LETTERS

Orbital and millennial-scale features of atmospheric CH_4 over the past 800,000 years

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Atmospheric methane is an important greenhouse gas and a sensitive indicator of climate change and millennial-scale temperature variability[1]. Its concentrations over the past 650,000 years have varied between ~350 and ~800 parts per 10^9 by volume (p.p.b.v.) during glacial and interglacial periods, respectively[2]. In comparison, present-day methane levels of ~1,770 p.p.b.v. have been reported[3]. Insights into the external forcing factors and internal feedbacks controlling atmospheric methane are essential for predicting the methane budget in a warmer world[3]. Here we present a detailed atmospheric methane record from the EPICA Dome C ice core that extends the history of this greenhouse gas to 800,000 yr before present. The average time resolution of the new data is ~380 yr and permits the identification of orbital and millennial-scale features. Spectral analyses indicate that the long-term variability in atmospheric methane levels is dominated by ~100,000 yr glacial–interglacial cycles up to ~400,000 yr ago with an increasing contribution of the precessional component during the four more recent climatic cycles. We suggest that changes in the strength of tropical methane sources and sinks (wetlands, atmospheric oxidation), possibly influenced by changes in monsoon systems and the position of the intertropical convergence zone, controlled the atmospheric methane budget, with an

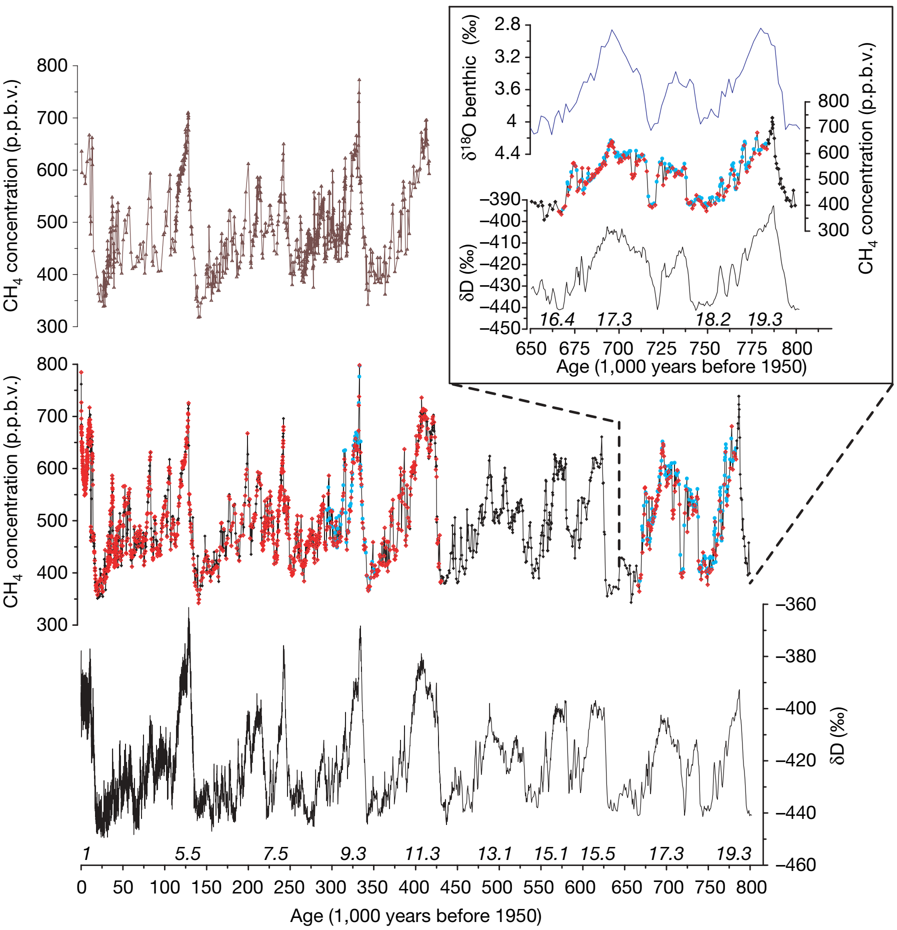

Figure 1 | Methane records and EPICA/Dome C δD. Bottom to top: δD record[9]; EDC methane record (previously published data[2], black diamonds; new data from LGGE, red diamonds; new data from Bern, blue dots); Vostok methane record[1]. Marine Isotope Stage numbering is given at the bottom of each interglacial. Insert: expanded view of the bottom section of EDC: δD values[9] (black line), CH_4 (black line) from EDC and stack benthic $\delta^{18}O$ values (blue line)[19] for the period from MIS 16 to 20.2, on their respective age scales. $\delta^{18}O = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{standard}] - 1$, where standard is vPDB; $\delta D = [(D/H)_{sample}/(D/H)_{standard}] - 1$ where standard is SMOW.

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additional source input during major terminations as the retreat of the northern ice sheet allowed higher methane emissions from extending periglacial wetlands. Millennial-scale changes in methane levels identified in our record as being associated with Antarctic isotope maxima events[1,4] are indicative of ubiquitous millennial-scale temperature variability during the past eight glacial cycles.

