

Sampling methane in basalt on Earth and Mars

Sean McMahon¹, John Parnell¹ and Nigel J.F. Blamey²

¹School of Geosciences, University of Aberdeen, Aberdeen AB24 3UE, UK
e-mail: sean.mcmahon@abdn.ac.uk

²Department of Earth and Environmental Science, New Mexico Tech, Socorro, NM 87801, USA

Abstract: If confirmed, the extremely low concentrations of methane (CH₄) detected in the Martian atmosphere may represent reservoirs and emission processes that would normally be considered negligible on Earth. One such process is the release of ancient volatiles from fluid inclusions and interstitial sites in rocks and minerals during erosion or geothermal activity. Using a highly sensitive rock-crushing and mass-spectrometry technique previously shown to detect CH₄ in serpentinites and hydrothermal mineral deposits, we have demonstrated that CH₄ and other ancient volatiles can be recovered from basalt, the dominant rock type on the Martian surface. Basalt samples from a wide range of ages and geological systems were tested, all of which released CH₄ when crushed. Oxidative weathering was associated with lower quantities of CH₄. Otherwise, CH₄ recoverability showed no relationship with age or geological context. Mineral veins, cross-cutting one locality were found to share the volatile composition of the basalt. In general, the results suggest that CH₄-release from ancient basalts could be a significant process on Mars, which could be further investigated by Martian rovers using a similar rock-crushing and mass spectrometry technique *in situ*.

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Introduction

Spatially and temporally variable methane (CH₄) concentrations on the order of tens of parts per billion by volume (ppbv) were detected in the Martian atmosphere by ground-based telescopes in 2003 (Mumma *et al.* 2009) and by the *Mars Express* orbiter in 2004 (Formisano *et al.* 2004). A 2010 re-analysis of earlier data from the *Mars Global Surveyor* orbiter also identified a seasonal CH₄ signature with maxima of about 50 ppbv over the Elysium, Tharsis, and Arabia Terrae regions in the northern hemisphere (Fonti & Marzo 2010). CH₄ concentrations apparently peak during northern-hemisphere summer and decline thereafter, with an inferred atmospheric lifetime of less than 200 Martian days (Lefèvre & Forget 2009).

These surprising but mutually supportive results remain controversial (Zahnle *et al.* 2011) and await confirmation by NASA's *Mars Science Laboratory* and ESA's *Trace Gas Orbiter* (currently intended to reach Mars in 2016). If verified, the presence of CH₄ indicates either or both: (1) extant biological or non-biological generation of CH₄; (2) periodic release – perhaps due to seasonal pressure and temperature changes – from a vestigial reservoir of ancient biogenic or abiogenic gas.

Earth's atmospheric CH₄ is predominantly biogenic, but methanogens are unlikely to be viable in the dry and oxidizing conditions at the CH₄ surface. On the other hand, they could have thrived there in the geological past, and the subsurface may remain habitable today (Fisk & Giovannoni 1999).

However, whereas Earth's atmospheric CH₄ is replenished by a yearly supply of 6×10^{14} g (Dentener *et al.* 2001), the low concentrations detected in Mars' tenuous atmosphere require an influx of only 2×10^8 g per year (Geminale *et al.* 2008). Hence, the production and emission mechanisms responsible for Martian atmospheric CH₄ may be of such low yield that they would normally be considered insignificant on Earth.

Candidate sources for Martian CH₄ include a range of geochemical processes known to reduce inorganic carbon in the terrestrial subsurface, of which serpentinization is the most significant (Oze & Sharma 2005). Serpentinization is the aqueous alteration of the common igneous minerals olivine and pyroxene to the hydrous mineral serpentine via several exothermic reactions favourable below 300 °C. These reactions evolve H₂, which reduces ambient CO₂ to CH₄. The CO₂ on Earth includes magmatic carbon in basalts, but also CO₂-rich groundwaters which interact with basalts so readily that the reactions have potential for sequestration of greenhouse gases (Schaefer *et al.* 2009, 2010). The CO₂ on Mars could ultimately be derived from mantle, atmospheric or meteoritic infall sources (Grady *et al.* 2004). Experiments have confirmed the production of H₂ and CH₄ from the aqueous alteration of olivine at temperatures as low as 30–70 °C (Neubeck *et al.* 2011). Olivine and pyroxene are major components of basalt, the glassy silicate rock that dominates the Martian crust. Liquid water has apparently been stable on the Martian surface for long periods of its history and may continue to circulate in the subsurface, driven by geothermal convection

(Travis *et al.* 2003). Thus, serpentinization is likely to have generated CH₄ in Mars' past and may continue to do so. Where carbon is available, e.g. from magmatic degassing, thermodynamic calculations predict that redox reactions with hydrothermal fluids could also generate CH₄ from basalt or magma (Lyons *et al.* 2005). Other reduced organic carbon molecules have already been detected in a range of Martian meteorites (Steele *et al.* 2012).

Intracrystalline 'fluid inclusions' and crystal boundaries in basalt and other mafic and ultramafic igneous rocks are known to incorporate and retain CH₄ and other volatiles (liquids and gases) formed by serpentinization as well as other geological processes (e.g. Welhan 1988; Kelley 1996). Clay minerals in altered basalts can also adsorb CH₄ (e.g. Gough *et al.* 2010). Thus, Martian basalt could serve as both a record of ancient methanogenic processes and a reservoir from which ancient CH₄ might escape. As a first step in evaluating the significance of this reservoir, we investigated the potential for sampling and detecting CH₄ in basalts using an incremental-crushing mass spectrometry technique previously found to detect CH₄ in serpentinites (Parnell *et al.* 2010), artificial impact craters (McMahon *et al.* 2012a) and hydrothermal minerals (McMahon *et al.* 2012b). This technique has potential for application *in situ* on the Martian surface.

