

ANALYSIS OF VOLATILE FLUIDS IN BASALT: A POSSIBLE SOURCE OF MARTIAN METHANE

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Introduction: Identifying the source of Martian atmospheric methane is a major objective for planetary science. Whereas Earth's atmospheric methane is replenished by a yearly supply of 6×10^{14} g from mostly biological sources [1], the low concentrations detected in Mars' tenuous atmosphere require an influx of only 2×10^8 g per year [2]. Thus, the production or emission processes responsible for Martian methane may be of such low yield that they would usually be considered insignificant on Earth. Release of ancient methane from intracrystalline fluid inclusions and intercrystalline cavities in basalt—a dominant rock type on Mars—is one such process. Basalt and other mafic and ultramafic igneous rocks are known to incorporate methane formed by biological and geological processes, chiefly the serpentinisation of olivine [3, 4]. As a first step in evaluating the significance of this potential Martian reservoir, we employed a rock-crushing and mass-spectrometry technique previously shown to detect ancient methane in serpentinites [5]. This technique could be adapted for automated *in situ* analysis of Martian rocks on future missions, or analysis following Mars Sample Return. Key questions were the following:

(1) *Can methane always be detected by this technique in basalts from Earth?*

(2) *Can we relate detected variations in methane quantity to the geological context of basalts, e.g. eruption depth and vesicularity?* An affirmative result could inform speculation about the quantity of methane likely to be retained in Martian basalt.

(3) *Does methane content vary systematically with basalt age?* Such trends might reflect: (a) secular changes in Earth's carbon cycle, or (b) diffusion, weathering or diagenetic processes.

(4) *Does oxidative weathering, which is pervasive on Mars, preclude or obscure measurements of ancient methane?* Methane might be gradually oxidised or analytically masked by carbon dioxide.

(5) *Does grain size affect the analysis?* A limited range of particle sizes may be available for *in situ* analysis on Mars [6]. It is therefore important to establish how methane recoverability varies with particle size.

(6) *Do mineral veins cross-cutting basalts acquire the same gas composition?* An affirmative result might suggest that hydrothermal systems can remobilise methane from basalt, a possible venting process.

Methods: A wide range of basalt samples were collected and analysed for methane by an incremental-crushing mass-spectrometry technique.

Sampling programme. To answer questions (1) and (2), ancient oceanic vesicular, amygdaloidal and non-vesicular basalts were sampled from seven localities in the British Isles and one in Ontario, Canada; and recent subaerial basalts were collected from near Lake Myvatn in Iceland and Kilauea in Hawaii. An olivine bomb (xenolith) derived from the upper mantle was also sampled from Recent basalt in Tenerife. To address question (3), Archean, Neoproterozoic, Ordovician, Tertiary and Recent basalts were sampled. Two localities yielding oxidised basalt were sampled to investigate question (4). Ordovician basalt from Helen's Bay in Co. Down, Northern Ireland was sampled along with two generations of cross-cutting veins (calcite, haematite), addressing question (6). One of these generations was oxidising (red in colour).

Basalt samples from Helen's Bay were fly-pressed and sieved through four mesh sizes—63 μm , 125 μm , 212 μm and 425 μm —in order to investigate question (5). All other samples were fly-pressed to obtain match-head-sized grains. All samples were then washed for about 5 minutes in H_2O_2 to remove surface organics, rinsed, and dried at room temperature.

CFS mass spectrometry. Volatiles were analysed by the crush-fast scan method [7–9]. Samples were analyzed by incremental cold-crush fast scan method under a vacuum (approx. 10^{-8} Torr) using Pfeiffer Prisma quadrupole mass spectrometers operating in fast-scan, peak-hopping mode. Two to six bursts of volatiles (up to $\sim 2 \times 10^{-11}$ l) were released per sample and analyzed for H_2 , N_2 , O_2 , CH_4 , CO_2 , and several other species. Calibration was checked against commercial standard gas mixtures, atmospheric capillary tubes and three fluid-inclusion standards as described by [10]. Instrumental blanks are also analysed routinely. Standard deviations are typically $\sim 0.5\%$.

The amount of each species was calculated by proprietary software, but crushing does not liberate all the entrapped gas from samples, so data are reported as ratios of molar percentages rather than bulk quantities. Here, methane is reported as CH_4/CO_2 .

Results: (1) *Can methane always be detected by this technique?* Methane and carbon dioxide were detected in all samples (Fig. 1). The CH_4/CO_2 and

H_2/N_2 ratios were both around $10 \times$ lower than previously discovered in serpentinites [5].