Atmospheric methane is an important climate forcing as well as a sensitive indicator of climate change and variability. Over the past 650 kyr, the ice-core record indicates that its abundance has varied from ~350 p.p.b.v. during glacial periods up to ~800 p.p.b.v. during interglacials[2]. In 2005, its global average was 1,774 ± 1.8 p.p.b.v (ref. 3), far exceeding the natural range of the past 650 kyr. Understanding the link between external forcings and internal feedbacks on the natural CH_4 budget is important for forecasting the latter in a warmer world. In addition, CH_4 is tightly linked to Northern Hemisphere millennial variability during the last glacial period[4]. Therefore, CH_4 variations can be used as a proxy for abrupt change further back in time[1].

Here, we present the most detailed and longest CH_4 record yet derived from a single ice core: EPICA Dome C (EDC, 75° 06′ S, 123° 20′ E, 3,233 m above sea level), reaching back to Marine Isotope Stage (MIS) 20.2 about 802 kyr before present (BP) and covering eight climatic cycles (Fig. 1). We have doubled the EDC CH_4 time resolution (Supplementary Fig. 2) between 0 and 215 kyr BP (MIS 1 to MIS 7, mean resolution: 210 yr) using a melt-refreezing method. EDC samples were measured between 230 and 420 kyr BP (MIS 7 to 11, mean resolution: 390 yr), whereas the record presented in Spahni *et al.*[2] relied on the existing Vostok record[1]. The deepest portion of the EDC core between 3,060.66 m and 3,190.53 m was analysed, providing the first CH_4 data for the time period from 666 to 799 kyr BP (MIS 16 to 20.2, mean resolution: 550 yr; see insert to Fig. 1). The EDC3 ice and gas timescales EDC3 (ref. 5) and EDC3_gas_a (ref. 6) are used hereafter, providing good agreement with the composite chronologies[7,8] from EPICA Dronning Maud Land and Greenland (Supplementary Fig. 1) over the last glacial cycle.

With a total of 2,245 individual measurements, the EDC CH_4 record is now complete from the surface down to 3,259.32 m. Because of stratigraphic disturbance in the deepest 60 m (ref. 9), we limit the discussion to the upper 3,190.53 m, which provide an average time resolution of 380 yr over the past 799 kyr. Within analytical uncertainties, our EDC data agree very well with the records of Vostok[1] over the past 420 kyr (Fig. 1) and with the millennial variability recorded in Greenland composite records[7,8] for the last glacial period (Supplementary Fig. 1). The homogeneity, accuracy and resolution of our EDC record make it a new reference for the atmospheric CH_4 temporal evolution on long timescales.

