

## Hypothesis Paper

### Martian CH<sub>4</sub>: Sources, Flux, and Detection

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#### ABSTRACT

Recent observations have detected trace amounts of CH<sub>4</sub> heterogeneously distributed in the martian atmosphere, which indicated a subsurface CH<sub>4</sub> flux of  $\sim 2 \times 10^5$  to  $2 \times 10^9$  cm<sup>-2</sup> s<sup>-1</sup>. Four different origins for this CH<sub>4</sub> were considered: (1) volcanogenic; (2) sublimation of hydrate-rich ice; (3) diffusive transport through hydrate-saturated cryosphere; and (4) microbial CH<sub>4</sub> generation above the cryosphere. A diffusive flux model of the martian crust for He, H<sub>2</sub>, and CH<sub>4</sub> was developed based upon measurements of deep fracture water samples from South Africa. This model distinguishes between abiogenic and microbial CH<sub>4</sub> sources based upon their isotopic composition, and couples microbial CH<sub>4</sub> production to H<sub>2</sub> generation by H<sub>2</sub>O radiolysis. For a He flux of  $\sim 10^5$  cm<sup>-2</sup> s<sup>-1</sup> this model yields an abiogenic CH<sub>4</sub> flux and a microbial CH<sub>4</sub> flux of  $\sim 10^6$  and  $\sim 10^9$  cm<sup>-2</sup> s<sup>-1</sup>, respectively. This flux will only reach the martian surface if CH<sub>4</sub> hydrate is saturated in the cryosphere; otherwise it will be captured within the cryosphere. The sublimation of a hydrate-rich cryosphere could generate the observed CH<sub>4</sub> flux, whereas microbial CH<sub>4</sub> production in a hypersaline environment above the hydrate stability zone only seems capable of supplying  $\sim 10^5$  cm<sup>-2</sup> s<sup>-1</sup> of CH<sub>4</sub>. The model predicts that He/H<sub>2</sub>/CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> abundances and the C and H isotopic values of CH<sub>4</sub> and the C isotopic composition of C<sub>2</sub>H<sub>6</sub> could reveal the different sources. Cavity ring-down spectrometers represent the instrument type that would be most capable of performing the C and H measurements of CH<sub>4</sub> on near future rover missions and pinpointing the cause and source of the CH<sub>4</sub> emissions. **Key Words:** Mars—Methane—Methanogens—Fischer-Tropsch reactions—Infrared spectroscopy. *Astrobiology* 6, 377–395.

#### INTRODUCTION

THE RECENT DETECTION of at least  $\sim 10$  parts per billion (ppbv) CH<sub>4</sub> in the martian atmosphere has fueled speculation that CH<sub>4</sub> may originate by microbial methanogenesis in the regolith of Mars

(Formisano *et al.*, 2004; Krasnopolsky *et al.*, 2004a,b; Mumma *et al.*, 2004). This is because the rate of photochemical destruction of CH<sub>4</sub> is approximately  $2.2 \times 10^5$  cm<sup>-2</sup> s<sup>-1</sup> ( $1.7 \times 10^7$  mol year<sup>-1</sup>), which translates into a CH<sub>4</sub> lifetime of  $\sim 340$  years for  $\sim 10$  ppbv (Krasnopolsky *et al.*,

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2004b). The short lifetime implies an active CH<sub>4</sub> source such as autotrophic methanogenesis (4H<sub>2</sub> + CO<sub>2</sub> → CH<sub>4</sub> + 2H<sub>2</sub>O) combined with diffusion through the regolith (where production occurs in near-surface brines) or through the underlying cryosphere (where production occurs in a subpermafrost aquifer), the sublimation or depressurization of hydrate-rich ground ice (Max and Clifford, 2000), or recent CH<sub>4</sub>-generating events such as cometary impact (Kress and McKay, 2004), igneous intrusion (Lyons *et al.*, 2005), volcanic eruption, or thermally generated gas discharge (Wong and Atreya, 2003). The last three mechanisms appear not to be supported by spacecraft observations and theoretical considerations (Krasnopolsky, 2005).

Satellite and ground-based observations indicate that the martian atmospheric CH<sub>4</sub> is not uniformly mixed, but concentrated in the equatorial region relative to the polar regions (Mumma *et al.*, 2004). Since the horizontal mixing time for the martian atmosphere is ~0.5 years (Krasnopolsky *et al.*, 2004b), this would imply that a CH<sub>4</sub> removal process more rapid than photochemical destruction must also exist. The sink could be some undefined surface oxidation phenomena or biological CH<sub>4</sub> oxidation equivalent to aerobic methanotrophy (CH<sub>4</sub> + 2O<sub>2</sub> → CO<sub>2</sub> + 2H<sub>2</sub>O) in terrestrial microorganisms that rely on the trace O<sub>2</sub> in the martian atmosphere [~1,300 parts per million (ppmv) or ~7 × 10<sup>7</sup> mol (Owen, 1992)]. Regardless of the mechanisms, the spatial heterogeneity in the CH<sub>4</sub> atmospheric abundance implies that the subsurface CH<sub>4</sub> flux could be much greater than the ~2 × 10<sup>5</sup> cm<sup>-2</sup> s<sup>-1</sup> required by the photochemical loss rate. An estimated flux is given by the following:

$$F = \Delta C M_a A / (S_M \tau s_{yr})$$

where  $\Delta C$  is the range in CH<sub>4</sub> concentration ~100 × 10<sup>-9</sup>,  $M_a$  is the martian atmosphere = 5.4 × 10<sup>17</sup> mol,  $A$  is Avogadro's number = 6.02 × 10<sup>23</sup> atoms mol<sup>-1</sup>,  $S_M$  is the surface area of Mars = 0.4 × 10<sup>18</sup> cm<sup>2</sup>,  $\tau$  is the mixing time in the Martian atmosphere = 0.5 year, and  $s_{yr}$  = 3.2 × 10<sup>7</sup> s year<sup>-1</sup>. This expression yields an estimated CH<sub>4</sub> flux of 2 × 10<sup>9</sup> cm<sup>-2</sup> s<sup>-1</sup>. The H<sub>2</sub> required to produce the CH<sub>4</sub> could originate in the martian atmosphere by photochemical destruction of H<sub>2</sub>O producing 15 ppmv of H<sub>2</sub>, which in turn could diffuse into the regolith at a rate of 9 × 10<sup>9</sup> cm<sup>-2</sup> s<sup>-1</sup> (Summers *et al.*, 2002). Given the 4:1 stoi-

chiometric ratio of H to C, a 2 × 10<sup>9</sup> cm<sup>-2</sup> s<sup>-1</sup> CH<sub>4</sub> flux should significantly deplete the H<sub>2</sub> concentration of the martian atmosphere.

This article examines whether an alternative CH<sub>4</sub> source—abiogenic CH<sub>4</sub>—and an alternative H<sub>2</sub> source—radiolytic H<sub>2</sub> produced in the martian crust—could sustain the recently reported subsurface CH<sub>4</sub> flux. This study first demonstrates the importance of both abiogenic CH<sub>4</sub> and radiolytic H<sub>2</sub> as the source of CH<sub>4</sub> flux in the South African Precambrian crust of the Witwatersrand Basin. This 2.9–2.5 × 10<sup>9</sup> year old (Ga) basin has not experienced volcanism in 200 × 10<sup>6</sup> years (Myr), and previous reports indicate that subsurface microbial communities are sustained by subsurface generation of H<sub>2</sub> through radiolysis of water (Lin *et al.*, 2005b; Sherwood Lollar *et al.*, 2005). A coupled reaction and diffusive transport model of this basin calibrated by He flux is used to model He, H<sub>2</sub>, and CH<sub>4</sub> in the martian subsurface and determine whether their rates can explain the estimated martian subsurface CH<sub>4</sub> flux. Four different origins for martian CH<sub>4</sub> are discussed in the context of this model: (1) volcanogenic; (2) sublimation of hydrate-rich ice; (3) diffusive transport through hydrate-saturated cryosphere; and (4) microbial CH<sub>4</sub> generation above the cryosphere. This article concludes with a discussion as to how to distinguish between the different CH<sub>4</sub> sources and what is the most capable analytical technology for characterizing the martian CH<sub>4</sub> in future rover missions.

## CH<sub>4</sub> IN PRECAMBRIAN SHIELDS

### *Isotopic composition of CH<sub>4</sub>–C<sub>4</sub>H<sub>10</sub> and abiogenic CH<sub>4</sub>*

To date, the characteristics of abiogenic hydrocarbons on Earth have not been well defined. The earliest reported abiogenic CH<sub>4</sub> occurrences were those identified by Welhan *et al.* (1979), which were discharging at the East Pacific Rise and very <sup>13</sup>C-rich due to their mantle-derived carbon source. Mantle-derived carbon sources have also been invoked to explain the <sup>13</sup>C-enriched CH<sub>4</sub> produced by serpentinization at the Zambales ophiolite sequence (Abrajano *et al.*, 1988, 1990) and the Lost City Hydrothermal Field (Kelley *et al.*, 2005) (Fig. 1).

Not all abiogenic CH<sub>4</sub> is mantle in origin. In continental crust, such as Precambrian Shield

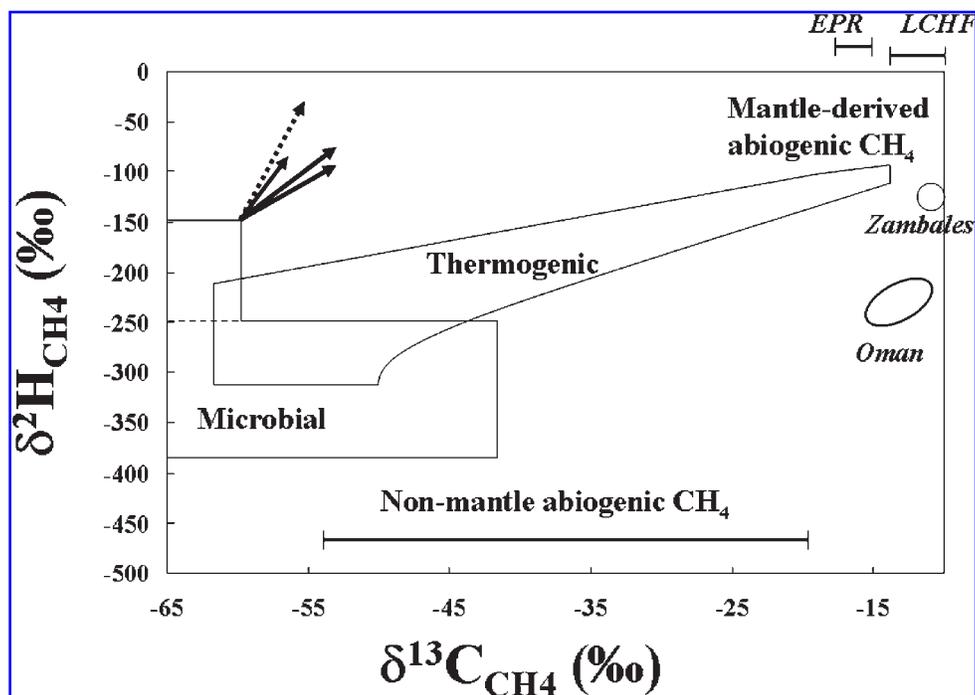


FIG. 1. C and H isotopic signatures for thermogenic, microbial, and abiogenic sources of CH<sub>4</sub> (adapted from Schoell, 1988). The range of  $\delta^{13}\text{C}$  values for suggested abiogenic CH<sub>4</sub> varies significantly depending on local carbon source. Where mantle carbon sources are invoked, highly enriched  $\delta^{13}\text{C}$  values have been reported, *e.g.*, East Pacific Rise (EPR) (Welhan and Craig, 1979), serpentinization-related CH<sub>4</sub> from the Lost City Hydrothermal Field (LCHF) (Kelley *et al.*, 2005), Zambales (Abrajano *et al.*, 1988), and Oman ophiolite sequences (Fritz *et al.*, 1992). Abiogenic CH<sub>4</sub> produced by non-mantle carbon sources produces a wide range of  $\delta^{13}\text{C}$  values as shown in experiments (Horita and Berndt, 1999) and Precambrian Shield field site studies (Sherwood Lollar *et al.*, 1993a, 2002, 2005). For some of these studies, only  $^{13}\text{C}$  values are available so a range of  $^{13}\text{C}$  values (horizontal lines) rather than plotted data are shown for comparison. The black arrows represent the stable isotope fractionation trend produced by aerobic methanotrophy (Coleman *et al.*, 1981; Reeburgh, 2003), the gray arrows represent anaerobic methanotrophy (Alperin *et al.*, 1988; Reeburgh, 2003), and the dashed arrow represents photochemical destruction of CH<sub>4</sub> (Nair *et al.*, 2005).