Objectives

The key questions were the following:

(i) Can CH₄ always be detected by this technique in basalts from Earth?

If all or most terrestrial basalts yield CH₄, we would expect the same on Mars, given evidence of comparable mineralogy (McSween *et al.* 2009). This expectation would be strengthened if CH₄ contents were consistently high across a wide range of altered, unaltered, recently erupted and ancient basalts in different eruptive settings.

(ii) Does particle size affect the sampling or analysis of gas?

A limited range of particle sizes may be available for *in situ* analysis on Mars. A future rover, for example, will carry a Sample Preparation and Distribution System (SPDS) capable of crushing geological samples to a broad grain-size distribution up to 400 µm (Schulte *et al.* 2008). It is therefore of particular interest to establish how CH₄ recoverability varies with particle size within this range. Most inclusion volatiles are present in relatively large (10s of µm) inclusions, which are opened and evacuated when grains are broken, whereas finer samples, having already lost these large volumes of volatiles, yield proportionally more crystal-boundary gas when crushed. CH₄/CO₂ ratios in hydrothermal calcite veins were previously observed to vary systematically with particle size, interpreted to suggest a difference in composition between inclusion volatiles and crystal-boundary volatiles (McMahon *et al.* 2012b).

(iii) Can we relate detected variations in CH₄ quantity to the geological context of basalts, e.g. eruption depth and vesicularity?

An affirmative result could constrain the quantity of CH₄ likely to be retained in Martian basalt and inform sampling strategies for lander missions.

(iv) Does CH₄ content vary systematically with basalt age?

It is important to establish the stability and consistency of volatile retention in basalts over geological time. Any trends in CH₄ recoverability might reflect: (a) secular changes in Earth's carbon cycle; (b) diffusion, weathering or diagenesis; (c) chance.

(v) Does oxidative weathering preclude or obscure measurements of ancient CH₄?

Oxidative weathering pervades the Martian near-surface and may affect the composition of interstitial volatiles. Crystal-boundary CH₄ in basalt may be gradually oxidized or analytically masked by CO₂. Oxidized basalts can be easily identified from their penetrative red discoloration.

(vi) Do mineral veins cross-cutting basalts share the same gas composition?

An affirmative result might suggest that hydrothermal systems can remobilize CH₄ from basalt, a possible venting mechanism. Hydrothermal systems are likely to occur on Mars as a result of geothermal heat (Travis *et al.* 2003) and may be locally increased by impact cratering and magmatic activity. Previous results demonstrate that terrestrial hydrothermal calcite veins entrain CH₄ in quantities varying according to the thermal maturity of organic-rich sediments through which they were injected (McMahon *et al.* 2012b).

Method

Sampling programme

An incremental-crushing mass-spectrometry technique was applied to a wide range of basalt samples (Table 1). To answer questions (i) and (iii) above, ancient oceanic vesicular, amygdaloidal and non-vesicular basalts were sampled from ten localities in the British Isles, one in Michigan, USA, one in Gävle, Sweden and one in Ontario, Canada; and recent sub-aerial basalts were collected from near Lake Myvatn in Iceland and Kilauea in Hawaii. An olivine bomb (xenolith) derived from the upper mantle was also collected from recent basalt in Tenerife. To address question (iv), Archean, Mesoproterozoic, Neoproterozoic, Carboniferous, Ordovician, Palaeocene and Recent basalts were sampled. At five localities basalts experienced contemporaneous oxidation (permeated by red discoloration due to weathering of lava flows) and were sampled to investigate question (iv). Ordovician basalt from Helen's Bay in County Down, Northern Ireland was sampled along with two generations of cross-cutting mineral veins, addressing question (v). The older vein, calcite, was sampled directly. The younger, haematite, was formed during Permo-Triassic uplift and weathering. Samples were removed from its (visibly oxidized) alteration halo.

Basalt samples from Helen's Bay were crushed in a press and sieved through four mesh sizes – 63, 125, 212 and 425 µm – in order to investigate question (ii). All other samples were crushed in a press to obtain grains about 3 mm in diameter. Care was taken to avoid unintentionally sampling veins, amygdaloids, or visible alteration halos. All samples were then

Table 1. Details of the basalt samples analysed for CH₄

Sample type	Locality	Age	Reference
Amygdaloidal pillow basalt	Schreiber, Ontario, Canada	Archean	Polat <i>et al.</i> (1998)
Pillow basalt	Hamrånge, Gävle, Sweden	Palaeoproterozoic	Ogenhall (2007)
Oxidized amygdaloidal basalt	Keweenaw Peninsula, Michigan, USA	Mesoproterozoic	Bornhorst & Rose (1994)
Amygdaloidal pillow basalt	Kiell's Jetty, Argyll, Scotland	Neoproterozoic	Gower (1977)
Pillow basalt	Penryn Nefyn, Gwynedd, Wales	Neoproterozoic	Kawai <i>et al.</i> (2007)
Oxidized pillow basalt	Ballantrae, South Ayrshire, Scotland	Ordovician	Bluck (1992)
Pillow basalt	Helen's Bay, Co. Down, Northern Ireland	Ordovician	Craig (1983)
Calcite veins			
Haematite vein oxidation halo			
Pillow basalt	Stonehaven, Aberdeenshire, Scotland	Ordovician	Thomas (1999)
Amygdaloidal basalt	Kinghorn, Fife, Scotland	Carboniferous	Browne & Woodhall (1999)
Oxidized subaerial basalt	Giant's Causeway, Co. Antrim, Northern Ireland	Palaeocene	Lyle & Preston (1993)
Pillow basalt	Glen Drynoch, Skye, Scotland	Palaeocene	Anderson & Dunham (1966)
Oxidized pillow basalt	Newtown Crommelin, Co. Antrim, Northern Ireland	Palaeocene	Eyles (1952)
Subaerial basalt	Portballintrae, Co. Antrim, Northern Ireland	Palaeocene	Lyle & Preston (1993)
Oxidized pillow basalt	Portree, Skye, Scotland	Palaeocene	Anderson & Dunham (1966)
Fresh subaerial basalt	Kilauea, Hawaii, USA	Recent	N/A
Fresh subaerial basalt	Lake Myvatn, Iceland	Recent	N/A
Olivine xenolith in basalt	Tenerife, Spain	Recent	N/A

