Reappraisal of the fossil methane budget and related emission from geologic sources

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[1] Converging evidence from new top-down and bottom-up estimates of fossil "radiocarbon-free" methane emissions indicates that natural geologic sources account for a substantial component of the atmospheric methane budget. Comparing emission estimates based on atmospheric $^{14}CH_4$ ("radiomethane") with geologic emissions from seepage, including terrestrial macroseeps, microseepage, marine seeps, and geothermal/volcanic emissions from the Earth's crust, shows that such "geo-CH_4" sources can be conservatively estimated at 53 ± 11 Tg yr^{-1} globally. This makes geo-CH_4 second in importance to wetlands as a natural methane source. Such a new appraisal can easily be accommodated within the uncertainty of the global methane budget as recently compiled, and recognizes the importance of geophysical out-gassing of methane generated within the lithosphere. We propose a new coherent contemporary budget in which 30 ± 5% (based on atmospheric radiomethane measurements) of the global source of 582 ± 87 Tg yr^{-1} has fossil origin, both natural and anthropogenic. **Citation:** Etiope, G., K. R. Lassey, R. W. Klusman, and E. Boschi (2008), Reappraisal of the fossil methane budget and related emission from geologic sources, *Geophys. Res. Lett.*, *35*, L09307, doi:10.1029/2008GL033623.

1. Introduction

[2] Methane is the most abundant hydrocarbon in the atmosphere and one of the primary greenhouse gases that contribute as much as 20% of the anthropogenic radiative forcing in the contemporary atmosphere. Although the efficacy of any reduction in anthropogenic methane emission depends upon the enduring level of its natural background, there remain large uncertainties and gaps in our knowledge of those natural emissions [*Lelieveld et al.*, 1998; *Houweling et al.*, 2000]. Methane sources can be "modern", incorporating radiocarbon (^{14}C) from contemporary biological activity (both natural such as wetlands, termites, wild animals, and anthropogenically mediated such as rice agriculture, ruminants, wastes, biomass burning), and radiocarbon-free "fossil", derived from natural gas formed and accumulated in the Earth crust in the geologic past. "Fossil methane" emissions include both anthropogenic, arising from coal, oil and natural gas exploitation as fossil fuels and their associated infrastructures, and natural arising from methane production in the lithosphere, its migration along tectonic dislocations, and seepage.

[3] The fossil component of the global methane source has long been accepted as about 20% (the "fossil fraction") [*Lelieveld et al.*, 1998; *Denman et al.*, 2007]. This value is traceable to an estimate of 18 ± 9% by *Quay et al.* [1999] based on a 9-year data set of atmospheric $^{14}CH_4$ (1987–1995) at Olympic Peninsula, near Seattle, Washington, USA. (All uncertainties cited in this paper are nominally $\pm 2\sigma$ or 95% confidence limits). A global methane source of 582 ± 87 Tg yr^{-1} [*Denman et al.*, 2007] would therefore imply a "fossil" emission of approximately 118 ± 17 Tg yr^{-1} (disregarding the uncertainty in the fossil fraction of 20%). Such a 'top-down' estimate of the global fossil emission is consistent with 'bottom-up' estimates of around 100 Tg yr^{-1} for anthropogenic sources together with a minor natural component from geologic seepage and gas hydrates not exceeding 15 Tg yr^{-1} [e.g., *Houweling et al.*, 2000].

[4] While such consistency is reassuring, it can also be flawed. In particular, the fossil fraction estimate has broad uncertainty, due to a limited data set and to poorly-quantified emissions of nucleogenic $^{14}CH_4$ from nuclear-power facilities. Furthermore, the natural fossil assessment was based on a few speculative and misquoted estimates of submarine seepage, without consideration of terrestrial seepages. In the last five years, a series of studies focused on fossil methane from two opposite perspectives: atmospheric measurements enable the top-down reassessment of the global fossil fraction and emission [*Lassey et al.*, 2007]; and improved coverage by geologic measurements enable better bottom-up assessment of the natural fossil CH_4 emission from the lithosphere (thermogenic, microbial and geothermal methane, i.e. "geo-CH_4") [*Etiope and Klusman*, 2002; *Etiope*, 2004; *Kvenvolden and Rogers*, 2005]. In this paper we update and compare the results of the two independent perspectives, and we formulate a new coherent view of the role of fossil methane in the global methane budget.

