

Isotopic signatures of CH₄ and higher hydrocarbon gases from Precambrian Shield sites: A model for abiogenic polymerization of hydrocarbons

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Abstract

Previous studies of methane and higher hydrocarbon gases in Precambrian Shield rocks in Canada and the Witwatersrand Basin of South Africa identified two major gas types. Paleometeoric waters were dominated by hydrocarbon gases with compositional and isotopic characteristics consistent with production by methanogens utilizing the CO₂ reduction pathway. In contrast the deepest, most saline fracture waters contained gases that did not resemble the products of microbial methanogenesis and were dominated by both high concentrations of H₂ gas, and CH₄ and higher hydrocarbon gases with isotopic signatures attributed to abiogenic processes of water–rock reaction in these high rock/water ratio, hydrogeologically-isolated fracture waters. Based on new data obtained for the higher hydrocarbon gases in particular, a model is proposed to account for carbon isotope variation between CH₄ and the higher hydrocarbon gases (specifically ethane, propane, butane, and pentane) consistent with abiogenic polymerization. Values of δ¹³C for CH₄ and the higher hydrocarbon gases predicted by the model are shown to match proposed abiogenic hydrocarbon gas end-members identified at five field sites (two in Canada and three in South Africa) suggesting that the carbon isotope patterns between the hydrocarbon homologs reflect the reaction mechanism. In addition, the δ²H isotope data for these gases are shown to be out of isotopic equilibrium, suggesting the consistent apparent fractionation observed between the hydrocarbon homologs may also reflect reaction mechanisms involved in the formation of the gases. Recent experimental and field studies of proposed abiogenic hydrocarbons such as those found at mid-ocean spreading centers and off-axis hydrothermal fields such as Lost City have begun to focus not only on the origin of CH₄, but on the compositional and isotopic information contained in the higher hydrocarbon gases. The model explored in this paper suggests that while the extent of fractionation in the first step in the hydrocarbon synthesis reaction chain may vary as a function of different reaction parameters, δ¹³C values for the higher hydrocarbon gases may be predicted by a simple mass balance model from the δ¹³C values of the lower molecular weight precursors, consistent with abiogenic polymerization. Integration of isotopic data for the higher hydrocarbon gases in addition to CH₄ may be critical for delineation of the origin of the hydrocarbons and investigation of formation mechanisms.

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1. INTRODUCTION

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Determination of the origin of methane (CH₄) and associated higher hydrocarbon gases collectively referred to as C₂⁺ (ethane—C₂H₆; propane—C₃H₈ and butane—C₄H₁₀),

has long relied on an interpretational framework developed by pioneers in the field of oil and gas exploration (Tissot and Welte, 1984; Whiticar et al., 1986; Schoell, 1988) whereby integration of carbon and hydrogen isotope values and additional parameters such as CH_4/C_2^+ ratios have been shown to effectively differentiate between different biogenic processes of methanogenesis including thermogenesis (thermal decomposition of high molecular weight organic precursors) and bacteriogenesis (microbial processes of hydrocarbon formation (definitions after Schoell, 1988)). The past decade has witnessed significant refinement and reevaluation of these traditional frameworks, in particular for isotope fractionation effects associated with microbial processes of hydrocarbon formation, based in part on the increased sensitivity of compound specific isotope analysis via online continuous flow mass spectrometry, and on an increased ability to integrate real-time isotope analysis with microbial culture experiments and molecular microbiological techniques. In particular, models for carbon and hydrogen isotope fractionation associated with microbial methanogenesis pathways (CO_2 reduction and the acetoclastic reaction) described by Whiticar et al. (1986) are undergoing substantial reexamination to incorporate the effects of growth phase and substrate availability (Whiticar, 1999; House et al., 2003; Valentine et al., 2004a), the role of enzymatically-induced hydrogen isotope exchange reactions (Balabane et al., 1987; de Graaf et al., 1996; Waldron et al., 1999; Chidthaisong et al., 2002; Valentine et al., 2004a,b) and proposed novel microbiological pathways for formation of high hydrocarbon gases (Hinrichs et al., 2006). Distinct differences in carbon and hydrogen isotope fractionation effects during microbial methanogenesis have also been identified for different microbial strains. For instance, moderate thermophiles have been found to produce a smaller isotope fractionation than previously thought between the CH_4 produced and the carbon source (CO_2 or the methyl position on acetate) (House et al., 2003; Valentine et al., 2004a).

Despite the large overlap in $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values typically found for microbial and thermogenic gases, attempts to distinguish between these two categories of biogenic gas are typically successfully resolved through integration of multiple lines of evidence including isotopic and compositional data, microbiological techniques, and hydrogeological and geological context. To date however, resolving such biogenic gases from proposed abiogenic hydrocarbons has been much more challenging, largely due to continuing uncertainty in the defining characteristics of hydrocarbon gases produced by abiogenic processes. Jenden et al. (1993) proposed three criteria for identification of mantle-derived abiogenic hydrocarbons: a $\delta^{13}\text{C}$ value for CH_4 more enriched than -25‰ ; a carbon isotope “inverse” trend of increasing isotopic depletion in ^{13}C with increasing molecular weight for CH_4 -ethane-propane-butane; and a $^3\text{He}/^4\text{He}$ ratio indicative of mantle-derived helium ($R/R_a > 0.1$). Over the past decade however, there has been a growing body of literature that indicates that not all abiogenic gases are mantle-derived. A variety of water-rock interactions have been shown to produce CH_4 , as well as higher hydrocarbons gases, by reactions such as surface-catalyzed

polymerization from reduction of CO or CO_2 in a Fischer-Tropsch-type synthesis (Anderson, 1984; Szatmari, 1989; Horita and Berndt, 1999; Foustoukos and Seyfried, 2004; McCollom and Seewald, 2006; Taran et al., 2007; Proskurowski et al., 2008); heating or metamorphism of graphite- or carbonate-bearing rocks (Giardini and Salotti, 1968; Holloway, 1984; Kenney et al., 2002; McCollom, 2003); and other gas-water-rock alteration reactions associated with serpentinization (McCollom and Seewald, 2001; Kelley et al., 2001, 2005; Charlou et al., 2002). Significantly, several experimental studies have demonstrated that production of abiogenic hydrocarbons by these types of water-rock interactions can result in $\delta^{13}\text{C}$ values as depleted as -57‰ , well within the range of isotopically “light” values that were once assumed to be an indication of biological activity (Szatmari, 1989; Yuen et al., 1990; Hu et al., 1998; Horita and Berndt, 1999; McCollom and Seewald, 2006; Taran et al., 2007). In a crustal-dominated geologic setting, gas-water-rock interactions can produce abiogenic hydrocarbons whose $\delta^{13}\text{C}$ values reflect local crustal carbon sources and will not necessarily have either ^{13}C -enriched $\delta^{13}\text{C}$ values or R/R_a values > 0.1 . In addition, it has become evident that the carbon isotope “inverse” trend is not observed in all cases and alone is insufficient to support an abiogenic origin (Du et al., 2003; McCollom and Seewald, 2006; Fu et al., 2007; Taran et al., 2007).

In a wide variety of different disciplines in earth and planetary sciences, the ability to distinguish between abiogenic and biogenic origins for CH_4 has become increasingly important. Recent suggested evidence for the earliest onset of microbial methanogenesis at >3.46 Ga years on the early Earth (in part based on $\delta^{13}\text{C}$ values for CH_4 -rich fluid inclusions) (Sherwood Lollar and McCollom, 2006; Ueno et al., 2006), as well as reports of “ CH_4 -powered” chemolithotrophic microbial communities at deep ocean hydrothermal fields such as Lost City (Kelley et al., 2005) wrestle with this challenge. In planetary exploration and astrobiology, criteria for distinguishing between abiogenic and biogenic CH_4 is not only critical to resolving the origin of CH_4 reportedly found in Mars’ atmosphere (Mumma, 2004; Formisano et al., 2004; Krasnopolsky et al., 2004) and on Titan and Enceladus, but for evaluating the significance of proposed CH_4 -generating processes for chemoautotrophic life on other planets and moon (Boston et al., 1992; Oze and Sharma, 2005; Lyons et al., 2005).

Several of the above applications are hampered by the difficulty of obtaining samples. This paper focuses on gases (CH_4 , C_2^+ , H_2 , He and N_2) shown to discharge from saline fracture waters at rates of 1 to >30 L of gas/min in 1- to 3-km-deep Precambrian age rocks on the Canadian Shield, Fennoscandian Shield and in the Witwatersand Basin of South Africa (Nurmi and Kukkonen, 1986; Sherwood Lollar et al., 1993a,b, 2002, 2006; Potter and Konnerup-Madsen, 2003). The large number of boreholes, significant volumes of gas, and a diversity of geologic settings provide an excellent opportunity to test proposed criteria for the identification of biogenic versus abiogenic CH_4 and higher hydrocarbon gases. At the site of an ancient (2700 Ma) hydrothermal sea-floor spreading center characterized by layered units of felsic, mafic and ultramafic rocks

(Bleeker and Parrish, 1996), the gases at the Kidd Creek Mine, Timmins, Canada on the Canadian Shield in particular are a potential ancient analog of the serpentinite-hosted gases recently reported at Lost City and other hydrothermal fields on the Mid-Atlantic Ridge (Kelley et al., 2001; Charlou et al., 2002; Kelley et al., 2005; Proskurowski et al., 2006, 2008). Unlike the Lost City vents where CH₄ and H₂ are thought to be produced contemporaneously, the deep Precambrian Shield H₂, CH₄ and higher hydrocarbons appear to be stored in sealed fracture systems in the host rock over geologic time scales (Sherwood Lollar et al., 2007b). While many of the other sites investigated on the Canadian Shield and in Finland are, like Kidd Creek Mine, sites with a significant proportion of ultramafic rock (Sherwood Lollar et al., 2007b), the present study incorporates samples from a wide variety of other geologic settings including the quartz-diorite dike offset of the Sudbury Igneous Complex (1840 Ma) (Copper Cliff South Mine, Sudbury, Canada); and the Archean intracratonic Witwatersrand Basin in South Africa (2700–2900 Ma) (Kloof, Driefontein and Mponeng mines). The geologic settings for all these sites are described in more detail in Sherwood Lollar et al. (2006, 2007b).

