

## LETTERS

# Observed variations of methane on Mars unexplained by known atmospheric chemistry and physics

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The detection of methane on Mars<sup>1–3</sup> has revived the possibility of past or extant life on this planet, despite the fact that an abiogenic origin is thought to be equally plausible<sup>4</sup>. An intriguing aspect of the recent observations of methane on Mars is that methane concentrations appear to be locally enhanced and change with the seasons<sup>3</sup>. However, methane has a photochemical lifetime of several centuries, and is therefore expected to have a spatially uniform distribution on the planet<sup>5</sup>. Here we use a global climate model of Mars with coupled chemistry<sup>6–8</sup> to examine the implications of the recently observed variations of Martian methane for our understanding of the chemistry of methane. We find that photochemistry as currently understood does not produce measurable variations in methane concentrations, even in the case of a current, local and episodic methane release. In contrast, we find that the condensation–sublimation cycle of Mars' carbon dioxide atmosphere can generate large-scale methane variations differing from those observed. In order to reproduce local methane enhancements similar to those recently reported<sup>3</sup>, we show that an atmospheric lifetime of less than 200 days is necessary, even if a local source of methane is only active around the time of the observation itself. This implies an unidentified methane loss process that is 600 times faster than predicted by standard photochemistry. The existence of such a fast loss in the Martian atmosphere is difficult to reconcile with the observed distribution of other trace gas species. In the case of a destruction mechanism only active at the surface of Mars, destruction of methane must occur with an even shorter timescale of the order of ~1 hour to explain the observations. If recent observations of spatial and temporal variations of methane are confirmed, this would suggest an extraordinarily harsh environment for the survival of organics on the planet.

The fact that methane concentration varies with time and location on Mars contradicts the logic that a gas of lifetime much longer than the time required for global mixing should have a constant and spatially uniform distribution. To examine the implications of the recently observed variations of Martian methane, we implemented methane chemistry in the Laboratoire de Météorologie Dynamique (LMD) global climate model (GCM) of Mars with on-line photochemistry<sup>6–8</sup>. In the 'conventional' atmospheric chemistry scheme, which explains correctly the observed distribution of methane on Earth, loss of methane on Mars occurs primarily by photolysis at heights above 60 km, and by oxidation by OH and O(<sup>1</sup>D) at lower altitudes. These constituents are produced respectively by the photolysis of water and ozone. The fact that the LMD GCM reproduces closely the observed seasonal and geographical variations of these species<sup>8</sup> is an important prerequisite for a precise estimate of the fate of methane in the Martian atmosphere.

To determine the atmospheric lifetime of methane, we first initialized the GCM with a uniform mixing ratio and monitored the

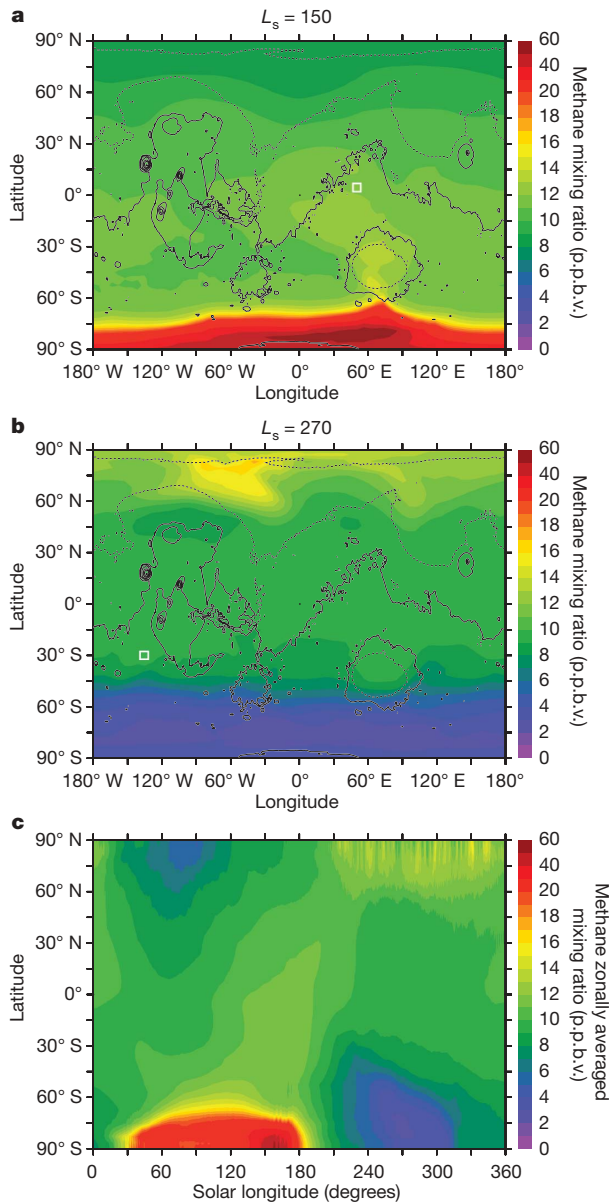
exponential decay of methane in a long-term simulation that did not include any source. We find that the global atmospheric mass of methane is reduced by a factor of  $e$  after 330 terrestrial years. This lifetime is consistent with past estimations based on globally averaged models (250–670 terrestrial years<sup>2,9,10</sup>), but here integrates the effects of spatial and seasonal variations in ultraviolet flux, water vapour and ozone. From this estimation, the source flux of methane at the Martian surface must be 260 tonnes per year ( $260 \text{ t yr}^{-1}$ ) for a steady-state value of 10 p.p.b.v. (parts per billion by volume). This may be compared with the terrestrial value of  $582 \times 10^6 \text{ t yr}^{-1}$  (ref. 11).

