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Gas flux to the atmosphere from mud volcanoes in eastern Romania

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ABSTRACT

Gas flux measurements have for the first time been taken from vents and soil of eastern Romania mud volcanoes, the largest geological structures in Europe releasing methane into the atmosphere. In the quiescent phase, the methane emission from single vents is up to 28 t yr^{-1}. Diffuse soil microseepage is of the order of 10^2–10^5 mg m^{-2} day^{-1}. A total output of at least 1200 tonnes of CH_4 per year can be conservatively estimated over the area investigated alone ($\sim$ 2.3 km^2). Helium fluxes are up to five orders of magnitude higher than the average flux in a stable continental area, pointing to a close link between mud volcanoes and crustal degassing through faults crossing the deep hydrocarbon reservoirs. These data represent a key contribution towards refining global CH_4-emission estimates, which indicate mud volcanoes as a significant and unavoidable source of greenhouse gases for the atmosphere.

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Introduction

Natural methane emission from geological sources has recently been recognized as an important component in the atmospheric methane budget. Some authors have only focused their attention on submarine gas seepage and gas hydrates (Judd, 2000; Kvenvolden *et al.*, 2001), recent studies have suggested that mud volcanoes (MVs) on land and microseepage in hydrocarbon-prone areas are also significant geological greenhouse-gas sources (Etiope and Klusman, 2002; Morner and Etiope, 2002; Etiope *et al.*, 2003; Milkov *et al.*, 2003; Etiope and Milkov, 2004). MVs, occurring both on land and on the seafloor, are cone-shaped structures produced by the advective upwelling of sediments (mud) fluidized by water and gas, generally comprising 90–99% CH_4, along faults in petroliferous sedimentary basins (at least 900 subaerial MVs are globally known; Etiope and Milkov, 2004). Although the genesis, geology and geochemistry of MVs have already been described in detail (e.g. Dimitrov, 2002; Kopf, 2002), methane flux to the atmosphere has been the subject of detailed studies only since 2001, when the first measurements, carried out on MVs in southern Italy (Etiope *et al.*, 2002), indicated a CH_4 output of 400 t yr^{-1} over an area of about 1.5 km^2, suggesting a specific flux of the order of 10^2–10^3 t km^{-2} yr^{-1}. Preliminary estimates suggest that MVs provide an annual global supply of the order of 5–10 million tonnes of CH_4 (Etiope and Klusman, 2002; Etiope and Milkov, 2004), i.e. 3–6% of the natural methane sources officially considered in the atmospheric methane budget.

Here we present early data concerning the methane output from the largest MVs in Europe, located in eastern Romania, in the southern part of the Eastern Carpathians Foredeep. Measurements have included localized emissions (vents and bubbling pools, t yr^{-1}) and diffuse soil degassing (mg m^{-2} day^{-1}), in a period with no paroxysmal activity in four areas with MVs and everlasting fires. Vent gases were also analysed to assess the helium (He), nitrogen (N_2) and carbon dioxide (CO_2) concentration and $^3He/^4He$ isotopic ratio as a tracer of gas origin.

Geotectonic setting and site characterization

The eastern boundary of the Carpathian chain consists of two main nappes (Fig. 1), the Cretaceous–Palaeogene (K-Pg) Flysch and the Sub-Carpathian Nappe with Miocene molassic sediments (Sandulescu, 1984). Mud volcano fields occur within the Berca–Arbanasi structure, a strongly tectonized anticlinal fold, orientated north–south and about 20 km long, located in the inner part of the foredeep. The numerous faults crossing the impermeable salt formation and reaching the hydrocarbon reservoirs provide preferential pathways for gas and mud upwelling, leading to MV formation (Paraschiv, 1979). The MVs investigated (Fig. 1) are called Paclele Mari (PMA), Paclele Mici (PMI) and Fierbatori (FI). The PMA and PMI areas host the largest mud volcanoes in Europe and have been declared natural reserves since 1924. The PMA is located in the middle zone of the Berca–Arbanasi structure, intersecting a strike-slip fault with the anticline axis (Fig. 2). The MVs develop across a circular, convex plateau, made up of eruptive products. The mud emerges from the top craters of dozens of domes and from several flank vents (Fig. 3), typically termed gryphons. The active domes and their recent products are distributed over an area of about 0.22 km^2, whereas the products of ancient eruptions occupy a surface of 1.62 km^2 (Sencu, 1985).

