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The geological methane budget at Continental Margins and its influence on climate change

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ABSTRACT

Geological methane, generated by microbial decay and the thermogenic breakdown of organic matter, migrates towards the surface (seabed) to be trapped in reservoirs, sequestered by gas hydrates or escape through natural gas seeps or mud volcanoes (via ebullition). The total annual geological contribution to the atmosphere is estimated as 16–40 Terragrammes (Tg) methane; much of this natural flux is 'fossil' in origin. Emissions are affected by surface conditions (particularly the extent of ice sheets and permafrost), eustatic sea-level and ocean bottom-water temperatures. However, the different reservoirs and pathways are affected in different ways. Consequently, geological sources provide both positive and negative feedback to global warming and global cooling. Gas hydrates are not the only geological contributors to feedback. It is suggested that, together, these geological sources and reservoirs influence the direction and speed of global climate change, and constrain the extremes of climate.

Key-words: climate change, gas hydrates, methane, mud volcanoes, seepage

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INTRODUCTION

Since the discovery of pockmarks off the coast of Nova Scotia (King & MacLean 1970) and the documentation of active natural gas seeps in the North Sea in 1983 (Hovland & Judd 1988), it has become increasingly clear that the migration of 'geofluids' (most significantly methane) is an important and ongoing geological process. In the last three decades, a wealth of evidence has shown that various features demonstrate fluid migration on continental margins. Furthermore, it is evident that features such as shallow gas accumulations, pockmarks, seeps, mud volcanoes and gas hydrates, often associated with cold seep communities and methane-derived authigenic carbonate, are present in a wide variety of geographical, oceanographic and geological environments: nearshore, continental shelf to deep ocean.

Hitherto, attempts to quantify the gas budget have focused on individual sites (Hornafius *et al.* 1999, etc.) or restricted areas (UK continental shelf — Judd *et al.* 1997, etc.). Some authors have attempted global extrapolations (Cranston 1994; Hovland *et al.* 1993), and some have presented global estimates based on available published data (Judd 2000). Collectively, these efforts have clearly demonstrated that fluxes of methane at the seabed and into the atmosphere are significant. Significant, that is, in terms of the global carbon budget. This is particularly interesting as the international authorities responsible for advising policy makers have failed to recognize the significance of geological processes in global climate change (see Fig. 1). Furthermore, most published drawings representing the global carbon cycle assume that there is no flux of carbon from geological sources, other than CO_2 from volcanoes and fossil fuels extracted by humans.

It is now time to challenge this paradigm by examining the role of natural geological processes which form part of the global carbon budget. The purpose of this paper is to consider the gas budget of the continental margins and its influence on the global climate.

SOURCES AND PATHWAYS OF GEOLOGICAL METHANE

The generation, migration and fate of gas are summarized in Fig. 2.

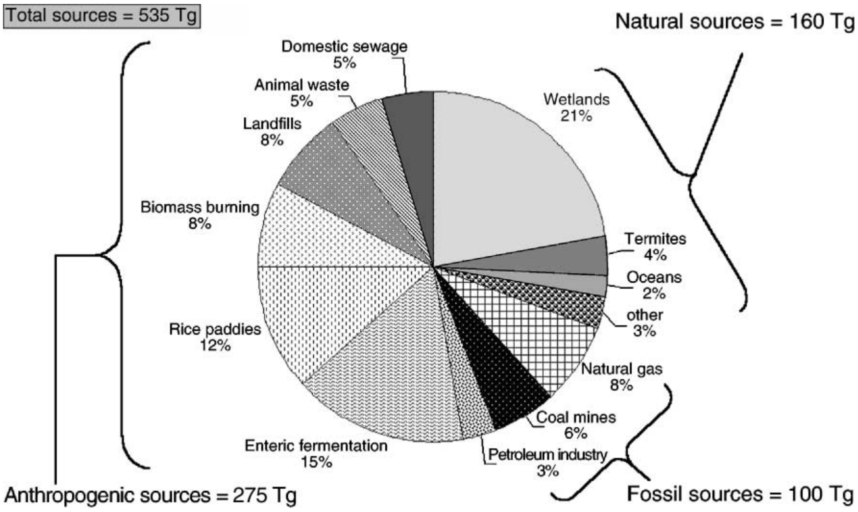

Fig. 1. Sources of atmospheric methane. Data from the Inter-Governmental Panel for Climate Change (IPCC) (Houghton *et al.* 1996).

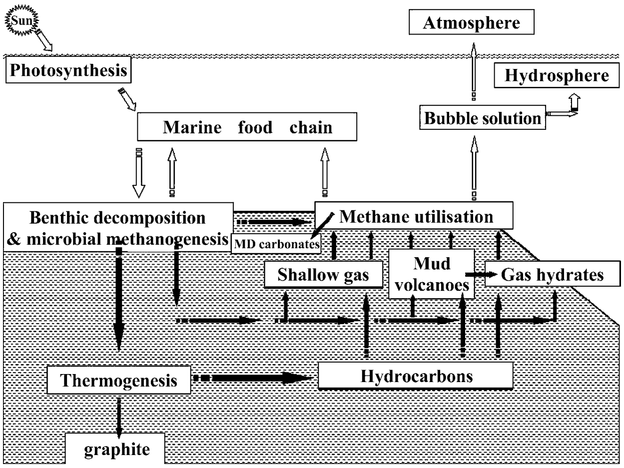

Fig. 2. Sources and pathways of geological methane. Organic matter, composed of molecules containing hydrogen and carbon, is formed during photosynthesis and enters the marine food chain. On death, this material is decomposed to simpler hydrocarbon compounds — near the seabed (by microbial decay) or at depth (by thermocatalytic breakdown). The smallest and lightest hydrocarbon is methane (CH_4). Unless trapped in reservoirs (petroleum or shallow gas reservoirs, or gas hydrates), these hydrocarbons migrate towards the seabed. Microbial utilization returns some of the hydrocarbon to the food chain, but some of the carbon is included in methane-derived authigenic carbonates. Escaping methane bubbles may be oxidized in the water column, but some escape to the atmosphere. In either case, methane will break down and its components may become available for 'recycling' during photosynthesis.

Geological sources of methane

Geological sources provide various gases to the atmosphere: SO_2, H_2O (water vapour), HCl and CO_2 from volcanoes; H_2, NO_2, CO_2 and CO from hydrothermal vents; He and Rn from magmatic sources, etc. However, methane is the most common geological gas. Methane is generated in sediments and sedimentary rocks by the natural destruction of pre-existing organic matter buried when the sediments were deposited.

Microbial (biogenic) methane is produced by methanogenic archaea as an end product of the decomposition of organic matter involving a consortium of diverse microorganisms. This process commences shortly after the organic matter is deposited and occurs mainly at relatively shallow depths within sediments in which sulphate levels have been depleted by the activities of sulphate-reducing bacteria. Where concentrations of reactive organic carbon permit, methane concentrations can rise to exceed methane solubility, permitting the formation of gas bubbles. As production rates may be seasonal (Martens *et al.* 1998), and the solubility of methane is temperature and pressure dependent, ebullition may be seasonal (controlled by bottom-water temperatures — Wever *et al.* 1998), triggered by tidal falls and atmospheric pressure variations (McQuaid & Mercer 1990) or triggered by earthquake events (e.g. Hasiotis *et al.* 1996). The advection of groundwater may also promote methanogenesis and the flux of methane to the seabed in coastal sediments (Bussmann & Suess 1998).

Residual organic carbon and the insoluble by-products of microbial decomposition remain within, and are buried with, the sediments. The generation of thermogenic methane (and other petroleum compounds) occurs when complex, long-chain organic molecules are broken down in the high-temperature, high-pressure conditions at depths typically in excess of 1 km (Floodgate & Judd 1992; Schoell 1988; Whiticar 1990).

Once generated, methane migrates towards the surface (land or seabed), although some becomes trapped to form natural gas accumulations, and some is sequestered by the formation of gas hydrates.

Reservoirs

Reservoirs of natural gas take the form of accumulations of free (bubble phase) gas within the sediments and gas hydrates.

Table 1 Marine geological environments in which gas seeps and shallow gas accumulations occur: representative examples.

Geological environment	Examples
Coastal environments of deposition* (bays, estuaries, rias, etc.)	Rías Bajas, Spain (García-García *et al.* 1999) Penobscott Bay, eastern USA (Scanlon & Knebel 1989) Aegean and Ionian Seas (Papatheodorou *et al.* 1993)
Major deltas*†	Yangtze, China (Milliman & Butenko 1985) Amazon (Manley & Flood 1988) Fraser, British Columbia, Canada (Hart & Hamilton 1993)
Hydrocarbon-bearing sedimentary basins on the continental shelf†	Persian (Arabian) Gulf (Uchupi *et al.* 1996) North Sea (Brekke *et al.* 1997) Vietnam (Traynar & Sladen 1997)
Hydrocarbon-bearing sedimentary basins on the continental slope and rise†	Gulf of Mexico (Kaluza & Doyle 1996) Offshore SW Spain (Baraza *et al.* 1999)
Hydrocarbon-bearing sedimentary basins on land†	Alabama, USA (Clayton *et al.* 1993) California, USA (USGS 2000) Great Britain (Selley 1992)
Accretionary prisms†	Costa Rica (Silver 1996) Makran (Pakistan) (von Rad & Tahir 1996)
Trapped beneath gas hydrates*†	Cape Fear Slide, eastern USA (Schmuck & Paull 1993) Niger Delta (Hovland *et al.* 1997)

*Microbial sources.
†Thermogenic sources.

Gas reservoirs

Gas bubbles accumulate within the pore spaces of coarse-grained sediments when migration is inhibited by the presence of narrow pore throats within overlying finer grained sediments. In fine-grained sediments, gas may occur within gas voids which are larger than the pore spaces (Judd & Sim 1998).

Commercially exploitable gas reservoirs tend to occur deep within the sedimentary sequence. However, accumulations may occur at any depth. Those found within the topmost kilometre or so of seabed sediments are termed 'shallow gas' reservoirs. Shallow gas has been reported from a range of geological environments (see Table 1). No attempt has been made recently to determine the global distribution of shallow gas, but it is clear that such accumulations are quite common.

Blow-outs caused by the accidental penetration of shallow gas pockets have demonstrated that considerable volumes of gas can accumulate; a single accumulation at a depth of less than 230 m beneath the seabed at the Gullfaks Field in the Norwegian North Sea contained an estimated 2.5×10^6 m^3 of gas (Hovland & Judd 1988), approximately 1.8×10^{-3} Terragrammes (Tg) methane.

Gas hydrates

Gas hydrates are ice-like mixtures of water and gas; gas (most commonly methane) molecules are trapped within a cage-like framework of hydrogen-bonded water molecules. These structures are formed under very specific temperature and pressure conditions where sediments contain both water and an adequate supply of gas. These conditions are found on land in polar regions, where surface temperatures are very cold ($< 0^\circ$C), and within seabed sediments where the water depth exceeds 300–500 m and the temperature of the sea bottom water is less than about 5°C (Ginsburg & Soloviev 1998; Kvenvolden 1998, 1999).

Gas hydrates may represent the greatest reservoir of methane carbon on the planet. Estimates vary. Kvenvolden (1999) suggested that the global amount of methane hydrate lies towards the lower or intermediate part of the range 10^{15}–10^{17} m^3 (approximately 7.14×10^5–7.14×10^7 Tg). However, the vast majority of this gas is safely 'locked' within the hydrates, and will remain there unless there is a change in the temperature/pressure conditions critical to hydrate stability.

