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**Carbon and Hydrogen Isotopic Composition of Methane and C₂+ Alkanes in
Electrical Spark Discharge: Implications for Identifying Sources of
Hydrocarbons in Terrestrial and Extraterrestrial Settings.**
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4 Carbon and hydrogen isotopic composition of methane and C₂⁺
5 alkanes in electrical spark discharge: implications for identifying
6 sources of hydrocarbons in terrestrial and extraterrestrial settings

7

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16 Running title: C and H isotopic signatures of alkanes

17

18 **Abstract**

19 The low molecular weight alkanes, methane, ethane, propane and butane, are
20 found in a wide range of terrestrial and extraterrestrial settings. The development
21 of robust criteria for distinguishing abiogenic from biogenic alkanes is essential for
22 current investigations of Mars' atmosphere and for future exobiology missions to
23 other planets and moons. Here, we show that alkanes synthesized during gas phase
24 radical recombination reactions in electrical discharge experiments have values of
25 $\delta^2\text{H}_{\text{methane}} > \delta^2\text{H}_{\text{ethane}} > \delta^2\text{H}_{\text{propane}}$, similar to those of the carbon isotopes. The
26 distribution of hydrogen isotopes in gas phase radical reactions is likely due to
27 kinetic fractionations from either i) the preferential incorporation of ^1H into longer
28 chain alkanes due to the more rapid rate of collisions of the smaller ^1H containing
29 molecules, or ii) by secondary ion effects. Similar $\delta^{13}\text{C}_{\text{C1-C2+}}$ and $\delta^2\text{H}_{\text{C1-C2+}}$ patterns
30 may be expected in a range of extraterrestrial environments where gas phase radical
31 reactions dominate, including interstellar space, the atmosphere and liquid
32 hydrocarbon lakes of Saturn's moon Titan, and the outer atmospheres of Jupiter,
33 Saturn, Neptune, and Uranus. Radical recombination reactions at high temperatures
34 and pressures may provide an explanation for the combined reversed $\delta^{13}\text{C}_{\text{C1-C2+}}$ and
35 $\delta^2\text{H}_{\text{C1-C2+}}$ patterns of terrestrial alkanes documented at a number of high
36 temperature/pressure crustal sites.

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38 **Key words:** Methane, Alkanes, Abiogenic, Carbon and hydrogen isotopes, Life

39 detection

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54 **Introduction**

55 Methane is often associated with the higher molecular weight alkanes such as
56 ethane, propane, and butane (C_{2+} alkanes), and is found in a wide range of
57 environments on Earth (Schoell, 1980), throughout our solar system (Woods and
58 Willacy, 2009), in interstellar space (Lacy et al., 1991), and in planetary
59 atmospheres in extrasolar systems (Swain et al., 2010). The development of robust
60 criteria for distinguishing abiogenic from biogenic alkanes, and differentiating
61 specific reactions involved in abiogenic synthesis, may provide insight into the
62 chemistry of organic synthesis before life evolved on Earth and define parameters
63 for the search for life on future exobiology missions (Boston et al., 1992;
64 McCollom, 1999; Fortes, 2000; Formisano et al., 2004; Krasnopolsky et al., 2004;
65 Sleep et al., 2004; Niemann et al., 2005).

66 On Earth, the absolute isotope ratios of methane ($\delta^{13}C_{CH_4}$ and $\delta^2H_{CH_4}$) and the
67 ratio of methane/ C_{2+} alkane concentrations are useful criteria for aiding in
68 distinguishing microbially generated (Archaeal) methane, thermogenic methane
69 (i.e., organic matter sourced), and abiogenic methane (Schoell, 1980; Welhan et al.,
70 1983; Jenden et al., 1993; Whiticar, 1999). Abiogenic methane and C_{2+} alkanes can
71 be either mantle-derived (Welhan et al., 1983; Jenden et al., 1993) or formed by a
72 variety of water-rock reactions in both oceanic and continental crust (Abrajano et
73 al., 1990; Sherwood Lollar et al., 1993; Berndt et al., 1996; Horita et al., 1999;