The PMI is situated about 2 km north of the PMA, also at the intersection of the anticline axis with a strike-slip dislocation. A central active cone, more than 15 m high, with 5–10° slopes, dominates the plateau. The area

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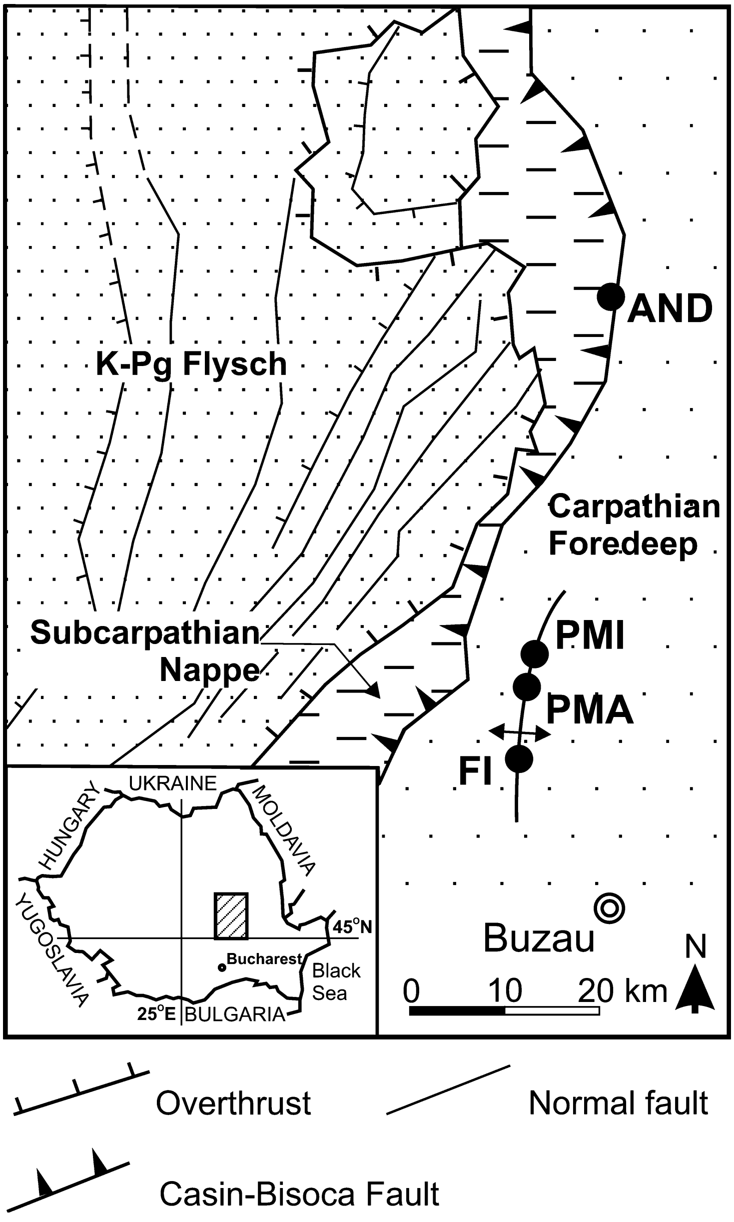

Fig. 1 Sketch map of the geostructural setting of the study area. AND = Andreiasu, PMI = Paclele Mici, PMA = Paclele Mari, FI = Fierbatori. PMI, PMA and FI belong to the wide Berca hydrocarbon-prone area.

with the current muddy products is 0.165 km^2 in size and surrounded by older products, covering a surface of about 0.63 km^2. Significant intermittent activity has been reported (Sencu, 1985) north of the PMI, in the Beciu area. An immense mudflow occurred in the summer of 1975. In November 1976 a huge eruption, with the mud column reaching 1 m in height for 24 h, was observed. In 30 days of activity, about 5000 tonnes of mud was erupted. During a local strong earthquake (M: 7.2) in 1977 the eruption was reactivated for 6 h (Sencu, 1985).

The FI area is located near the southern extremity of the anticline. The terrain is flat, without the convexity observed in the PMA and PMI areas. The mud is very fluid, generating small circular pools. The first mud eruptions were observed in 1881 (Cobalcescu, 1883).

