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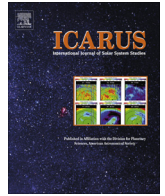
Numerical modelling of the transport of trace gases including methane in the subsurface of Mars

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ABSTRACT

We model the transport of gas through the martian subsurface in order to quantify the timescales of release of a trace gas with a source at depth using a Fickian model of diffusion through a putative martian regolith column. The model is then applied to the case of methane to determine if diffusive transport of gas can explain previous observations of methane in the martian atmosphere.

We investigate which parameters in the model have the greatest effect on transport timescales and show that the calculated diffusivity is very sensitive to the pressure profile of the subsurface, but relatively insensitive to the temperature profile, though diffusive transport may be affected by other temperature dependent properties of the subsurface such as the local vapour pressure. Uncertainties in the structure and physical conditions of the martian subsurface also introduce uncertainties in the timescales calculated.

It was found that methane may take several hundred thousand Mars-years to diffuse from a source at depth. Purely diffusive transport cannot explain transient release that varies on timescales of less than one martian year from sources such as serpentinization or methanogenic organisms at depths of more than 2 km. However, diffusion of gas released by the destabilisation of methane clathrate hydrates close to the surface, for example caused by transient mass wasting events or erosion, could produce a rapidly varying flux of methane into the atmosphere of more than 10^{-3} kg m^{-2} s^{-1} over a duration of less than half a martian year, consistent with observations of martian methane variability. Seismic events, magmatic intrusions or impacts could also potentially produce similar patterns of release, but are far more complex to simulate.

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1. Introduction

Processes active in the subsurface of Mars are currently inaccessible to conventional instruments. However, many proposed processes would have products that might be observed in the martian atmosphere. To use observations of trace gases to understand their production also requires an understanding of their transport from source to the atmosphere.

The mutually supportive detection of methane in the martian atmosphere by a number of different teams (Formisano et al., 2004; Mumma et al., 2009; Fonti and Marzo, 2010; Geminale et al., 2011; Mellon and Jakosky, 1993) has remained controversial (Zahnle et al., 2011) and recent *in situ* measurements have set an upper limit of atmospheric methane abundance around ten times lower than these observations (Webster et al., 2013).

The putative discovery of methane has led to the proposal of a number of potential sources in the martian atmosphere, surface and subsurface (Atreya et al., 2011). Many of these proposed sources would occur deep in the martian crust, and the observed methane could be an indication of active geological processes, where ultramafic rocks react with water in serpentinization reactions (Oze and Sharma, 2005), or could suggest the presence of methanogenic organisms in colonies hundreds of metres to kilometres down (Mancinelli, 2000). The deep subsurface would protect microbes from the near-surface radiation environment (Patel et al., 2003; Dartnell, 2011), the surface oxidising environment (Bertaux et al., 2000) and provide more habitable pressure and temperature conditions (Mancinelli, 2003). A shallower putative source is the decomposition of methane clathrate hydrate (MCH) deposits, which could be stable up to the surface at some latitudes (Chastain and Chevrier, 2007). However, the formation of MCH would still require a genetic source to provide methane from below.

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It remains unknown whether any of the processes described above are active today, or whether the observed methane is a remnant of a period when Mars was more geologically active and could have supported life. Gas released from geological or biological sources deep in the crust may take a significant amount of time to travel to the surface, depending on the mechanism of transport. Even release from shallower sources may not be immediately apparent in the atmosphere. Our incomplete knowledge of the martian subsurface environment makes it difficult to assess the rate of any such transport. The little we do know is derived mainly from secondary sources – extrapolation from surface measurements, modelling and terrestrial or lunar analogues. The exact structure of the subsurface, how porous the martian regolith is, how deep the open pore space extends, whether there may be extensive fracture networks that would enhance transport, the possible presence of ice, liquid water and therefore convective plumes, along with many other questions, all remain open.

Here we describe a numerical model designed to investigate the transport of trace gases from their potential sources in the martian crust through to the atmosphere. The aim of this study was to determine the timescale of trace gas transport by diffusion in the martian subsurface, and to identify and quantify which controlling parameters have the biggest influence, by comparing results with appropriate initial conditions. In particular, we will quantify how relevant parameters alter the time it takes a trace gas to be transported to the surface–atmosphere interface. Investigating these properties will allow us to determine whether the source scenarios presented are compatible with recent observations of the martian atmosphere.

Combining the results of this modelling with future observations of trace gas release will also allow us to begin to form a link between active processes in the crust, which are currently inaccessible to present-day instrumentation, to the atmosphere, where they can be observed by instruments such as the NOMAD instrument (Nadir and Occultation for MArs Discovery) on the ExoMars Trace Gas Orbiter (TGO), due to launch in 2016. Understanding the specifics of trace gas production and transport will aid in the interpretation of results from TGO.