74 Charlou et al., 2002; Sherwood Lollar et al., 2002; Fiebig et al., 2009; Etiope et al.,
75 2011; Tassi et al., 2012). Recent field measurements and laboratory experiments
76 have shown a blurring of the $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ boundaries between Archaeal,
77 thermogenic, and crustally derived (e.g., non-mantle) abiogenic methane and C_2^+
78 alkanes (Horita et al., 1999; Sherwood Lollar et al., 2002; Valentine et al., 2004;
79 McCollom and Seewald, 2006; Fu et al., 2007; Taran et al., 2007; Takai et al., 2008;
80 McCollom et al., 2010; Taran et al., 2010a). Interpreting the origin of methane and
81 resolving the relative contributions from multiple sources has arguably become
82 more complex, not less, as the plethora of recent field and experimental studies have
83 progressed. Clearly, multiple lines of evidence are essential, well beyond simply
84 measuring carbon and hydrogen isotope signatures, but a definitive set of
85 measurements for differentiating the origin of hydrocarbons is as yet unavailable.

86 Problems in interpreting the source of terrestrial volatile alkanes can be
87 exacerbated by the mixing of alkanes from different sources (Jenden et al., 1993;
88 Sherwood Lollar et al., 2006; Taran et al., 2007; Liu et al., 2008; Etiope et al., 2011),
89 and by microbially mediated oxidation of methane and/or C_{2+} alkanes (McLee et
90 al., 1972; Whiticar, 1999; Kinnaman et al., 2007; Bradley and Summons, 2010;
91 Etiope et al., 2011). In extraterrestrial settings, problems interpreting the
92 provenance of methane and C_{2+} alkanes by using $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^2\text{H}_{\text{CH}_4}$ criteria are
93 further compounded by uncertainties in the starting isotopic composition of the

94 reaction substrates, for example, due to the differing losses of volatiles during the
95 initial formation of planets or moons from the solar nebula (Woods and Willacy,
96 2009) or the differing fractionation of isotopes from mantle to crust during crustal
97 formation (Grady and Wright, 2006).

98 Intermolecular compound specific isotopic analysis can provide important
99 additional information into the reaction pathways that form methane and C₂₊
100 alkanes (Des Marais et al., 1981; Berner et al., 1995; Sherwood Lollar et al., 2002;
101 Fu et al., 2007; Sherwood Lollar et al., 2008; Taran et al., 2007; McCollom et al.,
102 2010; Taran et al., 2010a; Taran et al., 2010b; Etiope et al., 2011). For example,
103 thermogenic hydrocarbon deposits typically have $\delta^{13}\text{C}_{\text{methane}} < \delta^{13}\text{C}_{\text{ethane}} <$
104 $\delta^{13}\text{C}_{\text{propane}}$ etc. and $\delta^2\text{H}_{\text{methane}} < \delta^2\text{H}_{\text{ethane}} < \delta^2\text{H}_{\text{propane}}$ etc., known as “normal” isotopic
105 distributions (Berner et al., 1995). In contrast, gas phase radical reactions produce
106 reversed $\delta^{13}\text{C}_{\text{C1-C2+}}$ distribution patterns (Des Marais et al., 1981), while abiogenic
107 water-mineral reactions can produce a variety of normal, flat, or reversed $\delta^{13}\text{C}_{\text{C1-}}$
108 C2+ patterns (Fu et al., 2007; Taran et al., 2007; McCollom et al., 2010; Taran et al.,
109 2010a). There is at present, however, a paucity of $\delta^2\text{H}_{\text{C1-C2+}}$ alkane data from
110 abiogenic synthesis experiments, with experiments (utilizing the high temperature
111 Fischer-Tropsch reaction) producing, to date, either varied (Fu et al., 2007) or normal
112 (McCollom et al., 2010; Taran et al., 2010a; Shi and Jin, 2011) $\delta^2\text{H}$ alkane
113 intermolecular distribution patterns.