In correspondence with the Casin–Bisoca Fault, near the Andreiasu village (AND; Fig. 1), there are no muddy manifestations, but gas is emitted producing everlasting fires with flames up to 1 m high and bubbling water pools.

Field and laboratory methodologies

The gas output from the vents and diffuse soil degassing was measured by the same devices as reported in Etiope *et al.* (2002), which include the inverted funnel system and the closed-chamber method (Norman *et al.*, 1997; Etiope, 1999). Gas accumulated in the chambers was collected two or three times by syringes following time intervals from 20 s to 10 min from the box emplacement, and analysed by gas chromatography with micro-TCD detector (Etiope, 1997). The number, size and frequency of the bubble trains was recorded in all the pools and gryphons; the gas flux in those vents not accessible for direct field measurement was then estimated using a theoretical plot of bubble flux vs. bubble size vs. bubble frequency (Fig. 4) and compared with direct flux measurements.

Gas samples were collected from the gryphons and water pools in 30-mL Pyrex bottles sealed by two vacuum cocks at the ends for the laboratory analyses of CH_4, CO_2, N_2, He and $^3He/^4He$ isotopic ratio. Chemical analyses were carried out with a Perkin Elmer 8500 gas-chromatograph equipped with a 4-m Carbosieve 5A column and double-detector (flame ionization detector and hot wire detector). The detection limits are 5 ppm (by volume) for O_2 and N_2, and 1 ppm (by volume) for CH_4 and CO_2. Analytical errors are ± 3%. Isotopic analyses of helium were performed by a static vacuum mass spectrometer (VG5400, VG Isotopes modified by the addition of a 'split flight tube') on helium purified from 0.3 mL of gas sample in an ultrahigh-vacuum preparation system. Uncertainties are about ± 1% for $^3He/^4He$ ratios in the range of atmospheric values, below ± 0.1% for high-^3He samples and below ± 3% for low-^3He (radiogenic) samples.

Results

Table 1 lists the chemical composition of the gases sampled at the PMI, PMA,

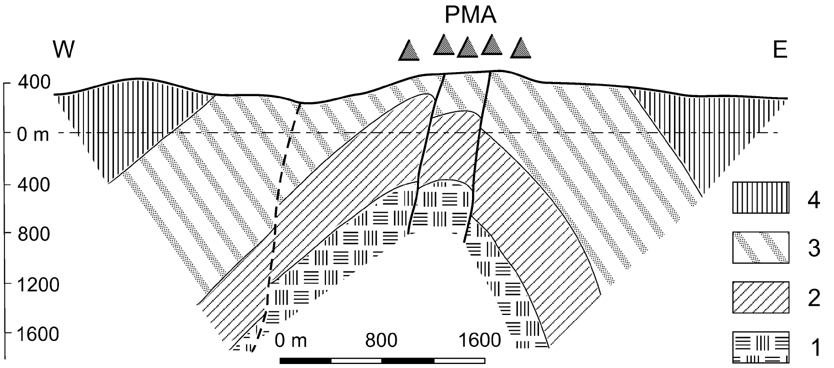

Fig. 2 Geological cross-section of Paclele Mari mud volcano area (modified after Ciocardel, 1949). 1, marls with sand intercalations and salt breccia intrusions (Middle Miocene); 2, sands and calcareous sandstones, oil-bearing formation (Upper Miocene); 3, marls, siltstones (Upper Miocene); 4, marls, siltstones, sands, coal and coaly schist intercalations (Pliocene).

FI and AND sites. The results, showing a CH_4-dominated gas phase, agree well with prior analyses performed over two decades at the PMA and PMI fields (Filipescu and Huma, 1979), which reported a composition of 95–98% CH_4, 0.1–1.2% superior hydrocarbons, 1.5–2.3% CO_2 and 0.1–0.6% N_2. Helium is always present in concentrations well above atmospheric with a $^3He/^4He$ isotope ratio ranging from 2 to 6×10^{-8}, thus showing a typical radiogenic (crustal) origin. Table 2 summarizes the CH_4 flux data. The measured output from single vents ranges from 0.36 to 28 t yr^{-1}. In the PMI area, 65 vents were counted, individually releasing from 1 to 28 t yr^{-1} of CH_4 into the atmosphere. The gas output estimated for all vents is about 255 t yr^{-1}. The mean flux from soil degassing is 470 mg m^{-2} day^{-1} (90–1200 mg m^{-2} day^{-1} from 14 points distributed over the entire muddy area), leading to 128 t yr^{-1} for the whole area. The total output for the PMI field is conservatively estimated at 383 t yr^{-1}.