Helium isotopic analysis for samples from the Canadian and Fennoscandian Shields, and from the Witwatersrand Basin confirm that there is no significant mantle-derived component associated with these gases (Sherwood Lollar et al., 1993b; Lippmann et al., 2003). The high salinities (up to hundreds of g/L), highly altered $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures, and both ^{36}Cl and measurements of co-occurring nucleogenic noble gases for these fracture waters are consistent with extensive water–rock interaction over geologically long time scales in these high rock/water ratio environments (Lippmann et al., 2003; Ward et al., 2004; Lin et al., 2006; Onstott et al., 2006; Sherwood Lollar et al., 2006). While the ultimate origin of these fluids has been attributed alternately to saline waters that penetrated the crystalline basement, formation water, or hydrothermal fluids in some cases, their geochemistry and isotopic signatures have typically been so profoundly overprinted by the effects of long-term water–rock interaction that, for the most saline end-members, little evidence of their primary composition remains (Frape and Fritz, 1982; Nurmi et al., 1988; Onstott et al., 2006).

While the earliest descriptions of these Precambrian Shield-type gases date back to the 1880s, the first scientific papers to describe the phenomenon in Canada (Fritz et al., 1987; Sherwood Lollar et al., 1993a; Sherwood Lollar et al., 1993b), Finland (Nurmi and Kukkonen, 1986), the Kola Peninsula (Khitrov et al., 1979); and the Ilimaussaq complex in Greenland (Konnerup-Madsen et al., 1979, 1988) largely focused on demonstrating that the majority of the gases were not consistent with known microbial or thermogenic gases and suggested a possible abiogenic origin in part by process of elimination. In contrast, the past several years have seen significant progress in understanding the controlling processes of gas formation in these environments, and the distribution of two major gas types.

Based on a ^{13}C -depletion in $\delta^{13}\text{C}$ values for higher hydrocarbon gases compared to $\delta^{13}\text{C}$ values for methane

(CH₄) similar to that observed for the Murchison meteorite *n*-alkanes, and on an inverse relationship between ^{13}C depletion and ^2H enrichment between CH₄ and ethane (C₂H₆ or C₂) consistent with Des Marais et al.'s (1981) model regarding fractionation during abiogenic polymerization, Sherwood Lollar et al. (2002) suggested that carbon and hydrogen isotope patterns for a suite of samples from Kidd Creek were consistent with an abiogenic formation mechanism. A set of time series samples for one of the boreholes at Kidd Creek showed a shift in $\delta^{13}\text{C}$ values and CH₄/C₂⁺ ratios over 19 months consistent with addition of a second component of microbial CH₄ eventually accounting for approximately 10–25% of the total gas in this groundwater (Sherwood Lollar et al., 2002). At sites in the Witwatersrand Basin, Ward et al. (2004) used both culture-based and molecular microbiological techniques to confirm the presence of active methanogenic communities in boreholes which also showed CH₄ isotopic signatures that suggested that microbial methanogenesis dominated the borehole gases at some sites. Sherwood Lollar et al. (2006) proposed a conceptual model to account for the range of hydrocarbon gas compositional and isotopic variability at sites both in Canada and South Africa based on variation between these two hydrocarbon gas end-members—one proposed to reflect an abiogenic CH₄ formation mechanism with the same pattern of ^{13}C and ^2H isotopic variation between CH₄–C₂⁺ originally identified at Kidd Creek (indicated by bold “A” in Fig. 1) and one dominated by microbial methanogenesis (indicated by bold “M” in Fig. 1). Fig. 1 summarizes this model in terms of the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values for CH₄, but as detailed in the cited papers, this two component isotopic model is supported by multiple lines of evidence including hydrocarbon gas compositions, and both culture-based and molecular microbiological evidence for active methanogenic communities in the same boreholes where the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values suggest a predominantly microbial end-member (M; Fig. 1). Sherwood Lollar et al. (2007b) subsequently demonstrated that this two-component variation in gas geochemistry and isotopic signatures was directly correlated with groundwater geochemistry as well. In the Witwatersrand Basin, gases with the proposed abiogenic signature (A) were found only in the most highly saline end-member fracture waters where ^{36}Cl and noble gas residence time estimates were on the order of 10–25 Ma (Lippmann et al., 2003). Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for these fracture waters fell well above the Global Meteoric Water Line (GMWL), a feature also consistent with long-term water–rock interactions over geologically long time scales (Onstott et al., 2006; Sherwood Lollar et al., 2007b). In contrast, the gas samples dominated by microbial methanogenesis were found exclusively with the younger, shallower, less saline groundwaters that not only still retained paleometeoric isotopic signatures falling along the GMWL, but had residence time estimates an order of magnitude lower (10 Ka to 1–5 Ma; (Lippmann et al., 2003; Sherwood Lollar et al., 2007b). Finally Sherwood Lollar et al., 2007b demonstrated that the distribution of H₂ is also consistent with this two-component model controlling gas and groundwater geochemistry. High H₂ levels (dissolved concentrations up to 7.5 mM) were exclusively

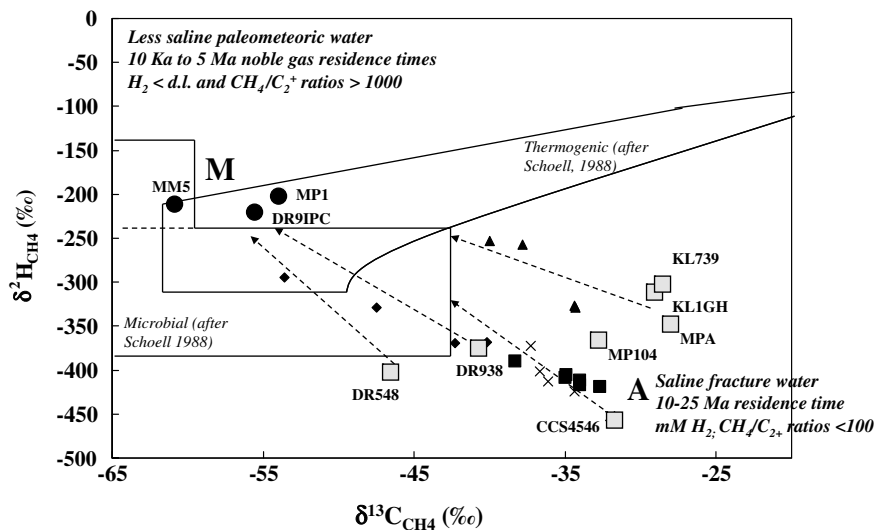
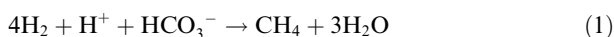


Fig. 1. Conceptual model of mixing between microbially-dominated (M), and proposed abiogenically-dominated (A) gas and groundwater end-members after Sherwood Lollar et al. (2007b). Briefly, culture-based and molecular microbiological evidence for the dominance of active methanogenic communities are found in the boreholes symbolized by black circles (see Ward et al., 2004; Sherwood Lollar et al., 2006 for further details). Black squares (Kidd Creek) and gray squares indicate boreholes in which predominantly abiogenic end-members have been proposed (see Sherwood Lollar et al., 2006 for further details on the gas geochemistry and Lin et al., 2006 for details on the microbiological community). Empirically derived ranges for conventional microbial and thermogenic CH_4 adapted after Schoell (1988). Error bars are smaller than the plotted symbols.

associated with hydrocarbon gases with the proposed abiogenic pattern (A) in the oldest most saline fracture waters whose geochemistry and isotopic compositions are dominated by the effects of water–rock interaction. In the younger, less saline paleometeoric waters with a dominance of microbial methanogenesis, dissolved H_2 levels were below detection limit, consistent with production of a more ^{13}C -depleted microbial CH_4 via the reaction:



In the past few years then, a two-component model has been established by multiple lines of evidence from groundwater and gas geochemistry, isotopic geochemistry, and microbiological evidence. While some sites have groundwaters consistent with the products of microbiological methanogenesis (Ward et al., 2004) (M; Fig. 1), the non-microbial end-member has been shown to have a set of characteristics consistently found only in the oldest, most highly saline and geochemically and isotopically altered fracture waters (Sherwood Lollar et al., 2006; Sherwood Lollar et al., 2007b). Specifically, Sherwood Lollar et al. (2006) demonstrated that for five different mines located both on the Canadian Shield and the Witwatersrand Basin, the same patterns first identified at Kidd Creek were also found— ^{13}C -depletion in $\delta^{13}\text{C}$ values of ethane, propane and butane with respect to CH_4 and an inverse correlation between ^{13}C -depletion and ^2H -enrichment between CH_4 and ethane. As noted, another key characteristic of this end-member is the close association of hydrocarbon gases with the proposed abiogenic isotopic signature (A) with high levels of H_2 , and a shift to microbial CH_4 isotopic end-members (M) correlated with H_2 -depletion consistent with Eq. (1). The trend lines in the conceptual model in Fig. 1 are schematic lines that suggest there is mixing be-

tween the two end-member types at many sites (Sherwood Lollar et al., 2007b). Certainly these linear trends are not attributable to any obvious secondary alteration processes such as microbial oxidation, as methanotrophy would be expected to produce a correlation of isotopic enrichment in both ^{13}C and ^2H in the residual CH_4 , not the inverse relationship seen in these gases. As summarized in previous work, while CH_4/C_2^+ ratios for the non-microbial end-members are similar to those of typical thermogenic hydrocarbons, the very $\delta^2\text{H}$ -depleted isotopic signature for the hydrocarbon gases, the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ relationships between CH_4 –ethane–propane–butane, and the high levels of H_2 , could not be reconciled with a thermogenic origin (Sherwood Lollar et al., 2002, 2006).

The primary objective of the present paper is to further investigate the origin of the non-microbial, proposed “abiogenic” end-members by a detailed examination of the isotopic relationships between the various hydrocarbon homologs. Hence the paper focuses not on all the boreholes sampled in past papers, but specifically on the end-members with the proposed abiogenic pattern from two sites in Canada and three in South Africa (samples represented by black and gray squares in Fig. 1) (Sherwood Lollar et al., 2002, 2006). To that end, this paper presents new data for the higher hydrocarbon gases at Kidd Creek and uses that data to develop a model to relate observed carbon isotopic variation to a possible abiogenic polymerization mechanism for the higher hydrocarbon gases. The paper then applies this model to hydrocarbons at other Precambrian Shield sites in both Canada and South Africa where abiogenic synthesis has been proposed in Sherwood Lollar et al. (2006) and demonstrates its ability to account for carbon isotope fractionation patterns in hydrocarbon gases at all these sites.