114 The only reported extraterrestrial $\delta^{13}\text{C}_{1-4}$ intermolecular alkane data is from the
115 Murchison meteorite, one of the carbonaceous chondrite group of meteorites (Yuen
116 et al., 1984). The heavy absolute $\delta^{13}\text{C}$ and $\delta^2\text{H}$ isotopic ratios (relative to terrestrial
117 values) of methane and the C_{2+} alkanes point to their extraterrestrial origin, likely
118 through low temperature (e.g., 10K to 100K) free radical reactions in interstellar
119 space (Yuen et al., 1984; Cronin and Chang, 1993). The $\delta^{13}\text{C}_{\text{C1-C2+}}$ of alkanes
120 extracted from the Murchison meteorite is reversed, similar to that produced during
121 radical recombination reactions in electrical spark discharge experiments (Des
122 Marais et al., 1981). The $\delta^2\text{H}_{1-4+}$ alkane intermolecular pattern of alkanes has yet to
123 be determined in any carbonaceous meteorite. It has been suggested, however, that
124 gas phase radical reactions in interstellar space or the cooling solar nebula produce
125 organic molecules with reversed $\delta^2\text{H}_{\text{C1-C2+}}$ as well as reversed $\delta^{13}\text{C}_{\text{C1-C2+}}$
126 intermolecular patterns (Huang et al., 2005). The latter hypothesis is based on the
127 combined reversed $\delta^{13}\text{C}_{\text{C3-C4+}}$ and $\delta^2\text{H}_{\text{C3-C4+}}$ intermolecular patterns of
128 monocarboxylic acids (MCAs) analyzed from the Murchison meteorite (Huang et
129 al., 2005). Alternatively, however, it has been proposed that isotopic exchange
130 during secondary hydrothermal reactions on asteroid parent bodies could have also
131 resulted in reversed isotopic intermolecular MCA patterns (Herd et al., 2011).

132 In this study, electrical spark discharge experiments were carried out to quantify
133 the combined $\delta^{13}\text{C}$ and $\delta^2\text{H}$ intermolecular alkane patterns produced from gas phase
134 radical recombination reactions. Methane was abiogenically polymerized to C_2^+

135 alkanes and their combined $\delta^2\text{H}$ and $\delta^{13}\text{C}$ intermolecular patterns determined. The
136 relevance of the results to interpreting the origin of hydrocarbons in terrestrial and
137 extraterrestrial settings is discussed.

138

139 **Materials and Methods**

140 **Experimental Apparatus**

141 Electrical spark discharge experiments were carried out in a similar apparatus
142 to that described by Des Marais et al. (1981) and Schlesinger and Miller (1983). In
143 the first experiment, the composition of the gases and $\delta^{13}\text{C}$ of methane, ethane,
144 propane, iso-butane, and n-butane were measured. The second experiment was
145 identical to the first with the exception that the $\delta^2\text{H}$ values of methane and C_2^+
146 alkanes were measured in addition to the $\delta^{13}\text{C}$ values. In both experiments, a four-
147 port 3 L borosilicate round bottomed flask was used, which was fitted with two pure
148 tungsten electrodes (1/16" diameter) with a spark gap of two centimetres. The
149 electrodes were inserted through silicone rubber bungs, and the tops of the bungs
150 were sealed to the glass with epoxy resin. An additional silicone rubber bung was
151 used to seal the sampling port. A high vacuum fitting allowed attachment of the
152 flask to a vacuum line. The flask was evacuated to a vacuum of better than 6×10^{-3}
153 torr and filled with 2.5 psi of reagent grade methane of known isotopic value

154 through a dry ice/isopentane trap (to remove any residual water vapor in the vacuum
155 line/flask). The electrical discharge was created by using model BD-10A (Electro-
156 Technic Products, Inc, USA) high frequency 50,000 volt tesla coils with a
157 frequency of approximately 1/2 megahertz, with no ground. Experiments were
158 sparked continuously for eight hours in both experiments to produce sufficient C₂⁺
159 alkanes for precise $\delta^2\text{H}$ determinations. Three separate tesla coils were rotated
160 every 15 minutes to prevent overheating of the units. The bottom third of the flask
161 was immersed in a -160°C isopropanol/liquid N₂ trap. The temperature/pressure
162 combination of -160°C and 2.5 psi was chosen to freeze out C₂⁺ alkanes but not
163 methane during the experiments and hence preserve the initial products of reaction
164 by preventing secondary exchange of hydrogen isotopes. Liquid N₂ was added as
165 required during the experiments to maintain the -160°C temperature, and periodic
166 testing of the slush with a digital thermistor confirmed that this temperature was
167 maintained throughout the experiments. Samples of gas were taken through the
168 silicone rubber sampling port with a 1 ml gas tight syringe at both the start and end
169 of the experiments, the latter after allowing the flask to thaw to room temperature.