The distribution of gas hydrates is difficult to ascertain. Bottom simulating reflections (BSRs) on seismic reflection profiles indicate their presence beneath the seabed, but in some places drilling through BSRs has failed to find gas hydrates, and in other cases gas hydrates have been found where there is no BSR. The most reliable estimations of their distribution are based on actual observations rather than 'remote sensing' indications. Present understanding (Ginsburg & Soloviev 1998) indicates that submarine gas hydrates occur in the range of geological environments shown in Table 2. Figure 3 provides an indication of gas hydrate distribution, but the current interest in them is such that this map is likely to become out of date very quickly. The largest area in which the presence of gas hydrates has been 'proved' is on the Blake Ridge, off the Atlantic coast of the USA. This area of

Table 2 Geological environments in which natural gas hydrates occur (details from Ginsburg & Soloviev 1998).

Geological environment	Examples
Deep-water basins of Mediterranean and marginal seas	Caspian, Black and Okhotsk Seas, the Gulf of Mexico
Continental slopes of convergent margins	Peru and Middle America Trenches, Nankai Trough and northern California and Cascadia margins
Submarine tectonic regions	Okushiri Ridge, Sea of Japan
Continental slopes of passive margins	Blake Outer Ridge, offshore eastern USA
Polar shelves	Arctic and Antarctic
Spreading basins	Guaymas Basin, Gulf of California

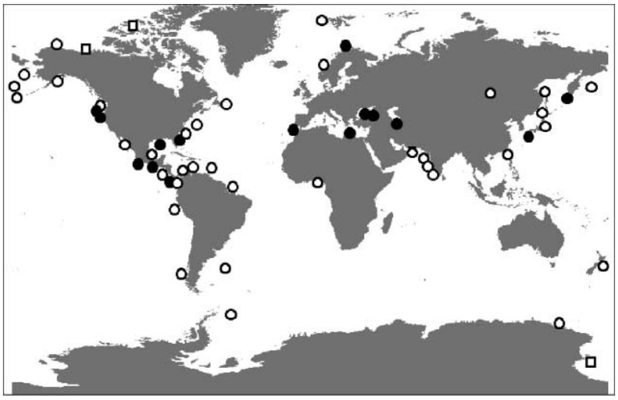

Fig. 3. Distribution of gas hydrates (data from Ginsburg & Soloviev 1998, Kvenvolden 2000, and others). Sampled (filled symbol) 'inferred' (open symbol) those for which evidence, such as bottom simulating reflections (BSRs), have been recorded on seismic profiles. Circles, in sediments of the outer continental margin; squares, in polar (permafrost) regions.

approximately 20 200 km^2 is thought to contain about 7.8×10^{13} m^3 (approximately 56 500 Tg) of methane gas (Max & Dillon 1998).

Utilization

Methane reaching the seabed sediments is subjected to oxidation. Current understanding of the processes involved points to the prevalence of anaerobic oxidation via sulphate reduction; dissolved methane is efficiently removed by syntrophic consortia of methanogenic archaea (operating in reverse) and sulphate-reducing bacteria. Although there are, as yet, no well-constrained data available, it seems that anaerobic oxidation removes a significant part of the dissolved methane (Boetius *et al.* 2000; Elvert *et al.* 2000; Hinrichs *et al.* 2000; Pancost *et al.* 2001).

Bicarbonate produced by the anaerobic oxidation of methane via sulphate reduction can lead to the precipitation of calcium carbonate to form rock-like 'methane-derived authigenic carbonates' (Dando & Hovland 1992; Hovland & Judd 1988; Thiel *et al.* 2001; Wallmann *et al.* 1997, etc.). Macrofaunal 'cold seep communities' capitalize on this microbial activity. Individual species derive their energy via thiotrophic or methanotrophic symbionts (Dando & Hovland 1992; Sibuet & Olu 1998; Suess *et al.* 1998, etc.).

Escape pathways

Methane bubbles rising through the seabed sediments too quickly to be consumed by oxidation escape through the seabed (Albert *et al.* 1998; Boone 2000; Martens *et al.* 1998). Observations and experimental research have shown that migration tends to be focused through discrete migration pathways. These pathways may be geological faults or, in fine-grained sediments, pathways formed specifically by the rising gas (Harrington & Horseman 1999; Horseman *et al.* 1999; Judd & Sim 1998) which feed seabed seeps. Mud volcanoes provide other pathways.

Natural gas seeps

The seepage of natural gas is known to be widespread in both land and marine environments (Clarke & Cleverly 1991; Hovland & Judd 1988; Kvenvolden & Harbaugh 1983; Landes 1973; Link 1952; Wilson *et al.* 1974). Gas seeps are known to be associated with leakage from gas reservoirs and shallow gas accumulations and from gas hydrates; consequently, they occur in all the environments identified in Tables 1 and 2.

Extensive surveys capable of detecting gas seeps have been undertaken; however, the majority have been undertaken by the petroleum industry, either during prospecting operations (Thrasher *et al.* 1996), or because of the need to survey drilling sites for potentially hazardous accumulations of 'shallow gas' (Prince 1990; Walker 1990). The details of such surveys are, largely, not in the public domain. Judd *et al.* (1997) demonstrated that published distributions of gas seeps are underestimates.

Mud volcanoes

Mud volcanoes are landforms that bear a morphological resemblance to true (igneous) volcanoes (see Fig. 4), but they

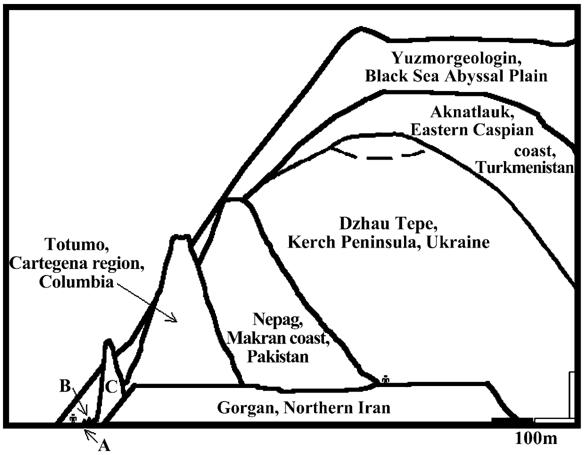

Fig. 4. Sizes and shapes of various terrestrial and submarine volcanoes. Mud volcanoes occur in an enormous range of sizes — both offshore and onshore. The smallest are less than a metre wide, the largest are >500 m tall and 3–4 km across the base. In some areas, the combined mud flows of groups of mud volcanoes cover >100 km^2. (A) Mangaehu Stream, New Zealand; (B) Volcanito, Cartegena region, Colombia; (C) Moruga Bouff, Trinidad.

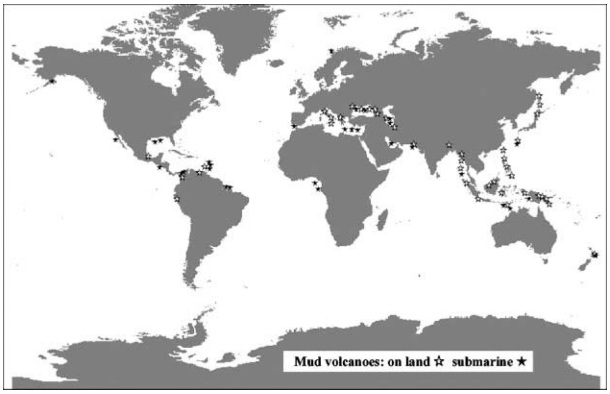

Fig. 5. Distribution of mud volcanoes. Mud volcanoes are found predominantly in areas with high rates of sedimentation and/or tectonic compression. For further details, see Dimitrov (2002).

are formed by the expulsion of water, gas and mud from sedimentary sequences. There has been a long history of the investigation of mud volcanoes which have been known for centuries; for example, they were described by Pliny in his '*Naturalis Historia*' (AD 77). Relatively recently it has become known that they also occur on the seabed.

Mud volcanoes have been described from many parts of the world: the southern Caspian Basin (Guliyiev & Feizullayev 1996; Sokolov *et al.* 1969), the Black Sea (Ivanov *et al.* 1996), Taiwan (Shih 1967), Indonesia (Barber *et al.* 1986), the West Indies (Brown & Westbrook 1988; Higgins & Saunders 1967), Alaska (Reitsema 1979) and the Mediterranean Ridge (Ivanov *et al.* 1996; Limonov *et al.* 1996), etc. Generally, they occur in zones of tectonic compression, the accretionary prisms formed by the collision of two tectonic plates. However, they also occur in tectonically inactive areas where sediment deposition rates are (or have been) high (e.g. the Amazon and Niger Deltas, the Dgungar Plain of China and the Norwegian and Black Seas, etc.). The distribution of mud volcanoes is shown in Fig. 5. It is estimated that there are more than 1700 such features (>1000 on land, >700 on the seabed; Dimitrov 2002).

Hedberg (1980), Brown (1990) and Milkov (2000) provided detailed discussions of the mechanism of mud volcano formation. Briefly, formation results from the rise of gas- and water-bearing muddy sediments from depth (in some cases several kilometres). The principal driving mechanism is an abnormally high pore fluid pressure caused by a combination of rapid sedimentation of fine-grained material, *in situ* gas generation and (in most, but not all, cases) tectonic compression. If pore fluids are unable to escape, the sediments become progressively less dense than the overlying, compacting sediments. At some stage, the density contrast is sufficient for buoyancy forces to initiate upward movement which, once started, is perpetuated as gases expand. As a result, either a body of gassy, semiliquid sediment rises through the overlying sediments *en masse*, or the fluids migrate, entraining some sediment material as they rise.

Kalinko (1964) classified mud volcanoes into three types.

(1) Lokbatan type: characterized by infrequent explosive activity, and the ignition of the emitted gases. The emitted sediments are very viscous so that steep, conical mud volcanoes are often formed. Usually, long passive periods are terminated by short periods of explosive activity when blocked feeder channels are cleared by excessive pore fluid pressure. The most recent eruption of Lokbatan itself was in October 2001.

(2) Chikishlyar type: characterized by calm, relatively weak and continuous activity during which gas is emitted at a more or less uniform rate. Mud volcanoes of this type tend to occur where there are water-bearing sediments at relatively shallow depths. They form low, flat domes or shallow, water-filled depressions.

(3) Schugin type: these are transitional between the above types and are characterized by weak activity interrupted by intermittent eruptive periods.

Dissolution in the water column

As bubbles rise from the seabed, a proportion of methane is lost to the hydrosphere by solution and microbial oxidation. In deep waters, plumes of methane-rich water have been identified rising from seep sites (e.g. Aleutian subduction zone — Suess *et al.* 1998; Hydrate Ridge on the Cascadia Margin — Suess *et al.* 1999), but it is generally considered that this methane does not reach the surface waters. However, surface waters with methane concentrations in excess of equilibrium with the atmosphere have been reported in shallower locations, for example over methane-rich sediments in the North Sea (Rehder *et al.* 1998) and Eckernförde Bay, Germany (Bussmann & Suess 1998). In such cases, the waters will be a source of atmospheric methane.

The ability of methane bubbles to survive passage through the water column is dependent upon the bubble size and rise velocity, and the presence of surfactants on the bubble surface (Judd *et al.* 1997; Leifer & Patro submitted). Surfacing bubble plumes are most likely to be found in shallow water, for example in Santa Barbara Channel, California (Hornafius *et al.* 1999; Leifer *et al.* 2000). However, Cranston *et al.* (1994) reported that bubbles were seen at the surface above a gas seep in 700 m of water in the Sea of Okhotsk.

