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Understanding the origin of methane on Mars through isotopic and molecular data from the ExoMars orbiter

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ABSTRACT

The identification of methane (CH_4) and its origin on Mars is a major mandate of the ExoMars mission, because this gas has potential links with biological activity. Starting in 2018, the NOMAD spectrometer suite of the ExoMars Trace Gas Orbiter can measure, in the martian atmosphere, important parameters that can contribute to identification of the origin of methane, i.e., its stable C isotope composition, its isotopologue $^{13}CH_3D$, and ethane concentrations. Assuming that the gas is produced in subsurface rocks and considering genetic and secondary, post-genetic alteration processes observed on Earth, it is anticipated that isotopic and molecular composition of the gas in the martian atmosphere may have a wide range of values, each reflecting a number of possible genetic mechanisms, microbial, thermogenic or abiotic. Due to oxidation and alterations during migration, the CH_4 isotopic signature observable in the martian atmosphere will likely be different from the one originally produced in the subsurface. Although there will likely be a considerable degree of uncertainty regarding the origin of any methane detected by NOMAD, integrating atmospheric with geological analysis can help to reduce the uncertainties.

1. Introduction

After a seven-month journey with the launch in March 2016, and aerobraking started in October 2016, in February of 2018 the ExoMars Trace Gas Orbiter (TGO) entered the orbit of Mars where it can start "sniffing" in search for methane (CH_4). The identification of CH_4 and its origin on Mars is a major mandate of ExoMars mission (http://exploration.esa.int/mars/46048-programme-overview*)*, because this gas has potential links with biological activity: microbial and thermogenic (cumulatively termed "biotic") CH_4, produced by microbes (methanogens) and degradation of organic matter in rocks, respectively, would represent a direct link with the existence (past or present) of life; abiotic CH_4, produced by geochemical processes (magma degassing or low temperature chemical synthesis, such as Sabatier reaction between CO_2 and H_2; Etiope and Sherwood Lollar, 2013), or by thermogenic degradation of abiotic organics (Oehler and Etiope, 2017), even if it is not directly originated from biological activity, may be source of energy (electron donor) for microbial activity and life origin (Russell et al. 2010). Although CH_4 has already been detected at very low concentrations (0.2–60 ppbv) in the martian atmosphere by terrestrial telescopes, martian orbiters and rovers (e.g., Formisano et al. 2004; Mumma et al., 2009; Fonti and Marzo, 2010; Webster et al., 2015), its origin is still elusive (potential origins are reviewed by Oehler and Etiope, 2017). Due to the relatively short lifetime of CH_4 in the martian atmosphere (300 years but potentially as short as 200 days; Lefèvre and Forget, 2009) and its varying abundance, an active gas source, below the ground (geological or biological) or above the ground (e.g., UV irradiation, meteor shower) must exist (e.g., Atreya et al. 2011). For the first time, ExoMars-TGO, through its NOMAD spectrometer suite (Vandaele et al. 2015), can analyse not only CH_4 concentration in the martian atmosphere, but also its stable C isotope composition ($^{13}C/^{12}C$, conventionally indicated as $\delta^{13}C$ vs. Vienna Peedee Belemnite standard, or VPDB), the isotopologue $^{13}CH_3D$, and the concentration of ethane (C_2H_6). CH_4 concentration data can also be provided by the TGO Atmospheric Chemistry Suite (ACS; Korablev et al. 2015). On Earth, combined CH_4 isotope-isotopologue and ethane data are known to provide useful information on the origin of methane, biotic (microbial or thermogenic) vs. abiotic. The interpretation of the NOMAD data, however, will not be easy and straightforward. In previous works, it was considered that ^{12}C-enriched CH_4 and high CH_4/C_2H_6 ratios on Mars may indicate the existence of microbial activity,

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while ^{13}C-enriched CH_4 should be attributed to abiotic gas (Allen et al. 2006; Atreya et al. 2007). But there are complications to that simple picture. Here, I briefly discuss the main interpretative problems and ambiguities that we will face in the upcoming atmospheric CH_4 measurements of ExoMars, assuming that the gas is released from the ground and considering genetic and secondary, post-genetic alteration processes similar to those observed on Earth. Integrating the NOMAD data with geological analysis of the areas of potential provenance of methane will help in mitigating the interpretation uncertainties.

