Atlantic Deep Water influence has been estimated as 0.1‰ to maintain the source of AABW over the freezing point[8]. Thus the maximum possible change in the whole vertical $\delta^{18}O$ gradient is 0.1‰.

These results indicate that the vertical salinity/$\delta^{18}O$ gradient in the northern Indian Ocean during LGM was not so different from the modern one. The sharp deep front between Intermediate and Deep Water is thus best explained by the decrease in Deep Water temperature in the Indian Ocean and development of a deep thermocline. The increased hydrological contrast between Intermediate and Deep Waters in the Indian Ocean has amplified the asymmetry between eastern and western Basins induced by the bottom topography of this ocean.

Our results demonstrate that the glacial Indian Ocean hydrological structure was different from modern conditions. Intermediate Water was of similar temperature but more ventilated than now. Similar observations about the intermediate-water ventilation during LGM are made for the Atlantic and Pacific Oceans[3,10,12,13], indicating the global nature of this phenomenon. By contrast, the deep world ocean was subject to drastic changes with a very weak ventilation and cooler temperatures. The description of the glacial ocean circulation has to take into account this strong stratification between intermediate and deep waters, which has, as described by Boyle[34], a potential influence on the regulation of the atmospheric pCO_2.

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Climatic and CH_4 cycle implications of glacial–interglacial CH_4 change in the Vostok ice core

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The atmospheric CH_4 increase from ~0.7 to 1.68 p.p.m.v. over about the past 300 years which has been documented from analysis of air trapped in ice cores[1–4] and from tropospheric measurements (see ref. 5 for example) is attributed to anthropogenic modifications of the CH_4 cycle. The concern about this increase is due to the radiatively and chemically active nature of CH_4. Here we present strong evidence from analysis of the Vostok ice core, that CH_4 concentrations increased from 0.34 to 0.62 p.p.m.v. between the end of the penultimate ice age and the following interglacial, about 160–120 kyr BP. This CH_4 change may be explained by considering the effect of the climatic change on the CH_4 cycle. Its contribution (including chemical feedback) to the global climatic warming is estimated to be about 25% of that due to CO_2.

The Vostok ice core provides a unique palaeoenvironmental record covering the past 160 kyr[6–8]. Our first aim has been to investigate whether atmospheric concentrations of CH_4 were different during full glacial conditions from those prevailing in an interglacial period. Seven depth levels were selected: three from the penultimate glaciation (~155 kyr BP), three from the following interglacial (~130 kyr BP) and one in the transition in between. We chose this time period in preference to the last glacial maximum (~18 kyr ago)–Holocene period because of potential problems linked with the presence of fractures in the upper part of the Vostok core[7].

Each ice sample (~40 g) is taken from the centre of the core and placed in a glass vessel sealed with vacuum silicone grease. The air surrounding the sample is evacuated, and the ice is melted. The meltwater is then slowly refrozen from the bottom. In this way, most of the air dissolved in the water is pushed out at the water–ice interface. Based on experimental tests, the efficiency of this extraction is estimated to be 99%. After refreezing the water, the gas is expanded in an extraction line and injected in a gas chromatograph (flame ionization detector).

Three successive injections from the same extracted air are performed and the system is calibrated using an air standard (Air Liquide) containing 1.2 ± 0.1 p.p.m.v. of CH_4 in a mixture of N_2, O_2 and CO_2. The analytical accuracy of each analysis (2σ), evaluated from the standard deviation of the residuals corresponding to the calibration regression, is 0.03 ± 0.02 p.p.m.v. Blank values are obtained by analysing standard gas in the same way as real samples, a cube of artificial bubble-free ice replacing the ice-core sample. Based on 12 tests, a correction that varies between about 0.04 and 0.1 p.p.m.v. has been applied to the results.

No trend appears between the three injections from the same sample, and our estimated overall accuracy (excluding the uncertainty due to the standard gas) is about 0.04 p.p.m.v. This value is consistent with the observed scattering (2σ) of the results obtained from the same ice-core section (Table 1), suggesting that CH_4 concentrations are homogeneous in a given core section.

