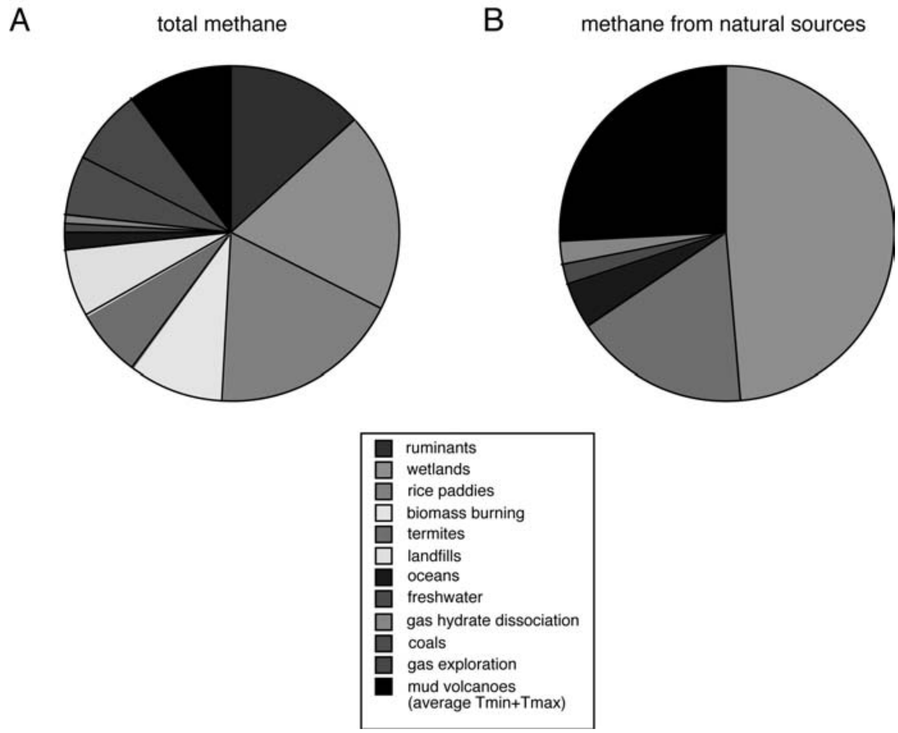

Fig. 3 Relative significance of methane contribution from mud volcanism during anthropogenic (1 ka to present; **A**) and ancient (**B**) times in the Earth's history compared to other sources (Cicerone and Oremland 1988). Note that legend starts at 12 o'clock and goes clockwise

methane budget prior to human influence is shown in Fig. 3B.

Discussion

The discussion is separated into two parts. The first part briefly focuses on three aspects: (1) the reliability of the CH_4 estimates in this study; (2) the impact of mud volcanic methane on the present greenhouse gas emissions; and (3) the significance and ramifications of this study on gas budgets and climate change when mud volcano emissions are extrapolated back into earlier Earth history without human influence. The second part of the discussion compares earlier mud volcano gas flux data with the refined, most recent estimates in this study.