rocks, processes of gas–water–rock interaction, including serpentinization, Fischer-Tropsch synthesis ( $3\text{H}_2 + \text{CO} = \text{CH}_4 + \text{H}_2\text{O}$ ), and the metamorphism of carbonate–graphite-bearing rocks ( $2\text{H}_2\text{O} + 2\text{C} = \text{CH}_4 + \text{CO}_2$ ) produce abiogenic hydrocarbons. This abiogenic CH<sub>4</sub> possesses  $^{12}\text{C}$ -rich signatures isotopically lighter than that of mantle-derived CH<sub>4</sub> and reflects local crustal carbon sources (Sherwood Lollar *et al.*, 1993a, 2005). Similarly, hydrothermal laboratory experiments have yielded CH<sub>4</sub> depleted in  $^{13}\text{C}$  with a  $\delta^{13}\text{C}$   $-67\%$  Vienna Pee Dee Formation Belemnite standard (VPDB) relative to the source CO<sub>2</sub> (Horita and Berndt, 1999) (Fig. 1).

A more rigorous test for distinguishing microbial from abiogenic hydrocarbons moves beyond comparing absolute  $\delta^{13}\text{C}$  values of the CH<sub>4</sub> to examining the pattern of stable isotope variation among CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>, as was done for the Murchison meteorite (Yuen *et al.*, 1984)

and abiogenic hydrocarbons produced in spark discharge experiments (Des Marais *et al.*, 1981). Substantial volumes of CH<sub>4</sub> gas are discharged from fractures and boreholes throughout the Precambrian Shield rocks of Canada, Fennoscandia, and South Africa (Ward *et al.*, 2004; Sherwood Lollar *et al.*, 1993a, 2002, 2005). Based on measurements of the  $^{13}\text{C}$  and  $^2\text{H}$  isotope variations in CH<sub>4</sub> and higher hydrocarbons in Precambrian Shield rock gases, Sherwood Lollar *et al.* (2002, 2005) proposed that an isotopic pattern of C isotope depletion in  $^{13}\text{C}$  and H isotope enrichment in  $^2\text{H}$  from CH<sub>4</sub> to C<sub>4</sub>H<sub>10</sub> was characteristic of abiogenically produced gases. This is based on the hypothesis that during polymerization of CH<sub>4</sub> to produce higher hydrocarbons there will be a preferential rate of reaction for the light isotopes, which results in the preferential incorporation of  $^{12}\text{C}$  into the products of the reaction concomitant with a preferential loss of  $^1\text{H}$  (Fig. 2).

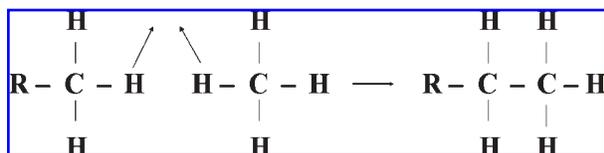


FIG. 2. The proposed carbon and hydrogen isotope fractionation process during abiogenic polymerization of  $C_2H_6$  from  $CH_4$ . With C addition, a preferential rate of reaction for  $^{12}C$  leads to  $^{13}C$ -depleted ethane [carbon isotope hypothesis from Des Marais *et al.* (1981)]. With H elimination, a preferential rate of reaction for  $^1H$  leads to  $^2H$ -enriched ethane [hydrogen isotope hypothesis from Sherwood Lollar *et al.* (2002)].

In the case of the 2.9-Ga Witwatersrand Basin of South Africa, the deep Au mines provide a unique opportunity to examine the regional distribution ( $350 \times 150$  km) and vertical distribution

(up to 3.3 km depth) of  $CH_4$  sources and sinks. The data have provided the first picture of the  $CH_4$  cycle for stable, Precambrian continental crust that has not experienced recent volcanic activity.

The isotopic composition and concentration of  $H_2$ , He, and  $CH_4$  to  $C_4H_{10}$  hydrocarbons and the sequences of the 16S rDNA were determined for fracture water samples collected at depths ranging from 0.2 to 3.3 km from the Witwatersrand Basin, South Africa (Lippmann *et al.*, 2003; Ward *et al.*, 2004; Onstott *et al.*, 2005). Samples were collected from the southernmost Welkom (shaded squares in Figs. 3–5), easternmost Evander (shaded diamonds in Figs. 3–5), and northernmost Carletonville (shaded triangles in Figs. 3–5) mining regions and from the overlying 2.45-Ga Transvaal

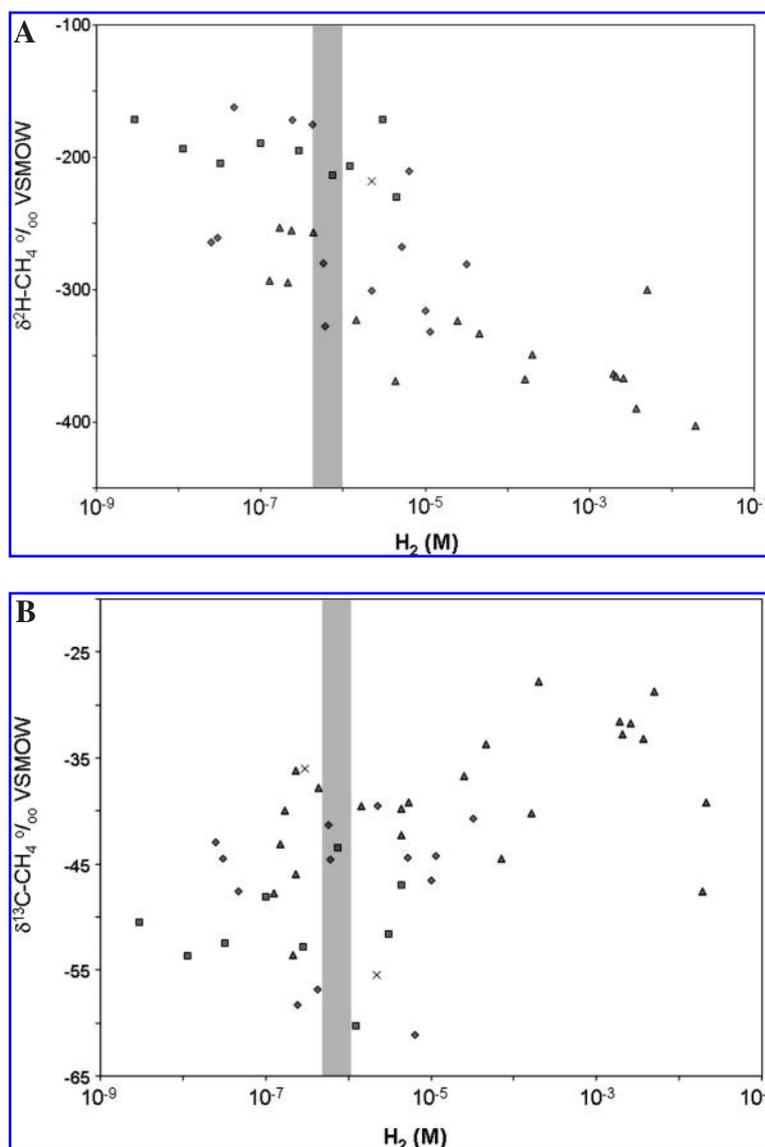
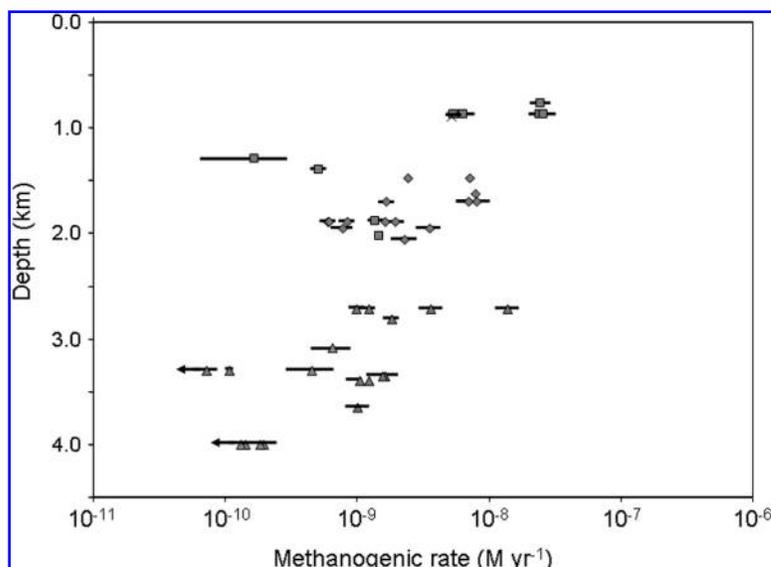


FIG. 3. A:  $\delta^2H$  of  $CH_4$  versus  $H_2$  concentration for fracture water samples from the Witwatersrand Basin, South Africa. Samples were collected from the Welkom (shaded squares), Evander (shaded diamonds), and Carletonville (shaded triangles) mining regions and from the overlying 2.45-Ga Transvaal dolomitic aquifer (x). Correlation coefficient is 0.58. B:  $\delta^{13}C$  of  $CH_4$  versus  $H_2$  concentration for fracture water samples from the Witwatersrand Basin, South Africa. Correlation coefficient is 0.32. Gray rectangle delineates the  $H_2$  concentration range for which the  $\Delta G$  of the reaction  $4H_2 + H^+ + HCO_3^- \rightarrow CH_4 + 3H_2O$  equals  $-20$  kJ mol $^{-1}$ . The  $\Delta G$  is more negative to the right of the gray rectangle and less negative to the left of the gray rectangle.

**FIG. 4. Methanogenic rate calculated from isotope model (see text for details) versus depth.** Samples were collected from the Welkom (shaded squares), Evander (shaded diamonds), and Carletonville (shaded diamonds) mining regions and from the overlying 2.45-Ga Transvaal dolomitic aquifer (×). Error bars represent 1 standard deviation from the average of three different estimates for the methanogenic rate from Eqs. 1, 3 and 4 in the text. Arrows indicates maximum estimate of methanogenic rate tolerated by the isotopic data.



dolomitic aquifer (crosses in Figs. 3–5) and the 250-Ma Karoo coal seams (asterisk in Fig. 4).

