A note on the fluxes of abiogenic methane and hydrogen from mid-ocean ridges

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[1] The concentrations of methane and hydrogen in hydrothermal vent fluids issuing from mid-ocean ridges tend to fall into two groups, one with high concentrations of these gases in ultramafic-hosted vent fields and a second group with relatively lower concentrations in basalt-hosted vent fluids. Ultramafic-hosted systems, however, appear to be restricted to slow-spreading ridges and constitute only a fraction of the hydrothermal systems found there. In this note, the hydrothermal fluxes of methane and hydrogen have been calculated by estimating the percentages of the total subsurface hydrothermal circulation that circulate through each type of host rock. Even though the percentage of the total subsurface flow that is affected by serpentinization appears to be rather small (8%), it still appears that this process produces about 70% of the total mid-ocean flux of these gases. The total production of methane and hydrogen is calculated to be about 20×10^9 mol yr^{-1} and 190×10^9 mol yr^{-1}, respectively. The hydrogen flux is comparable to that most recently calculated on the basis of the rate of hydration of mantle rock in newly formed crust and the stoichiometry of the serpentinization reaction. This suggests that, except for the production of methane, a major portion of the hydrogen produced in the subsurface is not consumed before venting. **Citation:** Keir, R. S. (2010), A note on the fluxes of abiogenic methane and hydrogen from mid-ocean ridges, *Geophys. Res. Lett.*, *37*, L24609, doi:10.1029/2010GL045362.

1. Introduction

[2] Although the sources of methane on earth today are predominately of biological origin, abiogenic production of this gas might have contributed to early pre-biotic warming [*Kasting*, 2005; *Emmanuel and Ague*, 2007] and might support the atmospheric mixing ratio in the present Martian atmosphere [*Oze and Sharma*, 2005; *Mumma et al.*, 2009]. A starting point for these considerations is the abiogenic source on earth today, but estimates of this flux range over 2 orders of magnitude [*Welhan and Craig*, 1983; *Kasting*, 2005; *Sorokhtin et al.*, 2001; *Emmanuel and Ague*, 2007; *Cannat et al.*, 2010]. In this note, hydrothermal fluxes of abiogenic methane and hydrogen from mid-ocean ridges are estimated on the basis of gas concentrations that have been observed in vent fluids and the dependence of these concentrations on the type of host rock.

[3] In most of the hydrothermal vents on mid-ocean ridges sampled to date, the carbon isotope ratio of methane occurs in a fairly narrow range ($\delta^{13}C = -9$ to -20‰, Table 1) and is distinctly heavier than in biological or thermogenic sources of this gas. The only 2 exceptions reported at oceanic spreading centers are the Guaymas Basin and the Endeavor Segment of the Juan de Fuca Ridge, both of which emit thermogenic methane with $\delta^{13}C \approx -50$‰ [*Welhan*, 1988; *Lilley et al.*, 1993]. The prevalence of relatively heavy isotope ratios implies that most of the methane generated on mid-ocean ridges is of abiogenic origin, formed either in basalts and extracted into the circulating fluid, or by the reaction of hydrogen with CO_2 within the fluids [*Welhan*, 1988]. The latter mechanism has become of particular interest in regard to serpentinization of mantle rock exposed on slow-spreading ridges [*Rona et al.*, 1987; *Charlou et al.*, 1998].

[4] Hydrothermal fluids exhibit a wide range of hydrogen concentrations (Table 1). Although the factors that control hydrogen generation are not well understood, an important mechanism appears to be the reduction of water with Fe^{2+} released by minerals into hydrothermal fluids to form hydrogen and magnetite. A large amount of Fe^{2+} is released during hydration of ultramafic rock because the resulting serpentine minerals largely exclude Fe(II) from their structure [*McCollom and Bach*, 2009]. High concentrations of hydrogen are found in all ultramafic-hosted vent fluids reported to date but are not limited to just these sites (Table 1). *McCollom and Bach* [2009] point out that release of Fe^{2+} from basalts also generates hydrogen, but usually at much lower concentrations because a greater proportion of the iron is taken as Fe(II) into the alteration minerals such as chlorite and amphibole. This may be perturbed by volcanic events. The highest concentration of H_2 found in hydrothermal fluids so far (40 mmol kg^{-1}) was measured shortly after emplacement of a dike at 9°46.5′N on the East Pacific Rise (EPR), after which the concentration rapidly declined [*Lilley et al.*, 2003]. The trend is that expected from initial hydration of gabbro/basalt until the intrusion of sulfate-bearing seawater oxidizes the fayalite/olivine component [*Seyfried and Ding*, 1995].

