UNDERSTANDING THE ORIGIN OF METHANE ON MARS THROUGH ISOTOPIC AND MOLECULAR DATA FROM NOMAD (EXOMARS): WILL THERE BE MORE ANSWERS OR QUESTIONS?

G. Etiope
[1]*Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy*

Introduction: The NOMAD spectrometer suite on ExoMars Trace Gas Orbiter (TGO) can measure the stable C isotope composition ($^{13}C/^{12}C$) of methane (CH_4) and the concentration of ethane (C_2H_6) in the atmosphere of Mars. On Earth, these parameters are known to provide useful, although not decisive, information on the origin of methane, biotic (microbial or thermogenic) vs. abiotic. Such information is therefore expected from ExoMars. In particular, it has been considered that ^{12}C-enriched CH_4 and high CH_4/C_2H_6 ratios on Mars may indicate the existence of microbial activity, while ^{13}C-enriched CH_4 should be attributed to abiotic (inorganic) gas [1,2]. But things are not exactly like that. The interpretation of isotopic and molecular gas data is not straightforward: not on Earth, and even less on Mars. Here, I briefly discuss the main interpretative problems and ambiguities that we will certainly face in the upcoming atmospheric measurements of Exomars.

Isotopic CH_4 composition

Today we know that methanes of different origins may have similar $^{13}C/^{12}C$ (or $\delta^{13}C$) values: for example, abiotic methane is not necessarily ^{13}C-enriched and may have isotopic composition similar to biotic gas (Fig. 1) [3-4]. Vice versa, microbes in special environments can produce relatively ^{12}C-depleted CH_4, with $\delta^{13}C$ values between -30 and -40‰, resembling thermogenic gas [4]. The CH_4 isotopic composition is basically controlled by the isotopic composition of its precursor (a carbonate or CO_2, considering only inorganic compounds), which on Mars may be quite variable. If CH_4 derives from atmospheric fractionated CO_2, with $\delta^{13}C$ ~ +46‰ [5], it will be likely very ^{13}C-enriched, with positive $\delta^{13}C$-CH_4 values, regardless its genetic mechanism. If the precursor CO_2 is atmospheric unfractionated or has a magmatic origin similar to CO_2 observed in Zagami meteorites (with $\delta^{13}C$ from -20 to 0‰; [6]), then CH_4 may have $\delta^{13}C$ values similar to those observed on Earth. Using CO_2 with $\delta^{13}C$ of -40‰, laboratory experiments of Sabatier reaction produced abiotic CH_4 with $\delta^{13}C$ as low as -140‰, resembling microbial gas [3]. Temperature and degree of reaction completeness influence the isotopic composition of produced CH_4.

In addition, post-genetic alterations, such as oxidation, can greatly modify the original CH_4 isotopic composition. On Mars, CH_4 oxidation, especially by hydrogen peroxide in the regolith, can increase the $\delta^{13}C$ value, transforming an apparent "microbial" signature into an "abiotic" one (Fig.1). Isotopic fractionation during diffusion in low permeability rocks can instead lead to ^{12}C-enrichment in the released gas. Although advection is the dominant mechanism of gas migration to the surface (seepage; [7]), diffusion steps may take place through less permeable, sealing rocks met by the gas on its way to the surface.

Methane/ethane ratio

Terrestrial microbes produce CH_4 and, in special conditions, trace amounts of C_2H_6. High C_1/C_2 values (>1000) are often suggestive of a dominantly microbial gas. Nevertheless, thermogenic gas, produced by thermal breakdown of organic matter at relatively high temperatures (over-mature source rocks), can have C_1/C_2 values, similar to those of microbial gas [4]. And abiotic gas has a wide range of C_1/C_2 ratios, overlapping microbial and thermogenic ranges (Fig. 1). Laboratory experiments have shown that the lower the temperature of the inorganic (Fischer-Tropsch Type) reaction, the lower the energy for polymerization of CH_4 molecules to form C_{2+} hydrocarbons [3]. Overall, the C_1/C_2 ratio is not a reliable indicator of gas origin. Also, we must consider the possibility that Martian microbes, if they exist, could produce more ethane, relative to methane, compared to terrestrial microbes.

In addition, chemical and physical post-genetic processes may change the original molecular composition of the gas. During gas migration in rocks, the C_1/C_2 ratio may increase because of molecular fractionation or segregation, a sort of filtration during advection in permeable, fractured rocks [4]. Also, once gas has reached the atmosphere, C_2H_6 is more rapidly oxidised than CH_4, resulting in a further increase of the C_1/C_2 ratio.