As reported by Ward *et al.* (2004) and Sherwood Lollar *et al.* (2005), the CH<sub>4</sub> of the Witwatersrand Basin represents a mixture of methanogenic CH<sub>4</sub> and abiogenic CH<sub>4</sub>. Microbially produced CH<sub>4</sub> was characterized by relatively depleted  $\delta^{13}\text{C}$  values, enriched  $\delta^2\text{H}$  values, and CH<sub>4</sub>/C<sub>2</sub>+ (C<sub>2</sub>+ = ethane + propane + butane) values on the order of 10<sup>3</sup>–10<sup>5</sup> (Schoell, 1988; Hunt, 1996). In contrast, the abiogenic component had substantially more C<sub>2</sub>+ relative to CH<sub>4</sub>, with CH<sub>4</sub>/C<sub>2</sub>+ ratios typically <100, and relatively enriched  $\delta^{13}\text{C}$  values and depleted  $\delta^2\text{H}$  values. Where microbial CH<sub>4</sub> was prevalent, 16S rDNA analyses generally confirmed the presence of methanogenic, sometimes autotrophic, microorganisms (Ward *et al.*, 2004).

Many of the Precambrian Shield sites contain substantial concentrations of H<sub>2</sub> (up to 5 mM) and He in addition to hydrocarbon gases (Sherwood Lollar *et al.*, 1993a, 2005). Sampling of the same boreholes over several years has shown that the high H<sub>2</sub> levels are not an artifact of drilling but a persistent natural phenomenon in this environment (Sherwood Lollar *et al.*, 1993b, 2002). The high He concentrations are caused by the radioactive decay of U and Th (Lippmann *et al.*, 2003). Like the hydrocarbon gases, the high quantities of H<sub>2</sub> are likely the product of abiogenic water–rock interactions in these highly impermeable, high rock-to-water ratio environments. Specific H<sub>2</sub>-generating reactions may vary from

one geological environment to another, ranging from serpentinization reactions in ultramafic rock (Abrajano *et al.*, 1990) to radiolytic decomposition of water in the U-rich continental crust (Lin *et al.*, 2005a,b). The association of high H<sub>2</sub> concentrations with a <sup>13</sup>C-enriched CH<sub>4</sub> component and low H<sub>2</sub> concentrations with the <sup>13</sup>C-depleted methanogenic component in South Africa suggests that H<sub>2</sub>-driven autotrophy supports methanogenesis in the deep subsurface (Sherwood Lollar *et al.*, 2005).

For Witwatersrand Basin fluids, the relationship between H<sub>2</sub> concentration and the  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  values for CH<sub>4</sub> is particularly pronounced (Fig. 3). The fracture water with dominantly abiogenic CH<sub>4</sub> contained millimolar H<sub>2</sub> concentrations, whereas fracture water with dominantly methanogenic CH<sub>4</sub> yielded micromolar H<sub>2</sub> concentrations. The presence of methanogenic CH<sub>4</sub> with H<sub>2</sub> concentrations greater than 10 nM is still consistent with autotrophic methanogenesis. Though CO<sub>2</sub>—the dominant electron acceptor—is limited, the environment is not H<sub>2</sub> limited (Onstott *et al.*, 2005). The minimal energy yield necessary for ATP synthesis (–20 kJ mol<sup>–1</sup>) (Shink, 1997) requires H<sub>2</sub> concentrations of at least 500–1,000 nM. This is not the case in marine sediments (Hoehler *et al.*, 1998).

#### *In situ rates of microbial CH<sub>4</sub> production and the abiogenic CH<sub>4</sub> flux*

The CH<sub>4</sub> concentration, isotopic composition, and surface flux for the South African crust were

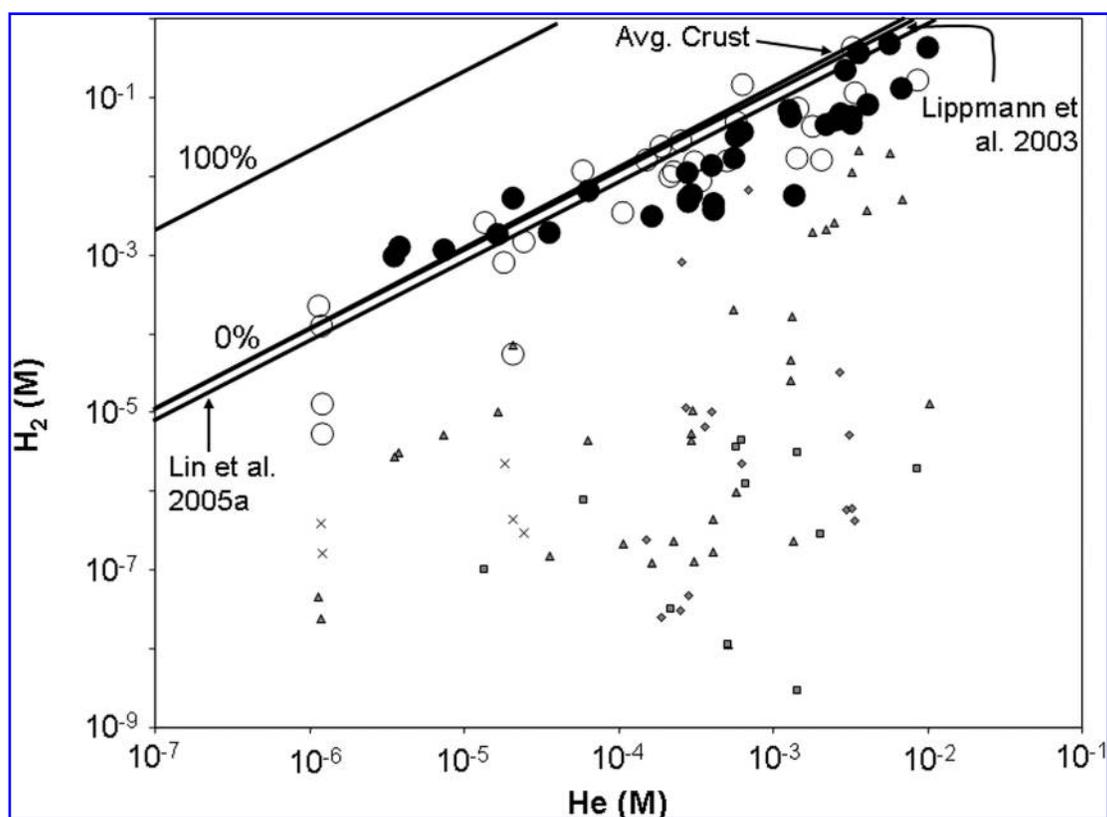


FIG. 5.  $H_2$  versus He concentration for fracture water samples from the Witwatersrand Basin, South Africa. Samples were collected from the Welkom (shaded squares), Evander (shaded diamonds), and Carletonville (shaded diamonds) mining regions and from the overlying 2.45-Ga Transvaal dolomitic aquifer ( $\times$ ).  $H_2$  concentrations that have been corrected for loss to  $CH_4$  by methanogenesis (open circles) and for loss to  $C_1$ – $C_4$  hydrocarbons by abiotic processes (solid circles) are also plotted for comparison (see text for details). The trend marked Avg. Crust represents the predicted  $H_2$  concentration from radiolysis of pore water (Spinks and Woods, 1990) and the He concentration in the pore water assuming that 0% of the  $\alpha$  particles from U and Th decay are retained by the mineral phases and that all of them diffuse into the pore water from the continental crust with 1% porosity and K, U, and Th concentrations of 3.4%, 2.8 ppm, and 10.8 ppm, respectively. The trend marked Lippmann et al. 2003 represents the predicted  $H_2$  yield from radiolysis of pore water for continental crust with 1% porosity and K, U, and Th concentrations of 3.4%, 520 ppm, and 10.8 ppm, respectively. The trend marked Lin et al. 2005a represents the predicted  $H_2$  concentration from radiolysis of pore water using the same crustal composition as Lippmann et al. (2003) but with the experimentally determined  $H_2$  yield of Lin et al. (2005a). The trend marked 100% is the same as the Average Crust trend, but assumes that 100% of the  $\alpha$  particles released within the mineral phases are retained and not lost by diffusion to the pore water.

modeled using an approach similar to that employed by Lippmann et al. (2003) to determine the He age of fracture water and interpret the  $H_2$  and  $CH_4$  data. The modeled  $CH_4$  concentration,  ${}^TCH_4$ , assumed to represent the sum of abiogenic  $CH_4$  flux and microbial  $CH_4$  generated *in situ*, is given by:

$${}^TCH_4 = {}^{He}t\{[J_{CH_4}/(\theta\rho_wz)] + [P_{CH_4}]\} \quad (1)$$

where  $J_{CH_4}$  is the abiogenic  $CH_4$  flux ( $\text{mol dm}^{-2} \text{ year}^{-1}$ ),  $\theta$  is the porosity (0.5–2%),  $z$  is depth (dm),  $P_{CH_4}$  is the rate of methanogenesis ( $M \text{ year}^{-1}$ ), and

${}^{He}t$  is the He age of the fracture water and is given by the equation from Lippmann et al. (2003):

$${}^{He}t = [He]/\{[J_{He}/(\theta\rho_wz)] + [\gamma_{He}(1 - \theta\rho_r/\theta\rho_w)P_{He}]\} \quad (2)$$

where  $[He]$  is the measured He concentration in the fracture water,  $J_{He}$  is the He flux,  $\rho_w$  is the fracture water density,  $\rho_r$  is the rock matrix density,  $\gamma_{He}$  is the fraction of He produced in the minerals that is released into the pore water, and  $P_{He}$  is the *in situ* production rate of He. For the Witwatersrand Basin, Lippmann et al. (2003) used

$J_{\text{He}} = 1.6 \times 10^{-8} \text{ mol dm}^{-2} \text{ year}^{-1}$  ( $3.1 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ ),  $\rho_w = 0.98\text{--}1.03 \text{ kg dm}^{-3}$ ,  $\rho_r = 2.65\text{--}2.70 \text{ kg dm}^{-3}$ , and  $P_{\text{He}} = 7.6 \times 10^{-12}\text{--}7.4 \times 10^{-10} \text{ mol dm}^{-3} \text{ year}^{-1}$  ( $1.5 \times 10^2\text{--}1.4 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ ). The range in  $P_{\text{He}}$  reflects the range in U concentrations in the rock strata. We calculated that the  $\gamma_{\text{He}}$  is  $\sim 0.6\%$ , given the 1% porosity (*i.e.*, the mean free path of the  $\alpha$  particle, 10–50  $\mu\text{m}$ , greatly exceeds that of the rock pore size,  $< 0.15 \mu\text{m}$  based upon Hg porosimetry data) and the relatively lower stopping power of water compared with that of silicates. Lippmann *et al.* (2003) argued that  $\gamma_{\text{He}}$  is  $\sim 100\%$ , because the ambient temperature of the rock strata bounding the fractures ranged from 40°C to 60°C, a temperature range that falls within the closure temperature range of the U-bearing minerals (Shuster *et al.*, 2004). Lippmann *et al.* (2003) assumed that since the rock strata have been at this temperature range for  $\sim 35 \text{ Myr}$  (Omar *et al.*, 2003), almost all of the He would have diffused out of the U-bearing mineral and into the pore water, making  $\gamma_{\text{He}}$  effectively  $\sim 100\%$ .