2. Isotopic CH_4 composition

The stable C isotope ratio, $^{13}C/^{12}C$ (or $\delta^{13}C$ vs VPDB) is a basic parameter for the study of the methane origin: low values (^{12}C-enrichment, $\delta^{13}C < -50‰$) are generally due to microbial production, while high values (^{13}C-enrichment, $\delta^{13}C > -50‰$) typically refer to thermogenic or abiotic gas production. A better identification of the methane origin is possible when the C isotope ratio is examined together with the stable H isotope ratio, $^{2}H/^{1}H$, as routinely made in natural gas geochemistry (Fig. 1). But the $^{2}H/^{1}H$ ratio is not measured by NOMAD. The problem with $^{13}C/^{12}C$ is that methane of different origins may have similar $^{13}C/^{12}C$ values: for example, abiotic methane is not necessarily ^{13}C-enriched and may have isotopic composition similar to biotic gas (Etiope and Sherwood Lollar, 2013; Etiope and Ionescu, 2015) (Fig. 1). Conversely, microbes in special environments can produce relatively ^{12}C-depleted CH_4, with $\delta^{13}C$ values between −30 and −40‰, resembling biotic thermogenic gas (Etiope, 2017 and references therein). 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 $\delta^{13}C \sim +46‰$ (Webster et al. 2013), it will be likely very ^{13}C-enriched, with positive $\delta^{13}C$-CH_4 values, regardless its origin. 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‰; Niles et al. 2010), then CH_4 may have $\delta^{13}C$ values similar to those observed on Earth (Etiope et al. 2010). In laboratory experiments of the Sabatier reaction between CO_2 and H_2, using CO_2 with $\delta^{13}C$ of −40‰, abiotic CH_4 was produced with $\delta^{13}C$ as low as −140‰, resembling microbial gas (Etiope and Ionescu, 2015). 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"

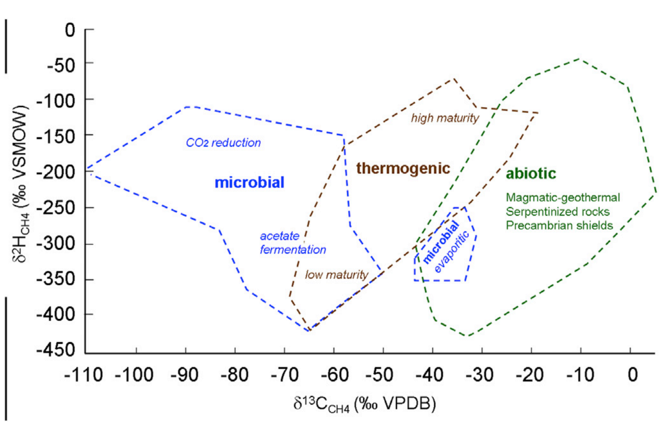

Figure 1. Stable C and H isotope diagrams used to identify methane origin on Earth. Re-drawn from Etiope (2017).

one (Fig. 2a). In addition, isotopic fractionation during diffusion in low permeability rocks can instead lead to ^{12}C-enrichment in the released gas (Fig. 2a). Although advection is the dominant mechanism of gas migration to the surface (seepage), diffusion steps may take place through less permeable, sealing rocks met by the gas on its way to the surface.

3. 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 biogenic organic matter at relatively high temperatures (over-mature source rocks), can have C_1/C_2 values, similar to those of microbial gas (Etiope, 2017 and references therein). And abiotic gas has a wide range of C_1/C_2 ratios, overlapping microbial and thermogenic ranges. Laboratory experiments have shown that the lower the temperature of the inorganic Sabatier reaction, the lower the energy for polymerization of CH_4 molecules to form C_{2+} hydrocarbons, resulting in very high C_1/C_2 ratios (Etiope and Ionescu, 2015). 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 (Fig. 2b). 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, as frequently observed on Earth (Etiope et al. 2009). 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.

4. CH_4 isotopologue $^{13}CH_3D$

The isotopologues (or clumped isotopes) of CH_4 can reveal the temperature of CH_4 formation and therefore may help in understanding its origin. But isotopologue thermometry is reliable only at high temperatures (generally >150 °C) when isotopologues are in thermodynamic equilibrium (Young et al. 2017). To understand whether the $^{13}CH_3D$ is in isotopologue equilibrium, a second parameter, $^{12}CH_2D_2$, is necessary (Young et al. 2017), which unfortunately cannot be measured by NOMAD. The combination of $^{13}CH_3D$ vs $^{12}CH_2D_2$ is also essential for unveiling possible microbial inputs (Young et al. 2017). Abiotic and microbial gas can be formed at the same low temperature, and in this case $^{13}CH_3D$ data alone are hard to interpret. The $^{13}CH_3D$ thermometry can however differentiate between biotic thermogenic (formed up to 250 °C) and magma-derived gas (formed at much higher temperatures, generally >300 °C).

5. The problem of analysing CH_4 in the atmosphere and the support of geological analysis

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 gas 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 taking into account atmospheric circulation modelling (Viscardy et al. 2016). For example, if a CH_4 source is traced to