Apart from the Vostok core, a section of another Antarctic core (D 57) has been analysed to compare the results obtained using our method with previously published data. The air occluded in the D 57 section was trapped around AD 1440, according to the dating based on volcanic horizons[9]. The mean

CH_4 concentration (Table 1) is 0.68 ± 0.04 p.p.m.v., in very good agreement with previous results[1-4] that indicate a CH_4 concentration of ~0.7 p.p.m.v. before the beginning of significant anthropogenic perturbation. The agreement is even better with results from three Byrd core samples[3] of about the same age, which give a mean CH_4 concentration of 0.67 p.p.m.v.

The results obtained on the seven Vostok core sections (27 samples analysed) and shown in Table 1, are plotted in Fig. 1 versus age, together with the isotopic temperature profile[6]. The age of the ice is from ref. 10 and the age of the air, which is younger, has been calculated according to the procedure described in ref. 7. The mean CH_4 concentration of the three interglacial levels (12 samples) is 0.62 p.p.m.v., with a maximum level value (0.65 p.p.m.v.) rather close to the fifteenth century value obtained from the D 57 ice core. We may also note a trend in the concentrations which parallels the temperature profile. The three levels (12 samples) covering the end of the penultimate glaciation give a mean CH_4 concentration of 0.34 p.p.m.v.. The level measured in the climatic transition shows an intermediate value of 0.46 p.p.m.v. The Vostok results thus indicate that the tropospheric CH_4 concentrations increased very significantly (by a factor 1.8) between the penultimate ice age and the following interglacial.

We now discuss whether the glacial-interglacial warming could itself have forced the CH_4 increase. We assume a similar warming for the last two glacial-interglacial transitions and use the estimate of 4.5 ± 1 °C (ref. 11) for such a global warming.

Oxidation of tropospheric CH_4 by OH ($CH_4 + OH \rightarrow CH_3 + H_2O$) is the main identified sink for CH_4. Because of the temperature dependence of the reaction rate coefficient, we expect an enhanced destruction of CH_4 by OH when the temperature increases. The strength of this sink may also increase because of an enhanced production of OH arising from the higher atmospheric H_2O levels produced by warmer temperatures[12,13]. Typical results obtained from a coupled climate-chemical model[12] show that, for a mean surface temperature increase of 3.1 °C, the enhanced sink strength leads to a tropospheric CH_4 decrease by 17%. Thus the effect of a 4.5 °C warming on this sink during the penultimate deglaciation could be a decrease in the CH_4 concentrations by about 20%. There is evidence that unsaturated soils also act as a CH_4 sink, but it is unlikely that they are important in the global CH_4 budget (see ref. 14 for example). If our estimate of the change in the sink strength is correct, the global source strength must have increased by a factor of 2.3 to account for the observed increase in CH_4 concentration (×1.8).

The sources of atmospheric CH_4 have been discussed by several authors[14]. Based on the different estimates of CH_4-emission rates and of their trends[15], we can assume that the flux of methane evolved from bacterial processes in freshwater wetland areas was the dominant source prevailing before the anthropogenic perturbation. Although there are only limited CH_4 flux measurements at freshwater wetland sites, increasing temperature may lead to an exponential response of CH_4-emission rate (as in ref. 12). Based on the CH_4-emission rate response given in ref. 12 and a temperature change of 4.5 °C, the interglacial source strength would be higher than the glacial by a factor of 1.7. The areal extent of such anaerobic environments should logically also have been larger during an interglacial than during a glacial period, because of wetter climate and more extended deglaciated area. A surface increase of ~35%, combined with the temperature impact on the freshwater wetland source strength, would account for the CH_4 increase from the ice age to the interglacial. We are aware that one could argue in favour of other sources (termites, wildfires, wild ruminants), but our aim is to stress that climatically induced changes of a global CH_4 source, like freshwater wetlands, could well account for the observed CH_4 increase and that this increase could be entirely explained as being a consequence of the climatic change.