At sites where gas hydrates are stable at the seabed, the possibility that methane may rise to the surface may be increased. Chunks of hydrate detached from the seabed rise rapidly. Although they dissociate as they rise, the methane bubbles produced are more likely to reach the surface than bubbles rising from the seabed (Rehder *et al.* 2001).

Exceptionally, major releases of gas from the seabed, from erupting mud volcanoes or sub-seabed reservoirs (including gas hydrates), may produce large volumes of gas which burst through the water into the atmosphere. Gas emitted during eruptions of Lokbatan-type seabed mud volcanoes may spontaneously combust on reaching the sea surface, sometimes producing flames tens or even hundreds of metres high.

THE METHANE BUDGET

Natural gas seeps

Global estimates of the contributions of atmospheric methane by seabed seeps have been undertaken by various authors. Ehhalt & Schmidt (1978) used the Wilson *et al.* (1974) study of the world-wide distribution of oil seepages for their calculation of the oceanic flux of methane. Trotsyuk & Avilov (1988) measured the disseminated flux of methane in the Black Sea and extrapolated world-wide. Lacroix (1993) calculated hydrocarbon reservoir depletion and migration rates and, by estimating the rate of removal by oxidation, etc., derived an estimate of the rate of emission to the atmosphere. Hovland *et al.* (1993) used published estimates of seabed flux rates and seepage distributions to arrive at a global estimate for the flux at the seabed. Cranston (1994) considered methane release by coastal sediments, marine sediments and gas hydrates. Hornafius *et al.* (1999) quantified the emissions from the prolific Coal Oil Point seeps, California, and used the resultant data to revise the global estimates of Hovland *et al.* (1993). They concluded that the natural gas seeps of the continental shelves account for between 3% and 9% of total global methane emissions. Judd *et al.* (1997) and Dimitrov (submitted) estimated the numbers of seeps on the continental shelves of the UK and Bulgaria, respectively, and used published seabed flux rates and models of loss to solution in the water column to derive estimated fluxes to the atmosphere. García-Gil *et al.* (submitted) applied a similar approach to Ría de Vigo, north-west Spain. These estimates are summarized in Table 3. Judd (2000) suggested that a total of 0.4–12.2 Tg year^{-1} is emitted to the atmosphere from natural seabed seeps world-wide.

Seeps which emit methane direct to the atmosphere also occur onshore, for example, in hydrocarbon (coal and petroleum)-bearing sedimentary basins (Clarke & Cleverly 1991; Clayton *et al.* 1993; Selley 1992; Simoneit *et al.* 1979; USGS 2000). Stadnik *et al.* (1986) showed that the measured atmospheric methane levels in 11 regions of the former USSR were consistently higher in petroliferous areas (1.97–6.6 p.p.m.; mean, 3.47 p.p.m) compared to the regional background (1.15–2.9 p.p.m.; mean, 1.85 p.p.m). However, no estimates of the atmospheric contributions made by onshore gas seeps are available, other than an estimate of 0.2–0.9 Tg CH_4 year^{-1} from the permafrost regions of the former USSR (Andronova & Karol 1993). The global contribution of these onshore areas is not considered in this paper, although the contribution they make is no doubt significant (Hornafius *et al.* 1999).

Gas hydrates

Gas seeps are also found in association with gas hydrates. Gas bubbles rising from gas hydrates exposed on the seabed have been described, for example from the Sea of Okhotsk (Cranston *et al.* 1994), the Gulf of Mexico (MacDonald *et al.* 1994) and Hydrate Ridge (Suess *et al.* 1999). However, because of the great water depths involved, the amount of methane contributed to the atmosphere by submarine gas hydrates is probably not great (about 3 Tg CH_4 year^{-1}, according to Kvenvolden 1988). The majority of methane escaping from deep-water hydrates is likely to dissolve in the water column rather than enter the atmosphere.

Mud volcanoes

The composition of the gases emitted by most mud volcanoes is dominated by methane, although some produce CO_2 and/or nitrogen. The volumes emitted are generally small, but during their short periods of catastrophic activity, Lokbatan-type mud volcanoes produce gas with sufficient force to eject enormous volumes of rock over a considerable area. The volumes of gases emitted during such eruptions are also considerable, although natural ignition reduces the effective flux to the atmosphere.

Several estimates have been made of the gas emissions from Azerbaijan and the southern Caspian mud volcano province. For example Hovland *et al.* (1998) estimated an annual emission of at least 800 m^3 (5.6×10^{-8} Tg) of gas, mainly

Table 3 Estimates of methane emissions from natural seabed seepages.

Location	Estimate ($Tg\,CH_4\,year^{-1}$)	At seabed or to atmosphere	Source	Notes
(a) Regional estimates				
United Kingdom continental shelf	0.12–3.5	Atmosphere	Judd *et al*. (1997)	
Coal Oil Point, California	0.029 ± 0.005	Atmosphere	Hornafius *et al*. (1999)	
Bulgarian Black Sea continental shelf	0.03–0.15	Atmosphere	Dimitrov (submitted)	
Ría de Vigo, north-west Spain	0.0001–0.004	Atmosphere	García-Gil *et al*. (submitted)	Similar fluxes probably occur in other rias in north-west Spain: Pontevedra, Arosa and Muros
Black Sea continental shelf	0.36–1.6	Atmosphere	Dimitrov (submitted)	Extrapolated from the Bulgarian continental shelf
(b) Global estimates				
World's oceans	1.3–16.6	Atmosphere	Ehhalt & Schmidt (1978)	Estimate based on the seep distribution of Wilson *et al*. (1974)
Continental shelves	1.9	Seabed	Trotsyuk & Avilov (1988)	The disseminated flux of methane in the Black Sea extrapolated world-wide
Continental shelves	8–65	Seabed	Hovland *et al*. (1993)	At seabed (no account made of losses to the water column)
Global	17 ± 14	Atmosphere	Lacroix (1993)	Based on estimates of hydrocarbon reservoir depletion and migration rates and the rate of removal by oxidation, etc.
World's oceans and marine sediments	1–10	Atmosphere	Cranston (1994)	Coastal sediments, marine sediments and gas hydrates
Continental shelves	18–48	Atmosphere	Hornafius *et al*. (1999)	Method of Hovland *et al*. (1993) applied to new data
Global seabed seeps	0.4–12.2	Atmosphere	Judd (2000)	Calculated using the method of Hovland *et al*. (1993), applied to data derived by Judd *et al*. (1997)

methane, from a single mud volcano, but few estimates have been made from elsewhere. These include estimates of continuous emissions by Chikishlyar-type mud volcanoes, and more problematic estimates of Lokbatan types (which involve estimating volumes per eruptive phase and the periodicity of eruptions). These estimates are summarized in Table 4. As a first approximation, it is estimated that the global emission of methane from mud volcanoes is between 7.8 and 10.1 Tg year^{-1}.

Total geological methane emissions

The methane generation sources and pathways described above, plus other geological sources, probably contribute between 13.5 and 37.5 Tg CH_4 year^{-1} to the atmosphere (see Table 5). This is thought to be a conservative estimate. In the absence of a reliable estimate of the proportion of the seabed (particularly on the continental shelves) associated with seepage, care has been taken to avoid overestimation; also, contributions from onshore seeps are largely unaccounted for. Seabed emissions also supply a considerable (but unquantified) amount of methane to the hydrosphere.

The significance of the continental margins

In the context of the total atmospheric methane budget (535 Tg year^{-1} — Houghton *et al.* 1996, table 3, p. 18), geological sources (shown in Table 5) represent about 2.4–6.7% of the total methane source, of which approximately 1.2–3.6% comes from the continental margins. This is a significant proportion and is more than is generally acknowledged by atmospheric scientists; note that the Inter-Governmental Panel for Climate Change (IPCC) budget (Houghton *et al.* 1996; Fig. 1) does not include a category called 'geological sources'. This contribution is particularly important in that it is largely 'fossil' methane (the exception being microbial methane currently being generated in seabed sediments). A total of 70–120 Tg year^{-1} (best estimate, 110 Tg year^{-1}) arises from fossil sources (Houghton *et al.* 1996, table 3, p. 18), of which 30–50 Tg is 'unaccounted for' (Crutzen 1991). It is normally assumed that the fossil

Table 4 Estimates of methane emissions from mud volcanoes (adapted from Dimitrov 2002).

	Estimate (Tg CH_4 year^{-1})				
Location	Calm period	Eruptive phase	Total	Source	Notes
Baku region, Azerbaijan	0.0008–0.00026	0.15–0.36	0.061	Sokolov *et al*. (1969)	Estimated average for the Quaternary period
Azerbaijan	0.014	0.18	0.2	Jakubov *et al*. (1971)	
Azerbaijan	0.36	0.25 0.36–0.72 up to 28.7		Zorkin *et al*. (1982) Kudryavtzev 1984*	
Southern Caspian mud volcano province	0.15	0.07–0.36	0.02–0.16	Geodekyan 1984*	Estimated average for the Quaternary period
Eastern Azerbaijan	0.14	0.015–0.36		Dadashev 1984*	
Kerch Peninsula, Ukraine	0.05			Plotnikov 1984*	
Azerbaijan	0.014		0.22	Guliyiev & Feizullayev (1996)	
Azerbaijan			0.125	Valyayev (1998)	Average over the past 1 million years
Kerch-Taman Peninsulas, Black Sea	0.00011–0.00052			Glebov & Shelting (1998)	
Seabed mud volcanoes near Barbados	0.00032 [0.003†]			Foucher & Henry (1996)	
	0.33–2.64	7.5	7.8–10.1	Dimitrov (2002)	Global — estimated by multiplying the average of the estimates by the estimated number of mud volcanoes

*Quoted in Ali-Zade *et al*. (1984).
†From dissociation of gas hydrates.

Table 5 Contributions to atmospheric methane from natural geological sources.

	Natural release pathways		
	Offshore (Tg CH_4 year^{-1})	Onshore (Tg CH_4 year^{-1})	Source
Natural seabed gas seeps	0.4–12.2	–	Judd (2000)
Mud volcanoes	3.2–4.3	4.6–5.8	Dimitrov (2002)
Gas hydrates	3	–	Kvenvolden (1988)
Onshore emissions (permafrost regions of the former USSR only)	–	0.2–0.9	Andronova & Karol (1993)
Hydrothermal/geothermal activity	–	0.9–3.2	Lacroix (1993) (land events only)
Volcanic activity	–	0.8–6.2	Lacroix (1993) (land events only)
Natural coal seam fires	–	<1	Lacroix (1993)
Total	6.6–19.5	6.5–16.1	13.1–35.6

fuel industries are solely responsible for fossil methane emissions. However, it is clear that they are not responsible for the natural emissions discussed in this paper; consequently, the contribution required of these industries to account for the 'missing' fossil methane can be reduced. A revised budget is presented in Fig. 6. Also, these geological sources predate the Industrial Revolution.