2. New Atmospheric "Fossil Fraction" Estimate

[5] Estimates of ~20% for the methane fossil fraction, f, presented in successive IPCC assessments [*Prather et al.*, 2001; *Denman et al.*, 2007] derive from interpretations of atmospheric $^{14}CH_4$ that are heavily affected by large uncertainties due to the ill-determined emission of $^{14}CH_4$ by nuclear-power industry. Recently, *Lassey et al.* [2007] have applied a regression approach to simultaneously estimate both f and the nuclear-power source strength. Based on a multi-investigator data set spanning both hemispheres from 1986 to 2000, *Lassey et al.* [2007] reestimated f at 30.0 ± 4.6%. While this estimate is 50% larger than the earlier estimate, the very large, but often over-looked, uncertainty

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Table 1. Global Emissions of Methane From Geologic Source Categories

	Emission, Tg yr^{-1}	References
Mud volcanoes	5–10	*Etiope and Klusman* [2002]
	10.3–12.6	*Dimitrov* [2002]
	6	*Milkov et al.* [2003]
	6–9	*Etiope and Milkov* [2004]
Other macro-seeps	3–4	This work
Marine seepage	18–48	*Hornafius et al.* [1999]
	10–30 (***20***)	*Kvenvolden et al.* [2001]
Microseepage	>7	*Klusman et al.* [1998]
	10–25	*Etiope and Klusman* [2008]
Geothermal/volcanic areas	1.7–9.4	*Lacroix* [1993]
	2.5–6.3[a]	*Etiope and Klusman* [2002]
	<1[b]	This work
Total[c]	30–70	*Etiope and Klusman* [2002]
	13–36[d]	*Judd* [2004]
	35–45[e]	*Etiope and Milkov* [2004]
	45[e]	*Kvenvolden and Rogers* [2005]
	40–60	*Etiope et al.* [2004]; *Etiope and Klusman* [2008]
	42–64	This work – best estimate
	30–80	This work – extended range

[a]Volcanoes not considered.
[b]Only volcanoes.
[c]Gas hydrates not considered.
[d]Microseepage not considered.
[e]Included former microseepage estimate.

in the latter (e.g., 18 ± 9%) [*Quay et al.*, 1999] means that the two estimates are nonetheless consistent.

[6] In avoiding the need to specify the nuclear-power emission strength, the approach of *Lassey et al.* [2007] yielded a much smaller uncertainty than for earlier estimates of *f*. The uncertainty cited is that in a regression fit to annually binned $^{14}CH_4$ data, and in general decreases with increasing regression interval. However, the longer the interval, the more unlikely it is that the methane budget can be taken as unchanging as is presumed. *Lassey et al.* [2007] argued that inventory changes were indiscernible during the 15-year duration used, 1986–2000. This was supported by regressions over 10-year sub-intervals 1986–1995 and 1991–2000 which yielded insignificantly different estimates for *f*, giving confidence in the robustness of *f* over 1986–2000.

[7] With the work by *Lassey et al.* [2007] predating the IPCC Fourth Assessment Report [*Denman et al.*, 2007], it is appropriate to recalculate *f* using revised budget data. Specifically, in place of 560 ± 80 Tg yr^{-1} used by Lassey et al. for the global source strength, the revised value 582 ± 87 Tg yr^{-1} leads to a recalculated value for *f* of 30.2 ± 4.6%. Furthermore, we now have $^{14}CH_4$ data to 2004, though post-2000 data is approximately semi-annual from a single site (Baring Head, New Zealand, which may be the only site at which $^{14}CH_4$ is now being measured). Using the 2001–2004 data in place of the noisy but multi-site, high-frequency data for 1986–1989 [*Lassey et al.*, 2007, Figure 1] allows a determination for *f* over the 15-year regression interval 1990–2004 that yields $f = 27.2 \pm 7.4\%$. This estimate is lower but insignificantly different from that for 1986–2000, and with a higher uncertainty that reflects the poorer data coverage of those last four years. In this paper we adopt 30 ± 5% for the "contemporary" value for *f*.

