

# The effects of subsurface transport on the isotopic signatures of methane release on Mars

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## Abstract

The ExoMars Trace Gas Orbiter (TGO) will have the ability to detect and characterise a broad suite of trace gases in the atmosphere of Mars. Interpreting the results of this mission will require an understanding of how these trace gases are transported from their sources, which may be deep underground, to the atmosphere, as this transport will change signatures that might identify the source of the gas. Here we present results of modeling designed to measure effect of transport on the release of gas from putative subsurface methane sources.

## 1. Introduction

Many of the proposed sources of the methane observed in Mars' atmosphere would occur hundreds of metres to several kilometres deep in the crust. Candidates include the serpentinisation of mafic rocks [1] and colonies of methanogenic organisms [2]. Shallower sources include the decomposition of deposits of methane clathrate hydrate in the cryosphere [3]. The gas produced from all of these sources and other gases produced geologically in the crust will potentially have to travel through the martian regolith before they can be observed in the atmosphere by missions such as the TGO.

Transport rates for gases of different molecular mass vary and therefore transport will cause a change in the isotopic fractionation that would be measured in the atmosphere from the fractionation of the original release. As measuring isotopic fractionation could be used a signature to help identify the original source of the methane [4], any change in fractionation caused by transport through the regolith could obscure such signatures.

We have developed a numerical model of subsurface transport from previous work [5] to quantify the change in isotopic fractionation of methane release in the subsurface.

## 2. The model

The model utilizes a discretized version of the the Dusty Gas Model, in the limit of a trace gas, with Darcy's law included:

$$\begin{aligned} \frac{\partial \phi \rho \omega_1}{\partial t} = & \frac{\partial}{\partial z} \left( \frac{D_{iK}}{D_z + D_{iK}} D_z \rho \frac{\partial \omega_1}{\partial z} \right) \\ & + \frac{\partial}{\partial z} \left( \frac{D_{iK}(D_z + D_{2K})}{D_z + D_{iK}} \rho \omega_1 \frac{1}{P} \frac{\partial P}{\partial z} \right) \\ & + \frac{\partial}{\partial z} \left( \frac{k}{\mu} \frac{\partial P}{\partial z} \right) \end{aligned} \quad (1)$$

where  $\omega_1$  is the mass fraction of the trace gas under scrutiny,  $z$  is the depth in the subsurface,  $t$  is time,  $\phi$  is the porosity of the porous medium,  $\rho$  is the gas density,  $D_z$  is the Fickian diffusivity modified for a porous medium,  $D_{iK}$  is the Knudsen diffusion coefficient of gas  $i$ ,  $P$  is the local gas pressure,  $k$  is the permeability of the porous medium and  $\mu$  is the viscosity of the gas.

## 3. Application

By transporting the  $\text{CH}_4$ ,  $^{13}\text{CH}_4$  and  $\text{CDH}_3$  isotopologues of methane from a source at a given depth with a given carbon and hydrogen fractionation, the change in these fractionation values due to transport through regolith can be quantified.

Our simulations show that the evolution of the concentration of both isotopologues in the topmost layer of the subsurface means that the isotopic fractionation measured there quickly reaches a steady state value that is different to the original source fractionation. This steady state value is used to quantify the difference from the original source fractionation and the observable atmospheric fractionation depends on a number of parameters of the original release, for example the source depth and the original source fractionation.

Given that different potential sources would produce methane of a different isotopic fractionation, the change in fractionation due to transport could mask the isotopic signatures of different sources, or even create 'false-positives'. For example, biogenic methane tends have a  $\delta^{13}\text{C}$  value more negative than around -50 ‰ [6], but a scenario could exist whereby methane released from an originally unfractionated source could appear to have an isotopic value close to or greater than standard biogenic values if it had been transported through a significant amount of regolith. A simple measurement of methane fractionation in the atmosphere would not be sufficient to unambiguously determine the subsurface source and other effects must be taken into consideration.

## 6. Summary and Conclusions

While MSL has set a low upper limit of methane in the martian atmosphere, if future missions such as the TGO confirm the presence of methane and, using high sensitivity instruments, begin to measure the isotopic fractionation of the methane, it will be possible to use multiple lines of evidence to constrain the potential sources of the methane.

If isotopic fractionation is used as a source signature, care must be taken to account for other processes that affect the fractionation. The model presented here quantifies changes due to transport through the martian regolith, but chemical reactions and adsorption with regolith grains will also contribute to a change in isotopic fractionation. Building up an understanding of these processes will allow much more rigorous examination of the signatures of any martian methane.

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