The microbial CH<sub>4</sub> production rate was also constrained by the isotopic composition of the CH<sub>4</sub>, which is given by the following expressions:

$$\delta^2\text{H} - \text{CH}_4 = {}^{\text{He}t} \times \{ [J_{\text{CH}_4} / (\theta \rho_w z) \times \delta^2\text{H}_{\text{CH}_4\text{A}}] + [P_{\text{CH}_4} \times \delta^2\text{H}_{\text{CH}_4\text{B}}] \} / T_{\text{CH}_4} \quad (3)$$

$$\delta^{13}\text{C} - \text{CH}_4 = {}^{\text{He}t} \times \{ [J_{\text{CH}_4} / (\theta \rho_w z) \times \delta^{13}\text{C}_{\text{CH}_4\text{A}}] + [P_{\text{CH}_4} \times \delta^{13}\text{C}_{\text{CH}_4\text{B}}] \} / T_{\text{CH}_4} \quad (4)$$

where  $\delta^2\text{H}_{\text{CH}_4\text{A}}$  and  $\delta^{13}\text{C}_{\text{CH}_4\text{A}}$  are the isotopic compositions of the abiogenic CH<sub>4</sub> component (Fig. 3) and  $\delta^2\text{H}_{\text{CH}_4\text{B}}$  and  $\delta^{13}\text{C}_{\text{CH}_4\text{B}}$  are the isotopic compositions of the microbial CH<sub>4</sub> (Fig. 3). Equations 1, 3, and 4 were solved simultaneously for the  $P_{\text{CH}_4}$  for each sample, the abiogenic CH<sub>4</sub> flux  $J_{\text{CH}_4}$ , and the isotopic composition of the microbial and abiogenic CH<sub>4</sub>. The data were best fit ( $\chi^2 = 0.2$ ) by an abiogenic CH<sub>4</sub> isotopic composition of  $\delta^2\text{H}_{\text{CH}_4\text{A}} = -360\%$  and  $\delta^{13}\text{C}_{\text{CH}_4\text{A}} = -30\%$ ; a microbial CH<sub>4</sub> isotopic composition of  $\delta^2\text{H}_{\text{CH}_4\text{B}} = -220\%$  and  $\delta^{13}\text{C}_{\text{CH}_4\text{B}} = -65\%$ ; and an abiogenic CH<sub>4</sub> flux of  $8.9 \times 10^{-8} \text{ mol dm}^{-2} \text{ year}^{-1}$  ( $1.8 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ ). For these model parameters the *in situ* microbial CH<sub>4</sub> production rates ranged from  $< 10^{-10}$  to  $10^{-7} \text{ mol dm}^{-3} \text{ year}^{-1}$  ( $< 2 \times 10^3$  to  $2 \times 10^6 \text{ cm}^{-3} \text{ s}^{-1}$ ). The lowest rates represent maximum estimates for the deepest CH<sub>4</sub> gas samples, which were isotopi-

cally indistinguishable from abiogenic CH<sub>4</sub>. Despite the fact that the fracture water samples come from three different mining regions that are separated by a distance of hundreds of kilometers and encompass a wide range of aqueous geochemical compositions, the methanogenic rates from different regions overlapped when plotted versus depth and displayed an exponential decline with depth (Fig. 4).

The slow rates of methanogenesis from CO<sub>2</sub> reduction and H<sub>2</sub> consumption imply a long-term H<sub>2</sub> source. When H<sub>2</sub> concentrations were compared with that of He for fracture water samples from the Witwatersrand Basin (Fig. 5), the H<sub>2</sub> concentration exhibited no obvious correlation with the fracture water age. When H<sub>2</sub> concentrations were corrected, however, for the loss to CH<sub>4</sub> by methanogenesis (open circles in Fig. 5) and for loss to C<sub>1</sub>–C<sub>4</sub> hydrocarbons by abiogenic processes (solid circles in Fig. 5), they exhibited a distinct positive correlation with He concentrations, *i.e.*, the H<sub>2</sub> concentrations increased as the fracture water age increased. Lin *et al.* (2005b) have shown that these corrected H<sub>2</sub> concentrations are consistent with a radiolytic source mechanism for the H<sub>2</sub>. The He effectively acts as a dosimeter for the  $\alpha$  dose if one assumes that 0% of the He generated by the decay of U- and Th-bearing minerals remains in the minerals ( $\gamma_{\text{He}} = 1$ ). The predicted trend is not significantly altered whether one uses the radiolytic yield for pure oxygenated water (Spinks and Woods, 1990) or that of saline anaerobic water (marked as Lin *et al.*, 2005a in Fig. 5). Nor do drastic variations in the (U + Th)/K ratio of the rock from  $7 \times 10^{-9}$  to  $3 \times 10^{-7}$  (Lippmann *et al.*, 2003) significantly affect the predicted H<sub>2</sub> versus He trend even though they do affect the production rates. Variations in the porosity between 0.01% and 5% change the relative production rates of H<sub>2</sub> and He by less than 10%. The relationship between H<sub>2</sub> and He is affected, however, by how much He is retained by the U-bearing minerals. If 100% of the  $\alpha$  particles released within the mineral phases are retained and not lost by diffusion to the pore water then the H<sub>2</sub>/He ratio increases by  $\sim 100$  (100% in Fig. 5).

#### *He-, H<sub>2</sub>-, and CH<sub>4</sub>-coupled flux model for South Africa*

To determine whether the radiolytic production of H<sub>2</sub> was sufficient to support the observed

*in situ* microbial CH<sub>4</sub> production rates, the subsurface fluxes of He, H<sub>2</sub>, and CH<sub>4</sub> were modeled for a 5-km-thick crust with diffusive flux coupled to *in situ* generation and consumption (MatLab version 7.1, The MathWorks, Inc., Natick, MA). The diffusion parameter for He in water was derived from Lippmann *et al.* (2003), and the diffusion parameters for H<sub>2</sub> and CH<sub>4</sub> in water were obtained from Cussler (1985) (Table 1). The matrix diffusivities were corrected for a porosity that varied with depth exponentially from a maximum of 2% and an  $e^{-1}$  decay parameter of 1.5 km. The diffusivities in water were also corrected for temperature and water viscosity using the geothermal gradient of 10°C km<sup>-1</sup> (Omar *et al.*, 2003). The kilometer scale diffusivity was treated as a 50:50 mixture of diffusion through water and matrix diffusion by the following approximation:

$$D_{\text{bulk}} = 0.5 \theta D_w + 0.5 D_w$$

This expression emulates fast diffusion through interconnected fracture networks with a fracture spacing of ~100 m and follows the He gas transport models of the Stripa granite (Andrews *et al.*, 1989). The surface concentrations of He, H<sub>2</sub>, and CH<sub>4</sub> were assumed to be zero.

Three models for He *in situ* generation and basal flux were tested. The first model is from Lippmann *et al.* (2003), has no basal flux of He, and relies strictly upon an He *in situ* generation rate of  $3.2 \times 10^{-13}$  mol dm<sup>-3</sup> year<sup>-1</sup> (Table 1), which corresponds to an average U concentration of 20 ppm and yields fracture water ages of tens to hundreds of millions of years. The second model is also from Lippmann *et al.* (2003) and uses a basal He flux of  $1.6 \times 10^{-8}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $3.1 \times 10^6$  cm<sup>-2</sup> s<sup>-1</sup>) and an He *in situ* generation rate of  $4.2 \times 10^{-12}$  mol dm<sup>-3</sup> year<sup>-1</sup> (Table 1), which corresponds to an average U concentration of 300 ppm and yields fracture water

ages of 1 to tens of millions of years (marked as Lippmann *et al.*, 2003 in Fig. 5). The third model utilizes an He *in situ* generation rate of  $7.6 \times 10^{-14}$  mol dm<sup>-3</sup> year<sup>-1</sup> (Table 1), which corresponds to an average continental crust U concentration of 3 ppm and a basal He flux of  $8.9 \times 10^{-8}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $1.5 \times 10^5$  cm<sup>-2</sup> s<sup>-1</sup>), and yields fracture water ages very similar to the second model (marked as Avg. Crust in Fig. 5). A Th concentration of the average continental crust (10.4 ppm) was used for all three models. In all three models the release of He from the mineral matrix was increased from 0.6% to 100% to simulate diffusive loss from the minerals to the pore water as the temperature increased with depth from 20°C to 70°C.

The CH<sub>4</sub> mixing model was evaluated for all three models. Because the second and third model yielded similar <sup>He</sup>*t*, their basal CH<sub>4</sub> flux was set equal to the  $8.9 \times 10^{-8}$  mol dm<sup>-2</sup> year<sup>-1</sup> abiogenic CH<sub>4</sub> flux derived in the calculations above, which were based upon the He parameters of the second model (Table 1). The first model, which possessed much greater <sup>He</sup>*t* values, yielded a lower abiogenic flux of  $2.2 \times 10^{-9}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $4.4 \times 10^3$  cm<sup>-2</sup> s<sup>-1</sup>).

A least squares fit of the data in Fig. 4 yielded the following expression for the *in situ* microbial CH<sub>4</sub> generation rate:

$$P_{\text{CH}_4} \text{ (mol dm}^{-3} \text{ year}^{-1}\text{)} = 1.2 \times 10^{-10} e^{(-0.0005z)} \quad (5)$$

For the third model the expression was  $3.0 \times 10^{-10} e^{(-0.0010z)}$ . For the first model with the much greater <sup>He</sup>*t* values, the *in situ* microbial CH<sub>4</sub> generation rate was much less,  $5.4 \times 10^{-12} e^{(-0.0004z)}$  (Table 1).

The basal H<sub>2</sub> flux was assumed to be zero. The *in situ* radiolytic H<sub>2</sub> generation rate was based on the model of Lin *et al.* (2005a), the radiolytic H<sub>2</sub>

TABLE 1. MODEL PARAMETERS FOR THE SOUTH AFRICAN CRUST

Species	$D_w$ m <sup>2</sup> year <sup>-1</sup>	Model	In situ production rate (mol dm <sup>-3</sup> year <sup>-1</sup> )	Basal flux (mol dm <sup>-2</sup> year <sup>-1</sup> )
He	$25.8 e^{[-11,700/(7.948 \times T)]}$	1	$3.2 \times 10^{-13}$	0
		2	$4.2 \times 10^{-12}$	$1.6 \times 10^{-8}$
		3	$7.6 \times 10^{-14}$	$8.9 \times 10^{-8}$
H <sub>2</sub>	$4.35 \times 10^{-13} T / (6\pi\mu 5.45 \times 10^{-9})^a$	1	$3.2 \times 10^{-11}$	0
		2	$4.2 \times 10^{-10}$	0
		3	$8.6 \times 10^{-12}$	0
CH <sub>4</sub>	$4.35 \times 10^{-13} T / (6\pi\mu 1.65 \times 10^{-8})$	1	$5.4 \times 10^{-12} e^{(-0.0004z)}$	$2.2 \times 10^{-9}$
		2	$1.2 \times 10^{-10} e^{(-0.0005z)}$	$8.9 \times 10^{-8}$
		3	$3.0 \times 10^{-10} e^{(-0.0010z)}$	$8.9 \times 10^{-8}$

<sup>a</sup> $\mu$  = viscosity of water at temperature *T*.

yield of Lin *et al.* (2005a), the U and Th concentrations for the three models stated above, the K concentration for the average continental crust of 3.4%, and the porosity stated above. The *in situ* radiolytic H<sub>2</sub> generation rates ranged from  $8.6 \times 10^{-12}$  mol dm<sup>-3</sup> year<sup>-1</sup> for the first model (lowest U content) to  $4.2 \times 10^{-10}$  mol dm<sup>-3</sup> year<sup>-1</sup> for the second model (highest U content) (Table 1). The model also assumed that the *in situ* H<sub>2</sub> consumption rate was four times that of the *in situ* microbial CH<sub>4</sub> production rate given the reaction stoichiometry.