170

171

172 Compositional and Isotopic Analyses

173 A Varian 3400 gas chromatograph (GC) equipped with a flame ionization
174 detector (FID) was used to determine the concentrations of methane, ethane,
175 propane, iso-butane, and n-butane. The hydrocarbons were separated on a J & W
176 Scientific GS-Q column (60 m x 0.32 mm ID) with a helium gas flow and the
177 following temperature program: 32°C for 6 min, ramping to 220°C at 20°C min⁻¹.
178 Reproducibility was ± 5%. A Varian 3800 GC equipped with a micro-TCD detector
179 was used to determine the concentration of H₂. H₂ was separated from other gases
180 with a Varian Molecular Sieve 5A PLOT column (25 m x 0.53 mm ID) with argon
181 as carrier gas and the following temperature program: 35°C for 6 min, ramping to
182 220°C at 20°C min⁻¹. Reproducibility was ± 5%.

183 $\delta^{13}\text{C}$ analyses were performed by gas chromatograph-combustion-isotope ratio
184 mass spectrometry (GC-C-IRMS) with the use of a Finnigan MAT 252 mass
185 spectrometer interfaced with a Varian 3400 GC with a 60 m GS-Q capillary column.
186 The following temperature program was used: 32°C for 6 min, ramping to 220°C
187 at 20°C min⁻¹. $\delta^2\text{H}$ analyses were measured by GC-C-IRMS with a Finnigan MAT
188 Delta+ XL mass spectrometer interfaced to a HP 6890 GC. A 60 m GS-Q capillary
189 column was used along with the same temperature program as for the $\delta^{13}\text{C}$ analyses.
190 A working laboratory standard of methane, ethane, propane, i-butane, and n-butane
191 was used to calibrate the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses. Total error for $\delta^{13}\text{C}$ analyses
192 incorporating both accuracy and reproducibility (after the method of Sherwood

193 Lollar et al., 2007) was ± 0.5 ‰ with respect to V-PDB standard over the range of
194 sample signal sizes in this study (0.5 V to 6V). Total error for $\delta^2\text{H}$ analyses
195 incorporating both accuracy and reproducibility was ± 5 ‰ with respect to V-
196 SMOW standard over the range of sample signal sizes in this study (1 V to 6 V).

197 The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of methane sampled from the experimental flask in initial
198 tests of the sampling and experimental set-up ($n=13$) and at the start of both
199 experiments were -41.1 ± 0.3 ‰ ($n = 15$) and -52 ± 2 ‰ ($n = 15$), respectively,
200 where error bars are one standard deviation (1σ). These values were
201 indistinguishable from isotopic values determined for the feedstock methane for the
202 experiment, a laboratory working standard with a $\delta^{13}\text{C}$ of -40.8 ± 0.3 ‰ (1σ , $n=38$)
203 and $\delta^2\text{H}$ of -52 ± 4 ‰ (1σ , $n=38$). This indicates that no detectable fractionation of
204 carbon or hydrogen isotopes occurred during the filling of the 3L flask on the
205 vacuum line or in sampling the gases from the flask.

206

207 **Results**

208 Methane and C_2^+ Alkane Concentrations

209 Ethane, propane, and butane were synthesized from methane during the spark
210 discharge experiments alongside substantial hydrogen production (Table 1), with a
211 logarithmic decrease in alkane concentration with increasing carbon chain length

212 (Fig. 1). These data are consistent with the higher molecular weight alkanes
213 originating via radical recombination from precursor methane. In both experiments,
214 the ratio of the branched chain iso-butane to the straight chained n-butane was 1:2.1.

215 The molar composition of the analyzed gases at the end of the experiments did
216 not quantitatively match that of the starting molar composition; 22.1 % of the
217 carbon and 14.4% of the hydrogen were unaccounted for in Expt 1, and 16.1% of
218 the carbon and 9.8% of the hydrogen were unaccounted for in Expt 2 (Table 1).
219 These apparent losses are likely due to the formation of higher molecular weight
220 gaseous and condensed hydrocarbons that were not analyzed in this study, a
221 conjecture supported by the visualization of a condensate at the electrodes at the
222 end of both experiments. The final H/C ratios in the two experiments (4.4 and 4.3)
223 were both higher than the starting ratio of 4 (Table 1), indicating that the undetected
224 hydrocarbons had lower H/C ratios than those of the C1-C4 alkanes, which is
225 consistent with longer chain alkanes.