[5] Following the initial discovery of hydrothermal vents in the ocean, *Welhan and Craig* [1983] calculated an abiogenic methane flux of 4×10^9 mol yr^{-1} from mid-ocean ridges according to the degassing rate of ^3He from the mantle and the $CH_4/^3He$ ratio observed at 21°N on the EPR. At that time, hydrothermal systems on slow-spreading ridges such as the Mid-Atlantic Ridge (MAR) had yet to be discovered. Since then, 16 active fields on the MAR have been visually identified, 7 of which are hosted in ultramafic rock (S. E. Beaulieu, InterRidge Global Database of Active Submarine Hydrothermal Vent Fields: prepared for Inter-

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Table 1. Concentrations of Selected Gases in Mid-Ocean Ridge Hydrothermal Fluids

Site	CH_4 (mmol/kg)	H_2 (mmol/kg)	^3He (pmol/kg)	$CH_4/^3He$ ($\times 10^{-6}$)	CH_4-($\delta^{13}C$‰)	References
				Pacific		
SJdF	0.09	0.4			−19	*Evans et al.* [1988]
EPR 21°N	0.06	0.4–1.7	10–14	4–6	−17	*Welhan and Craig* [1983]
EPR 13°N	0.05	5	21	2	−18	*Merlivat et al.* [1987]
EPR 9°50′N[c]	0.11	0.2–8	8[b]	13[a]	−20	*Proskurowski et al.* [2008a, 2008b] and *Love et al.* [2008]
				MAR-Basalt Hosted		
Snake Pit	0.06	0.48	13–24	2.5–4		*Jean-Baptiste et al.* [1991] and *Rudnicki and Elderfield* [1992]
TAG	0.14	0.15–0.37	17–20	8	−9	*Rudnicki and Elderfield* [1992] and *Charlou et al.* [1996]
Broken Spur	0.12	1.0–1.6			−18	*Lein et al.* [2000] and *Proskurowski et al.* [2006]
				Central Indian Ridge		
Kairei	0.15	8			−9	*Gamo et al.* [2001], *Gallant and Von Damm* [2006] and *Proskurowski et al.* [2006]
Edmond	0.4	0.02–0.2				*Gallant and Von Damm* [2006]
				MAR-Azores Hot Spot		
Lucky Strike	0.52	0.21	6–13	39–87	−13	*Charlou et al.* [2000]
Menez Gwen	1.7	0.04	16–24	70–105	−19	*Charlou et al.* [2000]
				MAR-Ultramafic Hosted		
Rainbow	2.5	16	25	108	−16	*Charlou et al.* [2002] and *Jean-Baptiste et al.* [2004]
Logatchev 1	2.1–4	19	21–40[b]	100[a]	−13	*Proskurowski et al.* [2006], *Lein et al.* [2000], and *Keir et al.* [2009]
Logatchev 2	1.2	11			−6	*Charlou et al.* [2010]
Drachenschlund	1.4	12	3.5[b]	400[a]	−14	*Melchert et al.* [2008] and *Keir et al.* [2008]
Lost City	1.4	1–14	2.9	480	−12	*Proskurowski et al.* [2006, 2008b]
Aschadze 1	0.5–1.2	8–19			−12	*Charlou et al.* [2010]
Aschadze 2	0.8	26			−9	*Charlou et al.* [2010]

[a] $CH_4/^3He$ ratio in near-field plume.
[b] Calculated from end-member CH_4 and plume $CH_4/^3He$.
[c] High-temperature fluids, excluding Vent A.