GEOLOGICAL METHANE AND CLIMATE CHANGE

Atmospheric methane concentrations have varied in sympathy with the rises and falls in temperature throughout the last 40 000 years in Greenland (Chapellaz *et al.* 1993) and for more than 150 000 years in Antarctica (Jouzel *et al.* 1993;

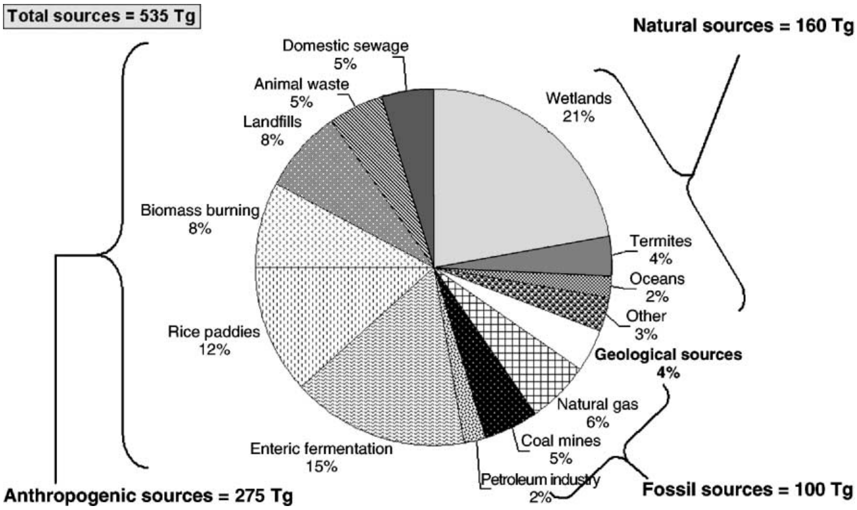

Fig. 6. Sources of atmospheric methane — a revised estimate (based on Fig. 1, plus natural geological sources identified in Table 5).

Raynaud *et al.* 1993) (see Fig. 7). Lowe & Walker (1997) recognized the apparent relationships between atmospheric gas concentrations (especially CO_2 and methane) and climatic change, and identified variations in the concentrations of these gases as one of the factors which may play a role in modulating or amplifying the Quaternary climatic shifts brought about, primarily, by orbital forcing. Woodwell *et al.* (1998) concluded that the oceans must have been a major source of atmospheric carbon during the period of warming since the last glacial maximum, enabling atmospheric concentrations to rise despite the net flow of carbon into the plants and soil of the land areas uncovered by the retreating ice.

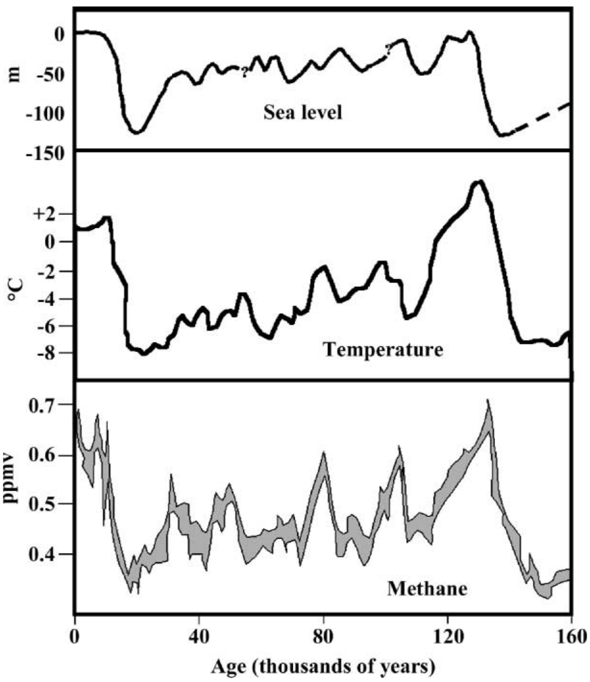

Fig. 7. Correlation between eustatic sea-level, temperature and atmospheric methane concentrations. Eustatic sea-level (in metres relative to present sea-level) taken as sea-level of the Huon Peninsula, New Guinea, corrected for local tectonic effects (redrawn from Chappell & Shackleton 1986). Temperature (in °C relative to present temperature) and atmospheric methane concentrations (in p.p.m. per volume) are from the Vostok Ice Core, Antarctica (redrawn from Houghton 1997, fig. 4.4, p. 54).

A link between the release of methane from gas hydrates into the atmosphere and changes in global temperature was suggested by Severinghaus *et al.* (1998), who considered that methane concentration rose as a consequence of the temperature rise. However, Nisbet (1992), Kennett *et al.* (1996, 2000) and Thorpe *et al.* (1996), amongst others (see Haq 1998, for a summary), postulated that sudden, catastrophic releases of methane from gas hydrates to the atmosphere may have acted as the trigger for the rises in global temperature at the beginning of each Dansgaard-Oeschger rapid global warming event during the last glacial; Kennett *et al.* (1996) referred to this as the 'clathrate-gun hypothesis'. Thorpe *et al.* (1996) used modelling to assess the impact on the global climate of a single methane release of this type. An implication which may be drawn from their work is that multiple catastrophic methane releases (multiple firings of the clathrate gun) may have been necessary to have made a significant contribution to the rapid temperature rise that brought about the end of glacial periods. Chapellaz *et al.* (1993) reported a lack of evidence of the 'spike' of methane concentration that would be expected to appear as a result of such events. Whereas Thorpe *et al.* (1996) considered this to be inconsequential (because of the poor resolution of the records), Raynaud *et al.* (1998) considered that the ice-core records would be capable of detecting such massive pulses of methane, but found none. However, Blunier *et al.* (1995) considered that the lack of evidence for methane 'spikes' in the ice-core record did not rule out continuous hydrate decomposition from melting permafrost as a methane source.

Previous discussions about geological methane and global climate change (Haq 1998; Nisbet 1990, 1992; Paull *et al.* 1991; Raynaud *et al.* 1998; Thorpe *et al.* 1996, 1998) have focused on the role of gas hydrates. However, it is clear from the previous sections that these are not the only geological sources of methane.

In common with Norris & Röhl (1999) and Katz *et al.* (1999), who considered the climate change event that marked the Palaeocene/Eocene boundary 55 Myr ago, we believe that geological methane releases may play a role in global climate change. However, we do not believe that gas hydrates are necessarily the sole geological agents. Rather, thermogenic gas seeps, microbial gas seeps, mud volcanoes and gas hydrates all play a role.

The rate of emission into the hydrosphere and the atmosphere of geological methane may have been affected by changing rates of generation and the effects of surface conditions on reservoirs and leakage pathways. Key differences between the surface environments of interglacial and glacial periods are, firstly, the geographical extent of permafrost, sea ice and ice sheets, and, secondly, changes in eustatic sea-level and the location of coastlines. At the last glacial maximum, approximately 23 000–18 000 BP, much of the land and continental shelf areas of northern North America, Europe and Asia were ice covered, or were affected by permafrost (Fig. 8). At this time, eustatic sea-level was approximately 120 m lower than it is today (see Fig. 7), exposing large areas of the present continental shelf.

Generation

The changes in surface conditions between glacial and interglacial periods may have affected the distribution and productivity of near-surface sources of microbial gas; however, deeper sources, particularly thermogenic sources, will not have been affected.

Thermogenic methane generation occurs over extended periods of geological time (measured in millions of years) once organic-rich source rocks have achieved thermal maturity. There is no reason to suppose that the migration of methane (and other hydrocarbons) from depth will not have continued throughout the Quaternary glacial and interglacial periods.

Organic-rich sediments, in which microbial methane generation occurs, accumulate in geological environments (see Table 1) which are largely controlled by sea-level. The cycle of falling and rising sea-level and, on land, groundwater level associated with the onset and demise of glacial conditions gives rise to four distinct sedimentary regimes (summarized in Fig. 9) on the continental shelves and slopes (Haq 1991).

(1) Falling sea-level (Fig. 9): continental shelves are progressively exposed and subjected to erosion, leading to the development of a prominent unconformity. Sediments are transported towards and down the continental slope to the basin where they form a basin floor fan during the early phase of lowstand time.

(2) Low sea stand (Fig. 9): sedimentation occurs primarily on the continental shelf margin (the slope fan and the lowstand wedge).

(3) Transgressive sea stand (Fig. 9): the beginning of relative sea-level rise from its lowest position provokes the cessation of stream incision and the infilling of existing incised valleys. As sea-level rise accelerates, the continental shelf is flooded and depocentres progressively migrate landwards, filling the former shelf valleys. This transgressive systems tract thins basinwards and fines upwards forming a condensed section.

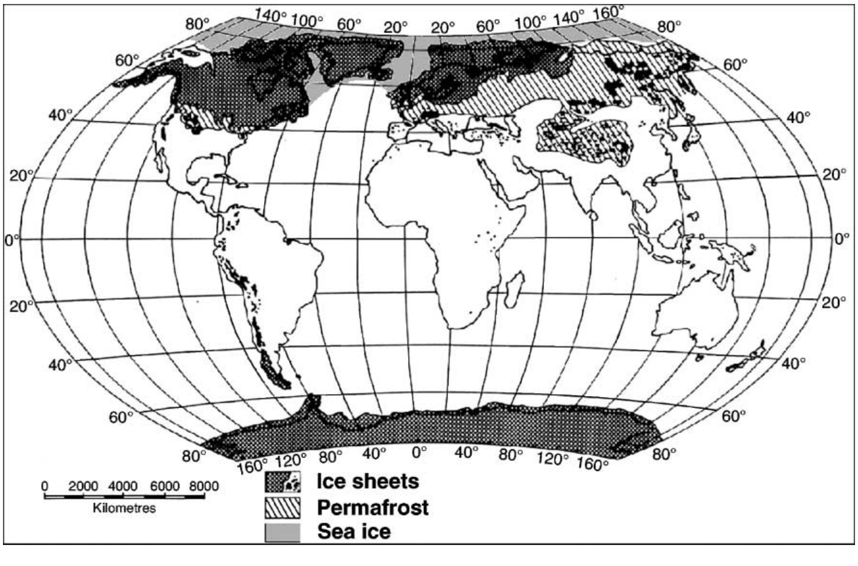

Fig. 8. Extent of ice sheets, permafrost and sea ice at the last glacial maximum (adapted from Williams *et al.* 1993).

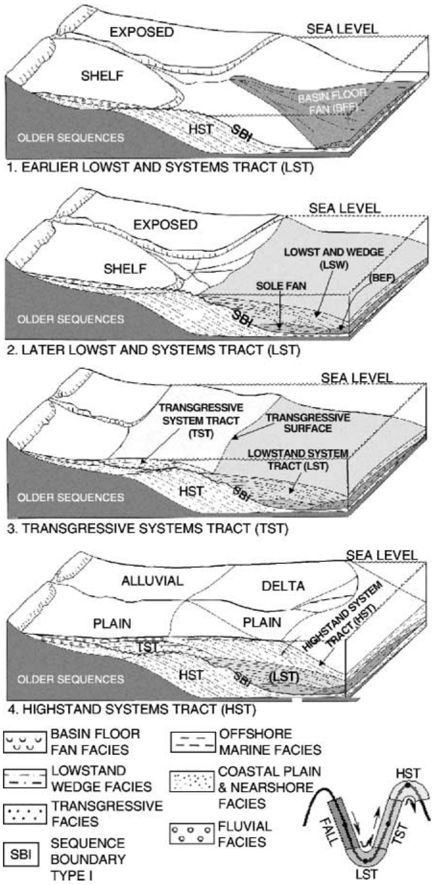

Fig. 9. Coastal depositional environments during a sea-level fall–rise cycle (adapted from Haq 1991). (1) Early lowstand systems tract. Low sea-level. The continental shelf is fully or partially exposed and subject to erosion. Sediment material is transported off the shelf to accumulate in deeper water. (2) Late lowstand systems tract. Shallow-water areas are now incised; deep-water areas have accommodated the sediment. (3) Transgressive systems tract. During sea-level rise sediments are pushed inland across the continental shelf. Sediments derived from rivers are deposited on the shelf. (4) Highstand systems tract. Rapid sedimentation occurs and the coastline builds seawards as sediments are deposited on the continental shelf.