2. MATERIALS AND METHODS

2.1. Sampling methods

In Canada and South Africa, gas phase and fracture water samples were collected from underground boreholes at the borehole collar after the method of Sherwood Lollar et al. (2002) and Ward et al. (2004). A packer was placed into the opening of the borehole and sealed to the inner rock walls below water level to seal the borehole from the mine air and eliminate air contamination. Gas and water were allowed to flow through the apparatus long enough to displace any air remaining in the borehole or the apparatus before sampling. Plastic tubing was attached to the end of the packer and the flow of gas and/or water from the borehole was directed into an inverted graduated collection device. Gases collected were transferred directly into evacuated vials through a needle that was attached to the top of the device. The gas sampling vials were pre-evacuated 130-ml borosilicate vials sealed with butyl blue rubber stoppers prepared after the method of Oremland and Des Marais (1983). Vials were pre-fixed with 50 μ l of a saturated HgCl₂ solution to kill any microbes contained in the sample so microbial activity post-sampling would not alter the gas composition and isotopic signatures. Previous studies comparing the isotopic values of gases taken at the borehole collars to values determined for gases in solution at depth in the same boreholes, showed that exsolution of the hydrocarbon gases from solution does not alter their isotopic signatures significantly (Sherwood Lollar et al., 1993a,b, 1994). Compositional and isotopic protocol tests were run with isotopically characterized working standards with known standard values to ensure that the vials and stoppers introduced no sampling artifacts for either compositional,

or for carbon or hydrogen isotopic analyses of the samples (Fu et al., 2007).

2.2. Compositional analysis

Compositional analyses of gas phase samples (Table 1a) were performed on a Varian 3400 gas chromatograph equipped with a flame ionization detector (FID) to determine concentrations of CH₄ and the higher hydrocarbon gases. The hydrocarbons were separated on a J&W Scientific GS-Q column (30 m \times 0.32 mm ID) with a helium gas flow and temperature program: initial 60 °C hold 2.5 min, increase to 120 °C at 5 °C/min. Both an HP 5830A and a Varian 3800 GC equipped with a micro-thermal conductivity detector (μ TCD) and Molecular Sieve 5A PLOT columns (25 m \times 0.53 mm ID) were used to determine concentrations of the inorganic gas components (H₂, He, O₂, CO₂ and N₂). To determine concentrations of He and H₂, the argon carrier gas flow rate was 2 ml/min and temperature program was: initial 10 °C hold 10 minutes, increase to 80 °C at 25 °C/min, hold 7 min. All analyses were run in triplicate and mean values are reported in Table 1a. Reproducibility for triplicate analyses was \pm 5%.

2.3. Isotopic analysis

Analyses for $\delta^{13}\text{C}$ values (Table 1b) were performed by continuous flow compound specific carbon isotope ratio mass spectrometry with a Finnigan MAT 252 mass spectrometer interfaced with a Varian 3400 capillary GC. Hydrocarbons were separated by a Poraplot QTM column (25 m \times 0.32 mm ID) with temperature program: initial 40 °C hold 1 min, increase to 190 °C at 5 °C/min, hold 5 min. Total error incorporating both accuracy and repro-

Table 1a
Compositional analysis (vol %) of Kidd Creek gas samples^a

Sample	He (vol %)	H ₂ (vol %)	N ₂ (vol %)	CH ₄ (vol %)	C ₂ H ₆ (vol %)	C ₃ H ₈ (vol %)	<i>iso</i> -C ₄ H ₁₀ (vol %)	<i>n</i> -C ₄ H ₁₀ (vol %)	<i>iso</i> -C ₅ H ₁₂ (vol %)	<i>n</i> -C ₅ H ₁₂ (vol %)
8558	2.45	1.97	9.06	74.2	10.6	1.99	0.17	0.42	0.06	0.10
8428	2.19	2.45	9.80	71.9	10.3	2.02	0.17	0.41	0.06	0.10
8282	2.12	1.30	10.7	69.3	11.7	2.42	0.20	0.57	0.07	0.14
8402	2.41	2.00	12.7	69.4	9.44	1.70	0.14	0.38	0.05	0.09
8539	1.83	1.34	8.41	72.2	9.93	1.88	0.16	0.41	0.05	0.09

^a All O₂ and CO₂ were < detection limit.

Table 1b
Carbon and hydrogen isotope values (‰) for Kidd Creek gas samples

Sample	$\delta^{13}\text{C}_{\text{CH}_4}$	$\delta^2\text{H}_{\text{CH}_4}$	$\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$	$\delta^2\text{H}_{\text{C}_2\text{H}_6}$	$\delta^{13}\text{C}_{\text{C}_3\text{H}_8}$	$\delta^2\text{H}_{\text{C}_3\text{H}_8}$	$\delta^{13}\text{C}_{\text{iso-C}_4\text{H}_{10}}$	$\delta^{13}\text{C}_{\text{n-C}_4\text{H}_{10}}$	$\delta^{13}\text{C}_{\text{iso-C}_5\text{H}_{12}}$	$\delta^{13}\text{C}_{\text{n-C}_5\text{H}_{12}}$
8558	-32.7	-419	-36.8	-321	-35.3	-264	-37.8	-34.8	-38.0	-33.6
8428	-34.0	-412	-36.4	-314	-34.9	-262	-37.7	-34.4	-36.8	-33.1
8282	-35.0	-409	-38.3	-316	-35.9	-269	-38.2	-35.6	-39.6	-34.3
8402	-34.9	-406	-38.1	-319	-36.8	-267	-39.8	-36.0	-39.4	-34.3
8539	-34.0	-417	-37.2	-320	-36.1	-270	-38.9	-35.6	-40.2	-33.9

Carbon and hydrogen isotope values for C1–C3 for the Kidd Creek samples from Sherwood Lollar et al. (2002).

Carbon and hydrogen isotope values for *n*-C₄, *iso*-C₄, *n*-C₅ and *iso*-C₅ never previously published.

ducibility is $\pm 0.5\%$ with respect to V-PDB standard (Sherwood Lollar et al., 2007a). The $\delta^2\text{H}$ analysis was performed on a continuous flow compound specific hydrogen isotope mass spectrometer which consists of an HP 6890 gas chromatograph (GC) interfaced with a micropyrolysis furnace (1465 °C) in line with a Finnigan MAT Delta⁺-XL isotope ratio mass spectrometer. H_2 and CH_4 were separated by a Molecular Sieve 5A column (25 m \times 0.32 mm ID) with a carrier gas flow rate of 1.2 mL/min. Temperature program was initial 20 °C, hold for 6 min, followed by an increase to 280 °C at 25 °C/min. Higher hydrocarbons were separated using the same column and temperature program as the carbon isotope analysis. Total error incorporating both accuracy and reproducibility is $\pm 5\%$ with respect to V-SMOW (Table 1b).

3. RESULTS AND DISCUSSION

Sherwood Lollar et al. (2002) suggested that the trends of carbon isotope depletion and hydrogen isotope enrichment between methane (CH_4 or C1) and ethane (C_2H_6 or C2) for the Kidd Creek gases were consistent with formation of ethane by abiogenic polymerization of methane precursors based on the preferential incorporation of ^{12}C , and preferential loss of ^1H during the initial step in the reaction. While $\delta^{13}\text{C}$ values for all the hydrocarbon compounds (ethane, propane and butane) were notably depleted in ^{13}C with respect to CH_4 in a pattern quite different from typical thermogenic gases, a detailed model could not be developed at that time to account for isotopic variation between the hydrocarbon homologs beyond the first two components, methane and ethane. In particular, the observation that the pattern of hydrogen isotopic variation was one of consistent ^2H enrichment with increasing molecular weight, while for carbon isotopes, $\delta^{13}\text{C}$ variation from one homolog to the next described a saw-tooth pattern of carbon isotope depletion (C1–C2); subsequent enrichment between ethane and propane

(C_3H_8 or C3); followed by isotopic depletion again between C3 and butane (C_4H_{10} or total C4) could not be explained (Sherwood Lollar et al., 2002).

Here we report new $\delta^{13}\text{C}$ and $\delta^2\text{H}$ data for the Kidd Creek site determined for the first time for pentane (C_5H_{12} or C5), and for separate determinations of *n*-C4, *iso*-C4, *n*-C5 and *iso*-C5 for the same suite of samples (Tables 1a and 1b). Hydrocarbon data sets in the literature often report $\delta^{13}\text{C}$ values only for total C4 (*n*-C4 + *iso*-C4) and total C5 (*n*-C5 + *iso*-C5). Fig. 2a and b shows that the new data determining separate $\delta^{13}\text{C}$ values for *iso*- and *n*-alkanes rather than $\delta^{13}\text{C}$ values for total C4 (butane) and total C5 (pentane) provide important insight into carbon isotope variation in these samples, and into possible reaction mechanisms. Values of $\delta^{13}\text{C}$ for all the higher hydrocarbon gases (C2–C5) are depleted in ^{13}C with respect to CH_4 (Table 1b) consistent with the original observations in Sherwood Lollar et al. (2002). Fig. 2a shows that for a plot of $\delta^{13}\text{C}$ values for straight chain alkanes alone however (C1–C3, *n*-C4 and *n*-C5), while C1–C2 shows a depletion trend, C2–C5 shows a consistent trend of isotopic enrichment in ^{13}C with increasing molecular weight. In contrast, the sawtooth pattern of carbon isotope depletion (C1–C2), enrichment (C2–C3) and depletion (C3–C4) in ^{13}C previously observed by Sherwood Lollar et al. (2002) is clearly a feature produced by the isotopic variation in C1–C3 and the branched hydrocarbons (*iso*-C4 and *iso*-C5) (Fig. 2b). The variability in $\delta^{13}\text{C}$ values of *iso*-C5 may be due to the presence of additional isomers of C5 (e.g. cyclo-pentane and neo-pentane) which could not be completely chromatographically resolved from *iso*-C5. Based on this observation, separate determinations of *iso*- and *n*-isomers for C4 and C5 should be a routine feature of the isotopic characterization for these Precambrian Shield gases. Unfortunately, this was not the case at the time of the analysis for the other sites for the Canadian Shield and Witwatersrand Basin, so they cannot be included in Fig. 2a and b for comparison at this time.

