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Abiogenic formation of alkanes in the Earth's crust as a minor source for global hydrocarbon reservoirs

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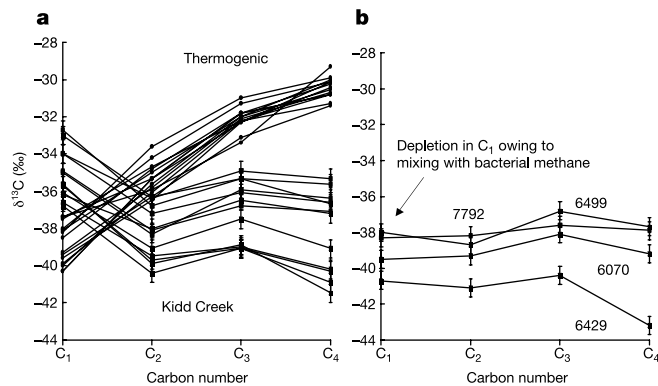*Stable Isotope Laboratory, University of Toronto, Toronto, Ontario, Canada M5S 3B1*

Figure 1 Plot of $\delta^{13}C$ values of individual *n*-alkanes against carbon number for gas samples from Kidd Creek mine, and for thermogenic gases from southwest Ontario natural-gas fields[29]. Error bars on all $\delta^{13}C$ values are ±0.5‰. **a**, Of 17 boreholes, 13 show a trend of ^{13}C depletion in $C_2–C_4$ with respect to C_1 (see text). **b**, For 4 of the 17 boreholes sampled at Kidd Creek, although the isotopic distribution still does not fit a typical thermogenic pattern, $\delta^{13}C_{C2}$ is within error of $\delta^{13}C_{C1}$, rather than depleted with respect to C_1. This is probably due to mixing of a Kidd Creek gas similar to those plotted in **a** with a component of bacterial methane such as reported in refs 18 and 19. For 8 of the 17 boreholes sampled in this study, time series data were collected over a period of 8–19 months. The isotopic compositions of $C_1–C_4$ alkanes for 7 of the boreholes are constant over time[30]. For the 6070 borehole however, a small increase in the $C_1/(C_2 + C_3)$ ratio and an isotopic depletion of 2.2‰ was observed for $\delta^{13}C_{C1}$ over the 19-month period after its completion, consistent with addition of 10–25% bacterial methane (based on typical compositional and isotopic values for bacterial gases[16]). Such a phenomenon could account for the fact that for this sample, $\delta^{13}C_{C1}$ is within error of $\delta^{13}C_{C2}$ rather than significantly enriched with respect to $C_2–C_4$ as in the majority of the samples. No time series data are available for boreholes 6499, 6429 and 7792 as they were only sampled once, but they may reflect the same phenomenon. Certainly, whereas the 5 other boreholes from the 6,900-foot level have very similar $\delta^{13}C$ and δ^2H values for C_1 (mean of 5 samples; $\delta^{13}C = -34.1 \pm 0.9$‰ and $\delta^2H = -413 \pm 5$‰), the isotopic values for C_1 from borehole 7792 are considerably more depleted in ^{13}C (-38.3‰) and enriched in ^2H (-390‰), consistent with mixing with a bacterial methane end-member (Table 1).

Natural hydrocarbons are largely formed by the thermal decomposition of organic matter (thermogenesis) or by microbial processes (bacteriogenesis). But the discovery of methane at an East Pacific Rise hydrothermal vent[1] and in other crustal fluids supports the occurrence of an abiogenic source of hydrocarbons[2–4]. These abiogenic hydrocarbons are generally formed by the reduction of carbon dioxide, a process which is thought to occur during magma cooling[5] and—more commonly—in hydrothermal systems during water–rock interactions, for example involving Fischer–Tropsch reactions and the serpentinization of ultramafic rocks[6–10]. Suggestions that abiogenic hydrocarbons make a significant contribution to economic hydrocarbon reservoirs[2] have been difficult to resolve, in part owing to uncertainty in the carbon isotopic signatures for abiogenic versus thermogenic hydrocarbons[4,10]. Here, using carbon and hydrogen isotope analyses of abiogenic methane and higher hydrocarbons in crystalline rocks of the Canadian shield, we show a clear distinction between abiogenic and thermogenic hydrocarbons. The progressive isotopic trends for the series of $C_1–C_4$ alkanes indicate that hydrocarbon formation occurs by way of polymerization of methane precursors. Given that these trends are not observed in the isotopic signatures of economic gas reservoirs, we can now rule out the presence of a globally significant abiogenic source of hydrocarbons.