Can such a faint source create variations in the observed methane field? Evidently, such variations are favoured if the source itself shows some degree of spatial or temporal variability. To investigate this possibility, we introduced a highly localized and sporadic source in the GCM. We chose the area and timing of the methane release to coincide with the important local maximum (40–50 p.p.b.v.) observed<sup>3</sup> in northern summer 2003: methane is released at the surface in a single grid cell of the model located in Syrtis Major ( $10^\circ \text{ N}$ ,  $50^\circ \text{ E}$ ), and the emission is assumed to occur for only 60 sols (one sol is a Martian day) around solar longitude  $L_s = 150^\circ$ . The amount of methane injected into the atmosphere during this period is constrained to balance the global photochemical loss integrated over the Martian year. Figure 1a displays the methane distribution obtained during the period of emission. The local release of methane does not produce any significant enhancement or plume in the source region. In contrast with the observation, the model shows an essentially well-mixed distribution over most of the planet. A striking feature, however, is the large methane enrichment that results from the condensation of  $\text{CO}_2$  gas at high southern latitudes. The enrichment in non-condensable species during the formation of the seasonal  $\text{CO}_2$  ice cap is a well established process, derived from observations of argon by the Gamma Ray Spectrometer on board Mars Odyssey<sup>12,13</sup>. In relative terms, the enhancement (or depletion) factor due to  $\text{CO}_2$  condensation (or sublimation) should be identical for all non-condensable species, and hence for methane and argon. The predicted enrichment factor of 4 to 5 for methane at  $L_s = 150^\circ$  is in good quantitative agreement with the argon enhancement measured by the Gamma Ray Spectrometer (ref. 14; Supplementary Information).

Moving the source to other regions has no effect on the GCM methane field. For instance, we attempted to reproduce the methane maximum reported in southern spring/summer over the south of Tharsis<sup>15</sup>. The signature of the short-lived release at  $L_s = 270^\circ$  remains invisible in the mixing ratio map (Fig. 1b). At the same time, the sublimation of the seasonal  $\text{CO}_2$  ice cap in the model leads to a depletion of methane that reaches ~70% at high southern latitudes, identical to the depletion of carbon monoxide (another non-condensable species) observed by the Mars Reconnaissance Orbiter<sup>16</sup>.

Figure 1c shows that the condensation–sublimation cycle of  $\text{CO}_2$  drives the entire seasonal cycle of methane calculated by the GCM