(4) High sea stand (Fig. 9): once the shelf is flooded to the highest level and the sea-level highstand stabilizes, the nearshore accommodation potential decreases and the shoreline begins to regress basinwards (highstand systems tract).

In the above sequence, the sediments of the transgressive and earlier highstand systems tract are the most important for microbial methane generation. The sediments accumulate in shallow water and coastal environments, and are characteristically organic rich due to the high productivity of such areas. They are immediately overlain by sediments of the highstand systems tract; consequently, there is a high potential for preservation. Stanley & Warne (1994) identified 36 deltas world-wide which did not start to form until the Holocene. The time range is consistently between 8500 and 6500 BP. Deltaic sediments and those of coastal environments (bays, estuaries, rias, etc.) are also typically rich in organic matter; shallow gas and gas seeps have been reported from many deltaic and coastal areas (see Table 1).

Reservoirs

Accumulations of both gas bubbles and gas hydrates are affected by variations in hydrostatic pressure caused by the cycle of sea-level changes accompanying glacial–interglacial cycles.

In gas reservoirs, a reduction in hydrostatic head caused by the lowering of sea-level or the exposure of the seabed as the coastline migrates seawards, effectively increases the gas overpressure within a gas reservoir, increasing the likelihood that trapped gas will escape. In contrast, the progressive increase in hydrostatic pressure as sea-level rises will encourage the formation of gas accumulations.

The conditions in which gas hydrates are stable are strictly controlled by temperature and pressure (Ginsburg & Soloviev 1998; Kvenvolden 1998); consequently, the changes in conditions (temperature and hydrostatic pressure) associated with glacial–interglacial cycles are thought to have resulted in significant shifts in the locations of gas hydrate stability zones. It is not necessary to explain this in detail in this paper as many authors have already rehearsed the arguments (see Haq 1998, for a summary); the following summary will suffice.

A 120 m sea-level fall during the last glaciation would have reduced hydrostatic pressure sufficiently to raise the lower boundary of the gas hydrate stability zone by approximately 20 m. The resultant dissociation of gas hydrates is thought to have been responsible for the triggering of massive seabed slope failures. Together, these events are thought to have caused massive gas escapes. During global warming, temperature increases in high latitudes would cause the melting of near-surface gas hydrates.

Kvenvolden (1993) and Haq (1993) suggested that these two processes interacted to provide a negative–positive feedback loop, constraining the severity of both cool and warm periods.

Leakage pathways

Hydrostatic pressure variations caused by varying sea-level and the extent of ice sheets and permafrost will have affected marine and high-latitude leakage pathways, respectively. However, the contributions to atmospheric methane by terrestrial geological sources beyond the maximum extent of ice sheets and permafrost will not have been affected during the Quaternary. It is assumed that their contribution will have been more or less continuous at the present rates. [The distribution of mud volcanoes on land is such that none will have been affected by glaciation during the Pleistocene (see Figs 5 and 8). Consequently, it may be assumed that their contribution will have remained more or less constant throughout this period.]

The lowering of sea-level will have had a double effect on marine leakage pathways, both mud volcanoes and seabed gas seeps. Firstly, the reduction in hydrostatic pressure will have encouraged migration towards, and seepage through, the seabed (as mentioned above). Mud volcanoes located on the seabed would have become underbalanced, and those with significant volumes of gas stored in porous sediments immediately beneath the seabed may have erupted. Secondly, the proportion of methane surviving passage through the water column would have increased as the depth of water decreased, particularly on the continental shelves. Indeed, many areas where seepage currently occurs at the seabed would have been above sea-level during part of the glacial period. A consequence of this may have been an increase in methane oxidation but, where flux rates were high, this process would have permitted uninhibited escape to the atmosphere.

It is anticipated that the majority of the gas (particularly thermogenic gas) generated in high-latitude areas will have been progressively cut off from the atmosphere as the ice-affected zones advanced, gas being either physically trapped beneath ice or permafrost, or sequestered by hydrates.

Lammers *et al.* (1995) and Kvenvolden *et al.* (1995) have both reported seasonal fluctuations in the concentration of dissolved methane in seas (the Okhotsk and Beaufort Seas, respectively) which are covered with ice in the winter. They indicated that the flux of methane to the atmosphere is significantly greater during the period of ice melt. Semiletov (1999) also reported that sea ice is an effective barrier, trapping methane in the Laptev Sea. However, he considered that the methane had come from the sediments to the seawater immediately beneath the ice primarily in the form of bubbles.

In view of the above, it seems logical to suggest that gas escape will also have been inhibited by 'permanent' (as opposed to seasonal) ice cover or permafrost. The following have provided evidence that gas has been trapped in this way. Long (1992) argued that the rate of pockmark formation in the central North Sea was not consistent over the postglacial period. Rather, there were periods characterized by unusually prolific pockmark formation (i.e. gas escape) which he correlated with periods of ground ice melting. Judd *et al.* (1994) demonstrated that an unusually large and active pockmark in the UK sector of the North Sea has been partially infilled since its formation (see Fig. 10). By dating the infilling sediments, they estimated that initial pockmark formation occurred, probably as a single 'catastrophic' gas escape event, approximately 13 000 BP. They related this event to the release of gas trapped beneath seabed ice or permafrost as melting occurred.

The event described by Judd *et al.* (1994) and the peak gas escape activity described by Long (1992) both occurred when warm North Atlantic waters entered the North Sea, causing a rapid rise in bottom-water temperatures. Solheim & Elverhøi (1993) reported that large seabed pockmarks in the Barents Sea may have formed by rapid degassing or blow-outs as a result of the destabilization of gas hydrates during the last deglaciation.

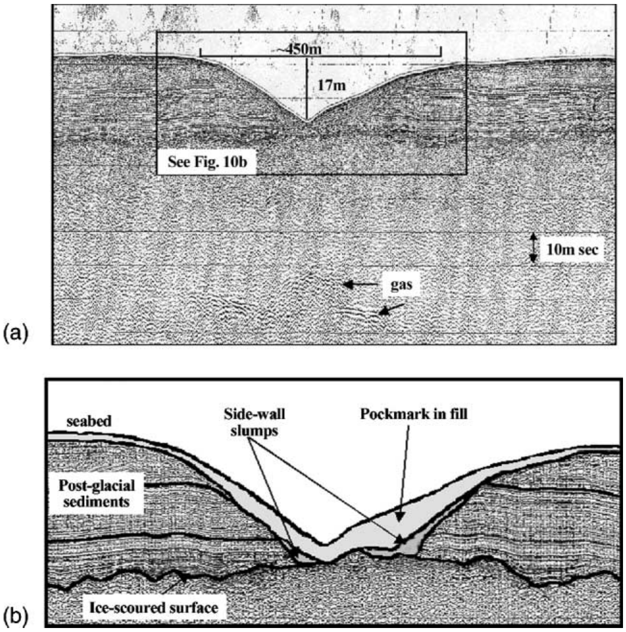

Fig. 10. Catastrophic pockmark formation caused by seabed ice melt. (a) Digital seismic (deep-towed boomer) profile, UK block 15/25, North Sea. (b) Detail showing postglacial sediments overlying an ice-scoured surface. The pockmark is partially infilled by sediments dated at 13 000 BP (Judd *et al.* 1994), indicating that the original pockmark formed before that time. Judd *et al.* (1994) considered that the pockmark formed catastrophically when seabed ice melted, releasing an accumulation of gas.

Together, these cases indicate that gas leakage is inhibited during glacial periods, and that accumulated gas escapes, sometimes catastrophically, during warming.

Seepage-prone continental shelves that were ice or permafrost covered during the last glacial maximum include the North Sea, Baltic Sea, Barents Sea, eastern seaboard of Canada, Bering Sea and Sea of Okhotsk, a total area of approximately 10 000 000 km^2 (see Fig. 8). Judd *et al.* (1997) suggested that the average methane flux to the atmosphere from the UK continental shelf (UKCS) is between 0.2 and 5.6 t km^{-2} year^{-1} [(0.2–5.6) × 10^{-6} Tg]. If these figures are applied to the continental shelf areas identified above, then approximately 2 000 000–56 000 000 t (2–56 Tg) of methane will have been prevented from reaching the atmosphere during each year of permafrost/ice cover.

CONCEPTUAL MODELS FOR NEGATIVE–POSITIVE FEEDBACK

It is evident from the previous section that the emission of natural gas from geological sources does not occur at a constant rate. Flux rates are affected by factors related to the changing climate, but some factors enhance gas emissions, whilst others inhibit them. It seems that the negative–positive feedback models proposed by Kvenvolden (1993) and Haq (1993) are too simplistic as they consider only gas hydrates. A more realistic model would recognize the competing influences of the various sources, reservoirs and leakage pathways. These are summarized as follows.

Global cooling scenarios

Positive feedback to cooling

High latitudes. The advance of permafrost, ice sheets, sea ice and 'polar' gas hydrates progressively inhibits the escape of gas.

Microbial sources in coastal areas and deltas. Organic-rich coastal sediments are removed by erosion as sea-level falls, so that this potential source of microbial methane is removed.

Neutral

Low latitudes — land areas. Sources on land (both seeps and mud volcanoes) are unaffected; present-day flux rates probably apply.

Negative feedback to cooling

Low latitudes — continental shelves. The reduction in hydrostatic pressure that accompanies the lowering of sea-level encourages the migration and escape of gas from both seeps and submarine mud volcanoes. Also, deeply buried offshore hydrocarbon reservoirs will loose confinement pressure and will therefore tend to leak more. The proportion of seeping methane that survives passage to the atmosphere increases because of the reduced depth of water. Seeps left above sea-level may provide methane direct to the atmosphere.

Continental slopes and deep sea. The gas hydrate stability zone migrates downslope as a result of a lowering in sea-level. Hydrates at higher levels dissociate, and significant volumes of methane are released. Major failures of the seabed are initiated by hydrate dissociation, and these are accompanied by releases of enormous volumes of methane (from the hydrates themselves, and from reservoirs capped by hydrates). (To some extent, cooling of ocean bottom waters may counteract this.)

Summary

The environments described above provide both positive and negative feedback to global cooling, as indicated in Fig. 11(A). Because of the enormity of the gas hydrate 'reservoir', it is probable that the most significant effect comes from catastrophic events associated with the decomposition of submarine gas hydrates, in which case the net effect will be a negative feedback, slowing global cooling.