Limitations and implications of this study

1. Arguably, an estimate like the one presented bears uncertainties which cannot easily be quantified by error analysis. However, this study represents a very conservative estimate of mud volcanic activity for various reasons. First of all, it can be safely postulated that only a fraction of the mud domes on Earth has actually been discovered. This is especially true for the marine realm, where mud domes and gas vents frequently transpire during sea-going expeditions (e.g., Milkov 2000; Kopf 2002). Hence, the number of mud volcanoes on the sea floor may easily exceed that compiled from the wealth of previous publications (Kopf 2002) by a factor of two or more. The presented estimates are even more conservative because CH_4 emission from marine features has been neglected in the mud volcano contribution during most of the discussion (see right columns in Tables 4a, 4b, termed $L_{average}$). A slight overestimation of methane flux may result from the fact that flux rates were taken for granted for the CH_4 calculations, although minor contributions (<<10 vol%) of other gases emanate from mud volcanoes. In rare cases [<<0.5% of all known mud volcano occurrences; see Kopf (2002)], namely when mud volcanism is associated with igneous volcanism (Chiodini et al. 1996), the gas phase may be dominated by CO_2. However, even if other gases contribute, they are usually radiative as well [but may have a lower GWP than CH_4; see ICPP report (2001), and below]. With respect to the other unknowns such as the episodicity of eruptions, number of dormant features, or size-dependent flux, much effort went into the research of the most solidly founded values available (for background see Tables 2a, 2b, 2c, and references therein).
2. Contemporary methane increase is unprecedented, at least during the past 160 ka, with two thirds of the present annual emissions being anthropogenic in nature (Cicerone and Oremland 1988). Among the natural sources, CH_4 degassing from mud volcanism approximately equals that from coals [5 e+13 g year^{-1}; Clayton et al. (1995)], and by far exceeds background flux from fresh water, gas hydrate destabilization, and the oceans [Cicerone and Oremland (1988); see also Fig. 3A). Unfortunately, little is known about to what extent mud volcanism contributes to the flux from the latter two sources. Gas hydrates are often associated with mud volcanism (Reed et al. 1990; De Lange and Brumsack 1998; Kopf 2002), and the deep-seated, warm fluids triggering mud volcanoes may dissociate considerable volumes of massive clathrates (Milkov 2000). Methane release from seawater is also connected with venting from mud domes. Although some CH_4 may be oxidized on or near the sea floor (e.g., Suess et al. 1999; Trehu et al. 1999), methane solubility in seawater (Kuo 1996) is insufficient to accommodate for lithospheric fluxes. Even at water depths of <75 m, a portion of the venting methane may be oxidized or dissolved and hence may not reach the atmosphere (Judd et al. 2002). At deeper water depths in subduction zone forearcs where arguably the majority of the mud domes are situated (Kopf 2002), it has been argued that much of the methane gets either precipitated at the sea floor (Fig. 2D), oxidized in the water column, or undergoes dissolution and biodegradation (ibid). A large bulk of literature exists on methane turnover times of ocean water bodies, which range from only several days, more than 14 years (Scranton and Brewer 1978), 30 years (Welhan and Craig 1979), 50 years (Rehder et al. 1999), and 70 years (Ward et al. 1987) to as long as several hundred years (Scranton and Brewer 1978). When excluding the highest values (from hydrothermal systems at spreading centers) and lowest values (from very old Pacific deep waters), methane oxidation to CO_2 takes on average a few decades. Note also that methane plumes have been shown to be stable with time, which allows time for oxidation (Suess et al. 1999). As a consequence, the majority of the methane very likely enters the atmosphere as CO and CO_2, whereas only in exceptional cases the methane may be transported rapidly to the sea floor (Sassen et al. 2001). Most of the methane, however, is clearly transformed into the less radiative CO and CO_2 (Logan et al. 1981), so that only a fraction of the total 1.8 e+14 g year^{-1} of natural CH_4 (Cicerone and Oremland 1988) may originate from mud volcanism.

   In a broader context, mud volcanic emissions even match values from passive and active (=eruptive) release of their igneous counterparts. If the conservative estimate of 2 e+12 g CO_2 year^{-1} from passive degassing (Williams et al. 1992) is multiplied by 21, the factor compensating for the higher GWP_{100} of methane (ICPP 2001), onshore mud volcanoes show a 1.72x higher contribution to greenhouse emissions (Table 4b). Compared with the igneous volcanic CO_2 estimates from active and passive degassing (Williams et al. 1992; Brantley and Koepenick 1995), onshore mud volcanism still reaches 5.4–10.1%. If all mud domes (T_{min}, T_{max} in Table 3) were considered, mud volcano CH_4 emissions range between 6% (minimum) and ~40x (maximum) of total CO_2 degassing from igneous volcanism (Table 4b). Compared with the annual CO_2 flux from mid-ocean ridges [Marty and Tolstikhin (1998); 6.11 e+10 g year^{-1}), mud volcanoes emit 2.69x more CH_4 (by weight), having a >56x larger global warming potential. No matter what the uncertainties within such estimates (from both this study and results compiled from the literature) are, it is apparent that mud volcanism potentially influences atmospheric gas levels and climate change.
3. Atmospheric methane concentrations have increased by ~150% during the past 250 years, with contributions from natural (wetlands, gas hydrate dissociation, etc.) and human-influenced sources [hydrocarbon exploration, agriculture, landfills, etc.; see Cicerone and Oremland (1988)]. However, higher than present