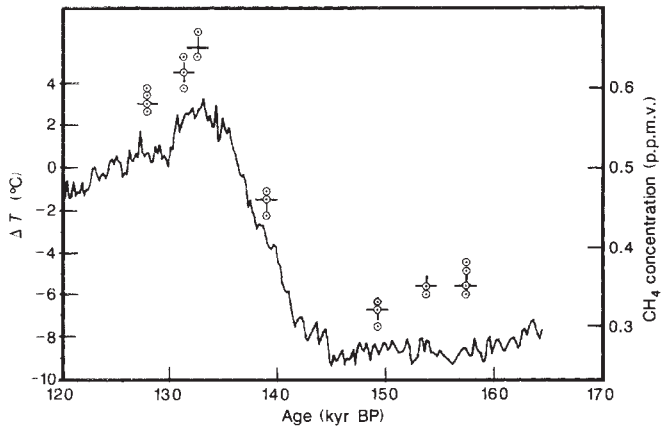

Fig. 1 Vostok ice core: CH_4 concentrations (+ indicate mean values) and isotope temperature profile (continuous line, from ref. 6) versus time.

Table 1 CH_4 concentrations in D 57 and Vostok ice cores with depths and ages

Depth (m)	Age of the ice (yr BP)	Mean age of the gas	CH_4 concentration (p.p.m.v.)	Mean CH_4 concentration ($\pm 2\sigma$) (p.p.m.v.)
D 57				
180.7	850	510	0.66, 0.72, 0.68 0.67, 0.68	0.68 (0.04)
Vostok				
1,789.2	130,080	127,800	0.58, 0.60, 0.57 0.58, 0.59, 0.58	0.58 (0.02)
1,834,7	133,360	131,100	0.64, 0.60, 0.62	0.62 (0.04)
1,852.3	134,650	132,400	0.67, 0.64, 0.64	0.65 (0.04)
1,932.1	141,600	138,800	0.44, 0.46, 0.47	0.46 (0.03)
2,016.4	153,420	149,100	0.30, 0.32, 0.33	0.32 (0.03)
2,042.5	157,790	153,600	0.35, 0.34, 0.35	0.35 (0.01)
2,063.7	161 [illegible]	157,300	0.37, 0.34, 0.34 0.35, 0.38, 0.34	0.35 (0.04)

Owing to the trapping process of the air by the ice, each level represents an average value of the age of the air—covering several hundred years in the case of Vostok[7] and ~50 years for D 57.

The climatic impact due to the observed glacial-interglacial CH_4 increase (0.34-0.62 p.p.m.v.) is an important issue. The corresponding direct radiative effect can be evaluated from radiative-convective models. The analytic expression provided by Hansen *et al.*[16], which fits the results of a one-dimensional radiative-convective climate model[17] within about 1%, leads to a global surface equilibrium warming of ~0.08 °C. Furthermore, under present-day conditions, increasing CH_4 produces higher levels of tropospheric O_3, another radiatively active gas, which in turn leads to a positive feedback on the surface temperature. Models taking this chemical feedback into account indicate an amplification of the direct CH_4 greenhouse effect by ~75% (ref. 18) and 58% (ref. 19). The assumption that these amplification factors also applied at the glacial-interglacial transition would lead to a radiative equilibrium warming of 0.13-0.14 °C due to the CH_4 increase and its chemical feedback. This is about four times less than the equilibrium warming (0.5 °C) obtained from the same model[16] for the CO_2 increase (from 195 to 270 p.p.m.v.) which occurred during the same time interval[7]

According to these calculations, the combined net greenhouse effect due to CO_2 and CH_4 changes (and excluding climatic feedbacks) would have increased the global surface equilibrium temperature by ~0.6 °C. We are aware of the uncertainties linked with the evaluation of the different climatic feedbacks, but if we adopt a climatic feedback factor of 3.5, as suggested in ref. 20 by the Goddard Institute Space Studies three-dimensional climate model (yielding a sensitivity of ~4 °C for doubling CO_2),

the global equilibrium warming arising from the CO_2 and CH_4 increases would be ~2.2 °C (0.5 °C for CH_4 alone). Hence, the combined net climatic forcing of CO_2 and CH_4 would be about 50% of a glacial–interglacial warming of 4.5 °C. If our suggestion that climate is initially forcing CH_4 changes is correct, we can expect a CH_4 contribution all along the temperature change observed during the last climatic cycle, and in particular in the isotope–temperature record obtained from the Vostok ice core. Further measurements of CH_4 concentrations from this ice core will help to clarify this point.