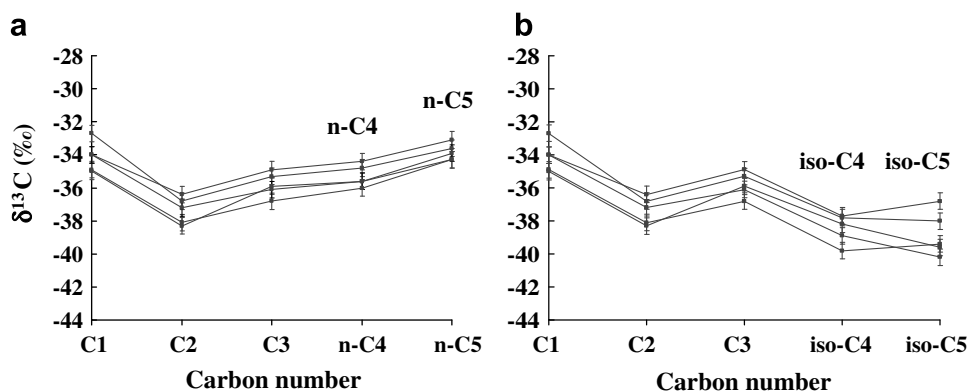


Fig. 2. (a) Carbon isotope values plotted versus carbon number for the straight chain alkanes from Kidd Creek—methane (C1), ethane (C2), propane (C3), *n*-butane (*n*-C4) and *n*-pentane (*n*-C5). While a carbon isotope depletion in ^{13}C occurs between C1 and C2, the rest of the pattern is a consistent carbon isotope enrichment trend with increasing molecular weight. Errors are $\pm 0.5\%$ for $\delta^{13}\text{C}$ values. (b) Carbon isotope values plotted versus carbon number for the straight chain alkanes from Kidd Creek—methane (C1), ethane (C2), propane (C3), and branched isomers of butane (*iso*-C4) and pentane (*iso*-C5). A saw-tooth pattern of alternating carbon isotope depletion in ^{13}C , and carbon isotope enrichment in ^{13}C is evident when the branched alkanes are characterized separately from the straight chain forms of *n*-C4 and *n*-C5 in (a). Errors are $\pm 0.5\%$ for $\delta^{13}\text{C}$ values.

3.1. Potential role of thermogenic gases

Overall variation in $\delta^{13}\text{C}$ for methane, ethane, propane and total butane and pentane is not consistent with the trend of increasing isotopic enrichment with increasing molecular weight well known for thermogenic gases (Sherwood Lollar et al., 2002). While the higher hydrocarbons all have $\delta^{13}\text{C}$ values more depleted than CH_4 , for straight chain C_2^+ alkanes alone however, $\delta^{13}\text{C}$ values do become increasingly isotopically enriched in ^{13}C with increasing carbon number (Fig. 2a). As discussed in Sherwood Lollar et al. (2002, 2006) however, the $\delta^2\text{H}$ values for the A-type gases are significantly depleted in ^2H compared to thermogenic gases. In a recent paper, Taran et al. (2007) suggested migration of a high-temperature, high-maturity thermogenic end-member (H) and mixing with a lower maturity (L) thermogenic gas might be able to account for the carbon and hydrogen isotopic distribution patterns observed in the A-type gases from the Shield sites. As demonstrated

in Fig. 3 however, it is unclear how such hypothesized end-members (which in any case have never been observed at the localities in question) could in fact account for the observed patterns at these sites. Compositional features of the A-type gases argue against a thermogenic origin for the C_2^+ gases and against complex mixing scenarios as well. Total C_2^+ content for these gases typically accounts for approximately 15% by volume of the gas phase, in contrast with mature thermogenic gases where C_2^+ levels account for only a few % of the gas phase (Schoell, 1980). In addition, the gas compositions for Kidd Creek also fit a Schulz–Flory distribution (Fig. 4). The Schulz–Flory distribution is a macromolecular (bulk chemistry) distribution of the hydrocarbon homologs that is controlled by chain growth probability factor for abiogenic stepwise polymerization where $(\text{C}_n + 1/\text{C}_n)$ is approximately constant (and C_n is the concentration in mole units) (Anderson, 1984; Taran et al., 2007). It is well known that this compositional distribution alone is not definitive evidence for an abiogenic origin for

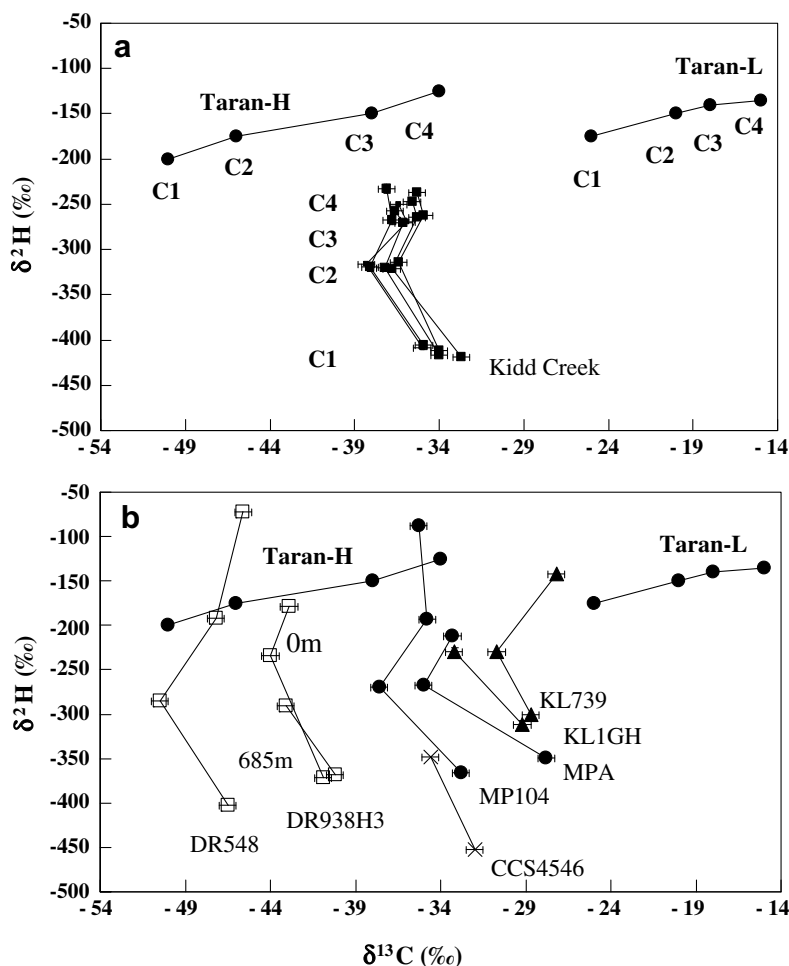


Fig. 3. Carbon and hydrogen isotopic patterns for methane, ethane, propane and butane for (a) Kidd Creek and for (b) four other Precambrian Shield sites for the proposed abiogenic end-members that are the focus of this paper (after Sherwood Lollar et al., 2006). While Taran et al. (2007) suggest that the observed patterns at these sites could be attributed to mixing between theoretical thermogenic end-members—a high-temperature and high maturity gas (H) and a lower maturity gas (L), it is difficult to see how such mixing can in fact account for the observed patterns at these sites (see text). Errors are $\pm 0.5\text{‰}$ for $\delta^{13}\text{C}$ values. Error bars for $\delta^2\text{H}$ values are $\pm 5\text{‰}$ and smaller than the plotted symbols.

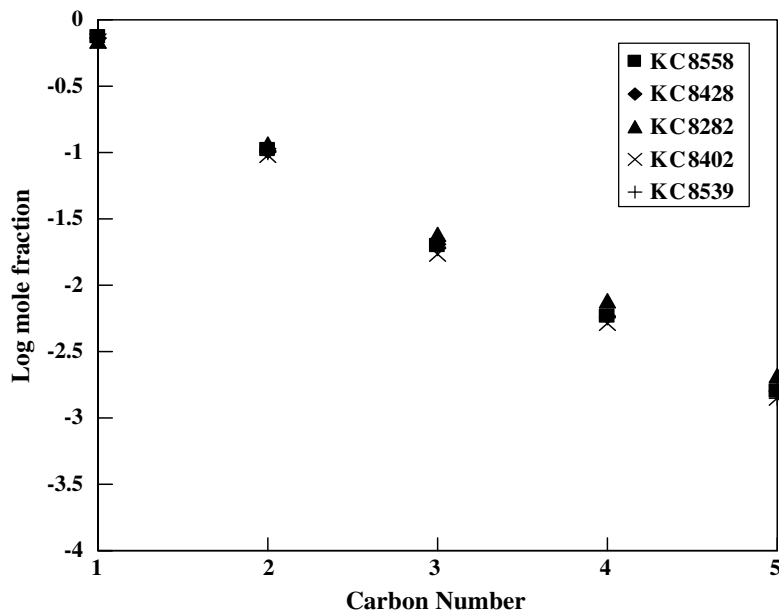


Fig. 4. Compositional data for all Kidd Creek samples fit a Schulz–Flory distribution with correlation coefficients better than $r^2 = 0.99$ for all samples. All A-type gases from Fig. 1 similarly fit a Schulz–Flory distribution (data not shown) with correlation coefficients between $r^2 = 0.97$ – 0.99 .

the hydrocarbons (Flory, 1936; Giggenbach, 1997). However it is difficult to envisage how mixing of a thermogenic C_2^+ component with a CH_4 component of a different non-thermogenic origin could fortuitously produce such a uniform compositional pattern for all A-type gases.

3.2. Potential for chemical and isotopic equilibrium

The fact that the Kidd Creek and all A-type gases from Fig. 1 fit a Schulz–Flory distribution is also significant in that it demonstrates that the hydrocarbon gas compositions are not controlled by chemical equilibrium (Schulz, 1935; Flory, 1936; Anderson, 1984; Taran et al., 2007; Proskurowski et al., 2008). Similarly there is no evidence for isotopic equilibration within the gases. Carbon isotope equilibrium would not be expected for these gases due to slow kinetics in such a low temperature system (measured groundwater temperatures are all less than 65 °C). Even for a system within which relatively rapid isotopic equilibrium might be expected, such as between $\delta^2H_{H_2O}$ and $\delta^2H_{H_2}$ (Lyon and Hulston, 1984; Horibe and Craig, 1995), calculated equilibration temperatures are significantly higher than the measured temperatures for co-existing gases and groundwaters (Fig. 5a). Similarly, temperature calculations based on the $\delta^2H_{CH_4}$ – $\delta^2H_{H_2}$ geothermometer of Horibe and Craig (1995) are also significantly higher than measured groundwater temperatures (Fig. 5b). Finally, the relationships between the $\delta^2H_{H_2O}$ and $\delta^2H_{CH_4}$ values do not suggest isotopic equilibration between the gases. Given that the maximum theoretical value for $1000 \ln \alpha_{H_2O(l)-CH_4(g)}$ is 276 (Horibe and Craig, 1995), the range of values for these samples (264–550) are not consistent with thermodynamic isotopic equilibrium. This is not surprising as H isotopic equilibration between H_2O and CH_4 is expected to be slow

(Lyon and Hulston, 1984). Even at temperatures of 200 °C, hydrogen exchange half-times for H_2O and CH_4 are estimated to be >0.6 Ma (Sessions et al., 2004) and the Witwatersrand Basin for instance has not experienced temperatures >70 – 120 °C for the past 80 Ma (Omar et al., 2003). Nonetheless the data set as a whole clearly indicates that the δ^2H isotopic values for H_2O – H_2 – CH_4 for these samples are not controlled by isotopic equilibrium.