Table 5 Comparison with other annual estimates of global methane seepage and mud volcanism

Literature source data	g CH_4 $year^{-1}$	Comment
This study	1.64 e+11	Onshore mud volcanism
	6.15 e+13	Marine and onshore mud volcanism
Dimitrov (2002)	14.85 e+11	Marine and onshore mud volcanism (Q)
	1.15 e+13	Marine and onshore mud volcanism (E)
Milkov et al. (2003)	1.59 e+13	Marine and onshore mud volcanism (Q)
	1.71 e+13	Marine and onshore mud volcanism (E)
Judd et al. (2002)	1.6–4 e+13	Seepage on shelves
Hovland et al. (1993)	0.8–6.5 e+13	Seepage on shelves
Etiope and Klusmann (2002)	2 e+12	Marine and onshore mud volcanism
	>7 e+12	Onshore hydrocarbon seepage
	1.8–4.8 e+13	Submarine hydrocarbon seepage

methane concentrations have been proposed for earlier periods during the Earth's history, although sources and sinks are poorly constrained. Some authors have further proposed that the abrupt pulses in climate change may have been caused by "methane-led" thermal runaway (Nisbet 1990). Other workers have linked specific events, like the Paleocene–Eocene thermal maximum, to elevated methane pulses (e.g., Dickens et al. 1995). Regardless of such events and their impacts on deglaciation and the Earth's climate, the long-term continuous methane flux owing to mud volcanic activity seems important. Compared with the present contribution (Fig. 3A), CH_4 from mud domes becomes incrementally more effective during times prior to human influence (i.e., only natural methane sources; Fig. 3B). Even the most conservative annual flux estimate from on-land mud domes alone ($L_{average}$=1.64 e+11 g $year^{-1}$; Table 3) would equal the total anthropogenic CH_4 input within less than 2.2 million years ($L_{average}$, Table 4a). Furthermore, given that conditions appropriate for mud volcano evolution have existed since ~1,400 Ma, when multicellular life (and, hence, abundant organic matter) evolved, an enormous amount of methane must have been emitted from mud domes during the Earth's history. It is not unlikely that mud volcanism due to plate convergence and dewatering of fluid-laden sediment occurred in a similar manner and abundance to that today since 1–1.5 Ga. As a consequence, mud volcanism may have been the major methane source during the Precambrian and early Proterozoic, before other natural sources like wetlands and termites (*Isoptera*, a group of wingless insects which evolved not earlier than the middle Devonian, i.e., ~400 Ma) began to play an increasing role in CH_4 emission.

Comparison of mud volcanic CH_4 emissions with other studies

While compiling and writing this paper, two similar studies have been published (Dimitrov 2002, Milkov et al. 2003), the second being basically an extension of the first. Here, these studies are briefly introduced and compared with this study. Dimitrov (2002) used 1,194 known + 572 inferred mud volcanoes, whereas Milkov et al. (2003) used 1,100 known + 5,000 inferred features for their calculations. Regarding the gas flux rates, the two studies also varied considerably, with Dimitrov [(2002), his Table 2] accessing 13 and Milkov et al. [(2003), their Table 1] accessing 9 publications to compile the gas emission during quiescent and eruptive periods. Both studies assume that all emitted gas contributes to atmospheric methane budgets, despite the fact that in Milkov et al.'s case 86% of the total mud domes are submarine and hence unlikely to contribute directly to atmospheric methane. Dimitrov (2002) estimates that the ~1,800 (known + inferred) mud domes presently degas at annual methane rates of 3.3–26.4 e+11 g $year^{-1}$ during quiescent periods plus 1.03–1.26 e+13 g $year^{-1}$ during eruptions (Table 5). In their less conservative estimate inferring an extra 5,000 deep-water mud domes, Milkov et al. (2003) propose that 1.59 e+13 g $year^{-1}$ (quiescence) and 1.71 e+13 g $year^{-1}$ (eruptions) of methane are emitted into the atmosphere.