2. Previous work

The majority of studies relating to trace gas transport on Mars to date concentrate on the transport of water vapour through the martian subsurface. These studies provide valuable insight into the possible diffusive properties of the martian subsurface, such as porosity and tortuosity, but cannot be directly applied to other trace gases, and have to be adapted and combined with other work as a starting point for a trace gas transport model.

Clifford and Hillel (1983), Mellon and Jakosky (1993), and Titov (2002) all produced numerical models to investigate the exchange of water between the atmosphere and subsurface, and therefore the stability of ice in the martian regolith. They describe the diffusive properties of the martian subsurface in detail using appropriate values and models from other literature, and the results are utilised here. Clifford and Hillel (1983) in particular detail the potential pore size distribution for the near-surface regolith. Their results show how the H_2O flux varies for different temperature and pore size distributions, and they calculate temperature, diffusion coefficient and ice density profiles for the martian subsurface, as well as mapping the depth of ice across the planet using mean surface temperatures. However, the models of Clifford and Hillel (1983), Mellon and Jakosky (1993), and Titov (2002) are limited in extent and consider the top layer of regolith to be isobaric and homogeneous, in the case of Mellon and Jakosky (1993) to depths of several metres and for Clifford and Hillel (1983) down to several

hundreds of metres. Other models that couple atmospheric, thermal and subsurface transport models include those of Zent et al. (1993) and Schorghofer and Aharonson (2005). Both investigate the cycling of water vapour and utilise thermal models resulting in realistic subsurface temperature profiles.

Hudson et al. (2007) investigated extensively the theoretical background of water vapour diffusion in the martian subsurface and derived diffusion coefficients for martian analogue regolith. Measuring the diffusive properties of some Mars regolith analogues formed the major part of the work of Sizemore and Mellon (2008), which measured the porosity, tortuosity, permeability, density, grain-size distribution, pore-size distribution and surface area of a range of analogue samples including glass beads, JSC Mars-1, Antarctic soils, dune sand and permafrost sediment, with a range of grain sizes where available. In all these investigations, the only diffusing species considered was water vapour, but some of the theoretical considerations and derived values are utilised in the model presented here.

These studies of water vapour diffusion can be adapted and extended to apply to other trace gases. However, while the description of the physical characteristics of the subsurface and the general methodology may be applicable to the diffusion more generally, the transport of water vapour in the subsurface will be very different to that of other trace gases. Local temperatures heavily influence vapour transport and phase changes must be taken into account in any modelling, which must include tracking of saturation pressures. Other processes such as adsorption will also affect water vapour differently to other trace gases. Therefore the knowledge of water vapour diffusion in the martian subsurface, while robust, cannot necessarily be applied directly to other gases. However, some studies have also turned their attention to the transport of other gases.

Bullock et al. (1994) created a coupled atmosphere and subsurface model for the transport of hydrogen peroxide. They included the catalytic destruction of H_2O_2 in the soil and photolysis in the atmosphere using appropriate rate coefficients, as well as phase partitioning to approximate adsorption onto grains, using methods that could be applied to a more extensive diffusive model.

Weiss et al. (2000) estimated the possible size of a methanogenic colony by constraining the possible supply of hydrogen and carbon monoxide. Discretising Fick's law as

$$J = -D\frac{\Delta n}{\Delta z} \tag{2.1}$$

where J is the molecular flux, D is the diffusivity, n is the number density and z is the depth, the diffusion coefficients for H_2 and CO were calculated, providing the supply rate of these gases to a given depth from the atmosphere. These supply rates would act as a limitation to the growth of any deep colonies of methanogenic organisms.

Krasnopolsky et al. (2004) included some discussion of methane diffusion from deep sources along with a description of methane detection and some hypothesised sources. In their considerations diffusion is approximated following Weiss et al. (2000), and they give approximate timescales of methane diffusion for a particular depth calculated using the standard 'diffusive timescale', $\tau = z^2/D$. If the high flux rates calculated by Krasnopolsky et al. (2004) are correct, then to match observations there must be a subsurface sink for methane that severely reduces this flux before it reaches the surface. The model used to obtain these results assumes that the martian regolith is homogeneous over vertical scales of several thousand metres – an assumption that is at odds with the evidence for a regolith column that varies significantly with depth (Clifford, 1993). Thus, the validity of the high flux rates calculated by Krasnopolsky et al. (2004) in appears questionable. The most applicable work to date is the coupled atmospheric-subsurface model of

Meslin et al. (2011), which investigates the adsorptive capacity of the martian regolith as a potential mechanism for the cycling of methane in the atmosphere, modelling gas transport over the top few metres of the subsurface. The treatment of diffusion is via a Fick's law type term, with the bulk diffusion coefficient accounting for the porous medium and including Knudsen diffusion explicitly. Their model neglects advection and is isobaric across the regolith region in question. The temperature is changed according to martian seasonal cycles to investigate the effect of adsorption. Meslin et al. (2011) draw particular attention to the difficulties of scaling the concentration between geometric and pore volume in diffusion equations when looking at porous media, which will be discussed later.