The second and third models yielded a (H<sub>2</sub> + CH<sub>4</sub>)/He concentration ratio of ~50, whereas the first model yielded a (H<sub>2</sub> + CH<sub>4</sub>)/He concentration ratio of ~75. Both values are consistent with the observed trend in (H<sub>2</sub> + CH<sub>4</sub>)/He (Fig. 5). Not surprisingly, the model results indicated that the *in situ* He generation rate in the top 5 km accounted for 99% of the surface flux of He, which varied from  $1 \times 10^{-8}$  to  $5 \times 10^{-7}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $2 \times 10^6$ – $1 \times 10^8$  cm<sup>-2</sup> s<sup>-1</sup>) for models 3 and 2, respectively. The *in situ* microbial CH<sub>4</sub> production rates increased the surface CH<sub>4</sub> flux to  $\sim 10^{-7}$  to  $10^{-5}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $2 \times 10^7$ – $2 \times 10^9$  cm<sup>-2</sup> s<sup>-1</sup>) for models 1 and 3, respectively. The model also demonstrated that the *in situ* H<sub>2</sub> generation rate more than sufficed to support the estimated microbial CH<sub>4</sub> production rates and still yielded a surface flux of  $\sim 10^{-6}$ – $5 \times 10^{-5}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $2 \times 10^8$ – $1 \times 10^{10}$  cm<sup>-2</sup> s<sup>-1</sup>) for models 3 and 2, respectively. Obviously such a surface flux is not observed as other electron-accepting microbial reactions quickly consume the H<sub>2</sub>. It is also possible that the abiogenic CH<sub>4</sub> is not rising from a deeper, hotter source as assumed in our model, but is forming within the upper 5 km of South African crust. Finally, the modeled CH<sub>4</sub> surface flux has to be considered a minimum estimate because our original model did not attempt to quantify any CH<sub>4</sub> oxidation rates even though the 16S rDNA sequences for both aerobic and anaerobic methane oxidizers have been detected in the shallowest groundwater boreholes.

### RELEVANCE TO THE ORIGIN OF MARTIAN CH<sub>4</sub>

As a conservative tracer, He provides a means of relating our South African crustal model to the conditions on Mars. The He abundance in the lower martian atmosphere was originally estimated to be ~1 ppm with an average lifetime of  $5 \times 10^4$  years due to loss to space at a rate of  $1.8 \times 10^5$  cm<sup>-2</sup> s<sup>-1</sup> ( $1.4 \times 10^7$  mol year<sup>-1</sup>) (Krasnopolsky *et al.*, 1994). This loss rate was presumed to be balanced by a subsurface flux of comparable value. Krasnopolsky and Gladstone (1996) revised the He abundance upward to  $\sim 4 \pm 2$  ppm, but kept the same subsurface flux and calculated an average lifetime of  $13 \times 10^4$  years (Krasnopolsky and Gladstone, 2005) while invoking an additional solar  $\alpha$  flux to explain the greater He abundance in the martian atmosphere. Recent papers that seek to constrain the origin of the martian CH<sub>4</sub> have ignored He subsurface flux from the martian crust (Krasnopolsky, 2005; Krasnopolsky and Gladstone, 2005), citing the lack of recent volcanism as justification for this assumption. Significant crustal He flux in the absence of volcanism has been documented for many places on Earth, including the South African Precambrian shield (Lippmann *et al.*, 2003). For the remainder of this paper we will assume that the modeled martian He subsurface flux of  $1$ – $3 \times 10^5$  cm<sup>-2</sup> s<sup>-1</sup> ( $1$ – $3 \times 10^7$  mol year<sup>-1</sup>) (Krasnopolsky and Gladstone, 1996) is still applicable.

In the Witwatersrand Basin, the ratio of the surface abiogenic CH<sub>4</sub> flux to He surface flux varied from ~10 to 1 in the three models. If we apply the same ratios to the martian subsurface He flux, the corresponding martian subsurface abiogenic CH<sub>4</sub> flux would be  $\sim 2 \times 10^5$ – $2 \times 10^6$  cm<sup>-2</sup> s<sup>-1</sup> ( $0.2$ – $1.5 \times 10^8$  mol year<sup>-1</sup>). Although this flux can sustain the photochemical loss rate of CH<sub>4</sub> from the martian atmosphere, it is less than the  $\sim 2 \times 10^9$  cm<sup>-2</sup> s<sup>-1</sup> of subsurface CH<sub>4</sub> flux required by the nonuniform CH<sub>4</sub> concentrations. If one considers the combined abiogenic and microbial South African CH<sub>4</sub> flux, the CH<sub>4</sub>/He flux ratio is 10–20, and the corresponding martian CH<sub>4</sub> flux would be  $2$ – $4 \times 10^6$  cm<sup>-2</sup> s<sup>-1</sup> ( $1.5$ – $3.0 \times 10^8$  mol year<sup>-1</sup>).

For abiogenic CH<sub>4</sub> generated by serpentinization of modern or ancient ocean crust, the ratio of CH<sub>4</sub> and H<sub>2</sub> to He ranges from ~200 to 200,000 (Fig. 6) (Abrajano *et al.*, 1988; Seyfried and Mottl, 1995). By applying this ratio to the martian subsurface He flux, the corresponding martian subsurface abiogenic CH<sub>4</sub> flux would be  $\sim 2.5 \times 10^7$ – $5.0 \times 10^{10}$  cm<sup>-2</sup> s<sup>-1</sup> ( $1.9 \times 10^9$ – $3.8 \times 10^{12}$  mol year<sup>-1</sup>). Oxidation of Fe-bearing olivine or pyroxene in basalt by water can potentially generate significant H<sub>2</sub> that could sustain abiogenic and microbial CH<sub>4</sub> production (Stevens and McKinley, 1995; Wallendahl and Treiman, 1999). The rates for these reactions increase with temperature in the presence of liquid H<sub>2</sub>O (Oze and

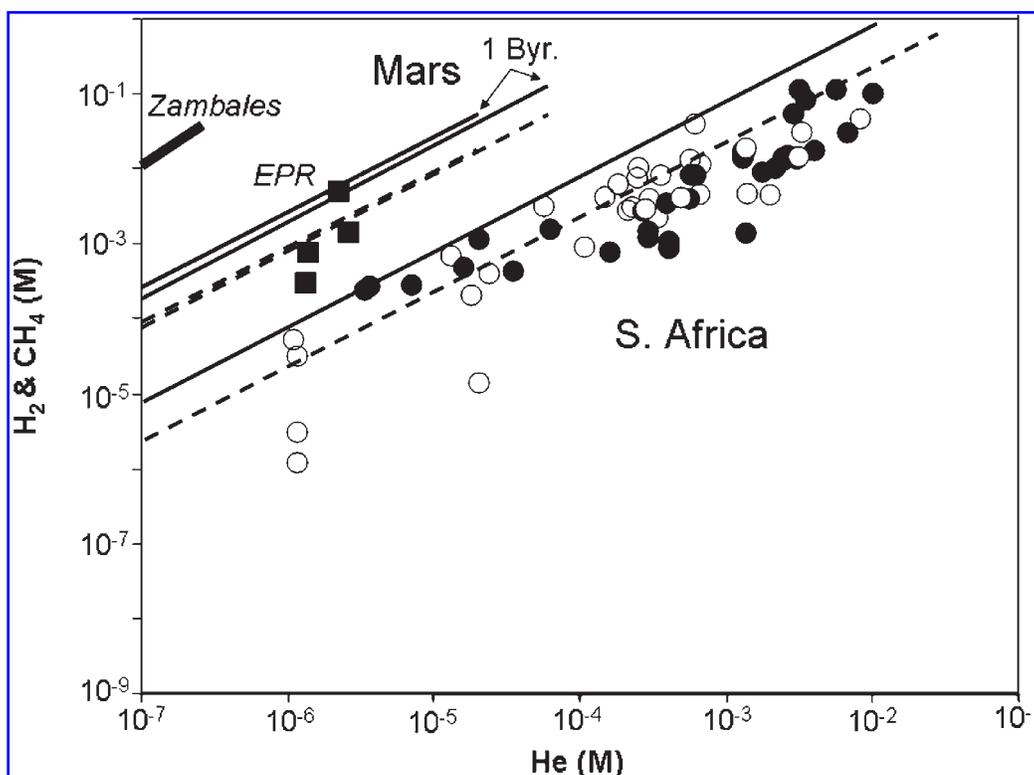


FIG. 6.  $H_2$  and  $CH_4$  versus He for fracture water samples from the Witwatersrand Basin, South Africa.  $H_2$  concentrations that have been corrected for loss to  $CH_4$  by methanogenesis (open circles) and for loss to  $C_1$ – $C_4$  hydrocarbons by abiotic processes (solid circles) are also plotted for comparison (see text for details). Solid squares represent the  $H_2 + 2 \times CH_4$  versus He concentrations of deep sea vent samples from the East Pacific Rise (EPR) and Endeavor (Seyfried and Mottl, 1995). Thick solid line labeled Zambales represents the  $H_2 + 2 \times CH_4$  versus He ratio for the Zambales ophiolite (Abrajano *et al.*, 1988). Solid lines represent the  $H_2$  versus He trends predicted by the radiolytic model. The dashed lines represent the  $H_2/4 = CH_4$  concentrations. Byr, billion years.

Sharma, 2005) deeper in the martian crust. With increasing depth, however,  $H_2O$  becomes less abundant because of diminishing porosity, and as found to be the case in South Africa,  $CO_2$  is stripped from solution as calcite because of increasing pH and  $Ca^{2+}$  with depth (Onstott *et al.*, 2005). If the rates implied above were extrapolated over  $4.5 \times 10^9$  years, the amount of  $H_2$  required would correspond to the serpentinization of a 50-m–113-km-thick global basalt layer composed of 10% FeO and producing magnetite.

#### In situ rates of He, $H_2$ , and microbial $CH_4$ production

A direct extrapolation of rates may not be appropriate given the uncertainties in the origin of He in the martian atmosphere and given that our hypothesized source of  $H_2$  is radiolysis of  $H_2O$  and the martian crust is much more mafic than that of southern Africa. Production of  $H_2$  by ra-

diolysis, however, can occur within the cryosphere where  $H_2O$  ice and  $CO_2$  are more abundant. To determine whether a radiolytic mechanism could generate sufficient  $H_2$  to produce the  $CH_4$  detected in the martian atmosphere, we applied the same numerical scheme for the He,  $H_2$ , and  $CH_4$  generation and diffusive transport to a 6.6-km-thick, martian crustal profile utilizing the model of Clifford (1993) and Clifford and Parker (2001). This model assumes that porosity varies as a function of depth according to the following expression:

$$\Phi(z) = \Phi(0) \exp(-z/2.82) \quad (6)$$

where the depth  $z$  is in km and  $\Phi(0) = 0.35$  (Clifford and Parker, 2001). Since the martian  $CH_4$  concentration is greatest in the equatorial regions of Mars (Mumma *et al.*, 2004), the thermal model of Clifford and Parker (2001) for the equator was used. For this model the porosity is filled with ice

from 0 to 2 km deep and with NaCl brine for the remaining 4.6 km (Clifford and Parker, 2001).

