



# 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  $10^{-3} \text{ kg m}^{-2} \text{ s}^{-1}$  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; Geminali 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<sub>2</sub>O 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<sub>2</sub>O<sub>2</sub> 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

$$J = -D \frac{\Delta n}{\Delta z} \quad (2.1)$$

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<sub>2</sub> 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

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