Work to date either focuses solely on the diffusion of water vapour in the martian regolith or, where other trace gases are considered, the models are either simplistic, only applied over short distance scales, or both. To investigate the transport of trace gases through a physically realistic upper crust, a model has been developed (described in the following section) that incorporates a pseudo-realistic subsurface environment, capable of simulating diffusive transport to a depth of 10 km, an approximation of the point at which the regolith pore space becomes negligible (Clifford, 1993; Hanna and Phillips, 2005).

3. The model

Diffusion of gas through the martian subsurface is modelled here using a modified form of Fick's laws. In the absence of source or sink processes, Fick's second law states that, in one dimension,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(D(z)\frac{\partial C}{\partial z}\right) \tag{3.1}$$

where C is the mass of fluid per unit volume, $D(z)$ is the diffusivity, t is time and z is distance, for the general case where D is not uniform.

The problem of diffusion through an inhomogeneous medium (where D is dependent on position) has no exact solution (Crank, 1956). Models of diffusion through regolith-like material (such as those listed in Section 2) typically reduce the problem to a distance range over which the medium can be considered as homogeneous, simplifying the solution. To model the behaviour of a gas transported through the estimated 10 km column of regolith, over which the physical environment can change a great deal, a numerical solution is employed.

The controlling factor in Eq. (3.1) is D, the diffusivity. This depends on the diffusing species and the fluid it is diffusing through, as well as the local temperature and pressure conditions. To modify Fick's law for a porous medium, the 'obstruction factor' given by Hudson et al. (2007) is used and the temperature and pressure dependence is scaled as by Clifford and Hillel (1983) via Wallace and Sagan (1979) and Schwertz and Brow (1951). The diffusivity is then calculated at each depth grid space using

$$D_z = \frac{\phi(z)}{\tau(z)} D_{12} \left(\frac{T(z)}{T_{ref}}\right)^{\frac{3}{2}} \frac{P_{ref}}{P(z)} \tag{3.2}$$

and applied to give

$$\frac{\partial C_{bulk}}{\partial t} = \frac{\partial}{\partial z}\left(D_z \frac{\partial C_{pore}}{\partial z}\right) \tag{3.3}$$

where $\phi(z)$ is the porosity at depth, $\tau(z)$ is the tortuosity at depth, D_{12} is the free gas diffusivity of gas 1 in gas 2, T is temperature, P is pressure, C_{bulk} is the concentration in the geometric volume and C_{pore} is the concentration in the pore space within that volume. The reference temperature and pressure are those for the quoted value of D_{12}, which, for the diffusivity of methane in carbon dioxide, was taken from Kestin and Yata (1968). Using this equation, which

is equivalent to the diffusive part of the model proposed by Meslin et al. (2011) but in this case neglects Knudsen diffusion, requires the concentration to be scaled between bulk geometric and pore volume. The distinction between geometric and pore volume concentration is critical, especially given that the porosity here is not uniform as in the majority of previous subsurface models and could otherwise generate unphysical transport in the absence of a concentration gradient.

The column of the subsurface under scrutiny is divided into a discrete, evenly spaced grid and Eq. (3.3) is discretised using a Crank–Nicolson finite difference scheme. The boundary conditions of the system use a constant zero value condition in the layer of atmosphere above the top of the regolith column to simulate the effect of having a well-mixed atmosphere above that moves diffused gas away at timescales shorter than the diffusion from the surface. As the diffusion timescale across one grid space is of the order $\Delta z^2/D$, methane is transported from the top layer of the subsurface to the bottom of the atmosphere in the order of 100 days. Estimates of vertical and horizontal mixing in the martian atmosphere are far below this value, on the order of a few hours to a few weeks, by boundary layer effects and, away from the surface, the global circulation (e.g. Spiga et al., 2010; Petrosyan et al., 2011). Lefèvre and Forget (2009) modelled the release of a passive tracer such as methane from a localised source and showed that the "plume" is dispersed across the atmosphere within half a Mars-year. We therefore consider any atmospheric concentration to be well mixed over timescales of more than 10^7 s, as 6×10^7 s is approximately one Mars-year. The pore closure limit, which is assumed to occur at a conservative estimate of 10 km (Clifford, 1993; Hanna and Phillips, 2005), sets the lower depth limit of the model.