 Table 2. Relative abundance of species recovered from a basalt sample (Penryn Nefyn, Gwynedd, Wales; Ordovician) using the CFS technique. Water is set to 0; percentages represent the remainder. SO₂ and organics other than CH₄ are usually excluded from analysis. This sample would be reported to have a CH₄/CO₂ ratio of 2.67/1.24 = 2.15

Species	Relative abundance, %				Mean weighted by burst size
	Crush 1	Crush 2	Crush 3	Crush 4	
H ₂	6.61	6.72	6.81	13.63	8.82
He	0.03	0.02	0.01	0.04	0.02
CH ₄	2.92	2.42	2.45	2.94	2.67
N ₂	86.41	88.54	88.63	81.33	86.04
O ₂	0.03	0.02	0.02	0.02	0.02
Ar	0.26	0.16	0.19	0.23	0.21
CO ₂	2.38	1.08	1.11	0.87	1.24
C ₂ H ₄	0.07	0.00	0.00	0.03	0.02
C ₂ H ₆	0.00	0.00	0.00	0.00	0.00
SO ₂	0.63	0.33	0.29	0.36	0.38
C ₃ H ₆	0.14	0.09	0.06	0.07	0.08
C ₃ H ₈	0.43	0.48	0.37	0.43	0.42
C ₄ H ₈	0.09	0.03	0.01	0.02	0.03
C ₄ H ₁₀	0.00	0.01	0.03	0.02	0.02
Benzene	0.00	0.09	0.02	0.02	0.03
Burst (amps)	1.02E-08	1.23E-08	2.04E-08	1.86E-08	

washed for about 5 minutes in H₂O₂ to remove surface organics, rinsed and dried at room temperature.

CFS mass spectrometry

Extraction and analysis of volatiles were performed by the crush-fast scan (CFS) method (Norman & Moore 1997; Moore *et al.* 2001; Parry & Blamey 2010; Blamey 2012), which offers very low detection limits (Blamey *et al.* 2012). Samples were loaded into a crushing chamber under an ultra-high vacuum (approximately 10⁻⁸ Torr) and crushed in swift increments, with each crush producing a burst of mixed volatiles. A typical sample size of about 250 mg (one or two 3 mm grains) released four to ten bursts of volatiles (up to ~2 × 10⁻¹¹ litres) into the vacuum chamber, which remained there for 8–10 analyser

scans (~ 2 seconds) before removal by the vacuum pump. This method does not require a carrier gas and volatiles are not separated from each other but released simultaneously into the chamber.

Bursts were analysed for H₂, He, CH₄, H₂O, N₂, H₂S (or O₂), Ar, CO₂, C₂H₄, C₂H₆, SO₂, C₃H₆, C₃H₈, C₄H₈, C₄H₁₀ and benzene using a Pfeiffer Prisma 'residual-gas' quadrupole mass spectrometers operating in fast-scan, peak-hopping mode at room temperature. In multiple ion-detection modes, both isotopic peaks and fragmentation peaks are observed; the major peaks for individual gases are generally selected but some exceptions occur. O₂ and H₂S cannot be analysed together because O₂ isotopologues at mass 34 obscure the typically much weaker H₂S signal at the same mass. In this

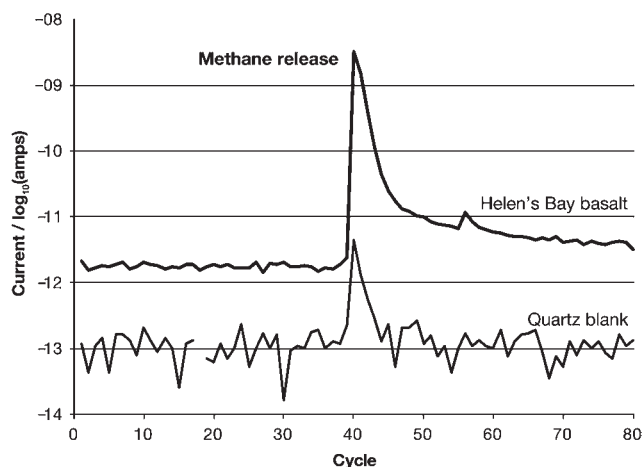


Fig. 1. Output from CFS-MS technique during CH_4 release. Output from CFS-MS over 80 cycles (approx. 27 seconds) at $m/z = 15$, representing ionized CH_4 released during sample-crushing. The ionized volatiles produce a current in the detector proportional to their amount. The signal from a basalt sample (Helen's Bay, Co. Down, Northern Ireland; $\text{CH}_4/\text{CO}_2 \approx 4$) is shown alongside a quartz blank with maxima aligned. The basalt's peak signal is about three orders of magnitude higher than the highest signal from the quartz blank.

study, most samples were analysed for O_2 (at mass 32) rather than H_2S . The samples generally produced much lower yields than routine aqueous fluid inclusions from geothermal systems or hydrothermal ore deposits for which the system was built. In order to enhance the detection of low-yield samples, a limited gas suite was selected for most samples, comprising H_2 , He, CH_4 , H_2O , N_2 , O_2 , Ar and CO_2 , thus removing higher organics and SO_2 . In preliminary work, samples were analysed for SO_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_4H_8 , C_4H_{10} and benzene, which were (each) found to constitute less than 1% of non-water volatiles on average; Ar typically constituted 0.1–1% and He typically constituted less than 0.1%.