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Note added in proof: After this paper was submitted, another paper[21] appeared sharing a very similar CH_4 change between the last ice age and the Holocene. The two sets of data together strongly suggest that the observed CH_4 increases as a general characteristic of the glacial–interglacial climatic transitions.

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Plume-asthenosphere mixing beneath the Galapagos archipelago

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Although the Galapagos Islands have long been cited as an example of intraplate volcanism resulting from a mantle plume[1,2], a number of features of the Galapagos appeared to conflict with a simple mantle-plume model. These include the non-linear arrangement of volcanoes, the non-time-transgressive nature of volcanism, and a tendency for the lavas to have more depleted trace-element and isotopic signatures towards the centre of the archipelago. The toroidal diapir model of Griffiths[3,4], in which depleted asthenosphere is drawn into the centre of the rising diapir with the original diapir material preserved in a torus, appears to resolve these conflicts and provides an explanation for many of the enigmatic aspects of Galapagos volcanism.

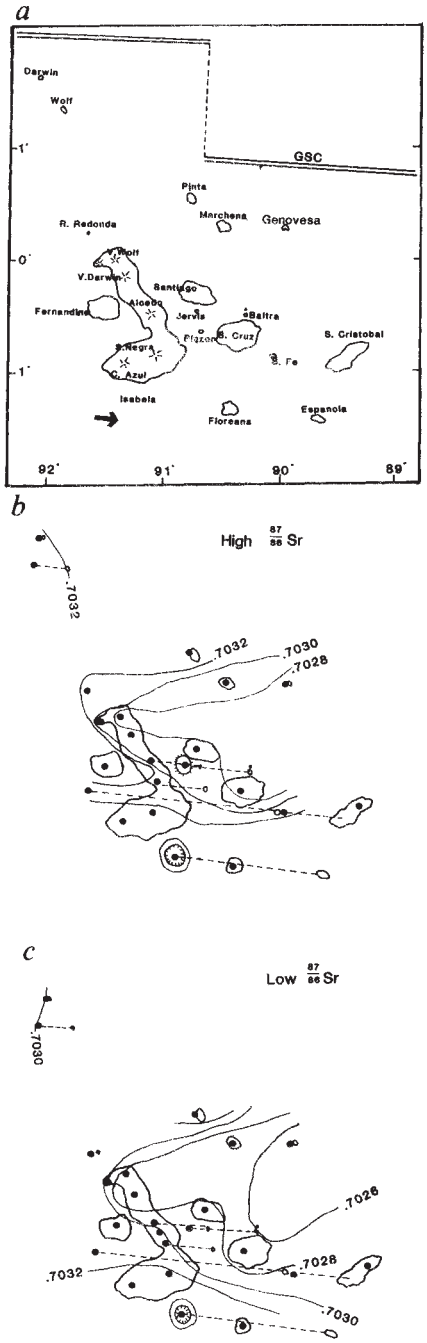

Fig. 1 *a*, Map indicating locations discussed in text. Arrow shows absolute motion of the Nazca Plate[19]. *b*, Galapagos Islands contoured by the highest $^{87}Sr/^{86}Sr$ ratios measured from each volcano. Position of each sample point has been adjusted (dashed lines) for its estimated age[8,9,13,14,17,25,26] and the velocity of the Nazca Plate[19]. *c*, Same as above, but for lowest measured $^{87}Sr/^{86}Sr$ from each volcano.

The Galapagos Islands are thought to be the manifestation of a mantle diapir that lies immediately adjacent to the Galapagos spreading centre (GSC), an active mid-oceanic ridge (Fig. 1). Interaction of the hotspot with the ridge is apparent from anomalous geochemical features in GSC lava, such as high $^{87}Sr/^{86}Sr$ and La/Sm and low $^{143}Nd/^{144}Nd$ ratios[5–7]. But the Galapagos differ from more familiar hotspots, such as Hawaii, in several important respects. First, the islands do not form a single linear chain; instead they are aligned in two oblique

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