3.3. Potential for enzymatically-mediated isotope exchange

Whiticar et al. (1986) proposed that microbial methanogenesis proceeds by two primary pathways, CO_2 reduction (Eq. (1)) and the acetoclastic reaction (Eq. (2)):



That paper further suggested that in moderate temperature terrestrial environments the latter pathway dominates, while in cold marine sediments CO_2 reduction is relatively more important. Recently this interpretational framework has undergone significant re-evaluation as isotopic fractionation for different methanogenic strains under different growth conditions and environmental conditions have been investigated. In particular, hydrogen isotope fractionation effects during both CO_2 reduction and the acetoclastic reaction have been re-evaluated in the light of possible enzymatically-mediated hydrogen isotope exchange under certain environmental conditions such as high H_2 and low SO_4 levels (Balabane et al., 1987; Whiticar, 1991; Burke, 1993; Sugimoto and Wada, 1995; Waldron et al., 1999). In a series of investigations of carbon and hydrogen isotopic fractionation by moderately thermophilic methanogens, Valentine et al. (2004a) demonstrated that different environmental growth conditions and different microbial strains

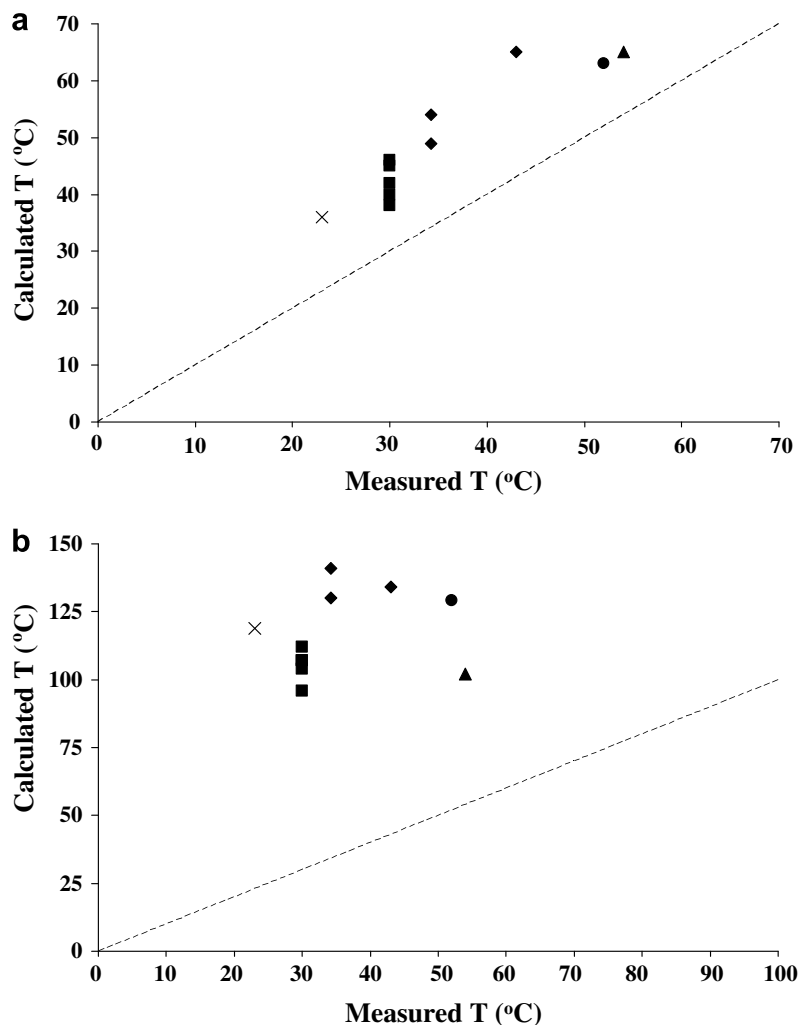


Fig. 5. Measured groundwater temperatures ($^{\circ}\text{C}$) for Kidd Creek samples (squares); Copper Cliff South (crosses); Dreifontein (diamonds) Mponeng (circles) and Kloof (triangles) versus temperatures calculated based on hydrogen isotope geothermometers for (a) $\text{H}_2\text{O}_{(l)}\text{-H}_{2(g)}$ and (b) $\text{CH}_4\text{-H}_2$ from Horibe and Craig (1995). All calculated temperatures are significantly higher than measured groundwater temperatures indicating the $\text{H}_2\text{O-H}_2\text{-CH}_4$ system is not at isotopic equilibrium. Data from Kidd Creek show a vertical distribution because all groundwaters have approximately the same measured temperature.

did indeed result in a wider range of values for carbon and hydrogen isotopic fractionation factors (α_{C} and α_{H}) for both pathways than previously suggested by Whiticar et al. (1986). In particular, for CO_2 reduction, suggested to be the dominant pathway for deep subsurface thermophiles, the study reported a wider range of fractionation factors related to growth phase and metabolic rate (Valentine et al., 2004a). In contrast to the α_{C} values of 1.095 to 1.055 and α_{H} values of 1.186–1.220 proposed for CO_2 reduction by Whiticar et al. (1986), Valentine et al. (2004a) reported α_{C} and α_{H} values between 1.023–1.064 and 1.16–1.43, respectively for CO_2 reduction, with the larger range of values in both cases associated with low H_2 and later growth phases in their experiments (Fig. 6). The authors hypothesized that carbon and hydrogen isotopic fractionation was related to changes in the enzymatic reactions, controlled by H_2 availability and/or growth phase and the impact of these factors on the reversibility of the catabolic reaction

(for α_{C}), and on the preferential expression of enzymes for H addition to the carbon substrate (for α_{H}) (Valentine et al., 2004a).

In the light of this new information on fractionation during microbial methanogenesis, both the microbial and proposed abiogenic end-members from Sherwood Lollar et al. (2006) are plotted on Fig. 6 for comparison. Based on both CH_4/C_2^+ ratios >1000 and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values for CH_4 from the boreholes, Ward et al. (2004) identified several sites where the paleometeoric waters were dominated by the products of microbial methanogenesis via CO_2 reduction (M; Figs. 1 and 6). This interpretation was further supported by enrichment cultures and 16S RNA gene cloning and *mcrA* (methyl coenzyme M reductase) gene cloning that indicated that a large % of the clone libraries for biomass from these groundwaters were highly (83–99%) related to known methanogens (Ward et al., 2004; Sherwood Lollar et al., 2006). Consistent with this

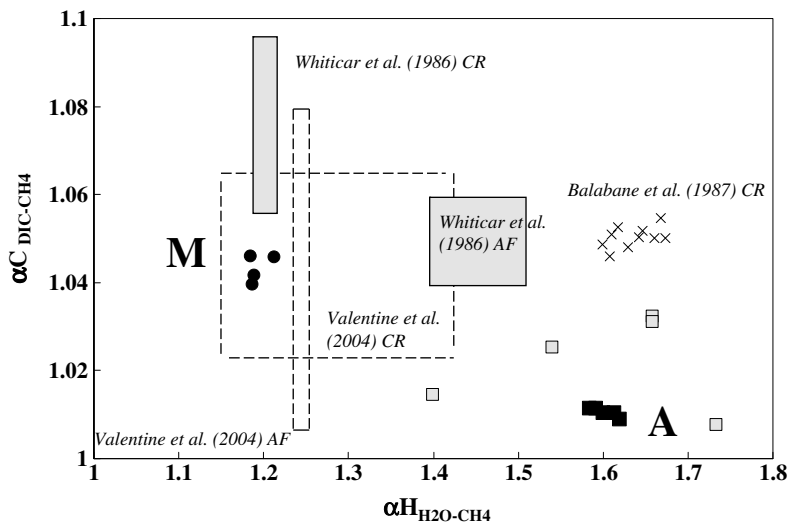


Fig. 6. Values of $\alpha_{\text{DIC-CH}_4}$ versus $\alpha_{\text{H}_2\text{O-CH}_4}$ for samples in this study compared to both Whiticar et al. (1986) and revised framework from Valentine et al. (2004a) for both CO_2 reduction (CR) and the aceticlastic pathway (AF). Following the conceptual model in Fig. 1, samples that have been interpreted as dominated by the products of autotrophic microbial methanogenesis (M) are shown in the solid black circles and are consistent with expected values of $\alpha_{\text{DIC-CH}_4}$ versus $\alpha_{\text{H}_2\text{O-CH}_4}$ for CO_2 reduction. In contrast the gases with a dominant or large component of a proposed abiogenic end-member (A) are indicated in black and gray squares and have small $\alpha_{\text{DIC-CH}_4}$ values and very large $\alpha_{\text{H}_2\text{O-CH}_4}$ values inconsistent with what has been previously reported for any known pathway for microbial methanogenesis. If values of $\alpha_{\text{DIC-CH}_4}$ are converted to $\alpha_{\text{CO}_2(\text{g})-\text{CH}_4}$ by incorporating pH, DIC speciation and fractionation associated with speciation of DIC, the values of α_{C} are even smaller but by an amount less than the plotted symbols, so measured $\delta^{13}\text{C}_{\text{DIC}}$ values were used to calculate α_{C} rather than corrected $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$.

interpretation, all gas samples interpreted as microbial in origin (M, Fig. 1) have α_{C} and α_{H} values that fall within the range determined by Valentine et al. (2004a) for CO_2 reduction, and very close to the range originally suggested by Whiticar et al. (1986) for that pathway (Fig. 6). Hence the microbial end-member in the conceptual model outlined in Fig. 1 is consistent with the literature on carbon and hydrogen isotopic fractionation during microbial methanogenesis via CO_2 reduction (Fig. 6).

3.4. Problem of the A-type end-members

In contrast, α_{C} and α_{H} values for the proposed abiogenic end-members do not fit the frameworks for carbon and hydrogen isotopic fractionation developed for microbial methanogenesis (Fig. 6). Values of α_{C} are very small (1.007 to a maximum of 1.032). While values of dissolved inorganic carbon for these samples are low (typically mg/L), they are not so low as to suggest carbon limitation in the fracture waters, so the small α_{C} values are not attributable to suppression of carbon isotopic fractionation due to quantitative conversion of substrate (DIC) to product (CH_4) (Lin et al., 2006). Valentine et al. (2004a) specifically addressed the issue of carbon and hydrogen isotope fractionation associated with thermophilic CO_2 reduction under excess H_2 conditions—demonstrating that under high H_2 conditions the fractionation between CO_2 (DIC) and resulting CH_4 would be minimized (as low as $\alpha_{\text{C}} = 1.023$; Fig. 6). That study also demonstrated that excess H_2 conditions would produce the smallest α_{H} fractionation however (as low as 1.16; Fig. 6), due to enzymatically-mediated hydrogen isotope exchange between H_2O

and H_2 under excess H_2 conditions. Hence this mechanism cannot account for the A-type end-members in Fig. 6, since samples with the lowest α_{C} are in fact associated with the largest α_{H} values—the opposite relationship to that predicted by Valentine et al. (2004a). Similarly, while a range of α_{C} values have been reported for the aceticlastic reaction pathway, from a low of 1.007 for thermophiles to a high of 1.079 for methylotrophic methanogenesis (Valentine et al., 2004a and references cited therein), again no other studies have reported corresponding α_{H} values for aceticlastic methanogenesis as large as the values observed for these Precambrian Shield end-members.