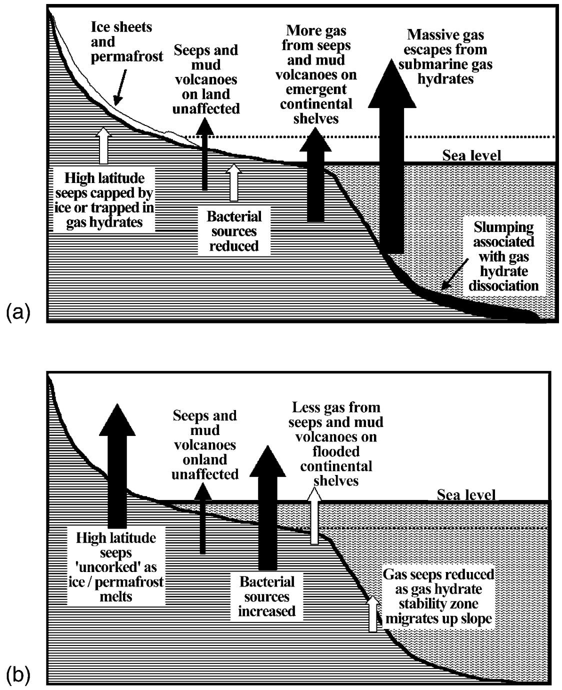

Fig. 11. Contributions of geological sources to atmospheric methane levels: conceptual models. (a) Global warming: high-latitude gas hydrates, ice sheets and permafrost retreat releasing gas. Rates of coastal deposition increase so that microbial methane generation is increased. At low latitudes, sea-level rise impedes seepage from marine sediments, and increases hydrostatic pressure, so that the proportion of seep gas dissolved in the water column rises. On the continental slope and in the deep sea, gas hydrate stability zones migrate upslope increasing the amount of gas sequestered. (b) Global cooling: high-latitude gas hydrates, ice sheets and permafrost advance trapping gas. Coastal sediments are removed by erosion, removing a source of microbial methane. The lowering of sea-level reduces hydrostatic pressure, encouraging seepage and enabling a higher proportion of seep bubbles to escape to the atmosphere. On the continental slope and in the deep sea, the lowering sea-level destabilizes gas hydrates, inducing slope failures — enormous volumes of gas are released. See text for a complete explanation.

Global warming scenarios

Positive feedback to warming

High latitudes. As the ice sheets retreat, permafrost melts and 'polar' gas hydrates dissociate, releasing trapped gas. These escapes may have a significant impact on global methane levels during the time period of glacial retreat.

Microbial sources in coastal areas and deltas. Significant increases in the deposition of organic-rich sediments on the continental shelves (especially in coastal and estuarine areas, and deltas) result in an increase in microbial methane generation (and seepage).

Neutral

Low latitudes — land areas. Sources on land (both seeps and mud volcanoes) are unaffected; present-day flux rates probably apply.

Negative feedback to warming

Low latitudes — continental shelves. Increasing hydrostatic pressure discourages gas migration towards the seabed, and the proportion of seabed seepage gas surviving passage through the water column decreases as the water depth increases.

Continental slopes and deep sea. The gas hydrate stability zone migrates upslope; consequently, the supply of gas from seeps in these areas is progressively reduced as the gas is sequestered in hydrates. (To some extent, warming of ocean bottom waters may counteract this.)

Summary

The environments described above provide both positive and negative feedback to global warming, as indicated in Fig. 11(B). Apparently, high-latitude and coastal environments have the greatest role in promoting climate change, whereas low-latitude and deep-water sources tend to act as buffers. It is probable that the most significant effects come from two sources: (i) the release of gas by retreating ice, permafrost and 'polar' gas hydrates (because of the magnitude of the 'reservoir'); and (ii) the generation of microbial methane in transgressive and highstand systems tract sediments of the continental shelves, coasts, estuaries and deltas (because of the considerable areas affected). Whereas the former commences as soon as the ice retreats, the latter is coincident with the late stages of global warming and subsequent interglacial periods. Together, the effects of these processes are probably dominant, and so the net effect is a positive feedback, accelerating global warming.

DISCUSSION

The processes by which geological methane is generated and released provide conflicting feedbacks to both global cooling and global warming. No doubt some are more influential than others. Perhaps some are most influential at particular phases of the cooling–warming cycle. For example, it is suggested that microbial methane generation in coastal, estuarine and deltaic sediments is most influential during the later stages of warming, and during interglacial periods.

The entrapment of thermogenic gas by submarine gas hydrates and high-latitude ice cover occurs at opposite stages of the glacial–interglacial cycle. In each case, gas entrapment or sequestration provides negative feedback to climate change as supplies of gas are progressively 'turned off'. When the cycle turns, the volume of gas released is dependent upon the duration of the previous cycle; the longer the previous cycle, the greater the reservoir of gas awaiting release. At individual locations, gas release events may be catastrophic, with large volumes of gas being emitted. However, these events will be phased as the ice retreats or the sea-level falls. Over any single time period, the impact of the gas release events will be a function of the number and size of the gas reservoirs, and the rate at which gas reservoirs are 'uncorked'.

It is possible that the geological sources of atmospheric methane and the processes discussed here effectively constrain glacial–interglacial cycles. Others have suggested that gas hydrates alone may perform this task, ensuring that neither cooling nor warming is allowed to 'run away'. The evidence presented here suggests that the situation is more complex than that, and that other geological factors contribute to the 'geological thermostat'. However, it would be short-sighted to think that geological sources alone can explain the vagaries of our climate. Non-geological influences on atmospheric methane levels must be recognized (Severinghaus *et al.* 1998 considered that wetlands were the dominant source of atmospheric methane prior to the Industrial Revolution), as must the role of other 'greenhouse gases', and the whole must be considered within the context of orbital cycles, etc.

In order to evaluate the role of geological sources of methane (i.e. to test the proposed model), both the magnitude and the timing of each of the individual processes must be established. In particular, the role of mud volcanoes (both the catastrophic Lokbatan-type outbursts and continuous Chikishlyar-type emissions) should be investigated, as should that of the sediments of coastal and continental shelf seas (identified by Bange *et al.* 1994 and Bates *et al.* 1996 as the most significant source in the 'oceans'). This work is now underway.

CONCLUSIONS

On the continental margins, the most important geological gas is methane formed by the destruction (microbial and thermogenic) of organic material in sediments and sedimentary rocks. Reservoirs of geological methane may occur within the sediments at any depth, right up to the seabed. Methane is also sequestered by gas hydrates.

Geological methane is released to the hydrosphere and the atmosphere by two main pathways: natural gas seeps and mud volcanoes. It is estimated that 6.6–19.5 Tg year^{-1} of methane from the continental margins enters the atmosphere, and a similar amount enters the hydrosphere. Clearly, this flux is significant and should be recognized as a component of the global carbon cycle. This is significant, particularly as the majority is 'fossil' (^{14}C-depleted) methane. The entire fossil methane budget should not be attributed to the fossil fuel industries. They can only be responsible for the portion not emitted naturally.

Whilst thermogenic methane generation continues at depth regardless of the surface conditions, rates of microbial methane generation may vary during the glacial–interglacial cycle; peak generation occurs during sea-level highstands (i.e. interglacials).

Positive and negative feedbacks to global climate change are made during all phases of glacial–interglacial cycles by geological methane from different sources and reservoirs. The net effect, whether positive or negative feedback, is dependent upon:

(1) the relative disposition of gas sources with respect to sea-level, and the extent of ice sheets, permafrost and gas hydrate stability zones;

(2) the amount of sea-level rise or fall;

(3) the duration of glacial–interglacial cycles;

(4) the rapidity of climate change.

It is suggested that geological methane (of which that associated with gas hydrates is just one component) is one of the influences on global climate, and that it may have an influence over the rapidity of climate change and the extremes of climate achieved. In particular, it is considered that the influences of mud volcanoes and of coastal and continental shelf sediments are worthy of more detailed investigation.

Lowe & Walker (1997) concluded that:

> ‘Conceptual models like those of Oerchger challenge us to examine more closely the importance of gas exchanges between the atmosphere and other reservoirs, and the ways in which these, and their potential feedback mechanisms, can affect the global climate system.’ (Lowe & Walker 1997, p. 371.)

We agree, and suggest that increased attention should be paid to geological sources of methane.

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REFERENCES

Albert DB, Martens CS, Alperin MJ (1998) Biogeochemical processes controlling methane in coastal sediments — Part 2. Groundwater flow control of acoustic turbidity in Eckernförde Bay sediments. *Continental Shelf Research*, **18**, 1771–94.

Ali-Zade A, Shnyokov E, Grigorianz B, Aliev A, Rahmanov R (1984) Geotektonicheskie uslovia proyavleniya gryazevih vulkanov mira i ih znachenie dlya prognozirovaniya gasoneftenosnosti nedr. *Proceedings of the 27th World Geological Congress*, **C13**, 166–72.

Andronova NG, Karol IL (1993) The contribution of USSR sources of global methane emission. *Chemosphere*, **26**, 111–26.

Bange HW, Bartell UH, Rapsomanikis S, Andreae MO (1994) Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. *Global Biogeochemical Cycles*, **8**, 465–80.

Baraza J, Ercilla G, Nelson CH (1999) Potential geologic hazards on the eastern Gulf of Cadiz slope (SW Spain). *Marine Geology*, **155**, 191–215.

Barber AJ, Tjokrosapoetro S, Charlton TR (1986) Mud volcanoes, shale diapirs, wrench faults and mélanges in accretionary complexes, eastern Indonesia. *American Association of Petroleum Geologists, Bulletin*, **70**, 1729–41.

Bates TS, Kelly KC, Johnson JE, Gammon RH (1996) A reevaluation of the open ocean source of methane to the atmosphere. *Journal of Geophysical Research*, **101**, 6953–61.

Blunier T, Chapellaz J, Schwander J, Stauffer B, Raynaud D (1995) Variations in atmospheric methane concentration during the Holocene epoch. *Nature*, **374**, 46–9.

Boetius A, Ravenschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A, Amann R, Jørgensen BB, Witte U, Pfannkuche O (2000) A marine microbial consortium apparently mediating anaerobic methane oxidation. *Nature*, **407**, 623–6.

Boone DR (2000) Biological formation and consumption of methane. In: *Atmospheric Methane: Its Role in the Global Environment* (ed. Khalil MAK), pp. 42–62. Springer, Berlin.

Brekke T, Lønne Ø, Ohm SV (1997) Light hydrocarbon gases in shallow sediments in the northern North Sea. *Marine Geology*, **137**, 81–108.

Brown KM (1990) The nature and hydrogeologic significance of mud diapirism and diatremes from accretionary systems. *Journal of Geophysical Research*, **95**, 8969–82.

Brown KM, Westbrook GK (1988) Mud diapirism and subcretion in the Barbados Ridge Complex. *Tectonics*, **7**, 613–40.

Bussmann I, Suess E (1998) Groundwater seepage in Eckernförde Bay (western Baltic Sea): effect on methane and salinity distribution of the water column. *Continental Shelf Research*, **18**, 1795–807.

Chapellaz J, Blunier T, Raynaud D, Barnola JM, Schwander J, Stauffer B (1993) Synchronous changes in atmospheric CH_4 and Greenland climate between 40 and 8 kyr BP. *Nature*, **366**, 443–5.

Chappell J, Shackleton NJ (1986) Oxygen isotopes and sea level. *Nature*, **324**, 137–40.

Clarke RH, Cleverly RW (1991) Petroleum seepage and post-accumulation migration. In: *Petroleum Migration, Geological Society Special Publication No. 59* (eds England WA, Fleet AJ), pp. 265–71. Geological Society of London, Bath.

Clayton JL, Leventhal JS, Rice DR, Pashin JC, Mosher D, Czepiel P (1993) Atmospheric methane flux from coals — preliminary investigations of coal mines and geologic structure in the Black Warrior Basin, Alabama. In: *The Future of Energy Gases, United States Geological Survey Prof. Paper 1570* (ed. Howell DG), pp. 471–92. United States Printing Office, Washington.

Cranston RE (1994) Marine sediments as a source of atmospheric methane. *Bulletin of the Geological Society of Denmark*, **14**, 101–9.