Ridge, version 2.0, 2010, available at http://www.interridge.org/IRvents). Mantle rock can outcrop at slow-spreading ridges because of their extensional tectonics [*Aumento and Loubat*, 1971; *Bonatti*, 1976; *Dick*, 1989; *Cannat et al.*, 1995, 1997]. This enables hydration of olivine and pyroxene minerals by fluids circulating in the crust to form serpentine, magnetite and hydrogen. The latter can reduce CO_2 to methane by catalytic reactions analogous to the Fischer-Tropsch synthesis [*Berndt et al.*, 1996]. In hydrothermal fluids from ultramafic hosted vents on the MAR, the $CH_4/^3He$ ratios are much higher than found on the EPR, and hydrogen concentrations are elevated as well (Table 1). Elevated methane concentration and high $CH_4/^3He$ ratios (but with low H_2) also appear in the basalt-hosted vent fields, Lucky Strike and Menez Gwen, which are located near the Azores hot spot on the MAR [*Charlou et al.*, 2000]. This seems to be related to enhanced degassing of CO_2 and CH_4 from a shallow magma chamber, although serpentinization at depth might also play a role. In general, variable $CH_4/^3He$ ratios occur in MAR hydrothermal systems, ratios that range from about 1 to 100 times those than found on the EPR. Thus, *Welhan and Craig*'s [1983] original assumption that the EPR $CH_4/^3He$ ratio is typical of the mid-ocean ridge system in general has not been borne out.

2. Abiogenic Methane Flux From Mid-Ocean Ridges

[6] In the compilation in Table 1, vent fluids tend to mostly fall into one of two classes, one with methane concentrations of about 0.1 mmol kg^{-1} and another with concentrations of about 1 to 4 mmol kg^{-1}. The former group includes many of the basalt-hosted systems found on ridges regardless of the spreading rate. The latter group consists of MAR ultramafic hosted fields as well as Menez Gwen near the Azores. Lucky Strike, which is also near the Azores, and Edmond on the Central Indian Ridge have methane concentrations in-between these two modes. From the flux of high-temperature vent fluid to the ocean and the partitioning of this flux between low and high concentration methane sources, one can in principle estimate the mid-ocean ridge abiogenic methane flux.

[7] The magnitude of the mid-ocean-ridge high-temperature fluid flux is rather controversial. From the difference between predicted and observed heat flow, the near axial

Table 2. Crustal Area Produced and Axial Hydrothermal Flow as a Function of Plate Spreading Rate

Spreading Rate (cm y^{-1})	Length[a] (km)	Rate of Area Increase (10^9 cm^2 y^{-1})	Fraction of Total Area Increase	Cumulative Percentage	Seawater Flow[b] (10^{13} kg y^{-1})
1	13,500	1.35	0.041	4.1	0.246
3	21,625	6.49	0.198	23.9	1.188
5	6500	3.25	0.099	33.8	0.594
7	13,250	9.28	0.283	62.1	1.698
9	3625	3.26	0.099	72.0	0.594
11	625	0.69	0.021	74.1	0.126
13	2500	3.25	0.099	84.0	0.594
15	3500	5.25	0.160	100.0	0.960
Total	65125	32.82	1.000		

[a]*Baker and German* [2004].
[b]Assuming total of 6×10^{13} kg y^{-1} (see text) and flow proportional to area spreading rate.

flow of seawater through the crust is estimated to be 3–9 × 10^{13} kg yr^{-1} [*Stein et al.*, 1995; *Kadko et al.*, 1995]. A Sr-isotope budget gave a similar flux (12 × 10^{13} kg yr^{-1} [*Palmer and Edmond*, 1989]). On the other hand, the budget of Tl-isotopes as well as calculations based on Li, Sr and S in ODP Hole 504B yield lower fluxes of high-temperature fluid, on the order of 0.7 × 10^{13} kg yr^{-1} [*Nielsen et al.*, 2006; *Chan et al.*, 2002; *Teagle et al.*, 1998, 2003].