Large volumes of methane gas discharge from fractures and exploration boreholes in hard rock mines operating throughout the Canadian and Fennoscandian shields. An abiogenic origin through water–rock interaction was proposed for these gases on the basis of $\delta^{13}C$ and δ^2H signatures for methane incompatible with bacterial or thermogenic methane[11]. Recent experimental studies[10,12,13] confirm that production of abiogenic methane by water–rock interaction can result in $\delta^{13}C$ values as depleted as those reported for methane from the above shields (-22.4‰ to -57.5‰)[11]. Nonetheless, the evidence for an abiogenic origin for these shield gases was hitherto largely circumstan-

tial. In this study, the unusual pattern of $\delta^{13}C$ values among the $C_1–C_4$ alkanes provides evidence of abiogenic formation mechanisms (Table 1; Fig. 1a). Thermogenic hydrocarbons have been shown empirically and experimentally to have a characteristic isotope distribution pattern whereby the $C_1–C_4$ alkanes become more enriched in ^{13}C (less negative $\delta^{13}C$ values) with increasing molecular mass. This orderly isotopic distribution results from kinetic fractionation effects, whereby alkyl groups separating from source organic matter cleave preferentially at weaker $^{12}C–^{12}C$ rather

Table 1 Carbon and hydrogen isotopic values for $C_1–C_4$ hydrocarbon gases

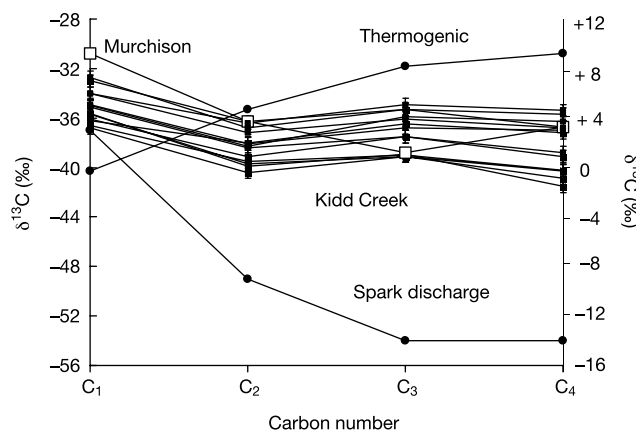| Borehole	$\delta^{13}C_{C1}$	δ^2H_{C1}	$\delta^{13}C_{C2}$	δ^2H_{C2}	$\delta^{13}C_{C3}$	δ^2H_{C3}	$\delta^{13}C_{C4}$	δ^2H_{C4}
6070	−39.5	NA	−39.3	NA	−38.1	NA	−39.2	NA
6080	−35.1	NA	−38.4	NA	−37.5	NA	−38.8	NA
6448	−33.0	NA	−36.3	NA	−35.3	NA	−36.7	NA
6499	−38.0	NA	−38.7	NA	−36.8	NA	−37.7	NA
6500A	−36.2	NA	−38.0	NA	−36.5	NA	−37.2	NA
6447	−35.6	NA	−39.9	NA	−38.9	NA	−41.5	NA
6500B	−36.1	NA	−39.1	NA	−37.5	NA	−39.1	NA
6298	−36.8	NA	−40.4	NA	−39.1	NA	−40.3	NA
6300	−35.7	NA	−39.7	NA	−39.1	NA	−40.9	NA
6429	−40.7	NA	−41.1	NA	−40.4	NA	−43.2	NA
6299	−36.6	NA	−39.5	NA	−39.0	NA	−40.2	NA
7792	−38.3	−390	−38.2	−299	−37.6	−256	−37.9	−224
8558	−32.7	−419	−36.8	−321	−35.3	−264	−35.7	−245
8428	−34.0	−412	−36.4	−314	−34.9	−262	−35.4	−236
8282	−35.0	−409	−38.3	−316	−35.9	−269	−36.3	−252
8402	−34.9	−406	−38.1	−319	−36.8	−267	−37.0	−234
8539	−34.0	−417	−37.2	−320	−36.1	−270	−36.8	−256

All values in ‰. NA, not analysed (see Methods).