At the PMA area, 62 vents release 300 t yr^{-1} of gas in total. The soil degassing flux is higher than in the PMI area. The measured values are in the range 360–1200 mg m^{-2} day^{-1}, with a mean value of 707 mg m^{-2} day^{-1}. Integrated over the 1.62-km^2 area, the output from the soil is about 430 t yr^{-1}. The estimated total output for the PMA field is thus provisionally about 730 t yr^{-1}.

The FI area is distinctly different from the other zones. Eighteen vents were counted over a relatively small area of about 0.025 km^2. The individual vent outputs do not exceed 5 t yr^{-1}, generally being around 1 t yr^{-1}. The output estimated for all the vents is about 17 t yr^{-1}. The soil degassing flux is not very different to values for the other fields. However, a high-degassing zone of about 1000 m^2 was outlined, with a mean value of 30 000 mg m^{-2} day^{-1}. The estimated total output for the FI area is 37 t yr^{-1}.

A highly diffuse degassing central zone can be identified in the Andreiasu fire area. Six main vents, including some bubbling pools, emit from

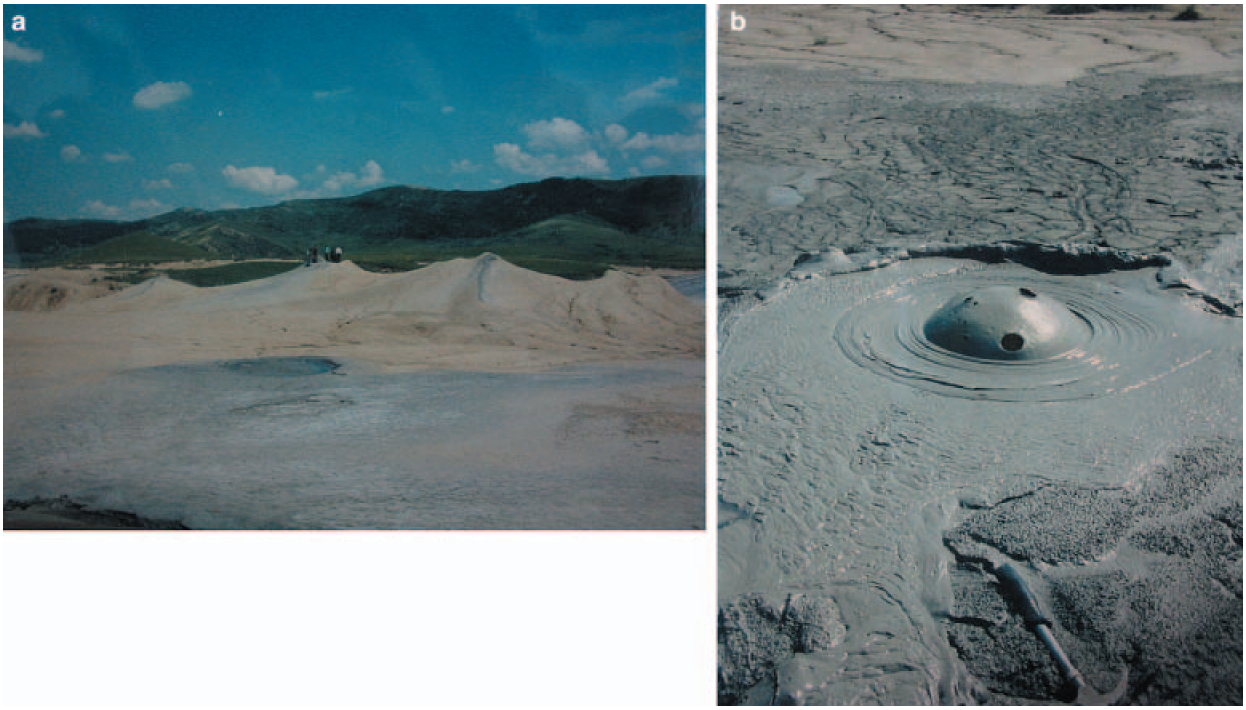

Fig. 3 Mud volcanoes (left) and bubbling crater (right) of the Paclele Mari.