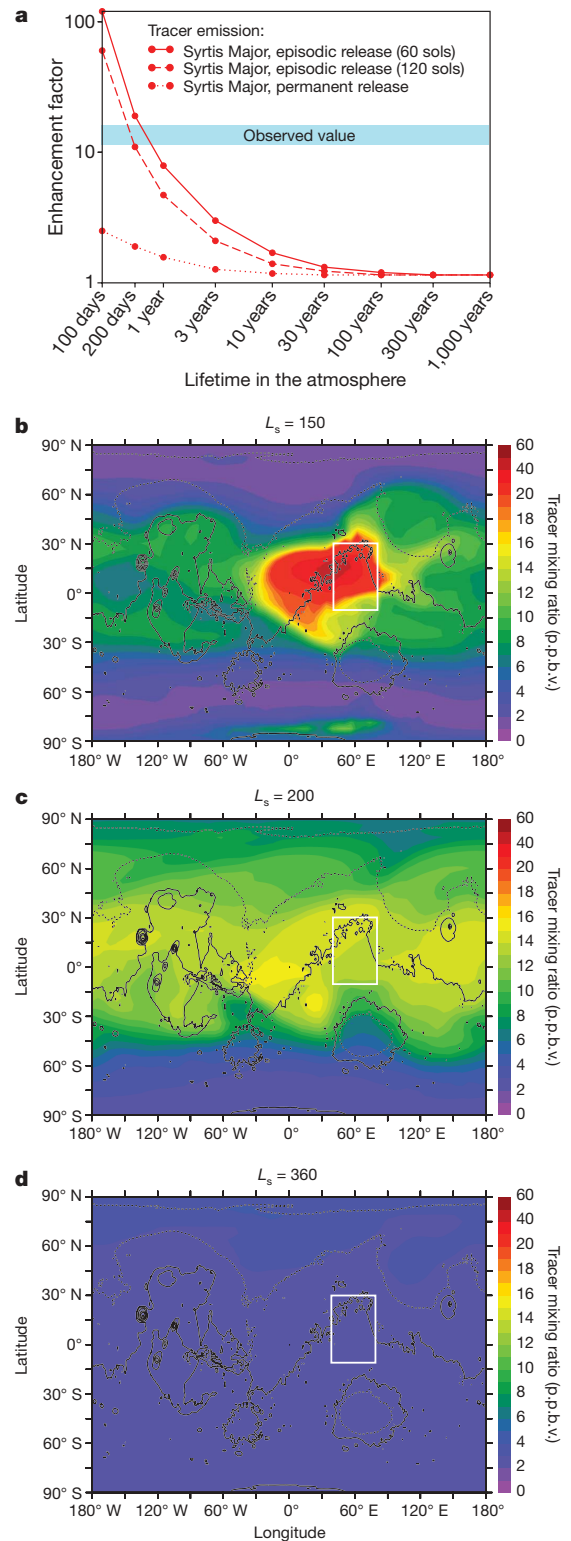
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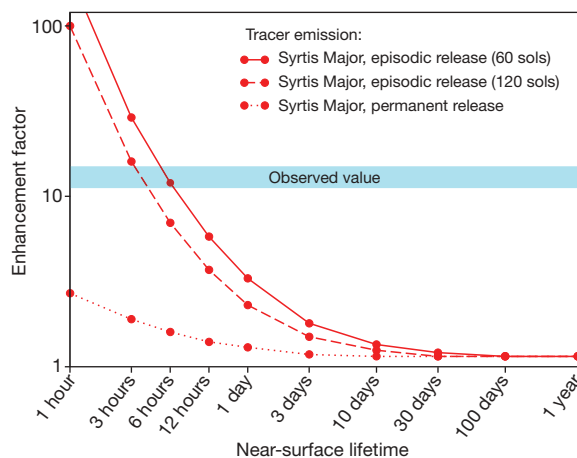
**Figure 1 | Column-averaged methane mixing ratio calculated by the global climate–chemical model.** The simulations include a local source at the surface indicated by the white square. The amount of methane released from the source balances the global photochemical loss integrated over the Martian year, assuming an equilibrium value of 10 p.p.b.v. **a**, Methane is emitted at 10° N 50° E for a period of 60 sols centred on  $L_s = 150^\circ$ . **b**, Methane is emitted at 30° S 135° W for a period of 60 sols centred on  $L_s = 270^\circ$ . Although shown during the period of emission, in both cases the methane maps do not show any signature of the local source. **c**, Seasonal evolution of the zonally averaged mixing ratio for the experiment shown in **a**.

with standard photochemistry. The largest variations are found during southern spring ( $L_s = 180\text{--}270^\circ$ ), when non-condensable species decrease rapidly south of 75° S. At mid-latitudes, the GCM simulation shows a weak seasonal modulation (2–3 p.p.b.v.) of the methane mixing ratio that is mainly related to slow variation in the global pressure of CO<sub>2</sub>. This contrasts with observations by the Planetary Fourier Spectrometer on board Mars Express, which suggest a methane increase from 5 p.p.b.v. to 20 p.p.b.v. between  $L_s = 360^\circ$  and  $L_s = 50^\circ$  (ref. 17). In addition, the GCM does not show any methane diurnal cycle, and no correlation is found with water vapour, contrary to what seems to be observed from Planetary Fourier Spectrometer spectra<sup>17</sup>.