The U, Th, and K concentrations of the martian crust were assumed to be 0.1 ppm, 0.4 ppm, and 0.25 wt%, respectively based upon the compositions of SNC meteorites (Chen and Wasserburg, 1985) and Alpha Particle X-ray Spectrometer analyses of rock units exposed on Meridiani Planum (Rieder *et al.*, 2004). Based on these parameters, assuming an H<sub>2</sub>O-saturated porosity and the Lin *et al.* (2005a) model, the *in situ* H<sub>2</sub> generation rate increased with depth from  $5.6 \times 10^{-12}$  to  $2.8 \times 10^{-11}$  mol dm<sup>-3</sup> year<sup>-1</sup>. The *in situ* He generation rate increased with depth from  $1.5$  to  $4 \times 10^{-15}$  mol m<sup>-3</sup> year<sup>-1</sup> as porosity diminished and temperature increased. With a mean annual surface temperature of 218K and a 17K km<sup>-1</sup> thermal gradient, no significant He loss from minerals occurred until ~4.5 km. Thus the *in situ* He generation rate within the upper 6.6 km of martian crust is much less than that of the South African crust (Table 2), whereas the *in situ* H<sub>2</sub> generation rate is comparable to the South African crust despite the lower U and Th content because of the higher porosity of the martian crust. The H<sub>2</sub>/He production ratios for the martian radiolytic model vary from 19,000 to 1,400 with increasing depth compared with ~100 for the Witwatersrand Basin (Tables 1 and 2 and Fig. 6).

For the *in situ* microbial CH<sub>4</sub> production rate, the same exponential decline with depth was used, but the pre-exponential term was initially assumed to be 10<sup>5</sup> times less than that for South Africa based upon the correlation between metabolic rate and temperature reported by Price and Sowers (2004). This assumes that the methanogenic biodensity is the same for the subsurface of South Africa and Mars despite the differences in porosity and the presence of ice. The *in situ* microbial CH<sub>4</sub> rate was then arbitrarily in-

creased until the H<sub>2</sub> flux resulting from *in situ* radiolytic production could just sustain it at steady state.

#### Surface flux for He, H<sub>2</sub>, and microbial CH<sub>4</sub>

The He and H<sub>2</sub> molecular diffusivities through the upper 2 km of ice were derived from Ikeda-Fukazawa *et al.* (2002) and Strauss *et al.* (1994), respectively (Table 2). The molecular diffusivity of CH<sub>4</sub> in ice is not well established but considered comparable to that of He (Ikeda-Fukazawa *et al.*, 2002), so a value four times less than that of He was adopted given the larger molecular size (Table 2). The formulas used to calculate the molecular diffusivities of He, H<sub>2</sub>, and CH<sub>4</sub> through the lower 4.6 km of pore water were the same as those used in the South African model (Table 1). As in the South African case, the crustal-scale diffusivity was considered a 50:50 mixture of fracture and matrix diffusion pathways.

The basal flux of He at 6.6 km was adjusted until the surface flux matched the modeled values of  $\sim 10^5$  cm<sup>-2</sup> s<sup>-1</sup> (Krasnopolsky *et al.*, 1994) at steady state. The corresponding basal abiogenic CH<sub>4</sub> flux was set to 10 times more than the basal He flux based upon the South African gas compositions. The basal H<sub>2</sub> flux was assumed to be zero.

Surface concentrations for He, H<sub>2</sub>, and CH<sub>4</sub> were approximated from the reported concentrations in the martian atmosphere and Henry's law coefficients for He, H<sub>2</sub>, and CH<sub>4</sub> derived from Smith and Kennedy (1983), Gordon *et al.* (1977), and Cygan (1991) for brines at 220K, respectively.

A basal He flux of  $1.9 \times 10^{-11}$  mol dm<sup>-2</sup> year<sup>-1</sup> ( $3.6 \times 10^3$  cm<sup>-2</sup> s<sup>-1</sup>) is required to produce a surface He flux of  $10^5$  cm<sup>-2</sup> s<sup>-1</sup> for this diffusivity structure and the *in situ* He generation rates. This indicates that crustal degassing by diffusion alone produces a He flux that is comparable with

TABLE 2. MODEL PARAMETERS FOR THE MARTIAN CRUST

Species	Ice diffusivity (m <sup>2</sup> year <sup>-1</sup> )	Supracryosphere diffusivity (m <sup>2</sup> year <sup>-1</sup> )	In situ production rate (mol dm <sup>-3</sup> year <sup>-1</sup> )	Basal flux (mol dm <sup>-2</sup> year <sup>-1</sup> )	Atmospheric partial pressure (atm)	Henry's constant (mol mol of H <sub>2</sub> O <sup>-1</sup> atm <sup>-1</sup> )	Atmospheric equilibrium concentration (mol dm <sup>-3</sup> )
He	$10.7 e^{(-11,300/RT)}$	$1 \times 10^{11}$	$1.5-4 \times 10^{-15}$	$1.9 \times 10^{-11}$	$6.6 \times 10^{-8}$	$2.7 \times 10^{-6}$	$7.9 \times 10^{-9}$
H <sub>2</sub>	$1.4 e^{(-750/RT)}$	$1 \times 10^{11}$	$5.6-28 \times 10^{-12}$	0	$2.0 \times 10^{-6}$	$5.2 \times 10^{-6}$	$5.7 \times 10^{-7}$
CH <sub>4</sub>	$2.5 e^{(-11,300/RT)}$	$1 \times 10^{11}$	$1.4 \times 10^{-10} e^{(-0.00136z)a}$	$1.9 \times 10^{-10}$	$1.7 \times 10^{-9}$	$6.5 \times 10^{-5}$	$5.4 \times 10^{-9}$

<sup>a</sup>*In situ* rate maximum sustainable by *in situ* H<sub>2</sub> production rate.

that estimated from earlier models (Krasnopolsky *et al.*, 1994; Krasnopolsky and Gladstone, 1996) and that volcanism is not a prerequisite for subsurface He flux. The subsurface abiogenic CH<sub>4</sub> flux corresponding to this basal He flux would be  $\sim 1.9 \times 10^{-10} \text{ mol dm}^{-2} \text{ year}^{-1}$  ( $3.6 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$ ). The maximum microbial CH<sub>4</sub> surface flux was  $\sim 1 \times 10^{-5} \text{ mol dm}^{-2} \text{ year}^{-1}$  ( $2 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ ). The surface H<sub>2</sub> flux in the absence of microbial CH<sub>4</sub> consumption was  $\sim 4 \times 10^{-6} \text{ mol dm}^{-2} \text{ year}^{-1}$  ( $8 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ ). We note that this surface H<sub>2</sub> flux is  $\sim 10\%$  of the  $8.8 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$  atmospheric production rate (Summers *et al.*, 2002) and, therefore, is not likely to significantly affect the  $\delta^2\text{H}$  content of martian atmospheric H<sub>2</sub> even if it was not consumed at all. The model predicts a (H<sub>2</sub> + CH<sub>4</sub>)/He surface flux ratio of  $\sim 2,500$ . This maximum *in situ* CH<sub>4</sub> production rate would only lead to a  $\sim 1\%$  conversion of pore water into pore hydrate after a billion years. The model indicates that radiolytically produced H<sub>2</sub> suffices to support the observed CH<sub>4</sub> surface flux in the absence of any other H<sub>2</sub> sources. Most likely subsurface H<sub>2</sub> generated by other processes and atmospheric H<sub>2</sub> all contribute to the potential microbial CH<sub>4</sub> production rate.

The CH<sub>4</sub> flux depends upon the crustal model in the following ways. If a significant vadose zone exists between the base of the cryosphere (Clifford and Parker, 2001) and the water table, then the H<sub>2</sub> and CH<sub>4</sub> production rates will be significantly less because the H<sub>2</sub> radiolytic production rate in water vapor and the rate of microbial methanogenesis in unsaturated pore space will both be significantly reduced. The decrease in the total CH<sub>4</sub> production rate will be partly compensated by the higher diffusive transport rate across the vadose zone. At higher latitudes, where the surface temperatures are much lower and the base of the cryosphere extends to much greater depths, the H<sub>2</sub> production rates will remain the same, whereas CH<sub>4</sub> production rates will be substantially less than those at the equator.

This simple diffusive transport model for CH<sub>4</sub>, H<sub>2</sub>, and He to the martian surface has two caveats. First, because the CH<sub>4</sub> will combine with water ice to form hydrate under appropriate conditions of temperature and pressure, which on Mars is found at depths ranging from  $\sim 15$  m below the surface to as much as a kilometer beneath the base of the cryosphere (Max and Clifford, 2000), it is unlikely to be able to diffuse through the cryosphere unless the potential storage ca-

capacity of the hydrate stability zone has been exceeded. This is not unreasonable because, regardless of whether the CH<sub>4</sub> is generated by biotic or abiotic processes, these processes have likely been active throughout Mars' geologic history. As the interior of the planet cooled, the freezing front at the base of the cryosphere propagated deeper into the crust at a rate of  $\sim 0.5 \text{ m Myr}^{-1}$  at the equator (Clifford and Parker, 2001). The models above predict that the sustainable rates of microbial CH<sub>4</sub> production would generate a subsurface flux of  $\sim 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ . If all of this CH<sub>4</sub> were trapped as hydrate at the base of the cryosphere, then the hydrate propagation rate would be  $\sim 0.07 \text{ m Myr}^{-1}$ . This suggests that the rate of cryosphere thickening has been more than sufficient to keep the hydrate stability zone from saturating. However, these simple models do not preclude the possibility that spatial or temporal spikes in the microbial methanogenesis rate could locally saturate the cryosphere with clathrates.

These arguments and model results suggest a means of distinguishing the four possible origins for the CH<sub>4</sub> that has been detected in the martian atmosphere: (1) volcanogenic; (2) sublimation of hydrate-rich ice; (3) diffusive transport through hydrate-saturated cryosphere; and (4) microbial CH<sub>4</sub> generation above the cryosphere. A volcanogenic source would generate  $\sim 20$  times greater He surface flux as a result of the greater crustal degassing. The C<sub>1</sub>–C<sub>4</sub> thermogenic compounds yield C and H isotopic profiles that distinguish them from abiogenic C<sub>1</sub>–C<sub>4</sub> compounds (Sherwood Lollar *et al.*, 2002). To the extent that water on the martian surface is enriched in <sup>2</sup>H, which is 5.2 times that of the Earth's, relative to the deep martian subsurface cryosphere or sub-cryosphere brine, the  $\delta^2\text{H}$  of deeply sourced CH<sub>4</sub> might reflect the H isotopic composition of deeply seated, unenriched H<sub>2</sub>O. Given the extent to which the H isotopic signature of hydrous phases of SNC meteorites records interaction with the enriched, near-surface H<sub>2</sub>O inventory (Watson *et al.*, 1994), it remains uncertain as to whether the CH<sub>4</sub> of modern volcanism would do the same.