3. Natural Fossil Methane Seepage: Refining the Global Emission Estimate

[8] The second and the third Assessment Reports of IPCC [*Schimel et al.*, 1996; *Prather et al.*, 2001], as well as most of methane budget literature [e.g., *Lelieveld et al.*, 1998; *Houweling et al.*, 2000], consider gas hydrates as dominating the natural geologic CH_4 emission. Nevertheless, most of the gas escaping from deep-sea hydrates dissolves in the seawater column rather than entering the atmosphere. The global gas hydrate emission to the atmosphere was reported to be between 3 and 10 Tg yr^{-1} [*Lelieveld et al.*, 1998], but these are "suggestions" that are not based on experimental data or verified estimation methodologies [*Kvenvolden and Rogers*, 2005]. Recent studies identify geologic sources that are presently much more important than gas hydrates. There has been growing consensus on the importance of marine seeps, independent from gas hydrates, as global contributors to the atmosphere [e.g., *Judd*, 2004]. In addition, studies since 2001 have reported abundant terrestrial releases of methane produced within the Earth crust [*Etiope and Klusman*, 2002; *Etiope et al.*, 2004, 2006, 2007a]. Major emissions are related to hydrocarbon production in sedimentary basins (microbial and thermogenic methane) and, subordinately, to geothermal areas (inorganic reactions or thermal breakdown of organic matter in magmatic or volcanic systems). Specifically, four main sources are distinguished: terrestrial macroseeps, microseepage, marine seeps and geothermal/volcanic emissions. These sources are widely described and discussed elsewhere [*Etiope and Klusman*, 2002; *Etiope et al.*, 2007b; *Judd*, 2004].

[9] Thanks to hundreds of flux measurements conducted in Europe, Asia and the USA, "emission factors" (emissive fluxes by seepage classification) of all geologic sources have become well established. Table 1 summarizes geo-CH_4 emission estimates. The global geo-CH_4 emission of about 40–60 Tg yr^{-1}, which is acknowledged in the 2007 IPCC Assessment Report [*Denman et al.*, 2007], was derived using estimates based on the largest available measurement data sets for the four categories of Table 1 (bold numbers): 6–9 Tg yr^{-1} for mud volcanoes, 10–25 Tg yr^{-1} for microseepage, ~20 Tg yr^{-1} for submarine seepage and

2.5–6.3 Tg yr^{-1} from geothermal systems. While the submarine emission estimate is a consensus value within a range of 10–30 Tg yr^{-1} [*Judd*, 2004] based on theoretical considerations [*Kvenvolden et al.*, 2001], the estimates of onshore emissions are based on direct measurements and upscaling procedures recommended by the EMEP/CORINAIR Guidelines, following the concepts of "emission factor" and "homogeneous area" or "point" sources [*European Environment Agency*, 2004; *Etiope et al.*, 2007b].

[10] We have rechecked these source strengths, using data acquired in the last 3 years. Based on new data from Italy, Romania and Taiwan [*Etiope et al.*, 2007a; *Hong and Yang*, 2007; *Etiope*, 2008], the emission factors for mud volcanoes and microseepage remain appropriate even if conservative. A small adjustment should be made to the volcanic emission estimates. *Kvenvolden and Rogers* [2005] favor an average value of ~4 Tg yr^{-1} taken from *Lacroix* [1993]. Recent reappraisals of the CH_4 content of volcanic gas [*Ryan et al.*, 2006; *Etiope et al.*, 2007b], however, suggest a lower CH_4 source potential. A simple calculation based on the average range of volcanic CO_2/CH_4 ratio (in the order of 10^3–10^4) and on the global volcanic CO_2 flux of 300 Tg yr^{-1} [*Mörner and Etiope*, 2002] suggests a global CH_4 output <1 Tg yr^{-1}, confirming that volcanoes are not an important CH_4 source [*Ryan et al.*, 2006]. Geothermal systems, often independent of active volcanoes, are much more important, as recently shown by bottom-up estimates in Europe [*Etiope et al.*, 2007b]. Other minor geologic sources not quantified here include natural efflux from coal-bearing rocks (generally influenced by mining activities), and outgassing from the crystalline basement and mantle.