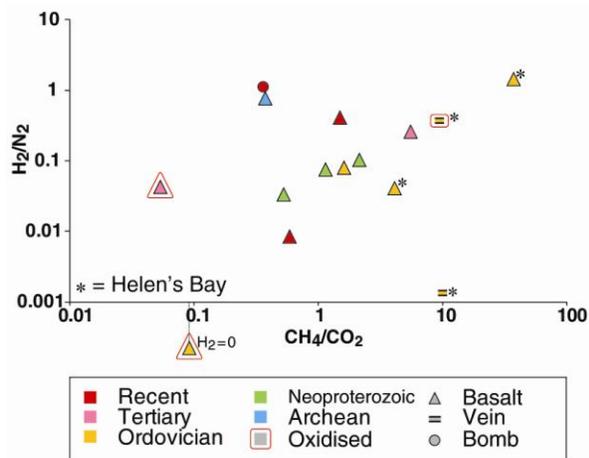


Figure 1. Cross-plot of H_2/N_2 and CH_4/CO_2 ratios in basalt, cross-cutting veins and an olivine bomb. Both H_2 and CH_4 are produced hydrothermally in reducing conditions and increase with H_2 fugacity (hence the weak correlation). Each point represents the mean weighted by burst size for a particular locality or for Helen's Bay (asterisked).

(2) *Can we relate detected variations in methane quantity to the geological context of basalts?* No consistent differences were found between vesicular and non-vesicular or subaqueous and subaerial basalts, or between the olivine bomb and the rest of the basalts.

(3) *Does methane content vary systematically with basalt age?* Similar compositions were observed for basalts of all ages. The data do not suggest long-term changes in the quantity of basalt included or retained by basalt.

(4) *Does oxidative weathering, which is pervasive on Mars, preclude or obscure measurements of ancient methane?* Surface reddening of basalt samples is associated with high O_2/N_2 ratios and low CH_4/CO_2 and H_2/N_2 ratios. This suggests that oxidative weathering may change the fluid composition of basalts. These trends were not observed in the veins, however.

(5) *Does grain size affect the analysis?* There was no clear correlation between grain size and CH_4/CO_2 ratio (Fig. 2).

(6) *Do mineral veins cross-cutting basalts acquire the same gas composition?* The veins cutting the Helen's Bay basalt yielded a similar CH_4/CO_2 ratio to the host rock, which is consistent with the possibility that they may have remobilised basaltic methane. More work is needed to confirm this conclusion.

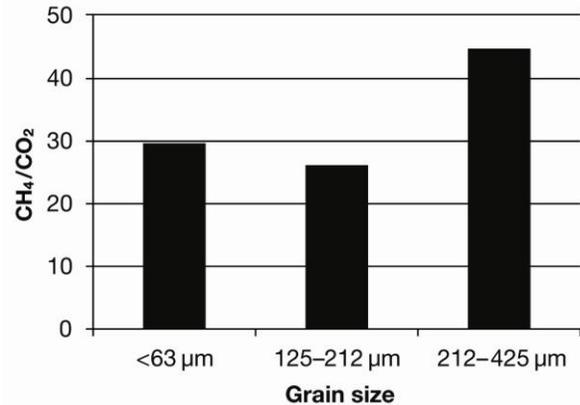


Figure 2. Mean CH_4/CO_2 ratios released from sieved crushed basalt from Helen's Bay, Ireland, weighted by volatile burst size.

Discussion: Basalt, a primitive undifferentiated silicate rock, is one of the most common rocks in the solar system. It is mineralogically susceptible to serpentinisation reactions, which generate methane in a wide range of geological settings on Earth. Basalts may also incorporate biogenic methane from sub-surface microbes.

These preliminary results show that methane is retained within a range of basalts, including xenoliths and cross-cutting mineral veins, which may be capable of remobilizing this methane and venting it to the atmosphere. More work is needed to understand causes of variation in methane retention.

These results also demonstrate the efficacy of the CFS technique in extracting and measuring this methane. The technique could be supplemented by isotopic analysis and adapted for use on Mars, perhaps by the modification of existing mass spectrometry techniques for Mars (e.g. the Sample Analysis at Mars package flying on NASA's Mars Science Laboratory).

References: [1] Houghton T. J. et al. (Eds.) (2001) *Climate Change 2001: The Scientific Basis*. [2] Geminalo A. et al. (2008) *Planet. & Space Sci.*, 56, 1194–1203. [3] Welhan J. A. (1988) *Canadian J. Earth Sci.*, 25, 38–48. [4] Kelley D. S. (1996) *J. Geophys. Res.*, 101, 2943–2962. [5] Parnell J. et al. (2010) *Int. J. Astrobiology*, 9, 193–200. [6] Schulte W. et al (2008) *Proc. i-SAIRAS IX*. [7] Norman D. I. and Moore J. N. (1997) *Euro. Current Res. Fluid Inclusions*, XIV, 243–244. [8] Moore J. N. et al. (2001) *Chemical Geology*, 173, 3–30. [9] Parry W. T. and Blamey N. J. F. (2010) *Chemical Geology*, 278, 105–119. [10] Norman D. I. and Blamey N. J. F. (2001) *Euro. Current Res. Fluid Inclusions*, XVI, 341–344.