Below the surface, the porosity of the bulk regolith is assumed to decrease exponentially towards the pore closure limit. The value at the surface has been measured by the Viking landers to be ∼50%, although values from 20% to 50% have also been proposed (Kieffer et al., 1992; Clifford, 1993). This exponential relationship means that the porosity of the regolith at a given depth is given by

$$\phi(z) = \phi_0 e^{\left(\frac{-z}{K}\right)} \tag{3.4}$$

where ϕ_0 is the surface porosity and K is a scaling factor set by the depth of pore closure (Clifford, 1993). The tortuosity, (z) is approximated as $\phi(z)^{-1/3}$ following Millington and Quirk (1961).

The temperature gradient in the subsurface is calculated using a constant thermal gradient following Michalski et al. (2013). This is a simplistic assumption as there is likely to be numerous distinct layers with different thermal gradients due to varying thermal conductivity (Clifford et al., 2010), but suffices here. The effect of temperature gradients between 10 and 30 K km^{-1} is shown in Fig. 1a. The temperature profile chosen makes little difference to the diffusivity.

The two limiting cases of the subsurface pressure gradient are a lithostatic and an atmospheric pressure gradient. If the pore spaces are closed then lithostatic pressure confines the gas in the pores, but if they are open it is only the weight of the gas above that generates pressure, giving rise to a much smaller pressure gradient (Schuerger et al., 2013). Full pore closure would inhibit diffusion, but the real pore pressure profile will most likely be some complex function between the two limits that depends on how connected the pore space is and whether the regolith is ice-saturated, dry, vapour saturated, fully consolidated, fully unconsolidated, or somewhere in between (Max and Clifford, 2001; Hanna and Phillips, 2005).

The pressure profile as a function of depth was calculated using a surface pressure of 600 Pa and a linear depth gradient using either a rock density of 2900 kg m^{-1} or atmospheric density of
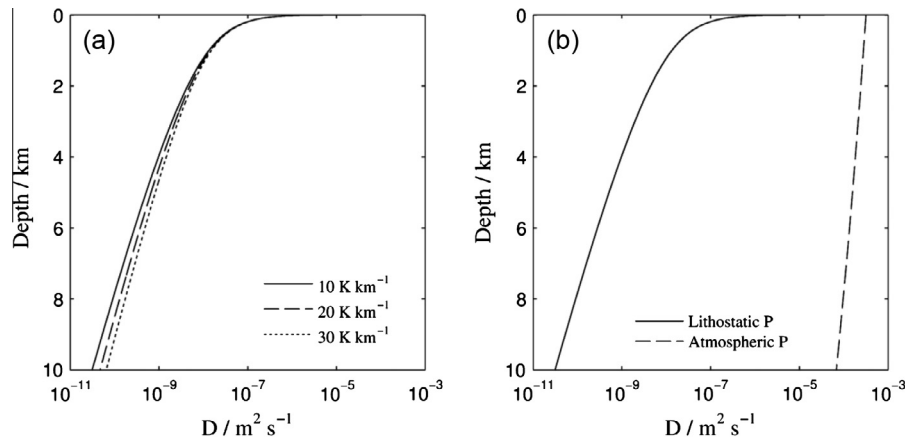
Fig. 1. The effect of subsurface: (a) temperature and (b) pressure profiles on the diffusivity.

0.02 kg m^{-1} and martian acceleration due to gravity (3.71 m s^{-2}). The effect of these two different forms of pressures profile upon the diffusivity is shown in Fig. 1b. In this case, the diffusivity is highly dependent upon the pressure profile chosen, with a variation of several orders of magnitude observed. The impact of these pressure profiles is investigated by their inclusion in the subsequent analyses as end member conditions. The calculation of pressure is a simplification, as the effects of gas density and temperature are not included, nor is the saturation of water vapour in the pore space, but these effects are beyond the scope of our model.

The source concentration is difficult to quantify. The different potential methane sources will have different methane production rates. From modelling of the martian cryosphere by Clifford et al. (2010), realistic depths for serpentinisation and biogenesis, which both require liquid water (Oze and Sharma, 2005; Tosca et al., 2008), would have to be below the base of the cryosphere at around 2–5 km. MCH could occur anywhere in the range of the hydrate stability zone (HSZ), which could potentially be at a depth of several tens of metres in equatorial regions, but only a few metres below the surface near the poles (Chastain and Chevrier, 2007), and may have formed in places beyond the range of the current HSZ in Mars' past.

Geochemical modelling shows that 1 kg of martian analogue rock can theoretically produce 10^{-8} kg of methane in a serpentinization reaction (Schwenzer, 2011). However, this value is a maximum and the specific environmental conditions of the reaction and the availability of reactants and catalysts are crucial factors, and are difficult to model concurrently (McCollom and Bach, 2009). Assuming a rock density of 2900 kg m^{-3}, this gives the maximum production of methane from 1 m^3 of mafic rock as 2.9×10^{-5} kg. However, given that the regolith column is porous down to the pore closure limit and this gas must occupy the pore space in the source region, this value will be reduced by a factor of $(1 - \phi(z))$.