[11] While macro-seepage in sedimentary basins should include both mud volcanoes and other types of gas vents that are independent of mud volcanism, global emission estimates have previously been proposed only for mud volcanoes. To complete the picture, we now incorporate a first estimate for other macro-seeps based on the wider data base currently available. Active seeps occur in most of the 112 countries hosting petroleum systems. The global number of terrestrial seeps exceeds 10,000 [*Clarke and Cleverly*, 1991]; an updated global database by Fugro Robertson Ltd (GIR™) reports 13,500 onshore seeps. The latter data set likely includes mud volcanoes of which about 930 are known onshore [*Etiope and Milkov*, 2004]. The actual number of seeps independent of mud volcanism would then be at least 12,500. We have constructed a database of fluxes directly measured or visually estimated from 66 gas seeps in 12 countries. For gas seeps with a diameter <1 m the flux is typically between 0.1 and 100 t yr^{-1}. Fluxes exceeding 1000 t yr^{-1} are associated with larger seeps with vigorous degassing. The aggregate emission from all 66 seeps is estimated at about 6600 t yr^{-1}. At a seep site, however, gas is released not only from the vents, but also pervasively over large areas of surrounding soil (orders of 10^3–10^4 m^2) [*Etiope et al.*, 2007a] because a vent is generally only the main expression of leakage from a larger gas-bearing fracture system. Numerous gas flux surveys show that the amount of gas released from the surrounding soil can be about 3 times higher than that from the vent alone [*Etiope et al.*, 2004, 2006, 2007a; *Hong and Yang*, 2007]. Accordingly, methane release from the 66 seeps is likely to sum to about 20,000 t yr^{-1}. Assuming they are statistically representative of the world seep population of ~12500 seeps, the total methane output would be about 3.8 Tg yr^{-1}. We can cross-check this macro-seepage estimate by applying an alternative extrapolative approach. The flux distribution of the 66 seeps suggests three different classes of flux: 79% of seeps have flux up to 30 t yr^{-1} (lower class), 15% have flux from 30 to 300 t yr^{-1} (medium class) and 6% have flux >300 t yr^{-1} (higher class). The average flux values in each class roughly correspond to 10, 100 and 1000 t yr^{-1}, respectively. Figure 1 shows the potential emission for macro-seeps on the basis of these low, medium and high emission factors, and the number of seeps. Assuming the 66 seeps are statistically representative in terms of flux distribution of the global macro-seep population, then the plot would suggest a total emission in the order of ~3 Tg yr^{-1}. Combining the two estimates, we suggest that 3–4 Tg yr^{-1} characterizes the global emission from macro-seeps other than mud volcanoes, an estimate that will improve as the seep-flux data set is extended. For comparison, Figure 1 also shows the microseepage potential. Incorporating this new macro-seep estimate, our best estimate for the global geo-CH_4 source is in the range 42–64 Tg yr^{-1}, or 53 ± 11 Tg yr^{-1} (Table 1).

4. Revised Budget

[12] Of the global methane source of 582 ± 87 Tg yr^{-1} [*Denman et al.*, 2007], a fossil fraction of 30 ± 5% implies a fossil source of 175 ± 39 Tg yr^{-1}. Identified fossil emissions from human activities aggregate to 90 ± 16 Tg yr^{-1}, based on the range of bottom-up estimates cited by *Denman et al.* [2007]. Adding the geo-CH_4 source of 53 ± 11 Tg yr^{-1} accounts for 143 ± 19 Tg yr^{-1}, leaving a residual fossil emission of 32 ± 42 Tg yr^{-1}. Though insignificantly different from zero, the residual emission may suggest that some natural and/or anthropogenic fossil emissions are yet to be identified or accounted for. In particular, abandoned coal mines are not included in the 90 ± 16 Tg yr^{-1}. The new estimate of the geo-CH_4 source makes it the second most important natural methane source behind wetlands with estimated global emission of 100–230 Tg yr^{-1} [*Denman et al.*, 2007].

5. Implications, Conclusion

[13] Contemporary global data sets of atmospheric radiomethane and geologic seepage emission factors have been independently reexamined, updated and compared. The results challenge the enduring view that natural "fossil methane" is a minor component of the global emission. Bottom-up assessments appraise the total methane emitted naturally from all geologic sources at more than 50 Tg yr^{-1} and potentially approaching 80 Tg yr^{-1} (Table 1).

