

UV induced methane and volatile organic carbon emission from the Murchison meteorite

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Abstract

Meteorites and interplanetary dust can deliver organics to the Mars. The fate of these organics is poorly understood. Long-term (>100 hours) irradiation studies of the Murchison meteorite show the emission of previously-reported methane (CH₄), along with 17 newly detected volatile organic carbons (VOCs), of which acetaldehyde, formaldehyde, and acetone/propanal are the most abundant. The data sheds new light on the contribution of extra-planetary material on the organic and CH₄ budgets of planets, e.g. Mars.

1. Introduction

The origin of CH₄ in the Martian atmosphere [e.g. 1] remains unclear. While on Earth the vast majority of CH₄ is biogenic, it is doubtful that this is the case on Mars. Other sources include release from clathrates [2] and emission as a photodegradation product of extra-Martian organic matter from meteorites and interplanetary dust particles [3], [4]. The possible contributions of these sources are poorly understood. To further investigate contributions of meteoritic CH₄, long-term experiments were conducted to determine its emission rates along with other VOCs from the Murchison meteorite as a result of UV irradiation.

1.1 Materials and methods

Small (~100mg) samples of Murchison meteorite (carbonaceous chondrite, CM2) material were ground and placed in an airtight glass container. All glassware was rinsed with water (18.2MΩ), acetone, and methanol, wrapped in aluminium foil and heated to 550°C for 3 hours. The sample was irradiated with a Xe-arc discharge lamp through a UV transparent Suprasil window. The lamps intensity is about seven times stronger than UV intensity on the Martian surface in the 250-320 nm range and roughly five times stronger in the 320-400 nm range [5]. The

sample chamber was flushed with pure N₂ gas and not shaken during experiments. The outflowing gas mixture was split and led to a Picarro cavity ring-down spectroscopy (CRDS) CH₄ analyzer and a proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS). The instruments measure CH₄ and VOCs every 5 and 1 seconds respectively. The data was analyzed using MatLab (CH₄) and PTRwid [6] (VOCs). Emission rates were calculated from concentrations using Eq. 1.

2. Results and discussion

Experiments indicated that CH₄ is emitted from meteorite material instantaneously when UV irradiation starts. After 200 hours, emission is still ~20 times larger than background emission (Fig. 1). The emission rate is described with a 3-term exponential function ($R^2=0.9985$ in Fig. 1). All six long-term experiments can be described by such a function, R^2 values are >0.99 in every experiment. The terms of this exponential function contribute a few %, ~15%, and ~80% to the total methane emission. The fundamental causes for this specific fit are still under investigation. In addition to methane, other VOCs were also emitted (Fig. 2). We detected 17 distinct masses after background corrections. The most abundant VOCs are acetaldehyde, acetone and/or propanal (both are at mass 59), methanol and formaldehyde. Fitting the emission data of the VOCs is more challenging than CH₄ since the concentrations are much closer to the PTR-TOF-MS detection limit and noise is therefore high. Nevertheless, formaldehyde, methanol, acetaldehyde, and acetone/propanal are well described by the aforementioned 3-term exponent (R^2 values of respectively 0.9927, 0.9346, 0.9892, and 0.9734). The mass of PTR-TOF-MS detectable VOCs was summed up and the total mass was three times higher than the total mass of CH₄. However, the molar CH₄ to VOC ratio is roughly 1:1. The total mass of all emitted compounds over 103 hours is still <0.5 wt.% of the initially present organics in the Murchison meteorite,

assuming 2 wt.% total organics. VOC emission are likely to include ethane, propene, and propane, as reported by [3], but those compounds are not detectable using this setup. Furthermore, the abundance of formaldehyde has a large error that could well be larger than the reported concentration itself, as the measured concentration is strongly influenced by e.g. humidity. The detected photodegradation products sheds new light on the atmosphere as a sink for extra-Martian organics.

3. Figures

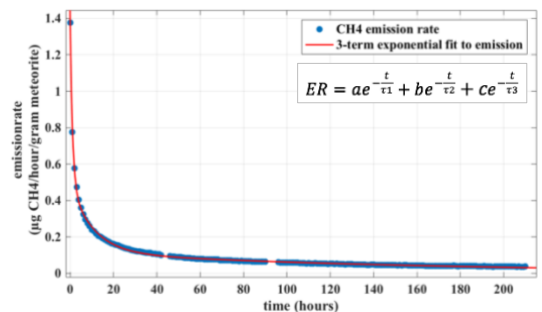


Figure 1: Plot of CH₄ emission rate against time.

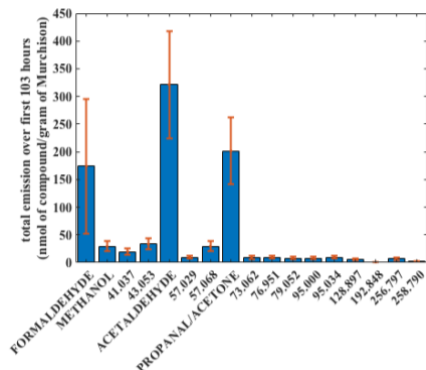


Figure 2: Total emitted VOCs after 103 hours of irradiation. Unidentified masses are protonated masses (+1 amu).

4. Equations

To calculate the emission rate (ER) we use air flow in ml/min (f), the concentration over background in ppm (ΔC), the molar volume of air in liters (V_{air}), the molar mass of CH₄ in g/mol (M_{CH_4}) and the sample mass in grams (m) in Eq. 1.

$$ER = \frac{f * \Delta C * M_{CH_4}}{V_{air} * m} \quad (1)$$

5. Summary and Conclusions

Long-term experiments confirm the previously reported emissions of CH₄ from carbonaceous chondrites under UV irradiation. In contrast to the first extrapolations by [3], we show CH₄ emission is still measurable after more than 200 hours. The emission of CH₄ can be mathematically described by a 3-term exponential function. Besides CH₄, VOCs are also emitted in a similar pattern. The mass of emitted VOCs is three times larger than the mass of emitted methane, while molar emissions are very similar to that of CH₄. Acetaldehyde, acetone/propanal, formaldehyde, and methanol are the most abundant emitted VOCs.

Acknowledgements

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