226 .

227

228

229 $\delta^{13}\text{C}$ and $\delta^2\text{H}$ Isotopic Values

230 There was a reversed intermolecular $\delta^{13}\text{C}$ pattern between methane, ethane, and
231 propane in both experiments (Fig. 2). The concentration of iso-butane in the first
232 experiment was insufficient for quantitative $\delta^{13}\text{C}$ analysis. The $\delta^{13}\text{C}$ value of iso-
233 butane was significantly lighter than n-butane in the second experiment, however,
234 contrary to the pattern previously documented in alkanes extracted from the
235 Murchison meteorite (Fig. 2). The $\delta^2\text{H}_{\text{C1-C2+}}$ pattern in the second spark discharge
236 experiment was similar to the $\delta^{13}\text{C}_{\text{C1-C2+}}$ pattern (Fig. 3a), with a positive correlation
237 between $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values ($r = 0.973$, $p < 0.01$, $n = 5$; Pearson's correlation, two-
238 tailed t-test; Fig. 3b).

239 The mean $\delta^{13}\text{C}$ of all analyzed compounds at the end of both experiments (-
240 39.1‰ and -40.2 ‰; Table 2) were slightly heavier than that of the starting methane
241 isotopic composition (-41.1‰; Table 2), indicating that the $\delta^{13}\text{C}$ of the undetected
242 hydrocarbons (likely those of higher molecular weight; see above) were isotopically
243 lighter than the detectable ones. Similarly, the mean $\delta^2\text{H}$ of all analyzed compounds
244 at the end of Expt. 2 (-44 ‰) was slightly heavier than that of the starting methane
245 composition (-52 ‰), indicating that the $\delta^2\text{H}$ of the undetected hydrocarbons were
246 also lighter than the detectable ones.

247

248 **Discussion**

249 Intermolecular $\delta^{13}\text{C}$ and $\delta^2\text{H}$ Signatures of Alkanes Formed Via Gas Phase Radical 250 Reactions

251 In this study, we replicated the reversed $\delta^{13}\text{C}_{\text{C1-C3}}$ pattern for gas phase radical
252 recombination reactions previously established by Des Marais et al. (1981) (Fig. 2)
253 and provide for the first time the complementary $\delta^2\text{H}$ values for all compounds. In
254 the 1981 study, the reversed $\delta^{13}\text{C}_{\text{C1-C3}}$ pattern was attributed to kinetic
255 fractionations during recombination due to $^{12}\text{CH}_3$ reacting faster than $^{13}\text{CH}_3$ to form
256 longer carbon chains, resulting in more ^{12}C incorporated into heavier alkanes (Des
257 Marais et al., 1981). Importantly, the $\delta^2\text{H}_{\text{C1-C2+}}$ and $\delta^{13}\text{C}_{\text{C1-C2+}}$ intermolecular
258 patterns in the spark discharge experiment were positively correlated (Fig. 3b). This
259 suggests that the distribution of hydrogen isotopes in gas phase radical reactions is
260 controlled by kinetic fractionations in an analogous way to the carbon isotopes. The
261 reversed $\delta^2\text{H}$ pattern may be due to the preferential incorporation of ^1H into longer
262 chain alkanes due to more rapid rate of collisions of the smaller ^1H containing
263 molecules (Huang et al., 2005). Alternatively, the reversed $\delta^2\text{H}$ pattern may be due
264 to secondary ion effects, that is, the presence of the lighter ^1H in $^1\text{H-C-C}$ causes a
265 weaker C-C bond than in $^2\text{H-C-C}$ (Bigeleisen, 1965). Significant secondary
266 hydrogen exchange in the spark discharge experiments is unlikely as the
267 experiments were designed to freeze out the initial C_2^+ alkane products and prevent
268 secondary hydrogen exchange reactions. Isotopic mass balance considerations