McCollom and Seewald (2001) provide estimates of timescales for serpentisation reactions based on previous work of Wegner and Ernst (1983). For temperatures appropriate to the subsurface depths we consider, McCollom and Seewald (2001) give a time for total conversion at 86,000 years. Assuming ideal reaction conditions and complete conversion to serpentinite, this gives a production rate of 1.07×10^{-17} kg s^{-1} in a 1 m^3 volume of solid rock. This is a very liberal estimate of the maximum production rate, and should not be thought of as descriptive of what might actually be happening – it is merely a starting point for modelling. Terrestrial measurements indicate that the production rate of methane at depth by methanogenic organisms is at the same order of

magnitude of the above estimate for serpentinisation (Onstott et al., 2006).

To estimate production from MCH requires a different method. As MCH does not generate methane but rather traps it until destabilised, the rate of release depends on the volume of hydrate destabilised. Given that 1 m^3 of MCH with 90% saturation can hold 164 m^3 of methane at STP (Max and Clifford, 2000), this means that a unit volume of MCH could release 6.8×10^3 moles of methane at a rate depending on how rapidly this volume of clathrate is destabilised. However, as the ice can only occupy the pore spaces of the regolith, this value must also be scaled by the local porosity within that volume.

4. Results

The purpose of this study was to investigate whether diffusive transport can be invoked to explain observations of methane in the atmosphere of Mars and what parameters control the timescales of this transport. Definition of the threshold amount of methane, which is used to calculate the diffusion timescale, that reaches the atmosphere is essentially arbitrary, and is defined here as when the concentration in the top layer of the subsurface is equal to 10^{-11} kg m^{-3}. This is equivalent to an atmospheric mixing ratio of 1 ppbv in the lower levels of the atmosphere, consistent with current observation limits set by the Curiosity rover of methane in the atmosphere of Mars.

4.1. Release timescales through dry regolith

As shown in Fig. 1b, the pressure environment of the subsurface is an important factor for diffusion. The diffusion timescales ('time to surface', defined by the time it takes to reach a concentration of 10^{-11} kg m^{-3} in the topmost layer of the subsurface) for the extremes of pressure variability profiles based on either lithostatic or atmospheric pressure gradient were calculated. Depths that approximate minimum present-day depth of the water table in the subsurface were used, taken from estimates by Clifford et al. (2010) that the minimum base of the cryosphere is around 2–5 km depending on latitude and the modelling parameters chosen and assuming that the subsurface is saturated with sufficient water to fill the pore space of the underlying crust. The effect of the production rates estimated above were also included to give a range of 'best-guess' estimates for the upper (lithostatic pressure) and lower (atmospheric pressure) extremes of methane diffusion timescales, listed in Table 1. "Zero production rate" means that a given mass of methane is injected at $t = 0$ and no more is added.

Table 1
Estimates of how long methane takes to reach the surface (to a threshold level of 1 ppbv) for a range of given parameters (in Mars-years).

Pressure gradient	Atmospheric		Lithostatic	
Source depth (km)	2	5	2	5
Zero production rate	1.25	13.4	23,800	719,000
Production rate 10^{-17} kg m^{-3} s^{-1}	1.25	13.3	23,500	665,000

These estimates are for the geologically context of a completely 'dry' regolith, *i.e.* one devoid of an extant cryosphere or groundwater system except where the methane is being produced. For this specific case, the intention is to determine a theoretical lower limit on the diffusive transport timescale of release from deep sources of methane. The effect of any extant cryosphere would be to increase the transport timescales, since ice will act to block pore spaces in the regolith and may in fact completely seal the deep subsurface from the atmosphere (Mellon and Jakosky, 1993; Clifford, 1993), and the use of source depths that occur in a more realistic 'unsaturated' groundwater layer would also extend transport timescales. It should be noted that even in the event that the cryosphere is disrupted, the cold-trapping of water vapour from beneath the cryosphere would likely reseal any unsaturated pores within the cryosphere on geologically short timescales (Clifford, 1993). These results therefore provide an approximation of the shortest timescale of release from these depths for a range of subsurface properties, assuming that transport occurs wholly by diffusion. Other transport mechanisms, such as convection, could produce more rapid transport.