[14] From the top-down perspective, the newly derived atmospheric fossil fraction f of ~30% would support a geo-CH_4 source strength that is at least 50% of the anthropogenic fossil emission of ~100 Tg yr^{-1}. The estimate for f appears quite robust over 1986–2000, though poor data coverage since 2000 at a time when global atmospheric CH_4 appears to have plateaued hinders post-2000 extension. This view of a significant geo-CH_4 role,

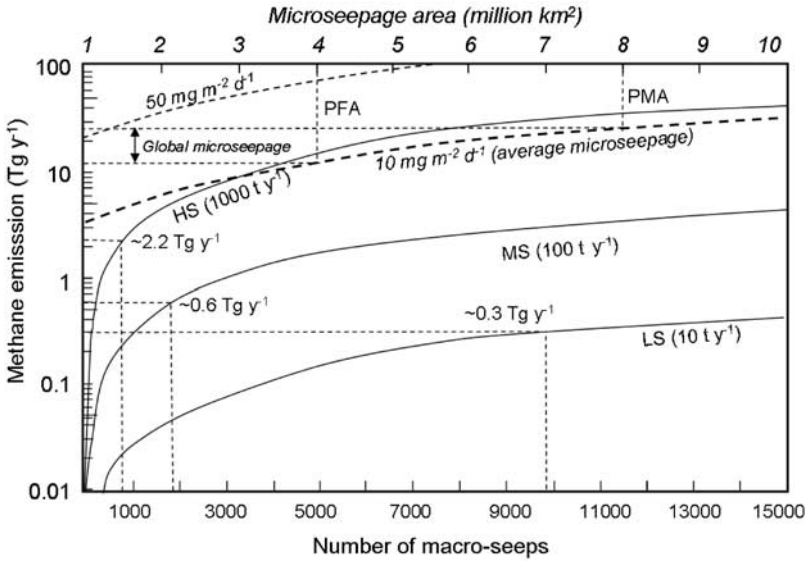

Figure 1. Plot of global methane emission potential from macro-seeps independent of mud volcanism. Macro-seep emission is drawn for Low-flux Seeps (LS), Medium-flux Seeps (MS) and High-flux Seeps (HS) emission factors, derived by the global data set discussed in this work. Considering a total number of 12,500 seeps, a first estimate of 3 Tg y^{-1} can be derived by assuming 750 HS + 1875 MS + 9875 LS (6%, 15% and 79%, respectively, following the flux distribution of the available data set). Microseepage lines (dashed) derived from a global data set by *Etiope and Klusman* [2008] are shown for comparison (10 mg $m^{-2}d^{-1}$ as conservative average flux; PFA, Potential Oil/Gas Field Area ~4 Mkm^2; PMA, Potential Microseepage Area ~8 Mkm^2).

summarized quantitatively in Figure 2, should be incorporated into future appraisals of preindustrial and contemporary methane budgets. Geo-CH_4 emission at the European scale (including Azerbaijan) has recently been estimated at about 3 Tg yr^{-1} [*Etiope*, 2008], which is ~5% of global emission. It is interesting to note that 5% is also the European fraction of global gas reserves. The reassessed geologic source is the second most important natural methane source after wetlands and about 30% of its magnitude; it also comprises about 1/3 of the total contemporary fossil CH_4 emission. This new geo-CH_4 emission estimate, acknowledged also in the latest IPCC assessment [*Denman et al.*, 2007], is based on a robust database covering a wide range of lithosphere degassing processes.

[15] Gas seepage results from advective migration processes, mainly driven by underground fluid pressures, gas buoyancy and fault-induced rock permeability, in turn determined by active tectonics [*Etiope et al.*, 2008]. Furthermore, it is well known that gas migration and surface gas anomalies, eruptions of mud volcanoes, and thus the gas flux into the atmosphere are stimulated by earthquakes [e.g., *Mellors et al.*, 2007]; therefore seismicity and neo-tectonics