CH_4 is detected at mass 15 (i.e. the CH_3^+ fragment; Fig. 1) to avoid interference by O^- fragments from water (the CH_4 peak at mass 15 is about 90% as intense as the peak at mass 16). CH_3^+ fragments generated by other organic compounds are typically much less abundant and can be corrected for.

Calibration was checked against commercial standard gas mixtures, atmospheric capillary tubes and three fluid-inclusion standards as described by Norman & Blamey (2001). Instrumental blanks are also analysed routinely.

The amount of each species was calculated by proprietary software to provide a quantitative analysis, which is corrected for the instrumental background. Crushing does not liberate all the entrapped gas from samples, so data are generated as molar percentages rather than moles. To circumvent the dependence of individual percentages on irrelevant species, we report CH_4 abundances as the ratio $(\text{mol}\% \text{CH}_4)/(\text{mol}\% \text{CO}_2)$, hydrogen abundances as $(\text{mol}\% \text{H}_2)/(\text{mol}\% \text{N}_2)$ and oxygen abundances as $(\text{mol}\% \text{O}_2)/(\text{mol}\% \text{N}_2)$ (hereafter CH_4/CO_2 , H_2/N_2 and O_2/N_2 , respectively). As predicted by thermodynamic calculations of redox equilibria, CO_2 is usually a dominant volatile

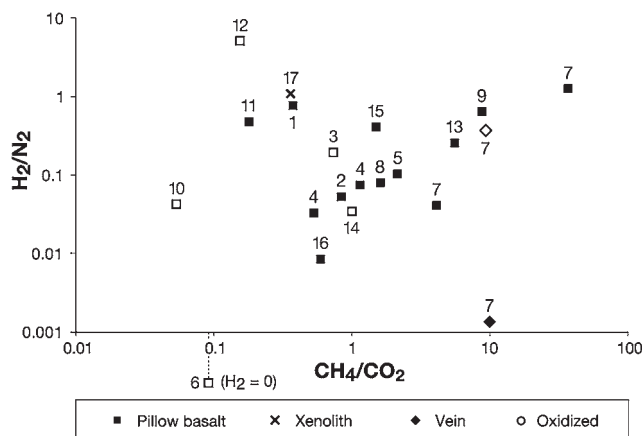


Fig. 2. Composition of volatile gases (CH_4/CO_2 against H_2/N_2 molar ratios) in basalt and related samples. Each point represents the mean molar ratios obtained from several volatiles bursts and weighted by burst size. Both ratios increase with H_2 fugacity, hence their apparent association. *Archean*: (1) Schreiber, Ontario, Canada. *Palaeoproterozoic*: (2) Hamrånge, Gävle, Sweden. *Mesoproterozoic*: (3) Keweenaw Peninsula, Michigan, USA. *Neoproterozoic*: (4) Kiehl's Jetty, Argyll, Scotland. (5) Penryn Nefyn, Gwynedd, Wales. *Ordovician*: (6) Ballantrae, South Ayrshire, Scotland. (7) Helen's Bay, Co. Down, Northern Ireland. (8) Stonehaven, Aberdeenshire, Scotland. *Carboniferous*: (9) Kinghorn, Fife, Scotland. *Palaeocene*: (10) Giant's Causeway, Co. Antrim, Northern Ireland. (11) Glen Drynoch, Skye, Scotland. (12) Newtown Crommelin, Co. Antrim, Northern Ireland. (13) Portballintrae, Co. Antrim, Northern Ireland. (14) Portree, Skye, Scotland. *Recent*: (15) Kilauea, Hawaii, USA. (16) Lake Myvatn, Iceland. (17) Tenerife, Spain. See Table 1 for more details.

in magmatic sources, second only to H_2O (Lowenstern 2001). High values of CH_4/CO_2 are therefore a good indicator of elevated CH_4 abundance in basalt.

Results

A typical set of results for a basalt sample is displayed in Table 2. H_2O typically exceeded 90% of all volatiles released. Of the remaining <10%, CH_4 , CO_2 , N_2 and H_2 were the most abundant constituents, each commonly accounting for between 0.1% and several% of total volatiles. Typical results for a basalt sample are shown in table 2. CH_4 and CO_2 were detected in all samples (Fig. 2), with CH_4/CO_2 ratios (means of several bursts, weighted by volatile burst size) ranging from 0.05 in oxidized Palaeocene basalt from Giant's Causeway (Co. Antrim, Northern Ireland) to 37.41 in non-oxidized Ordovician basalt from Helen's Bay (Co. Down, Northern Ireland). The mean mol% (of the remainder after subtracting H_2O) CH_4 was about 20. H_2/N_2 was weakly correlated with CH_4/CO_2 . Both ratios increase with H_2 fugacity, hence their apparent association.

Four grain-size fractions of basalt from Helen's Bay were analysed: <63, 63–125, 125–212 and 212–425 μm (Fig. 3). The 212–425 μm grains yielded the highest weighted mean CH_4/CO_2 ratio (44.7) followed by the 63–125 μm (37.1), the

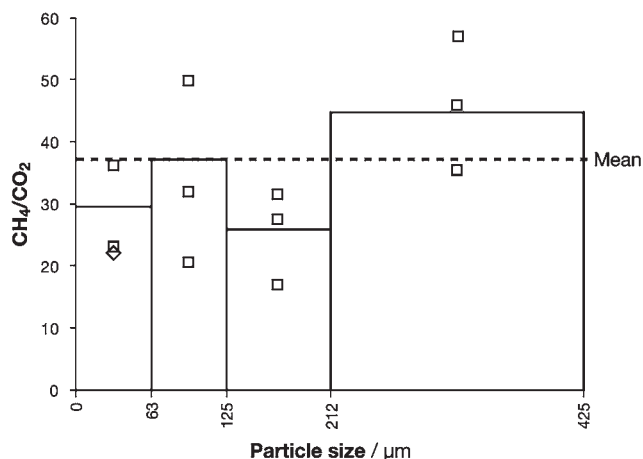


Fig. 3. Molar CH_4/CO_2 ratios in four particle-size fractions. The weighted mean ratio for each size fraction is presented as a bar; the individual bursts are presented as squares (or diamonds where points overlap). The dashed line represents the mean of all CH_4/CO_2 measurements of particles between 0 and 425 μm , weighted by burst size.