There is a difference of approximately an order of magnitude in timescale between source depths of 2 km and 5 km and several orders of magnitude for the two pressure profiles. A non-zero continuous production rate shortens timescales marginally. Following Eq. (3.2), the lower pressure at depth created by an atmospheric pressure gradient means that the diffusivity is several orders of magnitude higher than for a lithostatic profile, as shown in Fig. 1b. As *D* is inversely proportional to the pressure, a lower pressure gradient increases the rate of diffusive transport and means that the gas reaches the surface much faster. In the case of advective transport caused by pressurised release, the opposite would be true. Given that the lithostatic pressure profile is an extreme upper limit and unlikely to be close to reality except in cases of total pore closure and therefore zero gas transport, the atmospheric pressure profile is used for all further simulations.

The timescales in Table 1 show a significant range in the possible time taken for methane to move into the atmosphere from a subsurface source. A minimum of the order one Mars-year and maximum of the order several hundred thousand Mars-years means that without far more constraints on the subsurface environment, it is difficult to make reasonable estimates of diffusion timescales. However, as the results shown in Table 1 are likely to be conservative, and as the shortest is more than one Mars-year, anything but the shallowest of sources would mean that purely diffusive transport does not tie well with the variability of methane as observed in the martian atmosphere, which has shown significant variation over one Mars-year.

From a deep source, methane will take a long time to reach the surface by diffusion, potentially up to several hundred thousand Mars-years. This implies that gas produced by subsurface sources such as methanogenic organisms or serpentinization could only be observed in the atmosphere a long time after their release, with this timescale possibly increased by the presence of any ice in the subsurface during transport. The surface and subsurface environment of Mars is unlikely to have been significantly different several millions of years ago, but the planet may have been subject to significant obliquity and eccentricity variation over this timescale

(Laskar et al., 2004), which could have driven subsurface release, and transient processes such as large-scale faulting could create a path to the surface from deep sources. Since invoking the direct release of methane from a subcryosphere liquid water environment is inconsistent with current orbital or Earth-based observations, some alternative mechanisms for release of subsurface methane are now considered.

4.2. Release scenarios

While release from deep sources such as methanogenic organisms or serpentinisation will be slowed or completely stopped by the putative martian cryosphere, it is possible to conceive of several scenarios that include release from a shallower source such as MCH. The presence of MCH in the shallow martian subsurface has been proposed by a number of studies (Max and Clifford, 2000; Prieto-Ballesteros et al., 2006) and could be stable within the top few tens of metres of the subsurface in equatorial regions and at the surface at high latitudes (Chastain and Chevrier, 2007), therefore presenting a potential reservoir of methane much closer to the surface.

The actual presence of MCH in the subsurface will be dependent on the local temperature and pressure conditions as well as the abundance of methane and water and the thickness of the cryosphere, so the hydrate stability zone may not be completely filled. It is likely that MCH would not be stable if open to the atmosphere (under atmospheric pressure) and therefore is more likely to exist where it is closed-off from the atmosphere, though if the thermal conductivity of the regolith is high enough MCH can be stable in the subsurface even when open to the atmosphere.

Processes that either increase the subsurface temperature or decrease the local pressure could therefore destabilise some of the MCH in the subsurface and open pore space in the regolith, releasing the trapped methane. There are several plausible mechanisms by which this could occur. Seismic events, magmatic intrusions from the mantle, or impacts could all release confining pressure above MCH deposits or increase local subsurface temperatures. Simulating these processes is beyond the scope of this manuscript, but both surface erosion and mass wasting events would also release overburden pressure and are relatively easy to simulate. If the MCH is stable under closed conditions, the release mechanism must also act to open the pore space above the deposit to allow transport to occur, though it is possible that release of enough gas could be sufficient to open a pathway to the surface.

4.2.1. Erosion

The erosion of material at the surface will cause a reduction in overburden/confining pressure. This process has been invoked as a mechanism for the destabilisation of both terrestrial and martian clathrate hydrate deposits either over long timescales (erosion) or in rapid events (mass wasting) (Max and Clifford, 2001; Prieto-Ballesteros et al., 2006; Archer, 2007). There is evidence of rapid local erosional events in Mars' history, especially the large outflow channels have been observed across the surface but global erosion rates are typically low, similar to continental rates on Earth of 10^2–10^4 nm a^{-1} in Noachian terrains and several orders of magnitude lower for Amazonian terrains (Golombek and Bridges, 2000). As an example, Nilus Mensae, which is part of the Kasei Vallis outflow channel network, appears to have been formed by slow seepage weathering, and the morphology suggests an average erosion rate of 2 mm a^{-1} over its period of formation (Williams et al., 2000).

An erosion rate of 2 mm a^{-1} could destabilise a volume of MCH 3 mm in depth every year (over the area of the erosional event) due to the combined effect of overburden release and elevation of temperatures. This release can be modelled by the decomposition of a

volume of MCH across a unit area, multiplied by the timestep length and porosity (as the clathrate hydrate can only occupy the pore space), creating a slow and steady release of methane. This process is included in the model for depths of 10 m to 2 km.