Our results demonstrate that even in the most favourable case of a highly localized source only active around the time of the observation



**Figure 2 | Idealized tracer experiments.** **a**, Maximum enhancement created by a local source of tracer in a column-averaged tracer field, as a function of tracer lifetime in the Martian atmosphere. The release of tracer is either permanent or episodic (60 or 120 sols, centred on  $L_s = 150^\circ$ ) from the region where enhanced methane was observed<sup>3</sup>. Tracer loss occurs at all altitudes according to the designated lifetime. The enhancement factor is defined as the ratio of the tracer abundance in the emission area to the homogeneously mixed value at vernal equinox ( $L_s = 360^\circ$ ), and has an observed value of ~12 (ref. 3). **b**, Column-averaged mixing ratio at  $L_s = 150^\circ$  of a tracer with an atmospheric lifetime of 200 terrestrial days emitted for 120 sols ( $L_s = 120\text{--}183^\circ$ ). The area of emission is indicated by the white rectangle. **c**, As **b** but at  $L_s = 200^\circ$ . **d**, As **b** but at  $L_s = 360^\circ$ .



**Figure 3 | Maximum enhancement created by a local source of tracer in a column-averaged tracer field, as a function of tracer lifetime at the surface of Mars.** Scenarios of emission are identical to those of Fig. 2a. Tracer loss here only occurs in a 10-m-thick layer in contact with the surface, according to the designated lifetime.

itself, methane chemistry as currently understood cannot explain the spatial and temporal enhancements that have been reported. To create variations other than those due to  $\text{CO}_2$  condensation, a considerably more intense source is required. This in turn implies a greater sink, and hence a shorter lifetime in order to maintain the same quantity of methane in the atmosphere. To determine this lifetime in our simulations, we released idealized tracers from the region of Syrtis Major where enhanced methane was observed in 2003 (ref. 3). A particular atmospheric lifetime was attributed to each tracer, which we assumed to be identical on all vertical levels. For each emission scenario (permanent or restricted to 60 or 120 sols), the mass of tracer injected into the atmosphere balances exactly the integrated loss over the Martian year. Figure 2a quantifies the maximum tracer enhancement obtained in Syrtis Major for lifetimes between 100 terrestrial days and 100 terrestrial years. The enhancement factor is defined as the ratio of the tracer mixing ratio in the emission area to the homogeneously distributed value at vernal equinox ( $L_s = 0^\circ$ ), and has an observed value of  $\sim 12$  (ref. 3). This value is reached in our simulations for an episodic release and if the gas has a lifetime of about 200 terrestrial days, in agreement with the value obtained in ref. 3. Under these conditions, the GCM reproduces closely the observed spatial and temporal variability of the methane distribution. During the period of emission, at  $L_s = 150^\circ$ , the intense release of tracer maintains a plume of strong values ( $>40$  p.p.b.v.) over Syrtis Major (Fig. 2b). Rapid dispersion by the atmospheric circulation then occurs. At  $L_s = 200^\circ$  (Fig. 2c), less than 30 sols after the source ceased to emit, the region of emission is no longer identifiable in the tracer map. Mixing combined with the reduced chemical lifetime eventually leads to a quasi-uniform mixing ratio of 2–3 p.p.b.v. at  $L_s = 360^\circ$  (Fig. 2d). This optimum quantitative agreement with the methane observations is obtained with  $\sim 150,000$  t of methane emitted by the sporadic source. This amount is comparable to the yearly geochemical production of methane by serpentinization ( $50,000\text{--}130,000$   $\text{tyr}^{-1}$ ) along the entire Mid-Atlantic Ridge on Earth (ref. 18, and R. Keir, personal communication).

A lifetime of 200 terrestrial days implies the existence of an unknown methane sink that is 600 times more efficient than the loss predicted by the current consensus on terrestrial atmospheric chemistry. It has been proposed that methane can be destroyed on Mars by electrochemical processes triggered by the strong electric fields generated during dust storms<sup>4,19–21</sup>. We investigated this hypothesis by implementing in the GCM the dissociation of methane,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by energized electrons (refs 19, 20; see also Methods). In dust storms, these processes are expected to increase the methane destruction rate and to produce vast