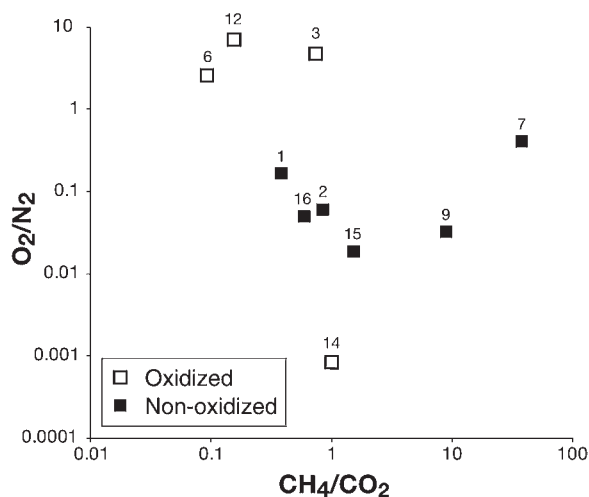


Fig. 4. O_2/N_2 plotted against CH_4/CO_2 molar ratios in oxidized and non-oxidized basalt. *Archean*: (1) Schreiber, Ontario, Canada. *Palaeoproterozoic*: (2) Hamrånge, Gävle, Sweden. *Mesoproterozoic*: (3) Keweenaw Peninsula, Michigan, USA. *Ordovician*: (6) Ballantrae, South Ayrshire, Scotland. (7) Helen's Bay, Co. Down, Northern Ireland. *Carboniferous*: (9) Kinghorn, Fife, Scotland. *Palaeocene*: (12) Newtown Crommelin, Co. Antrim, Northern Ireland. (14) Portree, Skye, Scotland. *Recent*: (15) Kilauea, Hawaii, USA. (16) Lake Myvatn, Iceland. Sample numbers are the same as in Figure 2. See Table 1 for more details.

<63 μm (29.6) and the 125–212 (26.1); hence, no clear trend was observed.

Of the ten basalt samples in which O_2/N_2 was measured, the three samples with the highest O_2/N_2 ratios were all oxidized, red basalt with low CH_4/CO_2 ratios. However, one other red basalt (Portree) yielded a very low O_2/N_2 ratio (Fig. 4). In general, pervasive reddening of basalt samples is broadly

associated with lower CH_4/CO_2 ratios (Fig. 2). However, the reddened halo of a haematite vein in Helen's Bay basalt, in which vein volatiles had evidently infiltrated and oxidized the basalt, was found to have a similar volatile composition to the rest of the basalt. A calcite vein cross-cutting the Helen's Bay basalt also released gas of a similar composition to the rest of the basalt.

Discussion

The results allow assessment against the original objectives of the study.

(i) Can CH_4 always be detected by this technique in basalts from Earth?

CH_4 and CO_2 were detected in all samples (Fig. 2). Most CH_4/CO_2 ratios were >0.5. The release of the gases during crushing implies that they were sealed within the sample before crushing, e.g. in fluid inclusions and on the tight crystal boundaries. The identification of CH_4 -bearing fluid inclusions in olivine crystals in other studies (Sachan *et al.* 2007; Arai *et al.* 2012) shows that significant quantities of CH_4 can become trapped in olivine. CH_4 can also be adsorbed on clay minerals produced by the alteration of basalt (e.g. Gough *et al.* 2010), which could also have contributed to the CH_4 released during crushing.

(ii) Does particle size affect the sampling or analysis of gas?

Variation in gas composition with grain size was small (CH_4/CO_2 fell within one order of magnitude) and no clear trend was observed in the basalt from Helen's Bay, Northern Ireland (Fig. 3). Given the reasonable assumption that finer particles yield proportionally more crystal-boundary (as opposed to fluid inclusion) gas when crushed, this result could suggest either that grain-boundary and inclusion volatiles shared a similar gas composition in this basalt or that one reservoir dominated the gas composition.

In previous work on hydrothermal calcite veins, grains below <63 μm yielded insufficient gas for analysis, having already liberated their volatiles during crushing and milling. It was suggested that this result provided an approximate lower limit to the particle size required for CFS. The new results are not consistent with that tentative conclusion, at least in the case of the basalt analysed. In any case, about 75–85% of the powder generated from basalt by the jaw crusher intended for the ExoMars rover (for example) falls within the range 63–400 μm (Schulte *et al.* 2008), so success in analysing the <63 μm fraction is not critical.

(iii) Can we relate detected variations in CH_4 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. This suggests that CH_4 is incorporated into basalt in a wide range of geological contexts, perhaps reflecting basalt's inherent mineralogical susceptibility to serpentinization or hydrothermal alteration, and does not depend strongly on local microbial methanogenesis; however, we did not assess the biogenicity of the gas

directly. The alteration process probably involves connate water, so the distinction of subaqueous and subaerial basalts may be of negligible importance.

(iv) Does CH₄ content vary systematically with basalt age?

Some samples close in age appear to share similar CH₄/CO₂ ratios (e.g. Recent), but the data do not demonstrate long-term changes in the quantity of CH₄ included or retained by basalt. It is unknown, however, whether CH₄ recovered from ancient basalt is itself ancient. Overall, similar volatile compositions were observed for basalts of all ages.

(v) Does oxidative weathering preclude or obscure measurements of ancient CH₄?