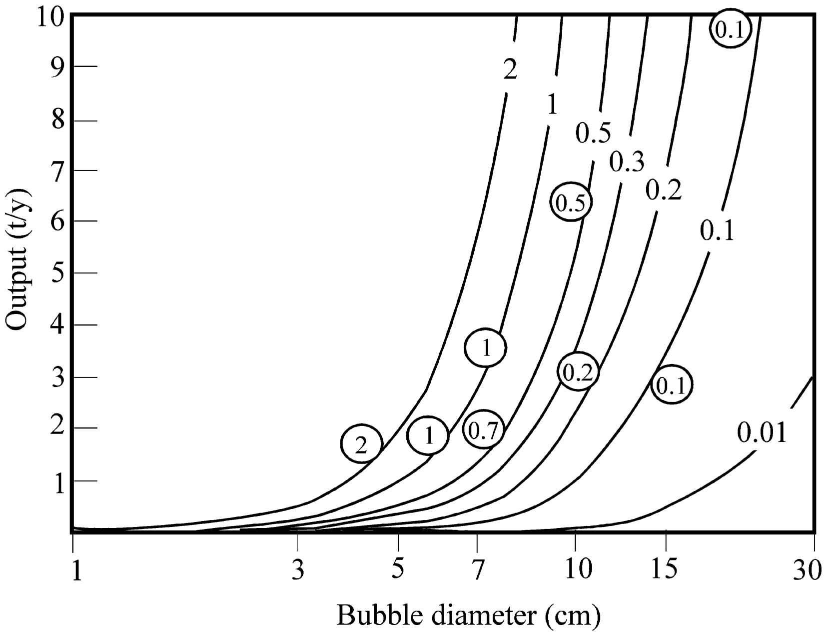

Fig. 4 Theoretical model for calculating the gas flux from bubble trains as a function of bubble diameter and bursting frequency. The curves are calculated for a bubbling rate in the range 2–0.01 bubbles per second. The open circles correspond to the output measured (inverted funnel method) at the PMA site. As the measured data are consistent with the theoretical curves, this model was used to estimate the fluxes in vents inaccessible to direct measurements.

Table 1 Chemical composition and isotopic ratios of helium for the sampled gases. He concentration in ppm by vol; CH_4, N_2 and CO_2 in vol.%

Sample	He	N_2	CH_4	CO_2	$^3He/^4He$
PMI	24.0	2.8	94.9	2.3	6.1×10^{-8}
PMA	25.1	15.3	82.7	2.0	6.1×10^{-8}
FI	14.3	6.2	91.3	2.5	2.1×10^{-8}
AND	10.3	2.2	95.8	2.0	4.3×10^{-8}

0.3 to 13.5 t yr^{-1} of CH_4 (at least 24 t yr^{-1} in total). The vents with the highest fluxes are liable to spontaneous ignition and give rise to spectacular everlasting fires. The mean gas flux from the soil is about 1.7×10^5 mg m^{-2} day^{-1} over an area of 400 m^2. A mean flux of about 100 mg m^{-2} day^{-1} was calculated for a surface area of 20 000 m^2. The estimated total CH_4 output of the AND area has a lower limit of 50 t yr^{-1}.

Discussion

We have estimated a total CH_4 output of at least 1200 t yr^{-1} from the Romanian MVs. The muddy area as a whole shows a high rate of pervasive soil degassing (namely microseepage) of the order of 10^2–10^5 mg m^{-2} day^{-1}. The total output of He, N_2 and CO_2 from vents and ponds can be estimated by scaling the CH_4 output with the concentration ratios of CH_4 relating to these gaseous species (Table 3). The CO_2 output from the vents of the whole Berca area is in the range 70–75 t yr^{-1}, which is negligible if compared with the CH_4 output. The CO_2 flux may, however, be highly variable with time owing to climatological variations and the area's tectonic activity. CO_2 migration is indeed strongly controlled by much higher solubility coefficients as compared with those of helium and methane (e.g. He = 8.75 mL L^{-1} whereas CO_2 = 759 mL L^{-1} at T = 25 °C and P = 1 atm; D'Amore and Truesdell, 1988), and by the seasonal variations in water table thickness. The local seismogenic processes (i.e. in the Beciu area) may then induce variations in crustal permeability, enhancing gas migration and consequent greenhouse gas output.

