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Daniel A. Stolper, Michael Lawson, Cara L. Davis, Alexandre A. Ferreira ...+8 more authors

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1   **Title: Formation temperatures of thermogenic and biogenic methane**

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3   **Authors:** D.A. Stolper[a1], M. Lawson[b], C.L. Davis[b], A.A. Ferreira[c], E.V. Santos Neto[c], G.S.

4   Ellis[d], M.D. Lewan[d], A.M. Martini[e], Y. Tang[f], M. Schoell[g], A.L. Sessions[a], J.M. Eiler[a]

5

6   *Affiliations: [a]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA*

7   *[b]ExxonMobil Upstream Research Company, Houston, TX, USA*

8   *[c]Division of Geochemistry, Petrobras Research and Development Center (CENPES), Rio de Janeiro, RJ, Brazil*

9   *[d]U.S. Geological Survey, Denver Federal Center, Denver, CO, USA*

10   *[e]Department of Geology, Amherst College, Amherst, MA, USA*

11   *[f]Power, Environmental, and Energy Research Institute, Covina, CA USA*

12   *[g]GasConsult International Inc, Berkeley, CA, USA*

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14

16   ***Abstract:*** *Methane is an important greenhouse gas and energy resource generated dominantly*

17   *by methanogens at low temperatures and through the breakdown of organic molecules at high*

18   *temperatures. However, methane formation temperatures in nature are often poorly constrained.*

19   *We measured formation temperatures of thermogenic and biogenic methane using a 'clumped*

20   *isotope' technique. Thermogenic gases yield formation temperatures between 157-221°C, within*

21   *the nominal gas window, and biogenic gases yield formation temperatures consistent with their*

22   *known lower formation temperatures (<50°C). In systems where gases have migrated and other*

23   *proxies for gas generation temperature yield ambiguous results, methane clumped-isotope*

[1] Corresponding author: 1200 E. California Blvd, Pasadena, CA 91125, dstolper@caltech.edu, 626-395-3753

24   *temperatures distinguish among and allow for independent tests of possible gas formation*

25   *models.*

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28   **Main Text:** The environmental conditions, rates, and mechanisms of methane formation

29   are critical to understanding the carbon cycle and for predicting where economically substantial

30   amounts of methane form. Conventional models of thermogenic methane formation predict that:

31   (i) gas formation is kinetically controlled by time, temperature, and organic matter composition

32   (*1*); (ii) gases co-generated with oil form below ~150-160°C (*2-4*); and (iii) gases created from

33   the breakdown (cracking) of oil or refractory kerogen form above ~150-160°C (*2-4*). Microbially

34   produced (biogenic) methane in nature is thought to form mostly below ~80°C (*5, 6*).

35   Our understanding of the kinetics of thermogenic methane formation is dominantly

36   constrained by extrapolating kinetic parameters from high-temperature (~>300˚C) laboratory

37   experiments to lower temperature (~100-200°C), geologically relevant conditions (*7*). These

38   experiments are sensitive to heating rates (*7*) and the activity of water (*1, 7-10*), minerals (*1*), and

39   transition metals (*11*); the observed range of derived kinetic parameters can result in divergent

40   predictions for natural methane formation temperatures (*1, 10*). Additionally, many thermogenic

41   gases have migrated from their source to a reservoir (*3, 12-14*). Although these migrated gases

42   dominate the datasets used to calibrate empirical models of thermogenic methane formation (*3,*

43   *13-15*), the ability to understand their thermal histories, and thus accurately calibrate models, is

44   hampered by: (i) a lack of independent constraints on the thermal histories of the source and

45   reservoir rocks and the timing of gas migration, and (ii) the possibility that a reservoir contains a

46   mixture of gases from different sources. Finally, biogenic gases are produced ubiquitously in

47   near-surface sedimentary environments (*6, 16*) and can co-mingle with thermogenic gases (*17*).

48   Despite the many empirical tools used to distinguish biogenic from thermogenic gases (*18*),

49   identifying the sources and quantifying relative contributions of biogenic and thermogenic gases

50   in nature remains challenging (*17*).