The only study to our knowledge to demonstrate α_{H} values as large as the A-type group in Fig. 6 were Balabane et al. (1987) who reported a similar range of α_{H} values for CO_2 reduction experiments with a pure culture mesophilic autotrophic methanogen (*Methanobacterium formicium*) (Fig. 6). The corresponding α_{C} values were also large however (Fig. 6) and most importantly, the mechanism invoked to explain these results (enzymatically mediated H isotope exchange due to the high ambient H_2 levels (80%) in the study's experiments) has subsequently been shown to have limited importance in systems which are dominated by sulfate reduction (de Graaf et al., 1996; Waldron et al., 1999), such as the Precambrian Shield fracture waters (Baker et al., 2003; Lin et al., 2006; Onstott et al., 2006).

The Precambrian Shield gases pose a unique challenge. For one end-member, all lines of evidence including compositional, isotopic ($\delta^{13}\text{C}$ and $\delta^2\text{H}$ values for CH_4 ; $\alpha_{\text{DIC-CH}_4}$ and $\alpha_{\text{H}_2\text{O-CH}_4}$ values) as well as culture-based and molecular microbiological evidence are consistent with existing expectations for microbial methanogenesis via CO_2 reduction. In

addition, these microbial end-members (M) are found within a particular geological and hydrogeologic context—within the less saline, more shallow paleometeoric waters (Sherwood Lollar et al., 2006, 2007b). Sherwood Lollar et al. (2006) showed that all samples from the Canadian Shield and South Africa fall on both an isotopic ($\delta^{13}\text{C}$ and $\delta^2\text{H}$ for CH_4 ; $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for H_2O) and a geochemical spectrum between these microbial end-members (M) and the non-microbial end-members (A) whose origin is the main subject of this paper. Unlike the microbial end-members, the proposed abiogenic gases do not readily fit any of the existing interpretational frameworks for either microbial or thermogenic gas, and do not appear to be controlled by either thermodynamic or enzymatically-mediated isotopic or chemical equilibrium. One interpretation could be that to date we have not yet as a field discovered the full range of isotopic fractionation effects that microbial communities can achieve. Recent experimental studies with methanogenic communities cited above have certainly established a hitherto unexpected variation in carbon and hydrogen isotope fractionation as a function of environmental parameters, growth phase, metabolic rate, temperature and microbial strains. A theoretical argument could be made that the proposed “abiogenic” end-members in this study are simply the product of a deep subsurface microbial community as yet not well understood and with novel metabolic processes and as yet unrecognized fractionation patterns. While we do not disagree that microbial processes clearly are capable of producing a wide variation in carbon and hydrogen isotopic fractionation patterns, we are not convinced by this argument alone. Given the lack of fit of these non-microbial end-members to all known microbial and thermogenic interpretational frameworks to date, alternative explanations for the compositional and isotopic features of these gases must be examined.

3.5. A model for abiogenic hydrocarbon synthesis via polymerization

3.5.1. Experimental studies to date

To that end, the final objective of this paper is to examine potential abiogenic formation processes. Recent literature has seen a number of different abiogenic hydrocarbon formation processes invoked including Fischer–Tropsch synthesis (Anderson, 1984; Szatmari, 1989; Horita and Berndt, 1999; Foustoukos and Seyfried, 2004; McCollom and Seewald, 2006; Taran et al., 2007; Proskurowski et al., 2008); heating or metamorphism of graphite- or carbonate-bearing rocks (Giardini and Salotti, 1968; Holloway, 1984; Kenney et al., 2002; McCollom, 2003); and other gas–water–rock alteration reactions associated with serpentinization (McCollom and Seewald, 2001; Kelley et al., 2001, 2005; Charlou et al., 2002). In part due to its extensive application in industrial chemical engineering, the most intensively studied processes of abiogenic hydrocarbon formation is the Fischer–Tropsch synthesis (FTS) which proceeds by a combination of polymerization and polycondensation (Anderson, 1984). Isotopic techniques in chemical engineering studies typically involve addition of heavy isotope labeled ^{13}C or ^2H to test reaction mechanisms and hence no detailed set of natural abundance fractionation factors exists that can be applied to interpreta-

tion of natural systems. While the state of knowledge of abiogenic fractionation factors is still limited then compared to what is known about carbon and hydrogen fractionation in microbial methanogenesis for instance, a number of recent experimental studies have begun to address this gap (Szatmari, 1989; Horita and Berndt, 1999; McCollom and Seewald, 2006; Fu et al., 2007; Taran et al., 2007). One major conclusion from this body of research is that abiogenic hydrocarbon formation reactions in general, and FTS specifically, do not always yield declining $\delta^{13}\text{C}$ values for hydrocarbons with increasing molecular weight (Fu et al., 2007; Taran et al., 2007). While the detailed controls on isotopic distribution patterns are still under investigation, the results indicate that both normal carbon isotope trends and inverse carbon isotope trends may be observed as a function of different experimental parameters such as catalysts and conversion ratios. In fact, experimental results from the chemical engineering literature for polymerization chain growth of hydrocarbons suggest that the very rapid reaction rate for polymerization of straight chain alkanes will result in negligible observed isotopic fractionation of the higher hydrocarbon gases (Mims and McCandlish, 1985; Mims and McCandlish, 1987). A recent study also suggested that the uniform $\delta^{13}\text{C}$ values for C_{12} – C_{27} hydrocarbons in abiogenic synthesis experiments, and the close similarity of those values to that of the precursor CH_4 , are also consistent with little or no discernable fractionation during the polymerization step (McCollom and Seewald, 2006).

3.5.2. Abiogenic polymerization model based on overall reaction chemistry

As noted previously, it is an important observation that the proposed abiogenic end-members in this paper have compositions that all fit the type of Schulz–Flory distribution associated with abiogenic synthesis, but while arguably necessary, this is generally considered an insufficient line of evidence. This paper draws on the isotopic experimental literature available to date to further test the hypothesis that the Kidd Creek gases are produced by abiogenic polymerization. While experiments can incorporate real-time analysis to constrain short-lived intermediates, field samples of proposed abiogenic origin will have long since lost their more reactive intermediates and reaction products. While important information can still be derived from the bulk chemical composition of samples from the field, deducing detailed mechanistic models including all intermediary steps and intermediates is likely not possible. Hence, using the observed $\delta^{13}\text{C}$ isotopic variation for the Kidd Creek data set to deduce potential reaction mechanisms consistent with the field observations, a model of isotopic variation during polymerization based on overall reaction chemistry is developed. If the Kidd Creek patterns are not in fact abiogenically-controlled but are produced by a complex combination of fractionation effects associated with secondary alteration processes such as oxidation or diffusion, or with mixing of hydrocarbons from additional thermogenic or microbial sources, then a first approximation model based on overall reaction chemistry for abiogenic polymerization should quickly fail to adequately reproduce the observed isotopic patterns in the Kidd Creek samples. In contrast, if such a

simple model does fit the data, it suggests that in fact abiogenic polymerization reactions are a useful alternative explanation for the Kidd Creek gases. While this is not as perfect an approach as attempting to identify the reaction mechanism responsible for the Kidd Creek gases by comparing observed fractionation factors to published values in the literature for all the different proposed abiogenic reaction mechanisms, until those fractionation factors become available, it is a reasonable first step.

While early experiments indicated that abiogenic production of hydrocarbons results in ethane that is isotopically depleted with respect to CH₄ from which it is formed (Des Marais et al., 1981), more recent experiments suggest this is not always the case and the extent of fractionation between CH₄ and ethane may vary as a function of the specific abiogenic formation mechanisms and reaction parameters such as catalysts or conversion ratios (McCullom and Seewald, 2006; Fu et al., 2007; Taran et al., 2007). For the Kidd Creek samples, the extent of fractionation observed between ethane and methane is very similar (Fig. 2a). Values of δ¹³C for ethane are more depleted than those of methane, with fractionation factors ranging from 0.9958 to 0.9975, and a mean fractionation factor (α) value for the sample set of 0.9967 ± 0.0006. This suggests then that if ethane is indeed formed by abiogenic polymerization of methane monomers, then this initial polymerization step is represented by a value of α = 0.9967 (Eq. (3), Table 2).

Unlike the Des Marais et al. (1981) data set, δ¹³C values for propane for Kidd Creek are more enriched in ¹³C with respect to ethane (Fig. 2a). This pattern is consistent with the literature that indicates that a very rapid reaction rate for polymerization of straight chain alkanes means observed fractionation in this step is negligible (Mims and McCandlish, 1985; Mims and McCandlish, 1987) and the δ¹³C value of propane can be related to the δ¹³C of the reactants methane and ethane by a simple overall mass balance reaction expressed in Eq. (4) (Table 2). Fig. 7 shows that although there is some divergence in the details for individual samples, starting with the measured δ¹³C_{CH₄} values for the Kidd Creek samples, the δ¹³C values for ethane and propane calculated via model Eqs. (3) and (4) (Table 2) yield a good fit to the measured data set.

Continuing to apply this model to production of *n*-C4 alkanes is more complex as several possible reactions could contribute to butane formation. Based on the measured data, reactions involving addition of two ethane molecules can be neglected because addition of two ¹³C-depleted ethanes cannot account for the ¹³C-enriched *n*-C4 observed for the Kidd Creek data (Fig. 2a). If however CH₄ and propane are assumed to be the main bulk reactants producing *n*-C4, and net observed fractionation associated with the rapid polymerization step is negligible as suggested by the literature (Mims and McCandlish, 1985; Mims and McCandlish, 1987), the δ¹³C values for *n*-C4 can be described by Eq. (5) (Table 2). Using the simplest assumptions for *n*-C5 formation, by straight chain polymerization from methane and *n*-C4, and again negligible fractionation due to rapid polymerization, the δ¹³C *n*-C5 can be described by Eq. (6) (Table 2). As Fig. 7 shows, the calculated δ¹³C values based on this model show a continued enrichment trend, and the calculated values for *n*-C4 closely approximate measured values. The calculated values from this model for *n*-C5 are not as enriched as the measured δ¹³C *n*-C5 values however. Given the increasing complexity of possible reaction mechanisms for *n*-C5 (i.e. methane plus *n*-C5; ethane plus propane addition, etc.) as well as the possible formation of cyclo-pentane or neo-pentane in addition to *n*-C5 and *iso*-C5, it is perhaps not surprising that the simple straight chain polymerization mass balance model breaks down at this point. The fact that such a simple model seems to approximate the measured δ¹³C values for CH₄-*n*-C4 so well however lends support for an abiogenic origin for these hydrocarbons. If any other of the other alternative processes of hydrocarbon formation (microbial, thermogenic) or complicating factors such as secondary alteration processes (oxidation, diffusion or mixing) were a significant factor at Kidd Creek, then this very simple approach should indicate that by quickly failing to reproduce the observed data.

