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Methane on Mars: A Perspective from Earth

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We discuss the potential of terrestrial abiotic gas seepage, either as focused flow or diffuse and widespread microseepage, as analog of possible degassing pathways on Mars. Newly discovered CH_4 isotopic data on Earth, may then provide a fundamentally new reference for understanding the Martian CH_4 origin.

Gas seepage from ophiolites on Earth: possible pathways of CH_4 degassing on Mars

If confirmed, the recently-discovered methane (CH_4) plume on Mars, in the Northern Summer of 2003, would reflect an emission of ~ 19 $x10^3$ tonnes y^{-1} and possibly even ~ 57 $x10^4$ tonnes y^{-1} (Mumma et al. 2009). Serpentinization in ophiolitic rocks is one of the main processes that are inferred for the origin of methane on Mars. Ophiolites or, hydrated mineral-bearing rocks in general on Earth could serve as analogues.

Currently, it is not clear whether low-temperature serpentinization can be an abiogenic methane "kitchen" where methane might be generated fast enough to sustain vigorous and long-lasting seeps. In cases of fluxes of the order of several tonnes per year, a pressurized accumulation must exist. In case of lower fluxes, probably gas accumulations are not necessary and low temperature serpentinization can be fast enough to charge episodic seeps. These concepts are fundamental to our understanding of potential sources and pathways for the Martian methane, and they need to be studied with the support of analogue seepage data on Earth.

We investigated a terrestrial abiogenic CH_4 seepage from ophiolitic rocks at the "eternal fires" of Chimaera in Turkey. Measured methane fluxes from the seep (>130 tonnes of CH_4 per year) suggest a great potential of gas production and subsurface accumulation from low-temperature serpentinization. We have also detected invisible microseepage of abiotic gas (as confirmed by isotopic analyses), far from Chimaera, in correspondence with serpentinized ophiolites (CH_4 fluxes up to 1000 mg m^{-2} day^{-1}). This microseepage process is quite common on Earth (Etiope and Klusman, 2010), and it could also occur on Mars, even if macro-seeps or mud volcanoes are lacking or are not active. Then, the plume-related ~19 kton/y on Mars could be supplied by a diffuse exhalation from an area of 500 to 5000 km^2 with a microseepage of ~10-100 mg m^{-2} day^{-1} or, alternatively, by a few hundreds macro-seeps like Chimaera. If a global Martian CH_4 source of around 100-300 t/y is required to maintain a 10 ppb atmospheric level (Atreya et al, 2006), then just one seep like Chimaera or a weak microseepage of 10 mg m^{-2} day^{-1} from only 30 to 90 km^2 would be sufficient. From these numbers we conclude that either localized (macro-seeps) or diffuse exhalations (microseepage) of abiotic methane from ophiolites may be effective pathways of methane degassing on Mars.

Abiogenic oxidation: a key process for understanding Martian CH_4

However, a vexing observation of Mars methane is the seasonal variation of methane concentrations (Fig.1 inset). Most importantly, as Mumma et al (2009) state: "the destruction lifetime for CH_4 is much shorter than the time scale (~350 years) estimated for photochemical destruction".

The Mars atmosphere contains oxidants like H_2O_2 and other superoxides which are likely scavenging all organic matter on the Mars surface and may "accelerate the loss of methane from the atmosphere" (Atreya et al. 2006). Mumma et al (2009) report a winter vs. summer variation of the CH_4 of 3 ppb and 6 ppb, respectively, i.e. 50% of the methane is removed at a rate that cannot be accounted for by photochemical processes. We found a terrestrial analog for abiotic oxidation of methane that could explain the excess removal process of methane on Mars. We discovered, in fact, a natural gas seep in Romania, close to Homorod village in Transylvania, with CH_4 characterised by values of deuterium concentrations, δD_{CH4}, up to +124‰ that far exceed those reported for any terrestrial gas (Etiope et al. 2010). This extreme value seems to be due to abiotic oxidation mediated by metals, and not by microbes. With this model, the isotope variations of methane on Mars would be similar to those we observed on Earth (see "Homorod" in Fig.1). Abiogenic oxidation similar to that occurring in the Homorod methane, may produce δD_{CH4} values beyond +200‰ which we also could expect in Mars methane. In particular, the observed seasonal variations, if caused by oxidation, should result in large seasonal variations of carbon and, in particular, hydrogen isotopes of Mars CH_4. Abiogenic oxidation would also apply to methane generated by psychrophilic methanogenic biota in cryoregimes that may exist on Mars (Onstott et al. 2006). As the isotopic composition of CO_2 on Mars is similar to that on Earth (Clayton and Mayeda 1988; Wright et al. 1990) one could infer that the enzymatically catalyzed biologic fractionation on Mars is similar to that on Earth which is at low temperatures (Schoell 1988).