269 suggest that higher molecular weight hydrocarbons have lighter $\delta^{13}\text{C}$ and $\delta^2\text{H}$
270 values than the $\text{C}_1\text{-C}_4$ alkanes (Table 2; Table 3). This suggests that the reversed
271 $\delta^{13}\text{C}$ and $\delta^2\text{H}$ patterns seen in these experiments are not only applicable to $\text{C}_1\text{-C}_4$
272 alkanes but also to higher molecular weight compounds via continued radical
273 recombination reactions. The experimental data of this study therefore support the
274 hypothesis that organic molecules formed by gas phase radical recombination
275 reactions in the low temperatures of interstellar space or the outer solar nebula will
276 have combined reversed $\delta^{13}\text{C}_{\text{C}_1\text{-C}_2+}$ and $\delta^2\text{H}_{\text{C}_1\text{-C}_2+}$ intermolecular patterns (Huang et
277 al., 2005). Although temperatures and pressures in interstellar space are
278 substantially lower than those used in the spark discharge experiments, the
279 mechanisms of radical recombination reactions (and the resulting isotopic
280 distribution patterns) should be similar. This is because radical recombination
281 reactions have very low activation energies and can take place at temperatures as
282 low as 10K (Herbst, 1995).

283 Reversed $\delta^2\text{H}_{\text{C}_1\text{-C}_2+}$ and $\delta^{13}\text{C}_{\text{C}_1\text{-C}_2+}$ patterns may also be typical of methane and
284 C_{2+} alkanes, and perhaps other low molecular weight organic molecules, formed by
285 gas phase radical reactions in a variety of extraterrestrial environments. One such
286 environment is the atmosphere and surface of Saturn's moon Titan where episodic
287 cryovolcanism releases gaseous methane from reservoirs of clathrate hydrates into
288 the atmosphere where it undergoes radical recombination reactions in the

289 atmosphere dominantly driven by UV-radiation photolysis, with further
290 contributions from cosmic ray radiation and magnetospheric electrons derived from
291 Saturn's magnetic field (Sagan and Thompson, 1984; Tobie et al., 2006). As the
292 average surface temperature of Titan is -179°C and the atmospheric pressure is 1.6
293 bars, the C_{2+} products (primarily ethane) condense out in liquid lakes on the surface
294 (Brown et al., 2008; Lunine and Atreya, 2008) or potentially on dust particles in the
295 atmosphere, which settle onto the surface (Hunten, 2006). Spectral measurements
296 on Titan's atmosphere have demonstrated that $\delta^{13}\text{C}_{\text{ethane}}$ is likely lighter than
297 $\delta^{13}\text{C}_{\text{methane}}$ by c. 8 ‰ (Jennings et al., 2009), while the $\delta^2\text{H}_{\text{C1-C2+}}$ has yet to be
298 measured.

299 Reversed $\delta^2\text{H}_{\text{C1-C2+}}$ and $\delta^{13}\text{C}_{\text{C1-C2+}}$ alkane patterns might also be present within
300 the upper atmospheres of the gas giant planets of Jupiter, Saturn, Neptune, and
301 Uranus where the polymerization of gaseous methane can be energized by lightning
302 strikes in addition to UV photolysis (Romani et al., 1993; Sada et al., 1996; Moses
303 et al. 2005; Hammel et al., 2006). Testing of this hypothesis awaits future more
304 precise measurements of the $\delta^2\text{H}$ and $\delta^{13}\text{C}$ of methane and ethane in the gas giants'
305 atmospheres.

306

307 Intermolecular $\delta^{13}\text{C}$ and $\delta^2\text{H}$ Signatures of Alkanes in Crustal Environments

308 Experimental data indicate that abiogenic hydrocarbons can have a wide range
309 of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ alkane distribution patterns (Sherwood Lollar et al., 2002;
310 McCollom and Seewald, 2006; Fu et al., 2007; Taran et al., 2007; Sherwood Lollar
311 et al., 2008; McCollom et al., 2010; Taran et al., 2010a; Taran et al., 2010b), which
312 likely reflects differences in reaction pathways, in catalysts and in kinetic
313 limitations such as absorption/desorption effects on catalyst surfaces (Sherwood
314 Lollar et al., 2008; McCollom et al., 2010; Taran et al., 2010a). To date, no high
315 temperature mineral-water experiments in the laboratory have, however, replicated
316 the combined reversed $\delta^{13}\text{C}$ and $\delta^2\text{H}$ distribution patterns documented in a number
317 of terrestrial abiogenic hydrocarbon deposits (Potter and Longstaffe, 2007;
318 Proskurowski et al., 2008; Taran et al., 2010b). It has been suggested that these
319 “completely” reversed hydrocarbons could be formed by radical reactions at
320 relatively high temperatures and pressures within the lower lithosphere (Du et al.,
321 2003; Taran et al., 2010a). The experimental results of the spark discharge
322 experiments (Fig. 1; Fig. 2; Fig. 3) provide the first experimental verification of this
323 hypothesis.