When excluding the inferred domes from both studies, the amounts of annual methane degassing of mud domes lie closer together. Dimitrov's (2002) data decrease to 2.2–17.4 e+13 g $year^{-1}$ during quiescent periods and 6.8–8.32 e+12 g $year^{-1}$ during eruptions (i.e., using ~1,200 of the total of ~1,800 domes for the calculations; see Table 5). The Milkov et al. (2003) estimates are reduced to 2.9 e+12 g $year^{-1}$ (quiescence) and 3.1 e+12 g $year^{-1}$ (eruptions) if only the known features are conservatively taken into account (Table 5). Note that in both studies it is still assumed that gas emitted at the sea floor may equally reach the atmosphere. In any case, the estimates based on known occurrences lie close to the results from preliminary data by Kopf (2002), who used very conservative flux estimates from Mediterranean mud domes and ~1,700 known features. The maximum annual methane emission estimated (quiescent + eruptive) was 1.39 e+12 g. This estimate has been refined using a wider set of gas flux measurements as well as a more detailed distinction of size, on/offshore setting, etc. in this study.

Given the wealth of literature on the subject [see bibliographies in Redwood (1913); Higgins and Saunders

(1974); Kopf (2002)], it is important to acknowledge that both Dimitrov (2002) and Milkov et al. (2003) provide a valuable foundation for estimates of methane flux from mud volcanoes and diapirs. However, it seems equally important to underline that both the number of mud volcanoes and some of the basic assumptions made by the above authors appear unrealistic, as will be discussed in the following section.

Mud volcano abundance

Despite the fact that there is clearly some uncertainty regarding the number of known mud volcanoes, it seems oversimplified to assume a spectrum over three orders of magnitude [i.e., 1,000–100,000; Milkov (2000)]. From the regional appendix in the review paper by Kopf (2002), a total number of ~1,700 known features can be compiled. Even here, not all features may be actively venting, nor do all of them emit methane. Although the abundance of known mud domes suggests that there are even larger numbers of yet to be discovered domes (see above), no number larger than the presently known one can safely be claimed as a conservative estimate. Still, Milkov et al. (2003) propose that 5,000 deep-water mud domes are conservative relative to the potential 100,000 features in this lower continental slope and abyssal plain setting, disregarding the fact that the deeper a submarine mud volcano is situated, the less likely it is to contribute to atmospheric methane budgets. In fact, the global distribution of mud domes suggests that a negligible number is situated on abyssal plains [the most prominent example probably being the area east of Barbados (Henry et al. 1996)]. In general, however, mud domes do not occur in the deep sea because of the absence of methane as a driving force for extrusion (see Fig. 1). Nutrient-rich waters and abundant organic matter in the subducted sediments are two of the major arguments for methane-derived fluids associated with mud domes, but clearly are restricted to continental margins and forearc slopes.

Size matters

Mud volcanoes are highly variable in size and geometry, with diameters and heights spanning the entire range from decimeters to tens of kilometers across [e.g., in the eastern Mediterranean (Kopf et al. 2001)] and up to 2 km high (e.g., in the Mariana Trough). When comparing all flux data published to date, it seems that there is a positive correlation between the size of active mud domes and the amount of gas being emitted. This includes passive as well as eruptive degassing. For example, the small features in Sicily (Etiope et al. 2002) release far less gas than larger domes in onshore (Azerbaijan, Trinidad, Sakhalin) as well as offshore (Mediterranean Ridge, Barbados) settings. Consequently, a thorough conservative estimate should subdivide the total of ~1,700 known mud volcanoes into categories of small (<100 m across), mid-size (100–1,000 m), and large (>1000 m) features for quantitative estimates, as has been done in this study (see Table 1).