Fig. 2 shows how the peak vertical methane flux at the surface (hereafter "outgassing flux") varies for periods of MCH destabilisation at different depths caused by continuous erosion at the surface as described above. In all cases the outgassing flux increases after the start of the erosional process, rising to a steady state condition that depends on the depth of the MCH source.

Comparing the outgassing fluxes calculated by the model to estimates made from the various detections of methane in martian atmosphere allows us to consider whether the subsurface transport simulated is consistent with these observations. For example, Mumma et al. (2009) calculate that a release rate of $\geqslant 0.63$ kg s^{-1} over a plume area of 9.7×10^6 km^2 is required to match their observations. Assuming homogeneous release, this equates to a flux of 6.5×10^{-14} kg m^{-2} s^{-1}. The outgassing flux shown in Fig. 2 is orders of magnitude greater than the value required to match the results of Mumma et al. (2009) in absolute quantity, but would also suggest that this large outgassing flux will occur continuously over the period of erosion, and is therefore inconsistent with suggestions that the "plumes" of methane are released and then quickly disperse or are destroyed.

4.2.2. Mass wasting

Mass wasting has been observed in a number of contexts on Mars but most notably in debris flows around gullies (Malin and Edgett, 2000; Costard et al., 2002). Large amounts of material can be moved in these debris flows, (Dundas et al., 2012, in press; Raack et al., in press), and total volumes have been estimated using orbital imagery and information from terrestrial analogues to be between 500 and 7000 m^3 per event (Conway et al., 2010). Assuming the rock portion of debris has a density of 2900 kg m^{-3} and that the debris flow has a low proportion of water, this gives an upper limit of 17.6×10^6 kg total mass of rock and water. If the sources of debris flows is assumed to be confined to an area of around 100 m^2 the overburden pressure could be reduced by 653 kPa over this area, decompressing the regolith and potentially destabilising up to 60 m of MCH in a single event. The volume changes involved
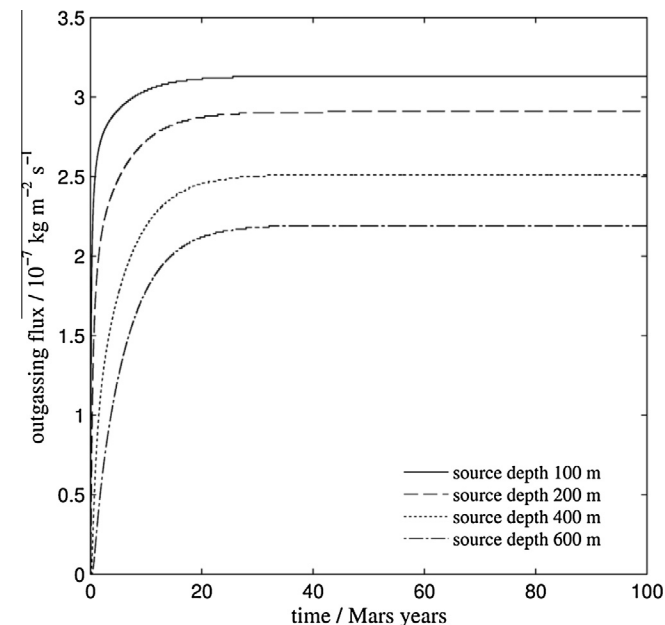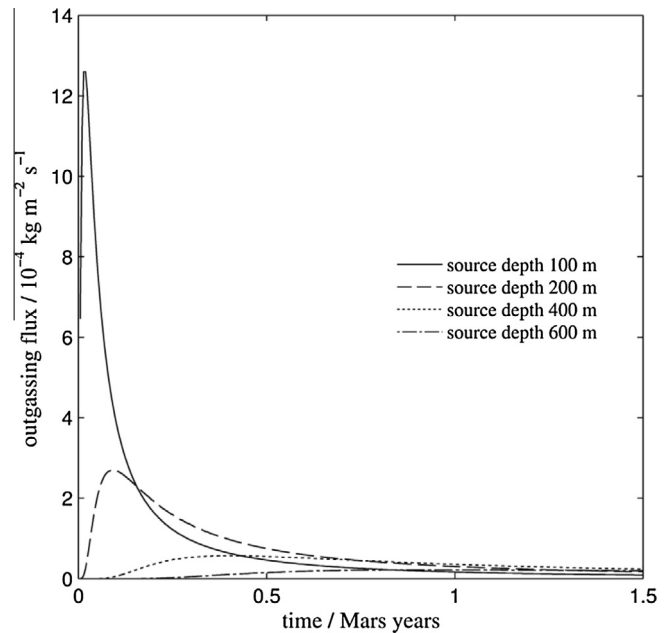
Fig. 3. The effect on source depth on outgassing flux over time for deposits of MCH at 100, 200, 400 and 600 m being destabilised by discrete mass wasting events.

in destabilising MCH could also provide a positive feedback, initiating further release (Max and Clifford, 2001).