324 Both experimental and field evidence indicate that, while relatively shallow,
325 “traditional” terrestrial thermogenic hydrocarbon deposits have normal $\delta^{13}\text{C}$ and
326 $\delta^2\text{H}$ intermolecular alkane patterns, hydrocarbons generated at high temperatures
327 and pressures deeper within the crust can have reversed $\delta^{13}\text{C}$ and $\delta^2\text{H}$ patterns
328 (Burruss and Laughrey, 2010). These reversed thermogenic $\delta^{13}\text{C}$ and $\delta^2\text{H}$ alkane

329 patterns have previously been interpreted in one of two ways: first, by the mixing
330 of different sources of alkanes (Liu et al., 2008) and second, by the combination of
331 mixing with either Rayleigh fractionation (for carbon isotopes) or the exchange of
332 methane hydrogen with formation water (for hydrogen isotopes) (Burruss and
333 Laughrey, 2010). The results of the spark discharge experiments (Fig. 1) suggest an
334 alternative possibility for the reversed $\delta^{13}\text{C}$ and $\delta^2\text{H}$ alkane patterns in “deep-
335 seated” thermogenic hydrocarbon deposits, which is that at high temperatures and
336 pressures C_{2+} alkanes are destroyed and then reformed via radical reactions,
337 producing similar reversed patterns to those seen in the spark discharge
338 experiments. Further support for the latter hypothesis is given by an experimental
339 study showing that completely reversed $\delta^{13}\text{C}_{1-4}$ alkane patterns are produced during
340 the high temperature/pressure (500-700°C, 1-3 GPa) pyrolysis of lignite (Du et al.,
341 2003).

342

343 Future Research

344 While current results, based on the bulk isotopic compositions of
345 compounds, do not as yet provide a definitive means by which to differentiate
346 abiogenic from biogenic hydrocarbons, experiments such as those described in this
347 paper represent important progress towards understanding reaction mechanisms
348 involved in abiogenic synthesis under different temperature and pressure

349 conditions. Future progress in this field may focus on the analysis of isotopologues
350 – the small set of molecules that contain more than one rare isotope, such as in the
351 case of methane $^{13}\text{C}^1\text{H}_3^2\text{H}$ (Wang et al., 2004; Ma et al., 2008). The proportion of
352 these isotopologues is likely to depend primarily on the temperature of formation
353 rather than the bulk isotopic composition, due to the relatively high stability of the
354 intermolecular bonds, suggesting the possibility of using isotopologues of methane
355 as a geothermometer (Wang et al., 2004; Ma et al., 2008), as has been done
356 successfully for CO_2 in carbonates (Eiler, 2011). Although there is some overlap in
357 the temperature fields of formation for microbial, thermogenic, and abiogenic
358 methane formation (Sherwood Lollar et al., 1993; Valentine et al., 2004;
359 Proskurowski et al., 2008), the future use of isotopologues alongside existing
360 geochemical and isotopic methods may provide a powerful means by which to
361 better distinguish the sources of hydrocarbons in both terrestrial and extraterrestrial
362 environments.

363

364 **Conclusions**

365 The results of this experimental study expand our understanding of the
366 intermolecular isotopic signatures of hydrocarbons formed in various
367 extraterrestrial and terrestrial environments. $\text{C}_2\text{-C}_4$ alkanes synthesized from
368 methane during gas phase radical recombination reactions have