Cranston RE, Ginsburg GD, Soloviev VA, Lorenson TD (1994) Gas venting and hydrate deposits in the Okhotsk Sea. *Bulletin of the Geological Society of Denmark*, **41**, 80–5.

Crutzen PJ (1991) Methane's sinks and sources. *Nature*, **350**, 380–1.

Dando PR, Hovland M (1992) Environmental effects of submarine seeping natural gas. *Continental Shelf Research*, **12**, 1197–208.

Dimitrov LI (2002) Mud volcanoes: the most important pathway for degassing deeply-buried sediments. *Earth Sciences Review*, in press.

Dimitrov LI (submitted) Contribution to atmospheric methane by natural seepages on the Bulgarian continental shelf. *Continental Shelf Research*, submitted .

Ehhalt DH, Schmidt U (1978) Sources and sinks of atmospheric methane. *Pure Applied Geophysics*, **116**, 452–64.

Elvert M, Suess E, Greinert J, Whiticar MJ (2000) Arachaea mediating anaerobic methane oxidation in deep-sea sediments at cold seeps of the eastern Aleutian subduction zone. *Organic Chemistry*, **31**, 1175–87.

Floodgate GD, Judd AG (1992) The origins of shallow gas. *Continental Shelf Research*, **12**, 1145–56.

Foucher JP, Henry P (1996) Fluid venting from mud diapiric structures: the example of the mud diapiric field seaward of the deformation front of the Barbados accretionary complex at 14°N. In: *Sedimentary Basins of the Mediterranean and Black Seas, 4th Post-Cruise Meeting of the TTR Program, 27 January–4 February 1996, Moscow.*

García-García A, Vilas F, García-Gil S (1999) A seeping sea-floor in a Ria environment. Ria de Vigo (NW Spain). *Environmental Geology*, **38**, 296–300.

García-Gil S, Vilas F, García-García A (submitted) Shallow gas features in incised-valley fills (Ría de Vigo NW Spain): a case study. *Continental Shelf Research* **submitted**.

Ginsburg GD, Soloviev VA (1998) *Submarine Gas Hydrates.* Statoil, Norway.

Glebov A, Shelting S (1998) Estesvennie vedelenija uglevodorodnih gasov v Chernom more. In: *Proceedings of the 1st International Symposium 'Environmental Aspects of the Exploration, Production and Transportation of the Oil and Gas in and through the Black Sea', Varna, Bulgaria*, pp. 45–47(in Russian).

Guliyiev IS, Feizullayev AA (1996) Geochemistry of hydrocarbon seepages in Azerbaijan. In: *Hydrocarbon Migration and its Near-Surface Expression, American Association of Petroleum Geologists Memoir, 66* (eds Schumacher D, Abrams MA), pp. 63–70. American Association of Petroleum Geologists, Tulsa.

Haq BU (1991) Sequence stratigraphy, sea-level change, and significance for the deep sea. *International Association of Sedimentologists, Special Publication*, **12**, 3–39.

Haq BU (1993) Deep sea response to eustatic change and the significance of gas hydrates for continental margin stratigraphy. *International Association of Sedimentologists, Special Publication*, **18**, 93–106.

Haq BU (1998) Natural gas hydrates: searching for the long-term climatic and slope-stability records. In: *Gas Hydrates: Relevance to World Margin Stability and Climate Change, Geological Society Special Publication No. 137* (eds Henriet J-P, Mienert J), pp. 303–18. Geological Society of London, Bath.

Harrington JF, Horseman ST (1999) Gas transport properties of clays and mudrocks. In: *Muds, Mudstones: Physical, Fluid Properties, Geological Society Special Publication No. 158* (eds Aplin AC, Fleet AJ, Macquaker JHS), pp. 107–24. Geological Society of London, Bath.

Hart BS, Hamilton TS (1993) High-resolution acoustic mapping of shallow gas in unconsolidated sediments beneath the Strait of Georgia, British Columbia. *Geo-Marine Letters*, **13**, 49–55.

Hasiotis T, Papatheodorou G, Kastanos N, Ferentinos G (1996) A pockmark field in the Patras Gulf (Greece) and its activation during the 14/7/93 seismic event. *Marine Geology*, **130**, 333–44.

Hedberg HD (1980) Methane generation and petroleum migration. In: *Problems of Petroleum Migration, American Association of Petroleum Geologists, Studies in Geology No. 10* (eds Roberts WH III, Cordell RJ), pp. 179–206. American Association of Petroleum Geologists, Tulsa.

Higgins GE, Saunders JB (1967) Report on 1964 Chatham mud island, Erin Bay, West Indies. *American Association of Petroleum Geologists, Bulletin*, **51**, 183–9.

Hinrichs K-U, Summons RE, Orphan V, Sylva SP, Hayes JM (2000) Molecular and isotopic analysis of anaerobic methane-oxidizing communities in marine sediments. *Organic Chemistry*, **31**, 1685–701.

Hornafius JS, Quigley D, Luyendyk BP (1999) The world's most spectacular marine hydrocarbon seeps (Coal Oil Point, Santa Barbara Channel, California): quantification of emissions. *Journal of Geophysical Research*, **104**, 20 703–11.

Horseman ST, Harrington JF, Sellin P (1999) Gas migration in clay barriers. *Engineering Geology*, **54**, 139–49.

Houghton JT (1997) *Global Warming: the Complete Briefing*, 2nd edn. Cambridge University Press, Cambridge.

Houghton JT, Meira Filho LG, Callander BA, Harris N, Kattenberg A, Maskell K (1996) *Climate Change 1995: The Science of Climate Change.* Cambridge University Press for the Inter-governmental Panel on Climate Change, Cambridge.

Hovland M, Gallagher JW, Clennell MB, Lekvam K (1997) Gas hydrate and free gas volumes in marine sediments: example from the Niger Delta. *Marine and Petroleum Geology*, **14**, 245–55.

Hovland M, Hill A, Stokes D (1998) The structure and geomorphology of the Dashgil mud volcano, Azerbaijan. *Geomorphology*, **21**, 1–15.

Hovland M, Judd AG (1988) *Seabed Pockmarks and Seepages: Impact on Geology, Biology and the Marine Environment.* Graham & Trotman, London.

Hovland M, Judd AG, Burke RA (1993) The global production of methane from shallow submarine sources. *Chemosphere*, **26**, 559–78.

Ivanov MK, Limonov AF, van Weering TjCE (1996) Comparative characteristics of the Black Sea and Mediterranean Sea mud volcanoes. *Marine Geology*, **132**, 253–71.

Jakubov A, Ali-Zade A, Zeinalov M (1971) *Atlas of Mud Volcanoes in the Azerbaijan SSR.* Azerbaijan Academy of Sciences, Baku.

Jouzel J, Barkov NI, Barnola JM, Bender M, Chapellaz J, Genthon C, Kotlyakov VM, Lipenov V, Lorius C, Petit JR, Raynaud D, Raisbeck G, Ritz C, Sowers T, Stievenard M, Yiou F, Yiou P (1993) Extending the Vostok ice-record of palaeo-climate to the penultimate glacial period. *Nature*, **364**, 407–11.

Judd AG (2000) Geological sources of methane. In: *Atmospheric Methane: Its Role in the Global Environment* (ed Khalil MAK), pp. 280–303. Springer, Berlin.

Judd AG, Davies G, Wilson J, Holmes R, Baron G, Bryden I (1997) Contributions to atmospheric methane by natural seepages on the UK continental shelf. *Marine Geology*, **137**, 427–55.

Judd AG, Long D, Sankey M (1994) Pockmark formation and activity, U.K. Block 15/25, North Sea. *Bulletin Geological Society of Denmark*, **14**, 34–49.

Judd AG, Sim R (1998) Shallow gas migration mechanisms in deep water sediments. In: *Offshore Site Investigation and Foundation Behaviour: New Frontiers* (eds Ardus DA, Hobbs R, Horsnell M, Jardine R, Long D, Sommerville J), pp. 163–74. Society of Underwater Technology, London.

Kalinko N (1964) Gryazevie vulkani, prichini ih vozniknovenia, razvitia i zatuhania. *VNIGRI*, **40**, 30–54 (in Russian).

Kaluza MJ, Doyle EH (1996) Detecting fluid migration in shallow sediments: continental slope environment, Gulf of Mexico. In: *Hydrocarbon Migration and its Near-Surface Expression, American Association of Petroleum Geologists Memoir 66* (eds Schumacher D, Abrams MA), pp. 15–26. American Association of Petroleum Geologists, Tulsa.

Katz ME, Pak DK, Dickens GR, Miller KG (1999) The source and fate of massive carbon input during the latest Palaeocene thermal maximum. *Science*, **286**, 1531–3.

Kennett JP, Cannariato KG, Hendy IL, Behl RJ (2000) Carbon isotope evidence for methane hydrate instability during Quaternary interstadials. *Science*, **288**, 128–33.

Kennett J, Hendy I, Behl R (1996) Late Quaternary foraminiferal carbon isotope record of Santa Barbara Basin: implications for rapid climate change (abstract). In: *Annual Meeting of the American Geophysical Union, pF292, San Francisco.*

King LH, MacLean B (1970) Pockmarks on the Scotian Shelf. *Geological Society of America Bulletin*, **81**, 3141–8.

Kvenvolden KA (1988) Methane hydrate and global climate. *Global Biogeochemical Cycles*, **2**, 221–9.

Kvenvolden KA (1993) Gas hydrates — geological perspective and global change. *Reviews of Geophysics*, **31**, 173–87.

Kvenvolden KA (1998) A primer of gas hydrates. In: *Gas Hydrates: Relevance to World Margin Stability and Climate Change, Geological Society Special Publication No. 137* (eds Henriet J-P, Mienert V), pp. 9–30. Geological Society of London, Bath.

Kvenvolden KA (1999) Potential effects of gas hydrate on human welfare. *Proceedings of the National Academy of Science, USA*, **96**, 3420–6.

Kvenvolden KA (2000) Gas hydrates and humans. Gas hydrates. *Annals of the New York Academy of Sciences*, **912**, 17–22.

Kvenvolden KA, Harbaugh JW (1983) Reassessment of the rates at which oil from natural sources enters the marine environment. *Marine Environmental Research*, **10**, 223–43.

Kvenvolden KA, Lilley MD, Lorenson TD (1995) The Beaufort Sea shelf as a seasonal source of atmospheric methane. *Geophysical Research Letters*, **20**, 2459–62.

Lacroix AV (1993) Unaccounted for sources of fossil and isotopically-enriched methane and their contribution to the emissions inventory: a review and synthesis,. *Chemosphere*, **26**, 507–58.

Lammers S, Suess E, Mansurov MN, Anikiev VV (1995) Variations of atmospheric methane supply from the Sea of Okhotsk induced by seasonal ice cover. *Global Biogeochemical Cycles*, **9**, 351–8.

Landes KK (1973) Mother nature as oil polluter. *American Association of Petroleum Geologists, Bulletin*, **53**, 2431–79.

Leifer I, Clark J, Chen R (2000) Modifications of the local environment by a natural marine hydrocarbon seep. *Geophysical Research Letters*, **27**, 3711–4.

Leifer I, Patro RK (submitted) The bubble mechanism for transport of methane from the shallow sea bed to the surface: a review and sensitivity study. *Continental Shelf Research* **submitted**.

Limonov AF, Woodside JM, Cita MB, Ivanov MK (1996) The Mediterranean Ridge and related mud diapirism: a background. *Marine Geology*, **132**, 7–19.