A previous CFS mass spectrometry study found no evidence that oxidative weathering affected gas compositions in hydrothermal calcite veins (McMahon *et al.* 2012b). In this study, however, pervasive reddening of basalt samples is broadly associated with lower CH₄/CO₂ ratios (Fig. 2). This suggests that oxidative weathering may change the volatile composition of basalts, for instance by oxidizing adsorbed and interstitial CH₄ to CO₂. Three out of four reddened basalts analysed for O₂/N₂ yielded high O₂/N₂ ratios and low CH₄/CO₂ ratios (Fig. 4). However, one reddened basalt yielded a very low O₂/N₂ ratio and a CH₄/CO₂ close to 1. Moreover, all oxidized samples released some CH₄ and the oxidation halo of the haematite vein in basalt from Helen's Bay showed no significant difference in CH₄/CO₂ ratio from non-oxidized basalt groundmass. Thus, the strength of the effect of oxidative weathering on gas composition is variable.

(vi) Do mineral veins cross-cutting basalts share the same gas composition?

Figure 5 shows the volatiles detected in two basalt samples and two veins, all from the Helen's Bay locality. Differences between the basalts may reflect differences in hydrothermal alteration, while the calcite vein shows a distinct volatile composition, most clearly by its lack of H₂. The veins yielded similar CH₄, CO₂ and CH₄/CO₂ ratios to the host rock (Fig. 2 and Fig. 5), which is consistent with the possibility that they may have remobilized basaltic CH₄, one of several plausible mechanisms for CH₄ release to the surface. This is a small-scale equivalent of the release of CH₄ through hydrothermal fracture systems on the sea floor (Charlou *et al.* 2002). Conversely, volatiles in hydrothermal fracture systems may also have influenced the gas composition of the basalt. This influence is less likely to have been significant at the other, less heavily veined localities.

Comparison with other datasets

Comparison of the basalt dataset with measurements from modern environments (sea floor hydrothermal fluids, Icelandic groundwaters and a hydrocarbon-bearing system; Charlou *et al.* 2002; Stefánsson & Arnórsson 2002; Parry & Blamey 2010) shows that higher CH₄/CO₂ ratios are recorded from the basalts (Fig. 6a). This is consistent with a progressive build-up of CH₄ in the basalts over time. Basalt data can also be compared with other geological materials previously analysed by the CFS technique (Fig. 6b; Parnell *et al.* 2010; McMahon *et al.* 2012b). This comparison reveals that most basalts in this

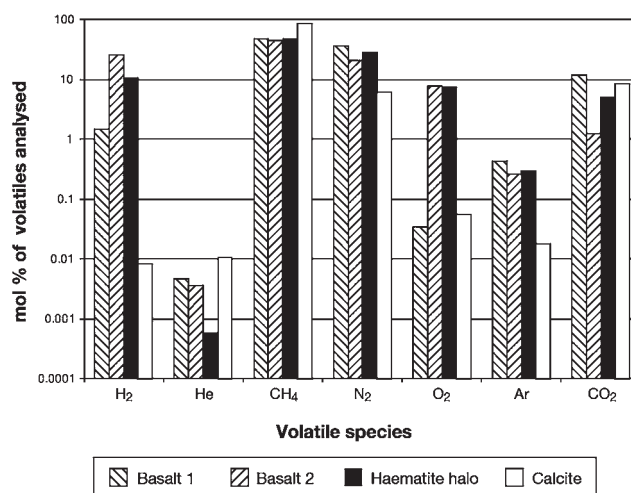


Fig. 5. Comparison of gas compositions in two basalt samples, a calcite vein, and the oxidation halo of a magnetite vein, all from Helen's Bay, Co. Down, Northern Ireland. Percentage abundances refer only to the seven volatiles presented; water is excluded and no other volatiles were analysed. The hatched bars represent two basalt samples, the black bars represent the alteration halo of a haematite vein through basalt, and the white bars represent a calcite vein in basalt. Differences between the basalts may reflect differences in hydrothermal alteration, while the calcite vein shows a distinct volatile composition, most clearly by its lack of H₂. However, CH₄ and CO₂ are similar for all four samples, which is consistent with gas exchange between the basalt and the veins.

study yielded lower CH₄/CO₂ ratios than previously studied serpentinites, which might be expected if the CH₄-enrichment of the basalts is mostly due to serpentinization. Nevertheless, some basalt yielded CH₄/CO₂ ratios as high as some serpentinites, despite the high concentration of CO₂ in magmatic systems.

Sources of CH₄ in terrestrial and Martian basalt

Although the present study did not seek to determine the ultimate sources of the CH₄ detected in terrestrial basalt, it would be an interesting question to explore further. Methanogens are known to thrive in hydrothermal systems associated with mid-ocean ridges, but are unlikely to have contributed significantly to the basalts formed in other settings. It is also possible that some CH₄ arrived in the basalt via the thermal breakdown of biogenic organic matter (kerogen) in sediments, sedimentary rock, and circulating fluid. Such 'thermogenic' gas commonly includes higher alkanes; we did not test for these in all samples, but found only trace amounts during preliminary work on samples from five localities. Ultimately, the biosphere is inextricable from the Earth's carbon cycle and subducted biological material may re-emerge in magmatic gases; Sleep *et al.* (2012) have recently shown that N₂ in mid-ocean ridge basalt derives from this source.