369 $\delta^2\text{H}_{\text{methane}} > \delta^2\text{H}_{\text{ethane}} > \delta^2\text{H}_{\text{propane}}$, similar to previously documented intermolecular
370 carbon distribution patterns ($\delta^{13}\text{C}_{\text{C1-C2+}}$) with $\delta^{13}\text{C}_{\text{methane}} > \delta^{13}\text{C}_{\text{ethane}} > \delta^{13}\text{C}_{\text{propane}}$.
371 These “reversed” patterns are likely typical of gas phase radical reactions in a
372 variety of extraterrestrial settings, including interstellar space, the atmosphere, the
373 liquid hydrocarbon lakes of Saturn’s moon Titan, and the outer atmospheres of
374 Jupiter, Saturn, Neptune, and Uranus. Radical recombination reactions at high
375 temperatures and pressures also provide a possible explanation for the combined
376 reversed $\delta^{13}\text{C}_{\text{C1-C2+}}$ and $\delta^2\text{H}_{\text{C1-C2+}}$ patterns of terrestrial alkanes documented at a
377 number of both abiogenic and high temperature/pressure thermogenic gas sites.

378

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385

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587 **TABLES**

588

589 **TABLE 1.** Composition of gases from spark discharge experiments

	Volume %						Mole % ¹		Ratio
	CH ₄	C ₂ H ₆	C ₃ H ₈	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	H ₂	Sum Carbon	Sum Hydrogen	H/C
Start	100	< 0.01	<0.01	<0.0003	<0.0002	< 0.04	100	100	4.0
Expt 1	37.7	10.7	4.4	0.44	0.9	39.0	77.6	85.4	4.4
Expt 2	31.5	12.4	6.2	0.7	1.5	44.2	83.7	90.1	4.3

590 ¹ Total molar volume composition of analyzed gases relative to start

591

592 **TABLE 2.** Carbon isotopic composition of gases from spark discharge
593 experiments

	$\delta^{13}\text{C}$ ‰					
	CH ₄	C ₂ H ₆	C ₃ H ₈	iso-C ₄ H ₁₀	n-C ₄ H ₁₀	Mean (C ₁ -C ₄ alkanes)
Start	-41.1					
Expt 1	-34.2	-42.0	-47.1		-44.8	-39.1
Expt 2	-34.8	-40.5	-46.7	-48	-43.7	-40.2

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597 **TABLE 3.** Hydrogen isotopic composition of gases from spark discharge
 598 experiments

	$\delta^2\text{H} \text{ ‰}$						
	CH_4	C_2H_6	C_3H_8	iso- C_4H_{10}	n- C_4H_{10}	H_2	Mean ($\text{C}_1\text{-C}_4$ alkanes and H_2)
Start	-52						
Expt 2	37	-8	-94	-129	-87	-149	-44

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614 **FIGURES**

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617 **FIG. 1.** Plot of % volume of alkanes versus carbon number produced in spark
618 discharge experiments. Open circles represent first experiment ($\delta^{13}\text{C}$ measurements
619 only), closed circles represent second experiment ($\delta^2\text{H}$ and $\delta^{13}\text{C}$ measurements).
620 Error bars (1σ) are smaller than the plotted symbols.

621

622 **FIG. 2.** $\delta^{13}\text{C}$ values of alkanes from spark discharge experiments. The $\delta^{13}\text{C}$ values
 623 of alkanes produced in both the first experiment (open circles) and second
 624 experiment (closed circles) show a pattern of decreasing isotopic value with
 625 increasing molecular weight between methane and propane. This decreasing $\delta^{13}\text{C}$
 626 trend with increasing molecular weight is similar to that documented in spark
 627 discharge experiments of Des Marais *et al.* (1981) (inverted solid triangles) and
 628 methane and C_2^+ alkanes extracted from the Murchison meteorite by Yuen *et al.*
 629 (1984) (open diamonds).

630

631 **FIG. 3. (a)** $\delta^2\text{H}$ values of alkanes from spark discharge experiments. The $\delta^2\text{H}$ values

632 of alkanes produced in the second experiment (open squares) show a similar pattern

633 to the carbon isotopes (closed circles), with a pattern of decreasing isotopic value

634 with increasing molecular weight. Error bars (1σ) are smaller than the plotted

635 symbols (b) $\delta^{13}\text{C}$ values versus $\delta^2\text{H}$ values of alkanes produced in the second spark

636 discharge experiment. There is a significant positive correlation between $\delta^{13}\text{C}$

637 values and $\delta^2\text{H}$ values ($r = 0.93$, $p < 0.01$, Pearson's correlation, two-tailed t-test).

638 Error bars (1σ) incorporate both accuracy and reproducibility.