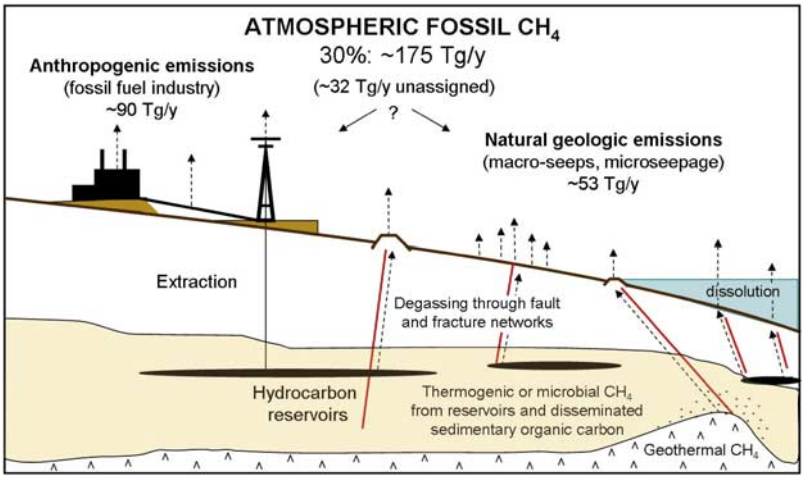

Figure 2. Schematic representation of natural and anthropogenic emissions of fossil methane. Rocks and tectonic discontinuities with enhanced permeability, such as faults or fracture networks, are the natural pathways of degassing. Estimates of uncertainties are omitted for clarity. About 32(±42) Tg y^{-1} of fossil CH_4 are still available to be assigned to man-made or natural sources.

may be significant determinants of methane injection into the atmosphere and its temporal variations. In other words, in view of the enormous amounts of methane released through seepage, the atmospheric greenhouse-gas budget is not independent of geophysical processes in the solid earth, emphasizing the multidisciplinary nature of methane-budget research.

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References

Clarke, R. H., and R. W. Cleverly (1991), Leakage and post-accumulation migration, in *Petroleum Migration*, edited by W. A. England and A. J. Fleet, *Geol. Soc. Spec. Publ.*, 59, 265–271.

Denman, K. L., et al. (2007), Couplings between changes in the climate system and biogeochemistry, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change,* edited by S. Solomon et al., chap. 7, pp. 499–587, Cambridge Univ. Press, Cambridge, U.K.

Dimitrov, L. (2002), Mud volcanoes—The most important pathway for degassing deeply buried sediments, *Earth Sci. Rev.*, *59*, 49–76.

Etiope, G. (2004), GEM—Geologic emissions of methane, the missing source in the atmospheric methane budget, *Atmos. Environ.*, *38*, 3099–3100.

Etiope, G. (2008), Natural emissions of methane from geological sources in Europe, *Atmos. Environ.*, doi:10.1016/j.atmosenv.2008.03.014, in press.

Etiope, G., and R. W. Klusman (2002), Geologic emissions of methane to the atmosphere, *Chemosphere*, *49*, 777–789.

Etiope, G., and R. W. Klusman (2008), Microseepage in drylands: Flux and implications in the global atmospheric source/sink budget of methane, *Global Planet. Change*, in press.

Etiope, G., and A. V. Milkov (2004), A new estimate of global methane flux from onshore and shallow submarine mud volcanoes to the atmosphere, *Environ. Geol.*, *46*, 997–1002.

Etiope, G., A. Feyzullayev, C. L. Baciu, and A. V. Milkov (2004), Methane emission from mud volcanoes in eastern Azerbaijan, *Geology*, *32*, 465–468.

Etiope, G., G. Papatheodorou, D. Christodoulou, G. Ferentinos, E. Sokos, and P. Favali (2006), Methane and hydrogen sulfide seepage in the NW Peloponnesus petroliferous basin (Greece): Origin and geohazard, *AAPG Bull.*, *90*, 701–713.

Etiope, G., G. Martinelli, A. Caracausi, and F. Italiano (2007a), Methane seeps and mud volcanoes in Italy: Gas origin, fractionation and emission to the atmosphere, *Geophys. Res. Lett.*, *34*, L14303, doi:10.1029/2007GL030341.

Etiope, G., T. Fridriksson, F. Italiano, W. Winiwarter, and J. Theloke (2007b), Natural emissions of methane from geothermal and volcanic sources in Europe, *J. Volcanol. Geotherm. Res.*, *165*, 76–86, doi:10.1016/j.jvolgeores.2007.04.014.