With either origin of methane, abiotic or microbial, extremely positive δD_{CH4} values would be the result of "oxidative pumping" (Fig. 1) and would be still compatible with biotic sources. The use of deuterium in CH_4 as an indicator of abiogenic methanogenesis is, then, invalidated. Although the D/H ratio is considered a fundamental biomarker, since biological systems prefer hydrogen (H) to deuterium (^{2}H), our results indicate that this preference can be masked by abiogenic oxidation, occurring in the absence of oxygen. This is important in the context of identifying extraterrestrial biomarkers and it shall be taken into account when CH_4 isotopic data will be hopefully available from the next Martian missions (Webster 2005).

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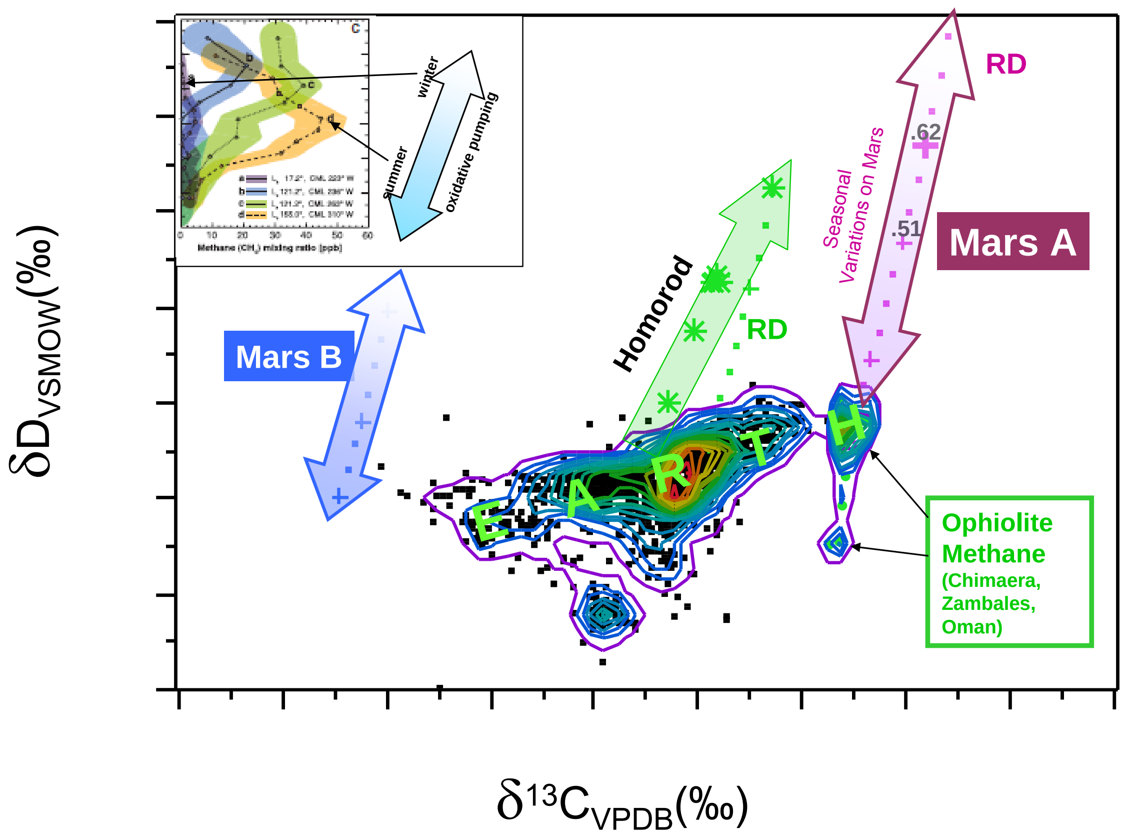

Figure 1

Carbon and hydrogen isotopic composition of methanes of different origins on Earth and potential methane isotope variations on Mars. We use isotopic data of terrestrial ophiolite methanes (Chimaera, Zambales, Oman) as possible analog of abiogenic Martian CH_4 ("MARS A"), and apply the Homorod abiogenic oxidation as analog for isotopic fractionation on Mars ("RD" for Rayleigh distillation). Summer-winter concentration variations (see inset from Mumma et al., 2009) would result in a seasonally cyclic variation of methane C and H isotopes. Microbial methane on Mars ("MARS B") is invoked as being formed from enzymatically catalyzed reduction of Mars CO_2 at low temperatures similar to methane formed in Antarctic shelf sediments.

Homorod: the terrestrial seep with the highest δD_{CH4} value, derived by abiogenic oxidation of thermogenic gas. "EARTH" data are from a global data-set of thermogenic and biogenic commercial gas (Schoell, unpublished). Homorod: Etiope et al, 2010a; Chimaera: Hosgormez et al 2008; Zambales: Abrajano et al. 1988; Oman: Fritz et al. 1992.