The helium outflow from the vents, estimated at between 6.7×10^9 and 7.7×10^{10} atoms m^{-2} s^{-1}, falls close to the typical continental value (2.8×10^{10} atoms m^{-2} s^{-1}; Dickin, 1995). Considering that the He/CH_4 ratio is unlikely to change even after interactions with shallow aquifers, we also estimated the total helium output basing the calculations on the total CH_4 output (vents and ponds + soil degassing). In this latter case, the output ranges between 1.8×10^{13} and 1.60×10^{15} atoms m^{-2} s^{-1}, up to five orders of magnitude higher than the typical value for a stable continental area. This suggests that soil microseepage is a significant component in helium degassing. CH_4 microseepage and helium fluxes at Andreiasu are the highest of those measured. This can be explained by considering that Andreiasu is located exactly over the Casin–Bisoca fault, where the clay cover is absent. Conversely, the Berca fault is a shallower local structure crossing less brittle sequences (evaporites) where gas–mud flows occur due to advection from pressurized reservoirs. $^3He/^4He$ ratios range between 2.1×10^{-8} and 6.1×10^{-8}, indicating everywhere that crustal rocks are the

Table 2 CH_4 output from the investigated areas. The 'area' is the one covered by mud volcanoes or mud (no vegetation). Soil degassing range and number of measures are in brackets (for AND only values of the high degassing zone are reported)

Site	PMI (Berca)	PMA (Berca)	FI (Berca)	AND (Andreiasu)
Area (km^2)	0.62	1.62	0.025	0.0004
Number of vents	65	62	18	6
Measured vents	14	8	8	6
Vent output (t yr^{-1})	255	300	17	24
Soil degassing (mg m^{-2} day^{-1})	470 (90–1200; n = 14)	707 (360–1200; n = 6)	354 (75–39 690; n = 8)	168 141 (87 000–245 000; n = 6)

Table 3 Mass output from vents. The CH_4 output was directly measured at the gas vents, whereas the N_2, CO_2 and He outputs are calculated on the basis of the concentration ratios with venting CH_4. Output units are in tonnes per year

Site	CH_4	CO_2	N_2	He
PMI	255	17.5	7.9	1.61×10^{-3}
PMA	300	19.9	25.9	2.27×10^{-3}
FI	17	1.3	0.9	6.70×10^{-5}
AND	24	1.4	0.6	6.45×10^{-5}

main He source in the gas reservoir. These data are in full agreement with those from similar tectonic environments, namely sedimentary basins formed by crustal loading (O'Nions and Oxburgh, 1988; Elliot *et al.*, 1993). The stable isotopic composition of CH_4 is still unknown, but other MVs closely connected to hydrocarbon reservoirs and with a strong helium component typically display thermogenic CH_4 (Etiope *et al.*, 2003; Yang, 2002).

Conclusions

This work is the first detailed investigation of the largest MVs in Europe. Mud volcanoes are typically located over areas where an enhanced vertical permeability allows high degassing rates. According to the results of Etiope *et al.* (2002), we can provisionally confirm that MVs typically emit a specific flux of between 10^2 and 10^3 t km^{-2} yr^{-1}. As experienced in southern Italy (Etiope *et al.*, 2002), a diffuse CH_4 flux also occurs outside the MV fields, up to distances of about 1 km from the muddy area. The existence of a positive CH_4 flux in tectonized dry lands, despite the absence of macroseepage, is thus confirmed, in agreement with previous works (Klusman and Jakel, 1998; Etiope, 1999; Klusman *et al.*, 2000; Etiope *et al.*, 2002). The venting gases have a crustal origin as revealed by the low $^3He/^4He$ ratios, in agreement with similar findings in other European sedimentary basins.

These data will be used to refine the global estimates of geological methane emissions into the atmosphere. The total geological CH_4 source, including MVs, seepage from the seafloor, microseepage in hydrocarbon-prone areas and geothermal sources, is currently given a conservative estimate of the order of 35–45 Mt yr^{-1} (Etiope and Milkov, 2004), that is the same level as or even higher than other CH_4 sources or sinks considered in the Intergovernmental Panel on Climate Change tables (IPCC, 2001), such as biomass burning (40 Mt yr^{-1}), termites (20 Mt yr^{-1}) and soil uptake (30 Mt yr^{-1}). The global geological CH_4 emission is still probably underestimated; its actual role in the atmospheric methane budget may be accurately assessed after further flux measurements from other MVs around the world and from soil microseepage in petroliferous areas.

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