A magmatic CH₄ source is thermodynamically unlikely. Redox equilibration between basaltic magma and hydrothermal C–O–H fluids is constrained by the QFM (quartz–fayalite–magnetite) mineral redox buffer, which predicts very

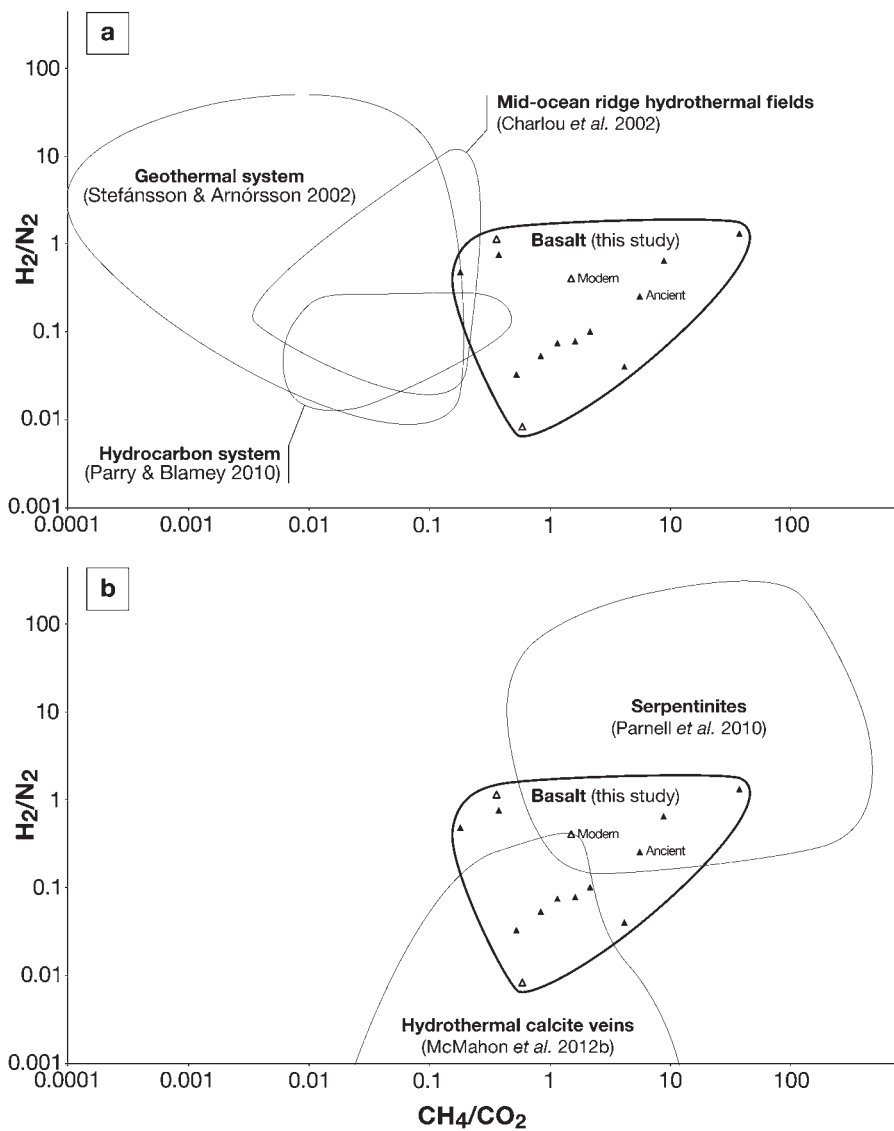


Fig. 6. Comparison of gas compositions in basalts with other CH_4 -bearing fluids and geological materials. (a) CH_4/CO_2 against H_2/N_2 molar ratios in evacuated volatiles from unweathered basalts in the present study (filled triangles = ancient basalts; unfilled triangles = Recent basalts) compared with three modern fluids (Parry & Blamey 2010; Charlou *et al.* 2002; Stefánsson & Arnórsson 2002). (b) CH_4/CO_2 against H_2/N_2 molar ratios in evacuated volatiles from unweathered basalts in the present study (filled triangles = ancient basalts; unfilled triangles = Recent basalts) compared with volatiles evacuated from serpentinites and hydrothermal calcite veins (Parnell *et al.* 2010; McMahon *et al.* 2012b).

low CH_4/CO_2 ratios at typically basalt quenching temperatures: less than 10^{-6} at 1000 °C (Giggenbach 1997). Where more reducing conditions occur, equilibrium is controlled by graphite and can generate CH_4/CO_2 ratios within the range we observed; however, it would be unusual for mid-ocean ridge basalts on Earth to form under these conditions.

In our view, the high CH_4/CO_2 ratios in these basalt samples are best explained by hydrothermal fluid- and/or water-rock reactions. Hydrothermal C–O–H fluids in contact with basalt are in redox equilibrium at high CH_4/CO_2 well below 500 °C, whether buffered by QFM or the FeO–FeO_{1.5} (quartz–fayalite–hematite) ‘rock buffer’ of Giggenbach (1987). Thus, Giggenbach (1997) describes CH_4 production in a ‘hydrothermal envelope surrounding the [volcanic] vent system.’ Additional H_2 and CH_4 are likely to have been supplied by

the low-temperature aqueous alteration of olivine and pyroxene (serpentinization) in local cumulates, in the underlying ultramafic layers of oceanic crust, and within the basalt itself, even the young Icelandic and Hawaiian basalt. These gases have been generated in the laboratory by the serpentinization of olivine at 30–70 °C on an experimental timescale (Neubeck *et al.* 2011).

Both of these mechanisms are likely to have operated on Mars. The surface of Mars is dominated by basalt (McSween *et al.* 2009), and evidence from orbit (Ehlmann *et al.* 2010) and meteorites (Changela & Bridges 2011) shows that the basalt is at least partially altered to serpentine and other silicates. Olivine and pyroxene cumulates, as preserved in the Chassigny and Nakhla Martian meteorites, respectively, are particularly vulnerable to serpentinization. The Martian mantle is also