Unlike formation of the straight chain alkanes, formation of the branched alkanes appears, like formation of ethane from CH₄, to involve a substantial carbon isotope fractionation. Abiogenic formation of *iso*-C4 and *iso*-C5 can proceed by a wide variety of different reaction pathways including both direct reaction of CH₄, ethane and propane,

Table 2
Model for carbon isotope variation between methane and higher hydrocarbons due to abiogenic polymerization

Step	Overall reaction	Hypothesis for fractionation
Ethane formation	$\text{CH}_4 + \text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$ $\delta^{13}\text{C}_{\text{C}_2\text{H}_6} = 1000 \ln \alpha + \delta^{13}\text{C}_{\text{CH}_4}$ where α = 0.9967	(3) C isotope depletion due to C addition; H isotope enrichment due to H elimination
Propane formation	$\text{CH}_4 + \text{C}_2\text{H}_6 \rightarrow \text{C}_3\text{H}_8 + \text{H}_2$ $\delta^{13}\text{C}_{\text{C}_3\text{H}_8} = 0.33\delta^{13}\text{C}_{\text{CH}_4} + 0.66\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$	(4) Negligible fractionation. Isotopic signature dominated by simple isotopic mass balance
<i>n</i> -Butane formation	$\text{CH}_4 + \text{C}_3\text{H}_6 \rightarrow \textit{n}\text{-C}_4\text{H}_{10} + \text{H}_2$ $\delta^{13}\text{C}_{\textit{n}\text{-C}_4\text{H}_{10}} = 0.25\delta^{13}\text{C}_{\text{CH}_4} + 0.75\delta^{13}\text{C}_{\text{C}_3\text{H}_6}$	(5) Negligible fractionation. Isotopic signature dominated by simple isotopic mass balance
<i>n</i> -Pentane formation	$\text{CH}_4 + \textit{n}\text{-C}_4\text{H}_{10} \rightarrow \textit{n}\text{-C}_5\text{H}_{12} + \text{H}_2$ $\delta^{13}\text{C}_{\textit{n}\text{-C}_5\text{H}_{12}} = 0.2\delta^{13}\text{C}_{\text{CH}_4} + 0.8\delta^{13}\text{C}_{\textit{n}\text{-C}_4\text{H}_{10}}$	(6) Negligible fractionation. Isotopic signature dominated by simple isotopic mass balance

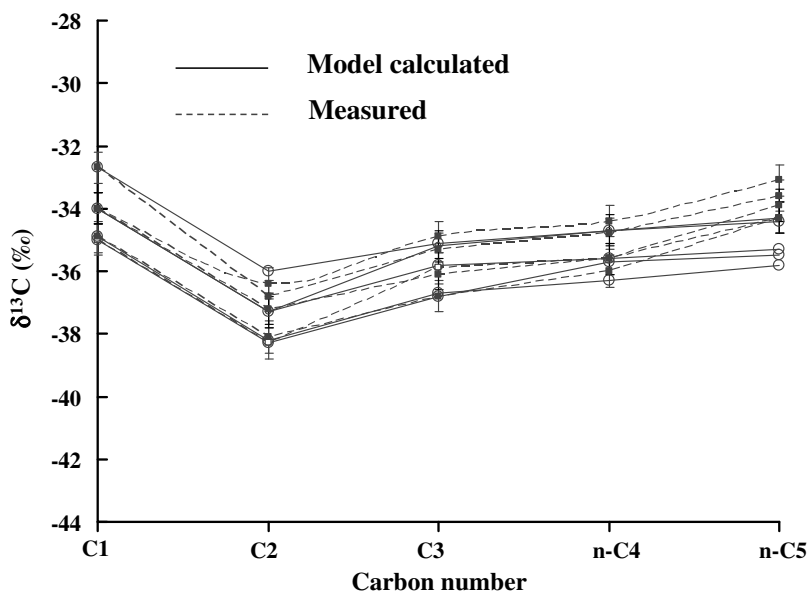


Fig. 7. Measured carbon isotope values (black squares and dotted lines) plotted versus carbon number for the straight chain alkanes—methane (C1), ethane (C2), propane (C3), *n*-butane (*n*-C4) and *n*-pentane (*n*-C5) for Kidd Creek gases. Errors are $\pm 0.5\text{‰}$ for $\delta^{13}\text{C}$ values. Carbon isotope values calculated based on the polymerization model equations in Table 2 are shown as open circles and solid lines. The model reproduces the C1–C2 depletion trend and C2–C5 enrichment trend in ^{13}C for straight chain alkanes, although the calculated $\delta^{13}\text{C}$ values for *n*-C5 are more depleted in ^{13}C than measured values (see text).

as well as formation of the branched isomers from the straight chain alkanes (Anderson, 1984; Mims and McCandlish, 1985; Mims and McCandlish, 1987). The significant ^{13}C -depletion in the *iso*-C4 and *iso*-C5 forms versus the straight chain alkanes may suggest formation of the branched isomers from *n*-C4 and *n*-C5.

3.6. Sensitivity of the abiogenic polymerization model

For each sample, the values of $\delta^{13}\text{C}$ calculated for C2, C3 and *n*-C4 by the model in Table 2 are within analytical uncertainty of the measured values ($\pm 0.5\text{‰}$ or $(\delta^{13}\text{C}_{\text{calculated}} - \delta^{13}\text{C}_{\text{measured}}) < 1\text{‰}$) (Fig. 7). This is illustrated in Fig. 8 by the hatched line which shows that 100% of the calculated values agree within 1‰ of the measured values, and in fact 80% of the calculated values from the model agree within 0.3‰ of the measured values. Fig. 8 demonstrates that the model is quite sensitive. If one assumes a change (Δ) in the input parameter of $\delta^{13}\text{C}_{\text{CH}_4}$ of as little as 0.5–1‰ in the direction of either more ^{13}C -enrichment or ^{13}C -depletion, the % of the calculated values for $\delta^{13}\text{C}$ for C2, C3 and *n*-C4 that agree with the measured values within analytical uncertainty drops significantly and the % that agree within 0.3‰ drops to 30–40%. This sensitivity analysis further underscores that if any other complicating factor such as thermogenic or microbial methanogenesis, additional fractionating processes such as oxidation and in particular any mixing of CH_4 from different sources were an important factor for the Kidd Creek samples, this simple model based on mass balance assumptions for rapid polymerization should fail to show a good agreement with the measured values.

Sherwood Lollar et al. (2006) suggested that the abiogenic hydrocarbons first identified at Kidd Creek could also be identified at a number of other Precambrian Shield sites in both Canada and South Africa. While many of the boreholes at these sites contained a component of microbially produced methane as well as proposed abiogenic hydrocarbons, the degree of mixing between these two sources of methane were estimated, and abiogenic end-members (where a microbial CH_4 component was estimated to be negligible) postulated at five sites based on $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values for methane, $\text{CH}_4/\text{C}_{2+}$ ratios and a correlation of ^{13}C -enriched and ^2H -depleted abiogenic end-members with high concentrations of H_2 gas (Sherwood Lollar et al., 2006). For seven samples from four different sites (Copper Cliff South, in Sudbury Canada and Driefontein, Kloof and Mponeng mines in South Africa) identified as abiogenic end-members (dark and gray squares in Fig. 1) (Sherwood Lollar et al., 2006), $\delta^{13}\text{C}$ values for the hydrocarbon gases are shown in Fig. 9a and b. Using the measured $\delta^{13}\text{C}$ CH_4 values for each of these samples, and the model developed in the present paper, $\delta^{13}\text{C}$ values for C2 were calculated via Eq. (3) and $\delta^{13}\text{C}$ values for C3 and *n*-C4 via Eqs. (4) and (5), respectively (Table 2). Fig. 9a shows that the model reproduces the overall pattern of carbon isotope variation between the homologs and provides a good approximation of the measured values for six of the seven samples. There is no obvious explanation for why the fit for the seventh sample (Fig. 9) is not as good as the other samples, but it is notable that for all other samples from these two Canadian Precambrian Shield sites (Kidd Creek in Timmins Ontario, Copper Cliff South in Sudbury, Ontario) and three South African Precambrian Shield sites,

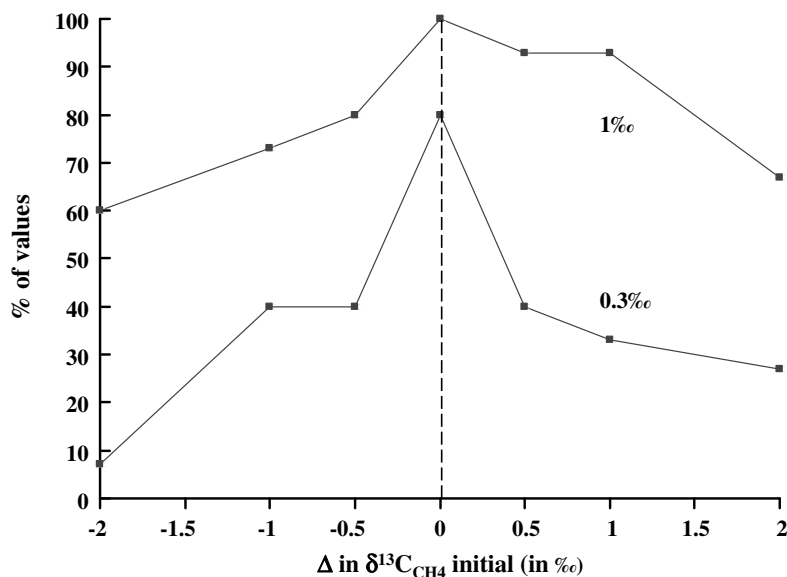


Fig. 8. Sensitivity of the model calculated values to changes in initial value parameter $\delta^{13}\text{C}_{\text{CH}_4}$ for methane. When $\delta^{13}\text{C}_{\text{CH}_4}$ is equal to the measured value ($\Delta = 0$), 100% of model calculated $\delta^{13}\text{C}$ values for C2, C3 and *n*-C4 for all samples are within 1‰ of the measured values ($\delta^{13}\text{C}_{\text{calculated}} - \delta^{13}\text{C}_{\text{measured}} < 1\text{‰}$) (see text). If Δ changes by as little as 0.5–1‰ in the direction of either more ^{13}C -enrichment or ^{13}C -depletion as would be the case if the primary methane isotope value was affected by mixing of gases from different sources or secondary fractionation processes, the percentage of calculated values which are in agreement with the measured values decreases significantly.

the patterns of isotopic fractionation between the hydrocarbon gases are consistent. The fit of this model to the observed data reinforces the evidence that production of hydrocarbons by abiogenic polymerization reactions may be a phenomenon common to Precambrian Shield crystalline rock environments.