Figure 2 Plot of $\delta^{13}C$ values of individual *n*-alkanes against carbon number. $\delta^{13}C_{C4}$ values include both iso- and *n*-butane. Error bars on $\delta^{13}C$ values for Kidd Creek samples are $\pm 0.5‰$. The isotopic pattern of C_1-C_4 *n*-alkanes for the Kidd Creek samples (filled squares, left *y* axis) are compared to the isotopic pattern for *n*-alkanes from the Murchison meteorite (open squares, right *y* axis). $\delta^{13}C$ values (circles, left *y* axis) for spark discharge experiments and thermogenic gas are from refs 14 and 29, respectively.

Figure 3 Plot of $\delta^{13}C$ versus δ^2H values for C_1-C_4 for the Kidd Creek samples, and for thermogenic gases from southwest Ontario natural-gas fields[29]. Error bars on Kidd Creek $\delta^{13}C$ values are $\pm 0.5‰$. Error bars on δ^2H values are $\pm 5‰$.

than $^{12}C-^{13}C$ bonds[14]. This isotopic distribution pattern is ubiquitous among thermogenically derived gases, and is considered to be diagnostic of gases produced by the thermal decomposition of high-molecular-mass organic matter.

In contrast, Fig. 1a shows a significant depletion in ^{13}C for C_2-C_4 with respect to C_1 for hydrocarbon gases from the Kidd Creek mine on the Canadian shield. For 13 of the 17 samples in this study, C_2 is significantly depleted in ^{13}C (by 2–4‰) with respect to C_1 (Fig. 1a). C_3 and C_4 are also isotopically depleted in ^{13}C compared to C_1 by 1–3‰ and by 1–6‰, respectively. No post-genetic alteration of typical thermogenic gas is known that could produce an isotopic enrichment in C_1 of the order of 10‰, and a simultaneous isotopic depletion in C_3 and C_4 relative to C_2, to produce the pattern exhibited by the Kidd Creek gases[15–17]. Although methanogenic bacteria have been identified in the ground waters of the Kidd Creek mine[18,19], addition of an isotopically depleted bacterial methane to the borehole gases would only reduce the C_1 enrichment observed in Fig. 1a and cannot account for the observed isotopic enrichment of C_1 relative to the higher-molecular-mass alkanes (Fig. 1b). A bacterial origin overall for the C_1-C_4 gases is ruled out on the basis of C_1/C_2+ ratios between 5.10 and 11.51, 2–4 orders of magnitude lower than for typical bacterial gas[16].

Natural occurrences of hydrocarbon gas exhibiting isotopic depletion in C_2-C_4 compared to C_1 are rare. Reported occurrences in the field include: C_1-C_3 hydrocarbons in two gas samples from fluid inclusions associated with the Khibiny massif on the Kola peninsula, Russia[20]; and C_1-C_2 hydrocarbons from six gas samples from fluid inclusions associated with the Ilimaussaq complex, South Greenland[21,22]. Unfortunately, none of these studies were able to obtain a significant number of $\delta^{13}C$ values for homologues higher than C_2. As apparent isotopic depletion of C_2 versus C_1 can occur owing to bacterial oxidation of methane, conclusive evidence of isotopic depletion of higher hydrocarbons with respect to C_1 requires comparison to a larger range of higher hydrocarbons, particularly C_3 and C_4. Only one isotopic data set exists for C_1-C_4 alkanes of undisputed abiogenic origin. Values of $\delta^{13}C$ obtained for C_2-C_4 *n*-alkanes for the Murchison meteorite show an isotopic depletion of 5–8‰ with respect to C_1 (Fig. 2). The absolute $\delta^{13}C$ values of the hydrocarbons from this meteorite are significantly more enriched in ^{13}C than the Kidd Creek samples, reflecting their extraterrestrial origin. Nonetheless, the Murchison and Kidd Creek samples show remarkable similarities in the isotopic distribution pattern between the C_1-C_4 *n*-alkanes (Fig. 2). Although C_3 in the
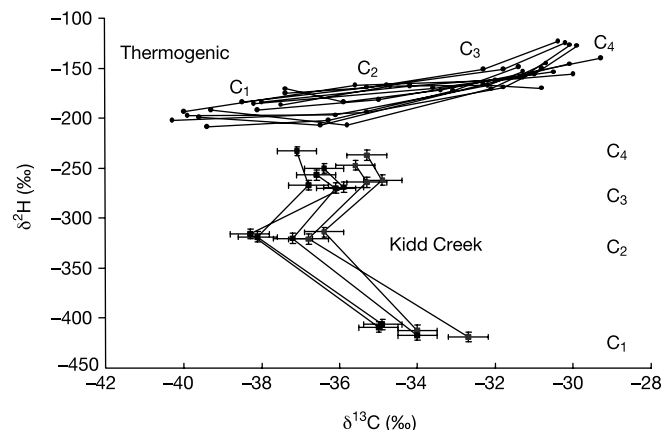
Murchison sample is more depleted relative to C_2 and C_4 than for the Kidd Creek samples, both sample sets show (1) significant depletion in $\delta^{13}C$ values of C_2-C_4 versus C_1, and (2) an isotopic pattern for C_1-C_4 alkanes distinctly different from the typical pattern for thermogenic gases.