amounts of hydrogen peroxide,  $\text{H}_2\text{O}_2$  (refs 4, 20, 21). The  $\text{H}_2\text{O}_2$  mixing ratio was determined to be 18 p.p.b.v. at  $20^\circ$  S in the dust storm season ( $L_s = 250^\circ$ , equivalent dust visible opacity of  $\sim 1$  at 7 hPa) that followed the detection of the methane plume in 2003 (ref. 22). This amount of  $\text{H}_2\text{O}_2$  is well reproduced by the GCM without the need for electrically charged dust<sup>8</sup>, which provides a lower limit on the dust threshold at which a large-scale impact of electrochemical processes on the chemistry can be envisaged. Using this constraint, we tested various parameterizations of the electric field coupled to the seasonal evolution of dust opacity observed by the Thermal Emission Spectrometer<sup>23</sup> in 2002–04. To obtain an electrochemical loss of methane that approaches the large-scale methane decrease observed between  $L_s \approx 150^\circ$  and  $L_s \approx 360^\circ$ , we find that the electric field must be close to the breakdown field strength value ( $\sim 25$   $\text{kV m}^{-1}$ ) in all the regions with visible dust opacity of  $\sim 2$  or above. The possibility that such extreme bulk electric fields can be sustained in the Martian lower atmosphere has recently been severely questioned<sup>24</sup>. Furthermore, the electrochemical dissociation of  $\text{CO}_2$  calculated in the same conditions rapidly leads to unrealistically large amounts of CO in the model ( $>15,000$  p.p.m.v. at  $L_s = 360^\circ$ ), exceeding the observations by a factor of  $\sim 20$  (ref. 16).

Alternatively, destruction of methane could take place in the Martian regolith. Heterogeneous loss of methane has been shown to be slow on mineral surfaces analogous to Martian materials<sup>25</sup>, but the presence of one or more strong oxidants in the Martian soil could accelerate this process.  $\text{H}_2\text{O}_2$  is a good candidate, which could form through the interaction of minerals with water<sup>26,27</sup> or accumulate in the soil following the precipitation of condensed  $\text{H}_2\text{O}_2$  produced in dust storms or dust devils<sup>21</sup>.

To simulate the loss of methane in the regolith, we assumed that the idealized tracers used previously are only destroyed in the first 10-m-thick atmospheric layer in contact with the surface. Clearly, this hypothesis places an even greater burden on the efficiency of the methane loss process. Figure 3 shows that the global-scale lifetime of methane in this near-surface layer must be in the range 3–6 h to obtain an enhancement factor that matches the observation. Given the turbulent fluxes calculated in the layer, this implies a lifetime of less than 1 h at the atmosphere–regolith interface. Such a lifetime suggests that organics are quite readily scavenged from the modern Martian environment, if reactions in the surface are the only cause of the observed methane variations. This would leave little hope that life as we know it can exist at present or that evidence of past life can be preserved in the shallow surface layer. The next Mars Science Laboratory (2011) and Exomars (2016) rovers will allow examination of this hypothesis, and should be able to determine *in situ* whether methane variations exist on Mars.

## METHODS SUMMARY

The LMD GCM was integrated at a resolution of  $3.75^\circ$  latitude  $\times$   $5.625^\circ$  longitude, on 32 vertical levels from the ground up to about 120 km. The photochemical code implemented in the GCM is an evolution of the model extensively described previously<sup>7</sup>, with updated kinetics and photochemical data<sup>28</sup>.

The simulations including electrochemical processes use the production rates of  $\text{CO/O}^-$  and  $\text{OH/H}^-$  pairs calculated as a function of the ambient electric field  $E$  in ref. 19. These rates published for surface conditions are scaled in the GCM by the local densities of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . For each value of the electric field, the production of  $\text{OH/H}^-$  is therefore constrained by the local vertical distribution of water vapour. The electron dissociation rate of methane as a function of  $E$  is taken from ref. 20.

The efficiency of electrochemical processes grows exponentially with  $E$  up to the atmospheric breakdown level, estimated to be  $\sim 25$   $\text{kV m}^{-1}$  (ref. 29). However, the actual value of  $E$  in Martian dust storms has never been measured. To get around this difficulty, we used the dust opacity  $\tau$  measured by the Thermal Emission Spectrometer<sup>23</sup> as a proxy for dust storm activity, and explored the sensitivity of our results to various linear or nonlinear relationships between  $\tau$  and  $E$ . The  $\tau$  field prescribed in our experiments<sup>30</sup> is three-dimensional, evolves with time, and reproduces the Thermal Emission Spectrometer observations of Martian year 26 (April 2002–March 2004), characterized by a peak in dust storm activity at  $L_s = 315^\circ$  (December 2003). This approach has the advantages of

providing a realistic distribution of the large-scale regions where strong  $E$  fields may be expected, and of constraining the GCM with observations of dust performed in the same Martian year during which enhanced methane was identified<sup>3</sup> (January–March 2003) and  $H_2O_2$  was measured<sup>22</sup> (September 2003).

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