The second, and currently most plausible, origin is that the crustal emissions result from the sublimation of near-surface, hydrate-rich ice at low latitudes, where ground ice and hydrate are both thermodynamically unstable when they are in diffusive contact with the atmosphere. Theoretical calculations suggest that the resulting sub-

limation front, at latitudes between  $\pm 30^\circ$ , may have propagated down to depths ranging from just a few tens of centimeters to as much as a kilometer below the surface, depending on the local thermal and diffusive properties of the crust and the extent of replenishment from deeper H<sub>2</sub>O reservoirs (Fanale *et al.*, 1986; Clifford, 1993; Mellon and Jakosky, 1993). For a sublimation rate of  $\sim 3\text{--}6 \times 10^{-2} \text{ m Myr}^{-1}$  (Fanale *et al.*, 1986) at the equator and a cryosphere that is  $\sim 14\%$  hydrate (from calculations above), the corresponding CH<sub>4</sub> surface flux would be  $\sim 2\text{--}4 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ . In this case, no correlation between CH<sub>4</sub> and He or H<sub>2</sub> surface flux would be observed, but a positive correlation between CH<sub>4</sub> and H<sub>2</sub>O surface flux would be expected. Also, the  $\delta^2\text{H}$  of the CH<sub>4</sub> should reflect the <sup>2</sup>H-enriched H<sub>2</sub>O of the martian surface.

If the cryosphere near the equator is effectively saturated with hydrate, then CH<sub>4</sub> may be originating from below the cryosphere and diffusing to the surface as modeled in this study. In this case the CH<sub>4</sub> and He surface flux would be correlated, but with higher (H<sub>2</sub> + CH<sub>4</sub>)/He surface flux ratios than in the case of volcanogenic origin. The C and H isotopic profiles of the C<sub>1</sub>–C<sub>4</sub> compounds, the C<sub>1</sub>–C<sub>4</sub> relative abundances, and the CH<sub>4</sub>/H<sub>2</sub> would all potentially distinguish microbial from abiogenic CH<sub>4</sub>. The  $\delta^2\text{H}$  of the CH<sub>4</sub> could reflect a mixture of CH<sub>4</sub> from the near-surface, <sup>2</sup>H-enriched H<sub>2</sub>O environment and deep-seated CH<sub>4</sub> from the unenriched H<sub>2</sub>O environment.

The final potential origin is that the atmospheric CH<sub>4</sub> is produced in the shallow subsurface (Krasnopolsky *et al.*, 2004b), either above the hydrate stability zone (*i.e.*,  $< 15 \text{ m}$  depth) or above the local depth of the sublimation front, which, again, may lie as much as a kilometer beneath the surface at the equator. In this case, microbial CH<sub>4</sub> generation in a CaCl<sub>2</sub>, or DEVIL, brine (Burt and Knauth, 2003) in a subsurface environment lying above the ice-saturated cryosphere might be sustained by a combination of radiolytic H<sub>2</sub> and atmospheric H<sub>2</sub>. Brines may occur at such shallow depth if they are composed of salts like CaCl<sub>2</sub> and LiCl, which are capable of depressing the freezing point to 218K and below (Brass, 1980; Clark and Van Hart, 1981; Burt and Knauth, 2003). Any significant flux of CO<sub>3</sub><sup>2-</sup> into this environment, however, would quickly strip calcium from the water and lead to freezing. This environment can only exist, therefore, if the pH is subneutral to

acidic or communication with the atmospheric CO<sub>2</sub> is limited. Given that low temperature, water–rock interactions lead to high pH because of hydrolysis of the silicates (Wallendahl and Treiman, 1999) the DEVIL brine environment would seem to require restricted access to the martian atmosphere. If the pore gas diffusivity for such an environment were  $10^{11} \text{ m}^2 \text{ year}^{-1}$  ( $0.32 \text{ cm}^2 \text{ s}^{-1}$ ), a value consistent with submicron pore throat sizes (Fanale *et al.*, 1986), and the environment were 100 m deep, then an *in situ* microbial CH<sub>4</sub> production rate of  $\sim 6 \times 10^{-6} \text{ mol dm}^{-3} \text{ year}^{-1}$  would be required to generate the CH<sub>4</sub> surface flux of  $1.8 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$  (Krasnopolsky *et al.*, 1994). This *in situ* rate could not be sustained by the combined radiolytic and atmospheric H<sub>2</sub> fluxes and would require a 100 times greater H<sub>2</sub> flux. Terrestrial autotrophic methanogens, which utilize H<sub>2</sub> as their electron donor, however, are not known to exist in highly saline environments probably because of the energy demands of maintaining a proper osmotic gradient (Oren, 1999). In South Africa, methanogens are noticeably absent from the deep residing brines, which may in part explain the decline in the *in situ* microbial CH<sub>4</sub> rate more than any other factor. If martian methanogens are operating within DEVIL brine-saturated pores in the upper levels of the martian crust, then they may be metabolizing methylated C<sub>1</sub> compounds or dimethyl sulfide like their terrestrial counterparts (Oremland and King, 1989) or have evolved a more energy-efficient means of maintaining osmotic stability. In this scenario, CH<sub>4</sub> emissions may be correlated with local depletions in atmospheric H<sub>2</sub> or CO and, depending upon the depth of the environment, with martian season. They may also be correlated with suspected locations of brine seeps. The  $\delta^2\text{H}$  of the CH<sub>4</sub> could reflect the depth of origin if the near-surface H<sub>2</sub>O is significantly <sup>2</sup>H enriched with respect to the deep-seated H<sub>2</sub>O.

## CH<sub>4</sub> DETECTION AND ANALYSIS ON MARS

The models in the preceding section suggest that measurements of the CH<sub>4</sub>, He, and H<sub>2</sub> concentrations can yield valuable insights as to the origin of the CH<sub>4</sub> and whether it is a biomarker. Equally important is the determination of its C and H isotopic composition. To distinguish abio-

genic from microbial CH<sub>4</sub>, measurement of the H and C isotopic composition of CH<sub>4</sub> and the abundance of higher hydrocarbons such as C<sub>2</sub>H<sub>6</sub> offer the best approach. Although astronomical determinations of the isotopic composition of CH<sub>4</sub> may be feasible, they lack the precision necessary to partition the sources of CH<sub>4</sub> and will have to be corrected for significant isotopic fractionation produced by photochemical reactions that occur at altitudes greater than 120 km (Nair *et al.*, 2005). The most reliable and useful approach from an exploration perspective is to measure the CH<sub>4</sub> isotopic composition from orbit with an airborne vehicle like a Mars plane, or from a rover.

In terms of analytical approaches, cavity ring-down spectroscopy (CRDS) is a high-sensitivity infrared tunable laser spectrometer method for detection of the absorption spectra of trace gases (Busch and Busch, 1999). The gas sample to be studied is inserted into a stable optical cavity formed by two or more "super mirrors" with a reflectivity,  $R$ , that is greater than 99.99%. This optical cavity is excited either with a short pulse of light or with continuous wave light that is rapidly turned off from a narrow line width tunable laser. This leads to light being trapped inside the cavity, and this light intensity decays exponentially with time at a rate proportional to both the loss due to the mirrors and any absorption or scattering loss as the light propagates through the gas sample. The intra-cavity light intensity is monitored by the intensity of light being transmitted by one of the highly reflective mirrors. Without absorption, the average number of passes through the cell that a photon will make is  $1/(1 - R)$ , which can be between  $10^4$  and  $10^5$  with current state-of-the-art mirrors or a path length of  $\sim 3$ – $30$  km for a 30-cm-length cavity. Unlike traditional absorption methods, CRDS is completely independent of amplitude noise in the optical source since a change in the excitation power only affects the amplitude of the resulting exponential signal decay, but not its decay rate, which depends only on the gas sample's absorption coefficient after correction for the background loss rate.

The noise in the absorption coefficient that CRDS can measure is given by  $(1 - R)/L$  ( $L$  being the distance between the mirrors, which for this illustration was chosen to be 30 cm) multiplied by the smallest fractional change in the ring-down decay rate that can be determined. The first factor can be as low as  $5 \times 10^{-7} \text{ cm}^{-1}$ , and the

second can be  $7.7 \times 10^{-4}$  or an overall noise-equivalent sensitivity of  $\sim 4 \times 10^{-10}/\sqrt{n} \text{ cm}^{-1}$ , where  $n$  is the number of ring-down events (Dudek *et al.*, 2003). For 1,000 ring-down events, equivalent to 0.07 s, the noise-equivalent sensitivity is  $\sim 1 \times 10^{-11} \text{ cm}^{-1}$ . This sensitivity is robust, both in controlled conditions and after transport and deployment in less ideal industrial settings (Yan *et al.*, 2001).

The possible use of CRDS to detect CH<sub>4</sub> in the martian atmosphere requires consideration of a number of factors. The strongest infrared absorption line of CH<sub>4</sub> is at 3067.3 cm<sup>-1</sup> with an integrated line strength of  $2.13 \times 10^{-19} \text{ cm molecule}^{-1}$  at room temperature (Rothman *et al.*, 2005). This absorption line falls within the range of quantum cascade lasers (Yang *et al.*, 2005). If we assume the martian atmosphere to have a pressure of 4.6 Torr, a temperature of 213K, and a pressure broadening coefficient (half-width at half-maximum) of the CH<sub>4</sub> line by CO<sub>2</sub> of  $0.085 \text{ cm}^{-1} \text{ atm}^{-1}$  (Walker and Philips, 1983), then the predicted CH<sub>4</sub> absorption cross section at the peak of the line is  $1.3 \times 10^{-16} \text{ cm}^2$ . The absorption coefficient, which determines the loss rate of the optical cavity in CRDS, is the product of the number density times the absorption cross section. Based upon the absorption sensitivity calculated above, we can predict a noise-equivalent CH<sub>4</sub> number density of  $3.9 \times 10^5 \text{ cm}^{-3}$  ( $1\sigma$  in 0.07 s), which translates to a concentration of only 2 parts per trillion (pptv). This is only 2 parts in  $10^4$  of the martian CH<sub>4</sub> concentration reported by Krasnopolsky *et al.* (2004b). This demonstrates that a CRDS instrument, because of its sensitivity, can rapidly measure small changes in the CH<sub>4</sub> concentration with current technology. This compares favorably to an estimated detection limit of  $\sim 100$  pptv for a hypothetical multipass Herriott cell with 40-m path length that integrates over eight absorption lines for <sup>12</sup>CH<sub>4</sub> in the 3.3 μm spectral region for several minutes (Webster, 2005).

CRDS instruments have measured small changes in isotopic abundance of sample gases, such as CO<sub>2</sub>, with a reported precision of  $\delta^{13}\text{C}$  of 0.22‰ (Crosson *et al.*, 2002). A study of the isotopic composition of CH<sub>4</sub> in ambient air using a CRDS reported a precision for  $\delta^{13}\text{C}$  of 11‰ for 10 2-s integrations, a precision that was limited by the poor signal-to-noise ratio of their CRDS instrument (the noise-equivalent sensitivity was  $2 \times 10^{-9} \text{ cm}^{-1}$ ), which could have been improved by better acoustic isolation and more highly reflective mirrors (Dahnke *et al.*, 2001).