[8] Estimation of the high-temperature fluid flux from the ocean ^{3}He flux gives a result similar to the higher estimates above based on near-axial heat flux. End-member ^{3}He concentrations in MOR vent fluids generally range between 7 and 30 pmol kg^{-1}, with an average value of 17 pmol kg^{-1} [*Jean-Baptiste et al.*, 2004] (see Table 1). The loss of ^{3}He from basalt must be balanced by the vertical flux of ^{3}He through the ocean, which is reasonably constrained to be about 1000 mol y^{-1} [*Craig et al.*, 1975; *Farley et al.*, 1995]. Since ^{3}He appears to be principally extracted into high temperature fluid, the circulation necessary to carry the helium flux is calculated to be in the range of 3 to 12 × 10^{13} kg yr^{-1}, similar to the heat-flux estimates. A value of 6 × 10^{13} kg yr^{-1} is obtained from the average ^{3}He concentration above and employed for the estimates of CH_4 and H_2 fluxes that follow. Note that the lower circulation estimates of <1 × 10^{13} kg yr^{-1} would necessitate vent fluid ^{3}He concentrations of >100 pmol kg^{-1}, which is greater than those that have been observed (Table 1).

[9] In order to partition the sub-surface circulation between venting with low and high methane concentrations, it is first assumed that the water flux occurs in proportion to the rate of areal increase of new crust. This is implied by the flux of ^{3}He to the ocean, which appears to occur in proportional to spreading rate [*Farley et al.*, 1995; *Dutay et al.*, 2004], while the ^{3}He concentration in vent fluids bears no apparent relation to spreading rate (Table 1). This is because the flux of ^{3}He is related to the frequency of vent field occurrence, and this in turn is correlated with the spreading rate [*Baker and German*, 2004]. Secondly, it is assumed that ultramafic rock outcrops mainly on ridges with spreading rates less than 4 cm yr^{-1}. Table 2 shows crustal production as a function of spreading rate, as calculated from the frequency of spreading rates given by *Baker and German* [2004, Figure 2c]. Slow and ultra-slow spreading ridges contribute 24% of the total crustal production. Thirdly, it is assumed that one-third of the hydrothermal fields on these ridges are affected by serpentinization. As mentioned earlier, 43% (7 of 16) of the active fields discovered thus far on the MAR are ultramafic hosted. Three of the 7 ultramafic sites, however, exhibit low-temperature venting (Lost City, Saldanha, Menez Hom). On the basis of gravity anomalies, *Cannat et al.* [1995, 2010] suggest that 23% of the seafloor created at slow-spreading ridges contains ultramafic rock. Here I assume the fraction of ultramafic-hosted vent fields on slow-spreading ridges is the average of these percentages. Accordingly, serpentinization appears to affect 8% of the global near-axis hydrothermal circulation. If this flow carries 3 mmol kg^{-1} methane, whereas the remaining 92% carries 0.1 mmol kg^{-1} on average (Table 1), and the total fluid flux = 6 × 10^{13} kg yr^{-1}, then the global abiogenic methane flux comes to the following: 0.48 $(10)^{13}$ kg yr^{-1} × 3 mmol kg^{-1} + 5.52 $(10)^{13}$ kg yr^{-1} × 0.1 mmol kg^{-1} = 19.9 × 10^9 mol yr^{-1}. The uncertainty in the flux estimate is at least plus/minus a factor of 2 due to that of the sub-surface seafloor circulation alone. Although serpentinization of ultramafic rock is presumed to occur within only 8% of the total circulation, this process appears to supply about 75% of the abiogenic methane from mid-ocean ridges.