3.7. Implications for developing criteria for abiogenic gases

The abiogenic hydrocarbon gas seen at the Precambrian Shield sites examined in this paper (Kidd Creek, Copper Cliff South, Kloof, Driefontein and Mponeng) all show consistency in the degree of isotopic discrimination between $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{C}_2}$, with a combined isotopic fractionation factor for all five sites of $\alpha = 0.9967$ yielding a good approximation of the measured values. While this approach suggests this fractionation may be characteristic of the underlying polymerization reaction at these specific sites, under different geochemical conditions the extent of fractionation in this first, most highly fractionating step will likely be different. While the model suggests that for abiogenic hydrocarbons produced by polymerization, the $\delta^{13}\text{C}$ value of ethane will be more depleted in ^{13}C than that of the CH_4 precursor (Des Marais et al., 1981; Sherwood Lollar et al., 2002) and the $\delta^2\text{H}$ more enriched in ^2H (Sherwood Lollar et al., 2002), the specific extent of the fractionation between methane and ethane will likely vary as a function of different reaction mechanisms and parameters such as catalysts or conversion ratio (McCullom and Seewald, 2006; Taran et al., 2007). In contrast, for the higher hydrocarbons, the rapid rate of chain polymerization is such that any net isotopic fractionation associated with subsequent carbon addition steps is negligible and suggests that the $\delta^{13}\text{C}$ values of ethane, propane and higher straight

chain alkanes may be predicted by simple mass balance from the $\delta^{13}\text{C}$ values of the lower molecular weight precursors, independent of the fractionation associated with the first step. This model suggests this pattern may be an important criteria for identifying abiogenic hydrocarbons whether in terrestrial and non-terrestrial systems.

3.8. Hydrogen isotope distribution patterns

Available literature on hydrogen isotope fractionation factors for abiogenic reactions are even more scarce than those for carbon isotope effects, making detailed mechanistic interpretations based on $\delta^2\text{H}$ values from field samples difficult. Nonetheless, two important observations can be made based on the $\delta^2\text{H}$ isotope values for the gases in this paper. The first is that, like the carbon isotope fractionation patterns between CH_4 and the higher hydrocarbon gases, the hydrogen isotope patterns are remarkably consistent not only within the Kidd Creek sample set but for all five Precambrian Shield sites examined in this paper (Table 3). If the apparent fractionation factors between CH_4 , ethane and propane are calculated, the mean $\alpha_{\text{CH}_4-\text{C}_2}$ value is $0.869 \pm 0.022\text{‰}$ —a tight range for such a large set of samples. Similarly, the values of $\alpha_{\text{CH}_4-\text{C}_3}$ and $\alpha_{\text{C}_2-\text{C}_3}$ are tightly constrained—with mean values of $0.753 \pm 0.087\text{‰}$, and $0.866 \pm 0.098\text{‰}$, respectively (Table 3). Since these $\delta^2\text{H}$ values are not controlled by chemical or isotopic equilibrium as shown earlier, this uniformity may possibly reflect intrinsic kinetic isotope effects associated with the hydrocarbon formation mechanism. Second, $\delta^2\text{H}$ isotope values for CH_4 –ethane–propane (butane and pentane were present at concentrations too low for hydrogen isotope analysis) show a consistent trend of isotopic enrichment in ^2H with increasing molecular weight as originally identified in

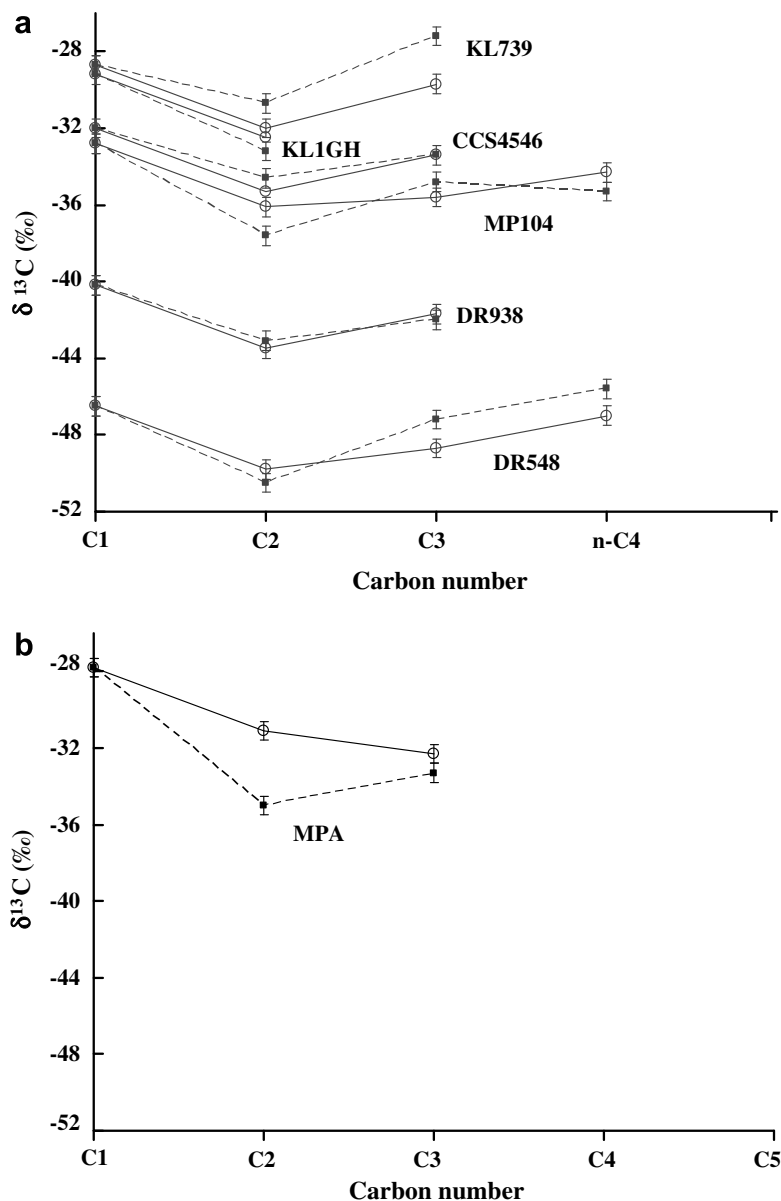


Fig. 9. (a) Calculated values $\delta^{13}\text{C}$ for hydrocarbons based on the polymerization model (shown as open circles and solid lines) are compared to measured data (black squares and dotted lines) for additional four sites in Precambrian Shield rocks in Canada and South Africa where proposed abiogenic end-members have been identified. Measured data from Sherwood Lollar et al. (2006). Errors are $\pm 0.5\text{‰}$ for $\delta^{13}\text{C}$ values. (b) Of the seven abiogenic end-member gases proposed in Sherwood Lollar et al. (2006) only one was not adequately reproduced by the model.

Sherwood Lollar et al. (2002). Such an isotopic enrichment trend is consistent with the preferential loss of ^1H involved in elimination of hydrogen atoms at each step of polymerization. While interpretation of the hydrogen isotope data is speculative until more experimental data can be generated, this initial data is nonetheless consistent with a polymerization hypothesis.

4. CONCLUSIONS

Research on the origin and evolution of life on earth and the potential for past life on Mars or elsewhere in the solar system has rapidly advanced the field of biosignature research as the role of fossil, chemical and isotopic

biomarkers and biomineralization features have been explored as potential diagnostic indicators of extinct or extant life. A necessary, though underexploited corollary is the development of abiosignature research to define diagnostic parameters that can reliably identify systems dominated by non-biological processes. As with the field of biosignature research, there is unlikely to be one definitive test for abiogenicity. Given the variety of possible reactions for synthesizing abiogenic hydrocarbons, there may be different compositional and isotopic characteristics for hydrocarbons produced by polymerization or by Fischer–Tropsch synthesis under different conditions or in the presence of different catalysts (Szatmari, 1989; Horita and Berndt, 1999; Foustoukos and Seyfried, 2004; McCollom and

Table 3

Apparent hydrogen isotopic fractionation factors between CH₄, ethane (C₂H₆) and propane (C₃H₈) where $\alpha = (1000 + \delta_A) / (1000 + \delta_B)$

Sample	$\alpha_{\text{CH}_4\text{-C}_2\text{H}_6}$	$\alpha_{\text{CH}_4\text{-C}_3\text{H}_8}$	$\alpha_{\text{C}_2\text{H}_6\text{-C}_3\text{H}_8}$
KC8558	0.856	0.789	0.923
KC8428	0.857	0.797	0.930
KC8282	0.864	0.808	0.936
KC8402	0.872	0.810	0.929
KC8539	0.857	0.799	0.932
MP104	0.868	0.786	0.905
MPA	0.888	0.826	0.930
KL739	0.909	0.816	0.897
KL1GH	0.894	0.688	0.770
CCS4546	0.840	0.548	0.652
DR938H3-0m	0.890	0.632	0.710
DR548	0.835	0.739	0.885
Mean KC samples	0.861	0.801	0.930
Std. Dev.	0.007	0.009	0.005
Mean all samples	0.869	0.753	0.866
Std. Dev.	0.022	0.087	0.098

Kidd Creek $\delta^2\text{H}$ values for the hydrocarbon gases from Sherwood Lollar et al. (2002). All other $\delta^2\text{H}$ values for the hydrocarbon gases from Sherwood Lollar et al. (2006).

Seewald, 2006; Fu et al., 2007; Taran et al., 2007), or by different reactions such as metamorphism of carbonates (McCullom, 2003), or other gas-water-rock reactions associated with serpentinization (Abrajano et al., 1990; McCullom and Seewald, 2001; Kelley et al., 2001, 2005) for instance. Nonetheless the model proposed in this paper provides what we believe is an important step forward in this process, as to our knowledge it is the first model to propose an explanation for $\delta^{13}\text{C}$ variation step by step in a hydrocarbon reaction chain for abiogenic polymerization of higher molecular weight hydrocarbons and to demonstrate the fit of such a model to field samples for which an abiogenic origin has been proposed. Future progress in biosignature and abiosignature research will require similar tests of models of abiogenic isotopic fractionation if we are to definitively distinguish non-biological processes from the signatures of extinct and extant life both on earth and elsewhere in the solar system.

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