The problem of analysing methane in the atmosphere

On Earth, we know that interpretation of the origin of CH_4 produced in the subsurface strictly depends on the type of system where gas is sampled and analysed (atmosphere, surface or subsurface water, soil, rocks). The atmosphere, in particular, is not the best place to study the origin of methane released from the ground. As described above, a series of post-genetic alterations may occur during seepage and, on Mars, significant isotopic and molecular fractionations are expected in the strongly oxidising atmosphere. Accordingly, the isotopic composition of CH_4 and the CH_4/C_2H_6 concentration observable by NOMAD can be totally different from those of the original gas produced in the subsurface. This problem can be mitigated by integrating the NOMAD observations with geological analyses of potential gas emission sites, whose location can be estimated by atmospheric circulation modelling [8]. In future missions, it would be desirable that gas be analysed directly in the soil or in the subsurface [7].

Conclusion

The isotopic composition of methane and the methane/ethane ratio observable by NOMAD in the Martian atmosphere may have a wide range of values; each value could reflect a number of possible genetic mechanisms (microbial, thermogenic and abiotic). In addition, the isotopic and compositional features observable in the Martian atmosphere will likely be different from those of the gas originally produced in the subsurface, and thus may not represent the genetic mechanism. However, the following general statements can be made:

(1) the $^{13}C/^{12}C$ ratio of CH_4 could be similar to that observed on Earth only if it derives from unfractionated or magmatic CO_2, or a C precursor with negative $\delta^{13}C$ values.

(2) If both methane and ethane are detected by NOMAD, then the gas could be abiotic, assuming that there are no ethane-producing microbes on Mars, and that there is no ancient organic matter in deep sedimentary rocks that could be degraded by temperature.

(3) if ethane is not detected, then we may hypothesize that the gas is: (a) microbial, (b) abiotic or thermogenic, both molecularly fractionated, (c) thermogenic from overmature organic-rich source rocks, or (d) abiotic generated at very low T.

In conclusion, there will be a considerable degree of uncertainty regarding the origin of any methane detected by NOMAD. Interpreting methane-ethane data will not be easy, and probably there will be more questions than answers. Atmospheric and geological analysis can add insight into gas origins, but in future missions, direct gas detection in the Martian subsoil, coupled with a better knowledge of subsurface geology (type of rocks, permeability, temperatures) should reduce the interpretative uncertainties.

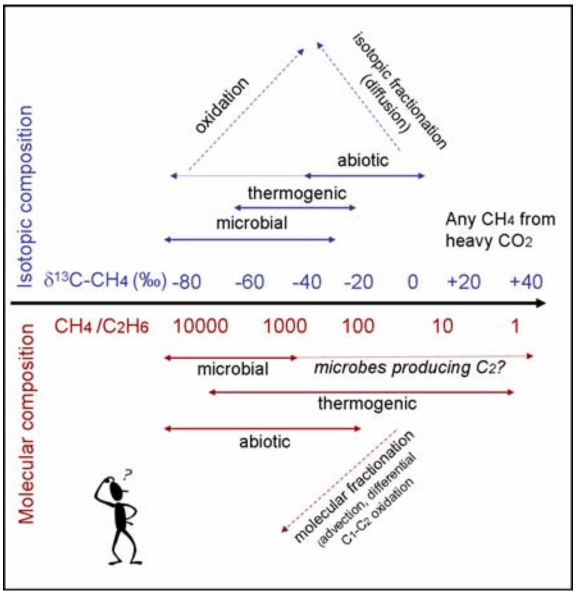

Figure 1: Ranges of terrestrial $\delta^{13}C$-CH_4 and C_1/C_2 values for the three classes of methane origin (microbial, thermogenic, abiotic), their possible extension to Mars (thin arrows) and potential post-genetic modifications (dashed arrows).

References:

[1] Allen M., Sherwood Lollar B., Runnegar B., Oehler D.Z., Lyons J.R., Manning C.E., Summers M.E., **EOS**, 87, 433-448, 2006.
[2] Atreya, S.K., Mahaffy, P.R., Wong, A.-S., **Planet. Space Sci.** 55, 358–369, 2007.
[3] Etiope G., Ionescu A., **Geofluids**, 15, 438-452, 2015.
[4] Etiope G., Natural Gas. **Encycl. of Geochemistry**, Earth Sciences Series, Springer, 1-5, 2017.
[5] Webster C.R., et al., **Science**, 341, 260-263, 2013.
[6] Niles, P.B., Boynton, W.V., Hoffman, J.H., Ming, D.W., Hamara, D., **Science** 329, 1334-1337, 2010.
[7] Oehler D., Etiope G., **Astrobiology**, http://dx.doi.org/10.1089/ast.2017.1657, 2017.
[8] Viscardy, S., Daerden, F., and Neary, L., **Geoph. Res. Lett.**, 43, 1868-1875, 2016.