The extended record reveals several new aspects of methane variability. First, the oldest interglacial MIS 19 shows a CH_4 maximum of ~740 p.p.b.v., much higher than during interglacials MIS 13 to 17. The EDC δD record indicates cooler and longer interglacials before 430 kyr, corresponding to the Mid-Brunhes Event transition[9]. This is reinforced by CO_2 (ref. 10) and CH_4 records until MIS 17. But the high CH_4 levels during MIS 19 break down this general trend. Amongst the past nine interglacials, MIS 9 and 19 appear decoupled (with unusually high methane levels) from the overall good correlation ($r^2 = 0.82$) observed between the maximum CH_4 value and the maximum Antarctic warmth[9] (Supplementary Fig. 3). Second, rapid and large fluctuations are identified. The glacial inception from MIS 19 to MIS 18 is accompanied by three distinct CH_4 peaks, having counterparts in the δD (ref. 9) and CO_2 (ref. 10) records. A large CH_4 oscillation (amplitude 170 p.p.b.v.) is identified at the end of MIS 18, comparable in shape with the Younger Dryas event[11], but with a longer duration (8 kyr between the surrounding maxima; Fig. 1). Its comparison with concomitant CO_2 levels[10] and marine records suggests that it does not reflect a bipolar seesaw sequence of events. A shorter and smaller oscillation (3 kyr between bracketing maxima, amplitude ~100 p.p.b.v.) is also observed during the early part of interglacial MIS 17.

Wetlands are by far the largest natural source of methane today. The largest wetland extents are found in boreal regions, with a second latitudinal belt between the tropics[12]. Their CH_4 emissions today are shared about one-third boreal and two-thirds tropics. The controversial alternative suggestion of direct plant CH_4 emissions[13] has been recently scaled down substantially[14]. Mean preindustrial CH_4 sources are estimated to be between 200 and 250 Tg yr^{-1}, 85% of which comes from wetlands[3]. Temperature changes and water-table variations are the dominant controls of wetland emissions on seasonal and interannual timescales[15]. The main sink of methane, oxidation by tropospheric OH radicals, directly feeds back on any CH_4 source change[3]. This is amplified by changes in emissions of volatile organic compounds, which may be related to the reduced extent of forests during glacial conditions[16]. To first order, CH_4 changes during the past 800 kyr should thus reflect varying extent of or emissions from wetlands in different latitudinal belts, and OH feedbacks associated