Fig. 3 shows how the outgassing flux varies for episodes of MCH destabilisation at different depths caused by discrete mass wasting events as detailed above. The time between the mass wasting event and the peak outgassing flux depends on depth, as does the magnitude of peak outgassing flux. The outgassing flux quickly decreases after the peak release, creating in the possibility for a significant change in flux over less than one Mars-year to occur in the scenario of release from deposits close to the surface. Even for a clathrate source at a depth of 1 km, the outgassing flux rises to a peak and then back to close to the previous value over a relatively short period of less than 10 Mars-years.

The release shown in Fig. 3 is broadly consistent with the type of plume described by Mumma et al. (2009). A mass wasting event over a small area above MCH deposits at depths of up to 200 m could easily produce a short lived plume with concentrations at or higher than those observed, with the atmosphere potentially being able to disperse this gas given that the outgassing flux reduces quickly over periods of less than a Mars-year.

5. Conclusions

The transport of methane produced in the subsurface of Mars has been modelled to assess the timescales of release into the atmosphere. These simulations show that it could potentially take up to several hundred thousand Mars-years for methane to diffuse from a source at a depth through the regolith column and into the atmosphere.

The transport of methane is influenced by a number of parameters, but most notably the profile of the pore pressure in the subsurface, which is currently poorly constrained. The timescales of an atmospheric *vs.* a lithostatic pressure gradient show several orders of magnitude difference. Shallower, stronger sources reach the surface faster, but the mixing of gas in the atmosphere is at much shorter timescales than transport by diffusion and so without very rapid release, spatially confined areas of high mixing ratio are unlikely to happen.

Results from simulations of release from methanogenesis or serpentinization at realistic depths, with a production rate based

Fig. 2. The effect on source depth on outgassing flux over time for deposits of MCH at 100, 200, 400 and 600 m being destabilised by continuous erosion at the surface.

on geochemical modelling of serpentinization, show a large variation in the potential timescale, with the major controlling parameters being the source depth and subsurface pressure profile chosen. All of the timescales calculated are too long to account for short timescale variations in the atmosphere, as observed by ground based and orbital spectroscopy, though short period release into the atmosphere is possible from very shallow sources. This implies that other sources such as the destabilisation of MCH deposits are more likely to be able to reproduce variable observations of methane in the atmosphere.

Additional simulations show that release of methane from destabilising clathrate hydrate sources due to transient mass wasting events could provide a sudden flux of methane into the atmosphere that could feasibly create a 'plume' such as observed by Mumma et al. (2009). Similar release caused by continuous erosion provides a slow and steady methane flux from the surface and therefore cannot explain methane observations that show variable abundance over time, but seasonally variable episodes of mass wasting or cycles of erosion and deposition could produce a 'cyclic' methane signature. Other processes such as seismic events or impacts could also serve to destabilise large volumes of MCH in a relatively short period of time.

The model described here is limited to considering diffusion, which is one of several possible transport mechanisms for trace gases in the subsurface. Advective transport is likely to play a role in transport, especially given the potentially complex pressure environment of the subsurface. Convection could also provide a method for transport, given that both methanogenesis and serpentinization would require elevated temperatures and liquid water, meaning that methane or other gases could be dissolved in convective plumes and transported rapidly upwards (Travis et al., 2003). Both of these mechanisms would most likely transport gas faster than purely diffusive transport and should be included in future modelling. Adsorption may also play a role in moderating transport, as gas can adsorb onto the regolith grains themselves, though this is unlikely to happen in the elevated temperature environment of the deep subsurface, but could have some effect near the surface. The inclusion of these additional mechanisms would significantly increase the complexity of a transport model and are reserved for future work. Understanding the specifics of trace gas production and transport will aid in the interpretation of results from the NOMAD instrument on the upcoming ExoMars Trace Gas Orbiter.

Constructing this model has again highlighted the current lack of knowledge of the martian subsurface environment in general. All the values used in this study are based on modelling from terrestrial or lunar analogues, or measurements of analogue samples, related to Mars using what surface measurements exist. Greater knowledge of the subsurface pressure environment in particular would help refine this work further – the real porosity and pore pressure variation are the environmental parameters that have the greatest influence on diffusion. Terrestrial pore pressure models generally relate to wet rocks, meaning that while they may be applicable to the part of the martian subsurface with an extant hydrosphere, it is difficult to assess the pressure profile in the layer of dry regolith above the permafrost. NASA's InSight mission, due to launch in 2016, could provide some limited constraints on the subsurface regolith properties via seismometry and the subsurface temperature environment via a heat flow probe.

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