Such depletion patterns in C_2-C_4 alkanes relative to C_1 have been shown to be produced by polymerization reactions, such as production of higher hydrocarbons from methane in a spark discharge experiment[14] (Fig. 2). This pattern results during kinetically controlled synthesis of higher-molecular-mass homologues from lower ones owing to the fact that $^{12}CH_4$ reacts faster than $^{13}CH_4$ to form chains, so that ^{12}C is more likely to be incorporated into larger hydrocarbon chains[14,23]. In other abiogenic polymerization reactions such as the Fischer–Tropsch synthesis, C_2-C_4 hydrocarbons produced from CO and H_2 are also isotopically depleted with respect to C_1, but the pattern of isotopic reversal ($\delta^{13}C_{C1} > \delta^{13}C_{C2} > \delta^{13}C_{C3} = \delta^{13}C_{C4}$) is not always as consistent as for the spark discharge experiment[12,13]. Experimental results to date certainly show that whether by spark discharge or Fischer–Tropsch synthesis, hydrocarbons produced by abiogenic polymerization reactions do not show the isotopic enrichment trends for C_1-C_4 typical of thermogenic gases. So although the $\delta^{13}C$ pattern between C_3 and C_4 in the Murchison sample is not identical to the spark discharge experimental results, a similar abiogenic polymerization reaction has been invoked[23] to explain the overall C_2-C_4 isotopic depletion pattern for the Murchison meteorite *n*-alkanes. For the Kidd Creek samples, the pronounced isotopic depletion of C_2-C_4, and the lack of a thermogenic-type enrichment trend for C_1-C_4 are as consistent with kinetically controlled polymerization reactions as the Murchison *n*-alkanes. Potential mechanisms for abiogenic gas synthesis in this geologic environment include: surface-catalysed polymerization from reduction of CO in the Fischer–Tropsch synthesis[24]; heating or metamorphism of graphite–carbonate-bearing rocks[25,26]; or other vapour–water–rock alteration reactions in the presence of catalytically active metals[27]. Confirmation of the exact mechanisms in natural systems will be dependent on constraining possible reactions with additional experimental data. Regardless of the specific mechanism, the Kidd Creek gases are (to our knowledge) the first reported terrestrial samples to demonstrate this consistent depletion of C_2-C_4 with respect to C_1 indicative of abiogenic formation reactions.

The δ^2H values for the Kidd Creek hydrocarbon gases provide additional support for an abiogenic origin. Figure 3 illustrates the positive correlation of $\delta^{13}C$ and δ^2H values that is an established pattern for thermogenic gas reservoirs worldwide, due to increasing isotopic enrichment in both ^{13}C and ^2H with increasing molecular

mass for the C_1-C_4 homologues[16]. In contrast, both the isotopically depleted absolute δ^2H values, and the relationship between $\delta^{13}C$ and δ^2H values for the Kidd Creek C_1-C_4 alkanes, are distinctly different from those of thermogenic gas. In particular, the inverse correlation of $\delta^{13}C$ and δ^2H values between C_1 and C_2 supports the participation of these compounds in an abiogenic polymerization reaction. It has been proposed[14] that in a kinetically controlled synthesis of higher-molecular-mass homologues from lower ones, the lighter isotope (^{12}C) will react faster than the heavy isotope (^{13}C) to form a 2-carbon chain. ^{12}C would be more likely to be incorporated into the product of the carbon addition reaction, and the resulting ethane would be depleted in ^{13}C versus the methane precursor. By analogy, owing to preferential cleavage of the weaker $^{12}C-^1H$ bond versus the $^{12}C-^2H$ bond, the light (^1H) isotope would be preferentially eliminated in a polymerization reaction. Hence, the resulting ethane would be expected to be isotopically enriched in ^2H, and isotopically depleted in ^{13}C, with respect to the methane precursor. This inverse relationship of ^{13}C isotope depletion and ^2H isotope enrichment between C_1 and C_2 for the Kidd Creek samples (Fig. 3) supports a polymerization reaction as the first step in the formation of the Kidd Creek higher hydrocarbons from a methane precursor.