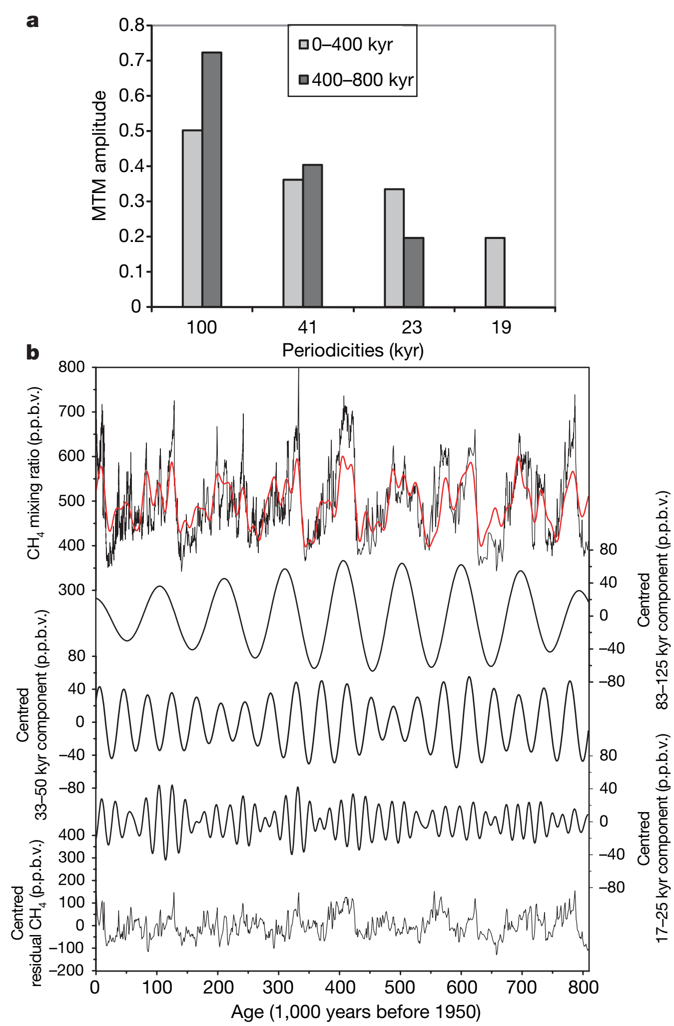

Figure 2 | Spectral analysis of the methane record. a, Amplitude of orbital periodicities in the methane record for the time ranges 0–400 kyr and 400–800 kyr, using the multi-taper method (MTM) with normalized data. The 19-kyr component is absent at 400–800 kyr because of its statistical non-significance (*F*-test <0.95, see Supplementary Information). **b,** Orbital components and residuals (expressed in p.p.b.v. on the centred signal) of the CH_4 record over the past 800 kyr. The red line combines the three periodicities. Note that the amplitude of the orbital components and residuals is similar (~200 p.p.b.v.). The residual CH_4 signal contains other statistically significant periodicities at 4.8 and 8.7 kyr and another periodicity at 10–11 kyr slightly below the confidence limit, not discussed here.

with vegetation changes. Other lesser sources could also have contributed either to long-term trends or to short events, such as biomass burning[17] and clathrate degassing[18].

The EDC CH_4 spectral analyses (Fig. 2) shed light on the response of methane sources and sinks to orbital forcing. They highlight the orbital periodicities of 100, 41, 23 and 19 kyr already found in the shorter Vostok record[1]. The 100-kyr component dominates the glacial–interglacial variability as in the δD (ref. 9) and global ice volume signals (ICE in Supplementary Fig. 4; deduced for simplification from the stacked oxygen isotopic composition of benthic foraminifera)[19]. But its contribution to the CH_4 variance clearly decreases after the Mid-Brunhes Event, opposed to the trend for δD (ref. 9). This goes together with an increasing contribution of the precessional component towards the present (Fig. 2), reaching the same magnitude as the obliquity component. At high northern latitudes, changes in ice-sheet volume should be the main driver on peat deposition rate, thawing and refreezing of the soil active layer and extent of seasonal snow cover, all affecting CH_4 emissions[20]. A comparison between the EDC CH_4 signal and global ice volume signal[19] does indeed indicate a strong coherency at 100 kyr. The two signals are in phase within current dating uncertainties[5] (Supplementary Fig. 4).

Orbital forcing modulates the latitudinal and land–sea temperature gradients in the Tropics and therefore is a major forcing of the tropical monsoon systems[21] and of the position of the intertropical convergence zone[22], which both drive the precipitation rate in the intertropical belt and will influence the areal variability of the large tropical wetlands found in southeast Asia, Africa and South America[12]. Feedbacks from OH associated with varying emissions of volatile organic compounds should closely follow a similar temporal pattern to the regional monsoon evolutions. The tropical climate is dominated mostly by precessional variability[23], as evidenced for instance by the loess magnetic susceptibility records (loess SUS[24]). Although the entire tropical region affects the methane budget, we compare the CH_4 signal only with the Asian summer monsoon reconstruction from SUS loess, which is currently the only available record of tropical climate variability that covers a time period comparable to our record. The CH_4 and the SUS loess are in phase within dating uncertainties (Supplementary Fig. 4) and show an increasing variance in the precessional band starting around 420 kyr BP, thus suggesting a dominant contribution of monsoon-related processes in the CH_4 variability at precessional periodicities. A picture thus emerges in which atmospheric CH_4 background levels have been modulated by tropical wetlands and/or volatile organic compound emissions from tropical forests during the late Quaternary, with overshoots every 100 kyr associated with varying extents of northern ice sheets and periglacial wetlands. This is in agreement with a recent isotopically constrained CH_4 budget between the last glacial