Both <sup>13</sup>CH<sub>4</sub> (3057.97 cm<sup>-1</sup>) and <sup>12</sup>C<sup>2</sup>HH<sub>3</sub> (3005.11 cm<sup>-1</sup>) have strong absorption lines in the same spectral region as <sup>12</sup>CH<sub>4</sub>, and these would be 1% and 0.06% as strong, assuming a CH<sub>4</sub> δ<sup>13</sup>C of -45‰ VPDB, with an abundance of 1.1237% for <sup>13</sup>C, and a CH<sub>4</sub> δ<sup>2</sup>H of 2,252‰ Vienna Standard Mean Ocean Water (VSMOW), with an abundance of 0.01558% for <sup>2</sup>H. This δ<sup>2</sup>H for CH<sub>4</sub> is equivalent to -350‰ relative to a martian hydrosphere that has 5.2 times the <sup>2</sup>H abundance of the Earth's. This isotopic composition corresponds to a <sup>13</sup>CH<sub>4</sub> concentration of 106 pptv and a <sup>12</sup>C<sup>2</sup>HH<sub>3</sub> concentration of 12.6 pptv for a CH<sub>4</sub> concentration of 10 ppbv. If we assume the CH<sub>4</sub> detection limit of 2 pptv limits the accuracy of the isotopic ratio, then we could determine the δ<sup>13</sup>C with a 1σ of 23‰ and the δ<sup>2</sup>H with a 1σ of 876‰. These limits will scale inversely with CH<sub>4</sub> concentration so that for a martian CH<sub>4</sub> as high as 100 ppbv (Formisano *et al.*, 2004), the predicted precision would be 2.3‰ for δ<sup>13</sup>C and 88‰ for δ<sup>2</sup>H. At these levels of precision it is possible to resolve isotopically some of the different CH<sub>4</sub> reservoirs found in terrestrial samples (Fig. 1). To attain an analytical precision approaching the ±0.5‰ and ±5‰ for δ<sup>13</sup>C and δ<sup>2</sup>H for compound-specific isotope ratio mass spectrometers (Ward *et al.*, 2004), the 10 ppbv CH<sub>4</sub> of the martian atmosphere would have to be *preconcentrated* by a factor of ~47 and ~175 times, respectively. These levels of *preconcentration* are much less than the factors of 300 and 4,000 required by the theoretical 40-m path length multipass instrument described by Webster (2005), which achieves much poorer precision levels of ±10‰ and ±50‰ for δ<sup>13</sup>C and δ<sup>2</sup>H, respectively. In fact, Webster (2005) concluded that determination of the δ<sup>2</sup>H for martian atmospheric CH<sub>4</sub> by his theoretical multipass instrument is probably not feasible. The advantages of utilizing laser spectroscopy over mass spectrometry for martian rover missions have already been summarized by Webster (2005). This analysis demonstrates that isotopic variation of martian atmospheric CH<sub>4</sub> can be monitored with CRDS instruments that can be constructed with current technology and an accuracy approaching that of isotope ratio mass spectrometers.

To distinguish abiogenic CH<sub>4</sub> from thermogenic or biogenic sources, however, requires comparison of the δ<sup>13</sup>C of C<sub>2</sub>H<sub>6</sub> with that of CH<sub>4</sub>. Although the CH<sub>4</sub>/C<sub>2</sub>+ ratio of abiogenic hydrocarbons on Mars is difficult to predict, we can start by assuming that it would be similar to what

we see in the Precambrian Shield gases on Earth with CH<sub>4</sub>/C<sub>2</sub>+ of 10:1. The photochemical depletion of C<sub>2</sub>H<sub>6</sub> with respect to CH<sub>4</sub> is ~25 (Krasnopolsky, 2005). If the source of the CH<sub>4</sub> were abiogenic, then concentration of 10 ppbv CH<sub>4</sub> would have corresponding C<sub>2</sub>H<sub>6</sub> concentrations of 40 pptv, which is above the CRDS instrument's detection limit. *Preconcentration* of the C<sub>2</sub>H<sub>6</sub> by a factor of ~1,000, however, would be required to achieve an isotopic determination of the δ<sup>13</sup>C of the C<sub>2</sub>H<sub>6</sub> with sufficient accuracy (±5‰). The isotopic fractionation associated with such a drastic *preconcentration* would have to be evaluated carefully.

Although a single determination of the δ<sup>13</sup>C and δ<sup>2</sup>H of CH<sub>4</sub> alone will not necessarily determine whether it is biogenic or abiogenic, the variation of its isotopic composition with concentration over time may. The CRDS instrument when deployed on a rover will be able to record diurnal and seasonal changes and spatial variations in the concentration and isotopic composition of CH<sub>4</sub> in the martian atmosphere. A rover would use this information in conjunction with other data to identify CH<sub>4</sub> sources and sinks and whether either or both are biological in nature. Temporal variability that could be related to temperature changes in the near subsurface of Mars would be consistent with a potential biological source, especially if the isotopic composition varied dramatically given the magnitude of microbial isotopic discrimination. If microbial oxidation of CH<sub>4</sub> by reduction of O<sub>2</sub> (aerobic methanotrophy) or by reduction of sulfate to sulfide (anaerobic methanotrophy) was occurring, it would produce large isotopic fractionation shifts in the δ<sup>13</sup>C of the residual CH<sub>4</sub> (Coleman *et al.*, 1981; Alperin *et al.*, 1988; Reeburgh, 2003) that might distinguish it from the isotopic shifts in δ<sup>2</sup>H of CH<sub>4</sub> produced by abiotic oxidation of CH<sub>4</sub> caused by photochemical destruction (Nair *et al.*, 2005; see Fig. 1). On the martian surface at low latitudes where intermittent brine might occur as a result of diurnal temperature variation (Kuznetz and Gan, 2002), simple thermodynamic analysis of the aerobic methanotroph reaction yields a negative free energy of -750 kJ mol<sup>-1</sup>, which is more than sufficient to sustain ATP production for terrestrial microorganisms. If methanotrophy is responsible for the CH<sub>4</sub> sink, then isotopic enrichment of the residual CH<sub>4</sub> will be substantial. Because the fractionation effects of photochemical destruction and microbial CH<sub>4</sub> ox-

idation are very similar based upon current data, the temporal observations of the martian CH<sub>4</sub> isotopic signature will be critical to resolving microbial from abiogenic signatures.

The final proof of microbial processes in the martian CH<sub>4</sub> cycle, however, requires direct detection of the cellular organic matter in a sample that exhibits a methanogenic or methanotrophic metabolism. For this reason, the principal importance of the CRDS would be to analyze spatial variations in concentration of atmospheric CH<sub>4</sub> and changes correlated with shifts in the wind direction that, in turn, could be utilized to steer the rover toward the source (or sink). The CRDS instrument could also be utilized for analyses of solid phases, *e.g.*, CH<sub>4</sub> hydrate, with an appropriate degassing/volatilization compartment, thus acting as a metabolic-based life detection tool. It is anticipated that, with minor modification, the instrument could be used to detect other molecular species present at low concentrations, most particularly other small hydrocarbons such as ethylene and ethane.

Given that a flight-capable CRDS instrument will not be available for the instrument packages already proposed for the Mars Surface Laboratory, the Astrobiology Field Laboratory is the next logical target for implementation of CRDS. This hypothetical post-Mars Surface Laboratory rover mission to Mars is named in various Mars Exploration Program Advisory Group pathways and could precede, parallel, or even follow a Mars Sample Return program. The Astrobiology Field Laboratory option essentially presumes that martian habitability, indeed past or present life itself on Mars, remains a real possibility warranting additional focused *in situ* study with a rover. The first possible launch opportunity considered is in 2013. The isotopic signature of CH<sub>4</sub> represents one biosignature for which a virtually limitless number of samples can be analyzed. Even though the CH<sub>4</sub> source or sinks may be beyond the reach of the Astrobiology Field Laboratory (*e.g.*, >1 m deep), it is conceivable that access to the subsurface via crater cuts or erosion channels may provide solid samples of the environmental niches that once supported ancient methanogenesis or methanotrophy.

Since the CRDS instrument measures air samples through a filter and does not come into direct contact with Mars surface samples, its degree of internal organic cleanliness and sterility does not have to match that of contact instruments. It

will be extremely important, however, for the *pre-concentrator* and sample/cavity interface to be free of any contaminating terrestrial methanogens and methanotrophs in the unlikely event that they become metabolically active on Mars and alter the CH<sub>4</sub> concentration and isotopic signature.

With regard to future deep-drilling missions on Mars (10–100 m), the CRDS instrument could provide real-time analyses of gases released from boreholes during drilling and aid in identifying rock layers that may require more detailed analyses of core samples or drill cuttings.

## CONCLUSIONS

Extrapolation of the South African He, H<sub>2</sub>, and CH<sub>4</sub> cycle to the martian subsurface indicates that the H<sub>2</sub> generation by radiolysis of ice and water can produce in reaction with CO<sub>2</sub> sufficient CH<sub>4</sub> to account for the recent observations of martian CH<sub>4</sub>. The estimated *in situ* rate of H<sub>2</sub> production by radiolysis is sufficient to support a CH<sub>4</sub> surface flux of  $\sim 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ , given a modeled martian He surface flux of  $\sim 10^5 \text{ cm}^{-2} \text{ s}^{-1}$ . Because of the colder environment, the predicted (CH<sub>4</sub> + H<sub>2</sub>)/He flux rates would be significantly greater than that observed in South Africa, and this parameter may provide a means of distinguishing hot, volcanogenic CH<sub>4</sub> sources from cold, cryospheric sources. Abiogenic CH<sub>4</sub> originating from deep beneath the cryosphere might be distinguishable from microbial CH<sub>4</sub> by determining its C and H isotopic composition relative to that of C<sub>2</sub>H<sub>6</sub>. If CH<sub>4</sub> hydrate exists within the cryosphere, then the CH<sub>4</sub> surface flux may be related to sublimation from the top of the cryosphere, in which case CH<sub>4</sub> atmospheric gas concentrations should be correlated to atmospheric H<sub>2</sub>O. Microbial CH<sub>4</sub> generated in near-surface hypersaline environments above the hydrate stability zone could contribute to the CH<sub>4</sub> surface flux, but only if a much greater electron donor flux is being tapped, in which case the CH<sub>4</sub> atmospheric gas concentrations may be negatively correlated with atmospheric H<sub>2</sub> and CO. If the martian hydrosphere is isotopically zoned with <sup>2</sup>H-enriched H<sub>2</sub>O located at the surface and <sup>2</sup>H-depleted H<sub>2</sub>O located at depth, then the  $\delta^{2\text{H}}$  of the CH<sub>4</sub> may reflect the depth of origin of the CH<sub>4</sub>. Diurnal and seasonal variations in the CH<sub>4</sub> abundance and isotopic composition would also constrain its ori-

gin and pinpoint the source of the emissions. A flight-capable version of a CRDS apparatus represents the type of instrument that has the sensitivity required to perform such an analyses. Such an instrument could be utilized to guide a rover to the location of CH<sub>4</sub> emissions or consumptions to perform life detection experiments.

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### ABBREVIATIONS

C<sub>2</sub>+, ethane + propane + butane; CRDS, cavity ring-down spectroscopy; Ga, × 10<sup>9</sup> year old; Myr, 10<sup>6</sup> years; ppbv, parts per billion; ppmv, parts per million; pptv, parts per trillion; VDPB, Vienna Pee Dee Formation Belemnite standard; VSMOW, Vienna Standard Mean Ocean Water.

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