The distinct carbon isotopic depletion trends observed for the Kidd Creek gases, and their similarity to the trends observed for the Murchison meteorite n-alkanes, provides evidence for production of these Canadian shield gases by abiogenic synthesis rather than by conventional thermogenic or bacteriogenic processes (Fig. 2). The pattern of ^{13}C isotopic depletion and ^2H enrichment between C_1 and C_2 in the Kidd Creek gases (Fig. 3) fits a model of isotopic fractionation involving hydrocarbon formation by kinetically controlled polymerization reactions. This study demonstrates that abiogenic processes that may have generated prebiotic organic molecules in the early Earth continued to play a significant role in the production of hydrocarbons in the crystalline rocks of the Canadian shield. The contrasting range of δ^2H values, and the markedly different relationship of $\delta^{13}C$ and δ^2H values demonstrated for abiogenic C_1-C_4 compared to thermogenic natural-gas reservoirs provide important criteria for distinguishing between these two sources. Based on the isotopic characteristics of abiogenic gases identified in this study, the ubiquitous positive correlation of $\delta^{13}C$ and δ^2H values for C_1-C_4 hydrocarbons in economic gas reservoirs world-wide is not consistent with any significant contribution from abiogenic gas. □

Methods

Kidd Creek mine, situated in the southern volcanic zone of the Abitibi greenstone belt (approximately 2,700 Myr old), 24 km north of Timmins, Ontario, is one of the world's largest volcanogenic massive sulphide deposits. All gas samples were collected from the 6,800- and 6,900-foot levels (2,072–2,100 m below land surface), from boreholes drilled approximately perpendicular to the steeply dipping felsic, mafic and ultramafic units[28]. Gases occur in association with saline ground waters and brines in pressurized 'pockets' formed by sealed fracture systems within the rocks. During exploration drilling, these systems are ruptured, triggering depressurization and gas release at rates as high as $30\,l\,min^{-1}$ per borehole. Samples were collected from freely discharging boreholes in evacuated glass sample vessels. Boreholes were sealed with packers, and samples collected from the packered interval to minimize any air contamination.

Gases are composed of methane (C_1, 69.3–78.1%), ethane (C_2, 5.55–11.7%), H_2 (0.40–12.7%) and N_2 (3.88–12.7%), along with minor concentrations of helium (1.83–2.45%), propane (C_3, 0.71–2.42%) and butane (C_4, 0.21–0.77%). CO_2 concentrations are all below detection. Compositional data are available as Supplementary Information. Compositional analyses were carried out as described in ref. 11. On the basis of crustal $^3He/^4He$ ratios for the shield gases, no mantle-derived component for the hydrocarbon gases is suggested[11].

Carbon isotopes were measured by compound specific isotope analysis using a Finnigan MAT 252 mass spectrometer interfaced with a Varian 3400 GC. Accuracy and reproducibility of $\delta^{13}C$ values are ±0.5‰ with respect to VPDB standard. $\delta^{13}C_{C_4}$ values include both n-butane and isobutane for all samples. Hydrogen isotopes were measured by compound specific isotope analysis using a Finnigan MAT delta + XL mass spectrometer interfaced with an HP6890 gas chromatograph. Accuracy and reproducibility of δ^2H values are ±5‰ with respect to VSMOW standard. 6000 series boreholes were sampled from the 6,800-foot level (2,072 m below land surface) of Kidd Creek mine in 1996–97. As this predates the availability of continuous flow compound specific hydrogen isotope

analysis, only $\delta^{13}C$ values could be analysed. 7,000 and 8,000 series boreholes were sampled from the 6,900-foot level (2,100 m below land surface) of Kidd Creek mine in 2000. Both $\delta^{13}C$ and δ^2H values are reported for these samples, and $\delta^2H_{C_4}$ values include both n-butane and iso-butane.

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Competing interests statement

The authors declare that they have no competing financial interests.

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