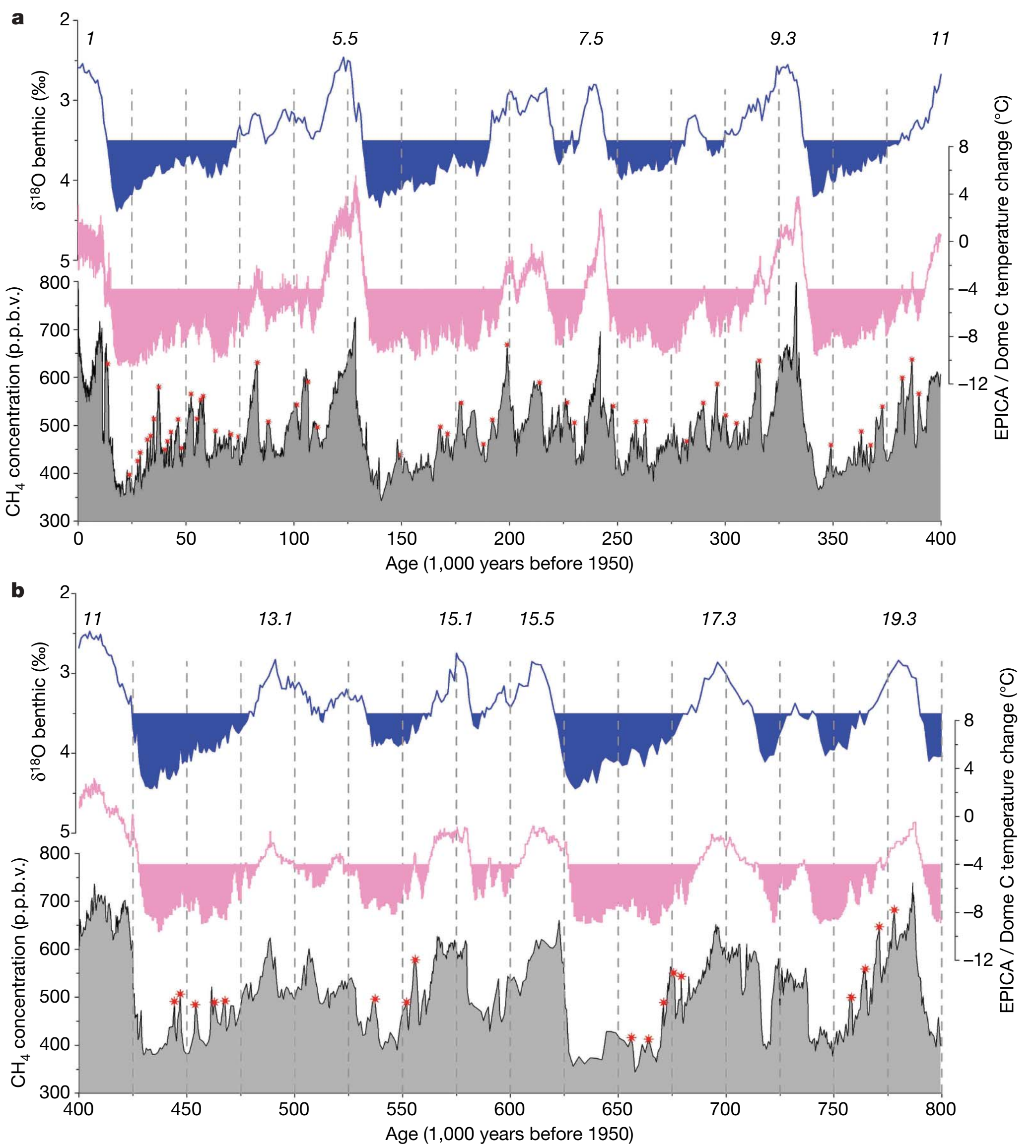

Figure 3 | Methane millennial variability. **a**, 0–400 kyr; **b**, 400–800 kyr. In each panel, from bottom to top, we show the methane signal (grey shaded curve) with 74 identified millennial changes (red stars, mean time between occurrences 6.2 kyr), based on a threshold amplitude of ~50 p.p.b.v. and a correspondence (occurrence and peak-to-peak synchroneity) with an Antarctic isotope maximum[9]. Glacial periods (pink shaded area) are defined by EPICA/Dome C temperature being at least 4 °C below late Holocene values[9]. Time periods of occurrence of millennial variability (blue shaded area) are defined by a threshold value of 3.5‰ in the North Atlantic $\delta^{18}O$ benthic record[27]. The benthic stack[19] is used to compare with the full CH_4 record over 800 kyr.

maximum and the early Holocene[25], suggesting a dominating contribution of tropical wetlands in the pre-industrial budget, a switch-on of boreal wetlands when the ice sheets decay and an amplification by the OH sink. Rigorous testing of this picture will require future model simulations of the Earth system that couple climate and the carbon cycle in transient mode over several glacial–interglacial cycles.

On even shorter timescales, high-resolution methane records can be used as a proxy of Northern Hemisphere millennial temperature fluctuations back in time[1], although the relationship between CH_4 and Greenland temperature is not linear during the last glacial period and the atmospheric CH_4 signal is slightly damped by gas trapping processes[26]. Our new EDC methane record represents a unique continuum of this millennial variability back through the past eight glacial periods with 99% of the record providing a time resolution better than 1,000 yr for the sequence MIS 1–11 (84.5% for MIS 11–20, when additional millennial changes may still be revealed with an improved time resolution). We find 74 millennial CH_4 changes (Fig. 3a and b), defined as an amplitude larger than 50 p.p.b.v. and an association (with peak-to-peak synchroneity) with Antarctic isotope maxima[8,9]. Marine records suggest that the millennial variability shows up whenever the ice-sheet volume, expressed