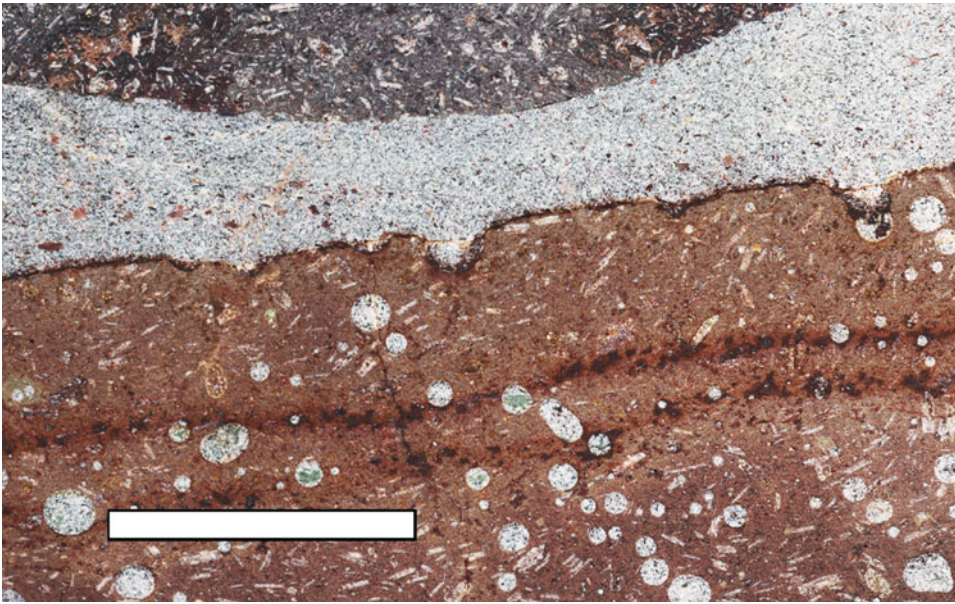


Fig. 7. Photograph of contemporaneously weathered basalt. Weathered basalt (red coloured by the oxidation of iron) in which vesicles have been filled with calcite (white) before erosion of basalt and incorporation into conglomerate, in which fine matrix intrudes into vesicles where calcite has been dissolved. This demonstrates rapid uptake of CO_2 (sequestered as calcite) into basalt, where interaction with hydrogen would yield CH_4 . The scale bar is 5 cm long.

believed to be more iron-rich than the Earth's, such that the Fe–Mg (solid-solution) minerals involved in serpentinization reactions are likely to contain more FeO and may thus release more H_2 and CH_4 (Sleep *et al.* 2004; Bridges & Warren 2006). Moreover, the Martian mantle is expected to be saturated with graphite and more reduced than QFM (and the Earth), such that hydrothermal fluids at equilibrium will contain a higher proportion of CH_4 (Lyons *et al.* 2005; Hirschmann & Withers 2008). Steele *et al.* (2012) have identified reduced organic macromolecular carbon in diverse Martian meteorites, which they interpret as a precipitate from C–O–H fluids.

There are several plausible mechanisms by which volatile-escape from altered ancient basalt could contribute to Martian atmospheric CH_4 : in the surface, wind abrasion, impact erosion due to micrometeorites and meteorites, freeze-thaw weathering, hot-cold weathering, or salt weathering; and in the subsurface, geochemical activity and hydrothermal fracturing enhanced by geothermal convection (Travis *et al.* 2003).

The gas data emphasize that basalts are sinks for carbon. This is why they are attracting strong attention for their potential in CO_2 sequestration (McGrail *et al.* 2006; Oelkers *et al.* 2008; Schaef *et al.* 2009, 2010). On Mars, there is growing evidence that carbonate formation is widespread (Michalski & Niles 2010; Niles *et al.* 2010; Chassefière & Leblanc 2011) and must be contributing to CO_2 drawdown. The occurrence of pre-terrestrial low-temperature carbonates in Martian meteorites (Carr *et al.* 1985; Changela & Bridges 2011) shows that basalts contribute to drawdown on Mars, as on Earth. At least some of this carbonate precipitation may have been surficial (Knauth *et al.* 2003; Halevy *et al.* 2011), as with carbonates in terrestrial basalts (Fig. 7). CO_2 extracted from the atmosphere in this way is available for conversion to CH_4 when coupled

with serpentinization in basalts. Thus, carbon from both atmosphere and lithosphere could contribute to fuelling a putative methanotrophic biosphere on Mars.

Conclusions

These results show that CH_4 is retained within a range of basalts, including cross-cutting hydrothermal mineral veins, which may be capable of remobilizing ancient CH_4 and venting it to the atmosphere. Several other mechanisms may also plausibly release CH_4 from Martian basalt. More work is needed to establish whether Martian basalts or meteorites contain quantities of ancient CH_4 comparable with their terrestrial counterparts and whether they are a likely source for the spatially and temporally variable CH_4 in the atmosphere. Indeed, the CFS technique demonstrated here could be 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).

Evidence of serpentinization or hydrothermal alteration on Mars would imply that liquid water, water-rock redox gradients, and gases including CO_2 , H_2 and CH_4 – all potential energy sources for metabolism – have all been present in the subsurface. These conditions are suggestive of a habitable environment. The products of serpentinization are known to support complex ecosystems in the Earth's oceanic crust and have also been implicated in the origin of life (Sleep *et al.* 2004, 2011; Kelley *et al.* 2005; Hellevang 2008). Biogenic CH_4 on Earth is classically distinguished from abiogenic CH_4 by its light carbon isotopic composition (i.e. very negative $\delta^{13}\text{C}$),

although this test for biogenicity can yield false positives where isotopic fractionation is induced by hydrothermal processes (Horita & Berndt 1999), as well as false negatives in circumstances where biogenic CH₄ is isotopically heavy (Takai *et al.* 2008). Moreover, interpretation of δ¹³C in Martian CH₄ will be challenging without a deeper understanding of the Martian carbon cycle than is presently available. Thus, other criteria including geological context, hydrogen isotope composition and degree of co-occurrence with higher hydrocarbons should also be considered in the determination of biogenicity. For this purpose, CFS analysis of CH₄ in basalts on Earth and Mars could be coupled with measurements of higher hydrocarbons and carbon- and hydrogen-isotopic analysis.

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