Link WK (1952) Significance of oil and gas seeps in world oil exploration. *American Association of Petroleum Geologists, Bulletin*, **36**, 1505–40.

Long DA (1992) Devensian late-glacial gas escape in the central North Sea. *Continental Shelf Research*, **12**, 1097–110.

Lowe JJ, Walker MJC (1997) *Reconstructing Quaternary Environments*, 2nd edn. Longman, London.

MacDonald IR, Guinasso NL, Sassen R, Brookes JM, Lee K, Scott KT (1994) Gas hydrate that breaches the seafloor on the continental slope of the Gulf of Mexico. *Geology*, **22**, 699–702.

Manley PL, Flood RD (1988) Cyclic sediment deposition within Amazon deep-sea fan. *American Association of Petroleum Geologists, Bulletin*, **72**, 912–25.

Martens CS, Albert DB, Alperin MJ (1998) Biogeochemical processes controlling methane in coastal sediments — Part 1. A model coupling organic matter flux to gas production, oxidation and transport. *Continental Shelf Research*, **18**, 1741–70.

Max MD, Dillon WP (1998) Oceanic methane hydrate: the character of the Blake Ridge hydrate stability zone, and the potential for methane extraction. *Journal of Petroleum Geology*, **21**, 343–57.

McQuaid J, Mercer A (1990) Air pressure and methane fluxes. *Nature*, **351**, 528.

Milkov AV (2000) Worldwide distribution of submarine mud volcanoes and associated gas hydrates. *Marine Geology*, **167**, 29–42.

Milliman JD, Butenko J (1985) Geohazards in the Yellow Sea and East China Sea. In: *Offshore Technology Conference, Houston, Texas, May 1985, paper 4965.*

Nisbet EG (1990) The end of the ice-age. *Canadian Journal of Earth Science*, **27**, 148–57.

Nisbet EG (1992) Sources of atmospheric CH_4 in early postglacial time. *Journal of Geophysical Research*, **97**, 12 859–67.

Norris RD, Röhl U (1999) Carbon cycling and chronology of climate warming during the Paleocene/Eocene transition. *Nature*, **401**, 775–9.

Pancost RD, Hopmans EC, Sinninghe Damsté JS and the MEDINAUT Shipboard Scientific Party (2001) Archael lipids in Mediterranean cold seeps: molecular proxies for anaerobic methane oxidation. *Geochimica et Cosmochimica Acta*, **65**, 1611–27.

Papatheodorou G, Hasiotis T, Ferentinos G (1993) Gas-charged sediments in the Aegean and Ionian Seas, Greece. *Marine Geology*, **112**, 171–84.

Paull C, Ussler W III, Dillon WP (1991) Is the extent of glaciation limited by gas hydrates? *Geophysical Research Letters*, **18**, 432–4.

Prince PK (1990) Current drilling practice and the occurrence of shallow gas. In: *Safety in Offshore Drilling: the Role of Shallow Gas Surveys* (eds Ardus DA, Green CD), pp. 3–26. Kluwer Academic Publishers, Dordrecht.

Raynaud D, Chapellaz J, Blünier T (1998) Ice-core record of atmospheric methane changes: relevance to climatic changes and possible gas hydrate sources. In: *Gas Hydrates: Relevance to World Margin Stability and Climate Change, Geological Society Special Publication No. 137* (eds Henriet J-P, Mienert J), pp. 327–31. Geological Society of London, Bath.

Raynaud D, Jouzel J, Barnola JM, Chapellaz J, Delmas RJ, Lorius C (1993) The ice record of greenhouse gases. *Science*, **259**, 926–34.

Rehder G, Brewer PG, Peltzer ET, Friederich G, Paull CK (2001) Effects of gas hydrate on oceanic methane transport (Abstract). In: EUG XI, Strasbourg, April 2001, *Journal of Conference Abstracts*, 6, p. 158.

Rehder G, Keir RS, Suess E, Pohlman T (1998) The multiple sources and patterns of methane in North Sea waters. *Aquatic Geochemistry*, **4**, 403–27.

Reitsema RH (1979) Gases of mud volcanoes in the Copper River Basin, Alaska. *Geochimica et Cosmochimica Acta*, **43**, 183–7.

Scanlon KM, Knebel HJ (1989) Pockmarks in the floor of Penobscot Bay, Maine. *Geo-Marine Letters*, **9**, 53–8.

Schmuck EA, Paull CK (1993) Evidence for gas accumulation associated with diapirism and gas hydrates at the head of the Cape Fear Slide. *Geo-Marine Letters*, **1**, 145–52.

Schoell M (1988) Multiple origins of methane in the earth. *Chemical Geology*, **71**, 1–10.

Selley RC (1992) Petroleum seepages and impregnations in Great Britain. *Marine and Petroleum Geology*, **9**, 226–44.

Semiletov IP (1999) Aquatic sources and sinks of CO_2 and CH_4 in the polar regions. *Journal of the Atmospheric Sciences*, **56**, 286–306.

Severinghaus JP, Sowers T, Brook EJ, Alley RB, Bender ML (1998) Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice. *Nature*, **391**, 141–6.

Shih TT (1967) A survey of the active mud volcanoes in Taiwan and a study of their types and the character of the mud. *Petroleum Geology of Taiwan*, **5**, 259–311.

Sibuet M, Olu K (1998) Biogeography, biodiversity and fluid dependence of deep-sea cold-seep communities at active and passive margins. *Deep-Sea Research*, **II 45**, 517–67.

Silver EA (1996) Introduction to the special section on fluid flow in the Costa Rica accretionary prism. *Geophysical Research Letters*, **23**, 88.

Simoneit BRT, Crisp PT, Rohrback BG, Didyk BM (1979) Chilean paraffin dirt — II. Natural gas seepage at an active site and its geochemical consequences. In: *Physics and Chemistry of the Earth*, **Vol. 12**: Advances in Geochemistry 1979 (Proceedings of the 9th International Meeting on Organic Geochemistry, Newcastle, September, 1979) (eds Douglas AG, Maxwell JR), pp. 171–6.

Sokolov VA, Buniat-Zade ZA, Geodekian AA, Dadashev FG (1969) The origin of gases of mud volcanoes and the regularities of the powerful eruptions. In: *Advances in Organic Chemistry — 1969* (eds Schenk P, Havemar I), pp. 473–84. Pergamon Press, Oxford.

Solheim A, Elverhøi A (1993) Gas-related sea floor craters in the Barents Sea. *Geo-Marine Letters*, **13**, 235–43.

Stadnik YeV, Sklyarenko I, Ya Guliyev IS, Feyzullayev AA (1986) Methane distribution in the atmosphere above tectonically different regions. *Transactions (Doklady) USSR Academy of Sciences, Earth Science Section*, **289**, 190–2.

Stanley DJ, Warne AG (1994) Worldwide initiation of Holocene marine deltas by deceleration of sea level rise. *Science*, **265**, 228–31.

Suess E, Bohrmann G, von Huene R, Linke P, Wallmann K, Lammers S, Sahling H (1998) Fluid venting in the eastern Aleutian subduction zone. *Journal of Geophysical Research*, **103**, 2597–614.

Suess E, Torres ME, Bohrmann G, Collier RW, Greinert J, Plinke P, Rehder G, Trehu A, Wallmann K, Winckler G, Zuleger E (1999) Gas hydrate destabilisation: enhanced dewatering, benthic material turnover and large methane plumes at the Cascadia convergent margin. *Earth and Planetary Science Letters*, **170**, 1–15.

Thiel V, Peckmann J, Richnow HH, Luth U, Reitner J, Michaelis W (2001) Molecular signals for anaerobic methane oxidation in Black Sea seep carbonates and a microbial mat. *Marine Chemistry*, **73**, 97–112.

Thorpe RB, Law KS, Bekki S, Pyle JA (1996) Is methane-driven deglaciation consistent with the ice-core record? *Journal of Geophysical Research*, **101**, 28 627–35.

Thorpe RB, Pyle JA, Nisbet EG (1998) What does the ice-core record imply concerning the maximum climatic impact of possible gas hydrate release at Termination 1A?. In: *Gas Hydrates: Relevance to World Margin Stability and Climate Change, Geological Society Special Publication No. 137* (eds Henriet J-P, Mienert J), pp. 319–26. Geological Society of London, Bath.

Thrasher J, Fleet AJ, Hay SJ, Hovland M, Düppenbecker S (1996) Understanding geology as the key to seepage in exploration: the spectrum of seepage styles. In: *Hydrocarbon Migration and its Near-Surface Expression, American Association of Petroleum Geologists Memoir 66* (eds Schumacher D, Abrams MA), pp. 223–42. American Association of Petroleum Geologists, Tulsa.

Traynar JJ, Sladen C (1997) Seepage in Vietnam — onshore and offshore examples. *Marine and Petroleum Geology*, **14**, 345–62.

Trotsyuk VY, Avilov VI (1988) Disseminated flux of hydrocarbon gases from the sea bottom and a method of measuring it. *Transactions (Doklady) USSR Academy of Sciences, Earth Science Section*, **291**, 218–20.

Uchupi E, Swift SA, Ross DA (1996) Gas venting and late Quaternary sedimentation in the Persian (Arabian) Gulf. *Marine Geology*, **129**, 237–69.

USGS (United States Geological Survey) (2000) Natural oil and gas seeps in California. http://seeps.wr.usgs.gov/.

Valyayev B (1998) Earth hydrocarbon degassing and oil/gas/ condensate field genesis. *Gasovaya Promishlennost (Gas Industry)*, **1/96**, 6–10.

Von Rad U, Tahir M (1996) Late Quaternary sedimentation on the outer Indus shelf and slope (Pakistan): evidence from high-resolution seismic data and coring, *Marine Geology*, **138**, 193–236.

Walker PM (1990) UKOOA recommended procedures for mobile drilling rig site surveys (geophysical and hydrographic) — shallow gas aspects. In: *Safety in Offshore Drilling: the Role of Shallow Gas Surveys* (eds Ardus DA, Green CD), pp. 257–90. Kluwer Academic Publishers, Dordrecht.

Wallmann K, Linke P, Suess E, Bohrmann G, Sahling H, Schlüter M, Dählmann A, Lammers S, Greinert J, von Mirbach N (1997) Quantifying fluid flow, solute mixing, and biogeochemical turnover at cold vents of the eastern Aleutian subduction zone. *Geochimica et Cosmochimica Acta*, **61**, 5209–19.

Wever ThF, Abegg F, Fiedler HM, Fechner G, Stender I (1998) Shallow gas in the muddy sediments of Eckernförder Bay, Germany. *Continental Shelf Research*, **18**, 1715–40.

Whiticar MJ (1990) A geochemical perspective of natural-gas and atmospheric methane. *Organic Geochemistry*, **16**, 531–47.

Williams MAJ, Dunkerley DJ, de Decker P, Kershaw AP, Stokes T (1993). *Quaternary Environments*. Edward Arnold, London.

Wilson RD, Monaghan PH, Osanik A, Price LC, Rogers MA (1974) Natural marine oil seepage. *Science*, **184**, 857–65.

Woodwell GM, Mackenzie FT, Houghton RA, Apps A, Gorham E, Davidson E (1998) Biotic feedbacks in the warming of the Earth. *Climatic Change*, **40**, 495–518.

Zorkin L, Dadashev F, Bairamova G (1982) Geozimicheskie poiski hefti I gasa v Azerbaijan. *Geological Hefti I Gasa*, **4**, 42–5(in Russian).