through the oxygen isotopic composition of benthic foraminifera, is above a threshold of 3.5‰ (ref. 27). Antarctic temperature change provides another proxy of glacial conditions, with the threshold considered to be at least 4 °C below late Holocene temperature[9]. Such thresholds, however, fail to capture millennial CH_4 events now identified during the early phase of glacial periods following the warmest interglacials (late MIS 5 and 7; early phase of MIS 8, 10 and 18). The hypothesis of constant lower thresholds is too permissive as it requires CH_4 variability during the lukewarm interglacials (MIS13 and 17), which is not supported by our data. The combination of CH_4 millennial variability and Antarctic isotope maxima therefore provides a better indicator of bipolar millennial variability, casting doubt on a straightforward link between ice volume or Antarctic cooling and climate instabilities.

METHODS SUMMARY

The analytical methods of CH_4 measurements in the two laboratories of Bern and LGGE have been already described in detail and compared[2]. The air from polar ice-core samples of about 40 g (Bern) and 50 g (LGGE) is extracted with a melt-refreezing method under vacuum, and the extracted gas is then analysed for CH_4 by gas chromatography. Two standard gases (408 p.p.b.v. CH_4, 1,050 p.p.b.v. CH_4) were used at Bern and one (499 p.p.b.v. CH_4) at LGGE, to calibrate the gas chromatographs. The mean CH_4 analytical uncertainty (1σ) is 10 p.p.b.v (ref. 2). Concentrations are not corrected for gravitational settling in the firn column as this effect corresponds to only about 1% of the measured levels. EPICA/Dome C CH_4 and δD data are on EDC3 age scales[5,6]. The Vostok data were synchronized on the EDC gas age scale by using the program Analyseries[28]. Orbital components and the residual in the CH_4 record are obtained by gaussian filters with the Analyseries program[28]. The precession band is calculated first ($f = 0.05 \pm 0.01$) on the CH_4 signal interpolated every 1 kyr, then the obliquity band on the first residual ($f = 0.025 \pm 0.005$) and then the ~100-kyr band on the second residual ($f = 0.01 \pm 0.002$).

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