Fate of submarine methane emissions

Both Dimitrov (2002) and Milkov et al. (2003) simplistically assume in their calculations that all methane emitted from submarine mud domes contributes to atmospheric budgets, although they acknowledge in their text that it may get oxidized. No explanation is given for this controversial approach, which causes a severe overestimation of the total mud volcanic CH_4. Although methane emissions from onshore mud volcanoes contribute directly to atmospheric concentrations [minus some negligible portion which may be combusted during violent, self-igniting eruptions (Bagirov et al. 1996); Fig. 2A], the picture changes in the marine realm. For exactly this reason the estimates in this study use mostly the continental features to support the significance of mud volcanic CH_4 emissions.

Global methane budgets

In recent years, numerous workers have pointed out the significant contribution of active mud volcanoes to the global atmospheric methane content and its implications (Dimitrov 2002; Etiope et al. 2002; Kopf 2002; Milkov et al. 2003). In fact, at present, mud volcanic emissions may well be the biggest source of natural methane released into the atmosphere, although approximately two thirds of the annual emissions are anthropogenic in nature (Cicerone and Oremland 1988). Also, there is little doubt about mud volcanic CH_4 emissions having contributed considerably to preindustrial methane budgets. However, given the present number of mud domes and the lack of a large number of either fossil or long-lived mud volcano examples, it does not seem sound to assume that more than half of the missing ~5 e+13 g year^{-1} (Quay et al. 1991) resulted from mud volcano degassing [as suggested in Milkov et al. (2003)]. Previous workers have pointed out that as much as 1.8–4.8 e+13 g CH_4 year^{-1} is set free by seepage along the continental shelves of passive and the forearc regions of active margins (Hornafius et al. 1999). The fundamentally wrong conclusion by Milkov et al. (2003) is that they oppose their mud volcanic estimates with the seepage estimates instead of acknowledging that mud volcanism is one of many mechanisms for devolatilization and gas seepage. The marine mud volcanic contribution from known domes [= 268/1,194 features according to Dimitrov (2002)] would then be 6.5 e+11 g year^{-1} (quiescent) and 0.7 e+12 g year^{-1} (eruptive) when following the Milkov et al. (2003) estimate of known features. Such a conservative approach would mean that the contribution of mud volcanoes to the overall seepage ranges between 1and 4%. This number is quite different from the 56% (2.7 e+13 g year^{-1} from "inferred deep-water mud volcanoes" relative to 1.8–4.8 e+13 g year^{-1} seepage) or more, as proposed by Milkov et al. (2003). Given the large number of other processes contributing to seepage [e.g., gas hydrate destabilization, diagenetic alteration, tectonic forcing, mineral transformation, etc.; Etiope and Klusmann (2002); Judd et al. (2002)], it does not seem reasonable to attribute to mud volcanism such an overpowering role. This is especially true since the area covered by mud extrusions relative to the total area of continental shelves and forearcs is small, their ratio being in fact very close to the 1–4% estimated conservatively. Such a value also lies much closer to the percentage of extruded mud relative to subducted and accreted sediment in forearc regions with abundant mud volcanism (Kopf 1999).

In summary, the various first-order quantitative estimates of mud volcanic gas flux clearly show the need to quantify their contribution to global methane budgets. However, the Milkov et al. (2003) estimate in particular attests that more careful investigation is required to make them reliable and powerful in the debate on climate change. Since there is no information concerning how many mud volcanoes may exist (or have existed previously), such careful estimates should be founded on known data. It has to be acknowledged that the uncertainty for the number as well as the gas emission rates for marine mud volcanoes is less well constrained than for continental outcrops. As a result, this study relies on those from on-shore mostly, whereas the Milkov et al. (2003) estimate is dominated by marine domes the majority of which was inferred.

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