3. Hydrogen Flux From Mid-Ocean Ridges

[10] The six MAR high-temperature ultramafic hosted vent fluids in Table 1 have relatively similar high concentrations of hydrogen. At Lost City, a low-temperature ultramafic hosted site, hydrogen concentrations range over an order of magnitude [*Proskurowski et al.*, 2006]. The upper end of this range (14 mmol kg^{-1}) corresponds to concentrations found in high-temperature ultramafic fields (Table 1). *Proskurowski et al.* [2006] suggest that the lower concentrations result from utilization by sub-surface sulfate-reducing bacteria in relatively cooler fluids before venting.

[11] The concentration of hydrogen in basalt-hosted vent-fluids varies more widely than methane, from 0.02 to greater than 8 mmol kg^{-1}, and this makes the estimation of the H_2 flux more uncertain. High values have been reported at 13°N on the EPR and at Kairei on the Central Indian Ridge (Table 1). At the latter site, it appears that the high hydrogen concentration arises from the serpentinization of troctolites at depth in the subsurface [*Nakamura et al.*, 2009]. Two segments north of Kairei and 1000 m deeper on the same ridge, the Edmond vent field exhibits some of the lowest hydrogen concentrations that have been reported, 0.02–0.2 mmol kg^{-1}. A large range of hydrogen concentrations has also been observed on the EPR at 9°50′N, where eruptive events

occurred in 1991 and 1992 [*Von Damm and Lilley*, 2004; *Proskurowski et al.*, 2008a]. The high concentrations occur in the high-temperature vent fluids, and these concentrations decrease in time following the eruptive events. Low hydrogen and high methane concentrations with relatively depleted ^{13}C ($\delta^{13}C \approx -30‰$) in the low-temperature diffuse fluids suggest that methanogenesis occurs below the seafloor at these temperatures (20–70°C [*Von Damm and Lilley*, 2004; *Proskurowski et al.*, 2008a]).

[12] For the purpose of a rough estimate, the geometric mean of hydrogen concentrations in basalted-hosted vents, 0.6 mmol kg^{-1} (Table 1), is applied to the axial flow through these systems, and 16 nmol kg^{-1} (arithmetic average in Table 1) is assumed to be representative of ultramafic vent fluids. Accordingly, the abiogenic hydrogen flux is calculated to be as follows: $0.48\ (10)^{13}$ kg yr^{-1} × 16 mmol kg^{-1} + $5.52\ (10)^{13}$ kg yr^{-1} × 0.6 mmol kg^{-1} = 110 × 10^9 mol yr^{-1}. Similar to methane, it appears that about 70% of the hydrogen flux is supplied by serpentinization. This flux, however, is the net hydrogen flux emitted with the vent fluids. Since hydrogen is a precursor of methane, the total production must be higher. If all of the sub-surface hydrogen consumption were due to reduction of CO_2 to form abiogenic methane according to

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O,$$

then the 5.5 to 1 overall ratio of hydrogen to methane flux above would imply that 42% of the total hydrothermal hydrogen production is converted to methane. Accordingly, the total amount of hydrogen produced would be 73% higher than the net flux and equal to 190 × 10^9 mol yr^{-1}.

4. Concluding Remarks

[13] Mid-ocean ridge fluxes of hydrogen and methane appear to be mainly supplied by serpentinization of ultramafic rock. The total hydrogen and methane produced by serpentinization are calculated in this work to be 133 × 10^9 mol yr^{-1} and 14 × 10^9 mol yr^{-1}. These fluxes are slightly lower than those calculated by *Cannat et al.* [2010] according to the rate of mantle rock exhumation and the stoichiometry of olivine hydration (167 × 10^9 mol yr^{-1} for H_2 and 25 × 10^9 mol yr^{-1} for CH_4). Although this difference could be due to subsurface consumption of hydrogen by reactions other than CO_2 reduction, all of these results are within the uncertainty of plus/minus a factor of 2 inherent to these estimates. The net venting flux of serpentinization produced H_2 calculated above (77 × 10^9 mol yr^{-1}) agrees well with a recent estimate by *Charlou et al.* [2010] (90 × 10^9 mol yr^{-1}) using the estimated heat flux of slow-spreading ridges.

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