Etiope, G., A. V. Milkov, and E. Derbyshire (2008), Did geologic emissions of methane play any role in Quaternary climate change?, *Global Planet. Change*, *61*, 79–88, doi:10.1016/j.gloplacha.2007.08.008.

European Environment Agency (2004), *Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook,* 4th ed., Copenhagen. (Available at http://reports.eea.eu.int/EMEPCORINAIR4/en.)

Hong, W. L., and T .F. Yang (2007), Methane flux from accretionary prism through mud volcano area in Taiwan: From present to the past, paper presented at 9th International Conference on Gas Geochemistry, Natl. Taiwan Univ., Taipei, Taiwan.

Hornafius, J. S., D. Quigley, and B. P. Luyendyk (1999), The world's most spectacular marine hydrocarbon seeps (Coal Oil Point, Santa Barbara Channel, California): Quantification of emissions, *J. Geophys. Res.*, *104*, 20703–20711.

Houweling, S., F. Dentener, and J. Lelieveld (2000), Simulation of preindustrial methane to constrain the global source strength of natural wetlands, *J. Geophys. Res.*, *105*, 17243–17255.

Judd, A. G. (2004), Natural seabed seeps as sources of atmospheric methane, *Environ. Geol.*, *46*, 988–996.

Klusman, R. W., M. E. Jakel, and M. P. LeRoy (1998), Does microseepage of methane and light hydrocarbons contribute to the atmospheric budget of methane and to global climate change?, *Assoc. Pet. Geochem. Explor. Bull.*, *11*, 1–55.

Kvenvolden, K. A., and B. W. Rogers (2005), Gaia's breath—Global methane exhalations, *Mar. Pet. Geol.*, *22*, 579–590.

Kvenvolden, K. A., T. D. Lorenson, and W. Reeburgh (2001), Attention turns to naturally occurring methane seepage, *Eos Trans. AGU*, *82*, 457, 2001.

Lacroix, A. V. (1993), Unaccounted-for sources of fossil and isotopically enriched methane and their contribution to the emissions inventory: A review and synthesis, *Chemosphere*, *26*, 507–557.

Lassey, K. R., D. C. Lowe, and A. M. Smith (2007), The atmospheric cycling of radiomethane and the "fossil fraction" of the methane source, *Atmos. Chem. Phys.*, *7*, 2141–2149.

Lelieveld, J., P. J. Crutzen, and F. J. Dentener (1998), Changing concentration, lifetime and climate forcing of atmospheric methane, *Tellus, Ser. B*, *50*, 128–150.

Mellors, R., D. Kilb, A. Aliyev, A. Gasanov, and G. Yetirmishli (2007), Correlations between earthquakes and large mud volcano eruptions, *J. Geophys. Res.*, *112*, B04304, doi:10.1029/2006JB004489.

Milkov, A. V., R. Sassen, T. V. Apanasovich, and F. G. Dadashev (2003), Global gas flux from mud volcanoes: A significant source of fossil methane in the atmosphere and the ocean, *Geophys. Res. Lett.*, *30*(2), 1037, doi:10.1029/2002GL016358.

Mörner, N.-A., and G. Etiope (2002), Carbon degassing from the lithosphere, *Global Planet. Change*, *33*, 185–203.

Prather, M., et al. (2001) Atmospheric chemistry and greenhouse gases, in *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton et al., pp. 239–287, Cambridge Univ. Press, Cambridge, U.K.

Quay, P., J. Stutsman, D. Wilbur, A. Snover, E. Dlugokencky, and T. Brown (1999), The isotopic composition of atmospheric methane, *Global Biogeochem. Cycles*, *13*, 445–461.

Ryan, S., E. J. Dlugokencky, P. P. Tans, and M. E. Trudeau (2006), Mauna Loa volcano is not a methane source: Implications for Mars, *Geophys. Res. Lett.*, *33*, L12301, doi:10.1029/2006GL026223.

Schimel, D., et al. (1996), Radiative forcing of climate change, in *Climate Change 1995: The Science of Climate Change*, edited by J. T. Houghton et al., pp. 65–131, Cambridge Univ. Press, Cambridge, U.K.

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