51   We measured multiply substituted ('clumped') isotope temperatures of methane (*19*)

52   generated via the experimental pyrolysis of larger organic molecules and sampled from natural

53   thermogenic deposits of the Haynesville Shale (USA), Marcellus Shale (USA) and Potiguar

54   Basin (Brazil) (*20*), and from natural systems with methanogens from the Gulf of Mexico and

55   Antrim Shale (USA). We quantified the abundance of both $^{13}CH_3D$ and $^{12}CH_2D_2$, two clumped

56   isotopologues of methane, relative to a random isotopic distribution via the parameter Δ_{18} (*20*).

57   For isotopically equilibrated systems, Δ_{18} values are a function of temperature, dependent only

58   on the isotopic composition of methane, and thus can be used to calculate methane formation

59   temperatures (Fig. 1A; *19, 20, 21*). It was not obvious prior to this work what Δ_{18}-based

60   temperatures of natural samples would mean, in part because conventional models assume that

61   methane forms via kinetically (as opposed to equilibrium) controlled reactions (*1-3, 8, 22-24*).

62   We generated methane from larger hydrocarbon molecules at constant temperatures in

63   two experiments: pyrolysis of propane at 600°C (*20*) and closed-system hydrous pyrolysis (*7, 9*)

64   of organic matter at 360°C (*20*). For both, Δ_{18} temperatures are within 2σ of experimental

65   temperatures (Fig. 1A; Table S1). This supports the suggestion in (*19*) that measured Δ_{18}-based

66   temperatures of thermogenic methane could record formation temperatures.

67   We next examined thermogenic shale gases from the Haynesville Shale (*25*). In shale-gas

68   systems, the shale is both the source and reservoir for generated hydrocarbons (*26*), thus

69   minimizing complications associated with gas migration for our interpretations. Geological

70 constraints indicate that the Haynesville Shale has undergone minimal uplift (~<0.5 km; *20*)

71 since reaching maximum burial temperatures (modeled to currently be within 5-17°C of

72 maximum burial temperatures; Tables S2,3; *20*). Measured Δ_{18} temperatures range from 169-

73 207°C, overlapping, within uncertainty, current reservoir temperatures (163-190°C; Fig. 1A,B;

74 Table S2). We also compared the Δ_{18} temperatures to independently calculated gas-formation

75 temperatures using the generation kinetics of Burnham (*20, 27*). Modeled average gas-formation

76 temperatures from secondary oil breakdown range from 168-175°C (Table S3; *20*). The modeled

77 temperatures are lower than, but within uncertainty of, measured Δ_{18} temperatures (Table S2).

78 This difference likely reflects the fact that the model calculates an average formation temperature

79 that includes all hydrocarbon gases (i.e., C_{1-5} alkanes), but the types of experiments used to

80 calibrate the model generate methane at a higher average temperature than other hydrocarbon

81 gases (*28*). Thus, average methane formation temperatures should be higher than those modeled

82 for average hydrocarbon gas-formation temperatures. Consequently, Δ_{18} temperatures are

83 consistent with expected methane formation temperatures. However, in this case, it is also

84 possible that methane re-equilibrated from some other, initial Δ_{18} value to one consistent with its

85 subsequent storage temperatures.

86   Next, we considered shale gases from uplifted rocks (>3 km of uplift after maximum

87 burial; *20*) in the Marcellus Shale (*29*), which reached modeled maximum burial temperatures of

88 183-219°C, but today are 60-70°C (Tables S2,3; *20*). This system allows us to examine the

89 effects of gradual cooling and long-term storage at temperatures colder than methane formation

90 temperatures on Δ_{18} values. Samples yield Δ_{18} temperatures from 179-207°C, overlapping those

91 for the Haynesville Shale and hotter than current reservoir temperatures (Fig. 1B). Modeled

92 formation temperatures (using the Burnham kinetics as above; *27*) are 171-173°C (Table S3) –

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93   the modeled temperatures are again slightly lower than the measured Δ_{18} temperatures (for

94   reasons discussed above), but the two are within analytical uncertainty (Table S2). We conclude

95   that Δ_{18} temperatures of Marcellus Shale methane are indistinguishable from independent

96   expectations regarding methane formation temperatures and were not noticeably influenced by

97   later cooling.

98   We also examined thermogenic gases from the southwestern sector of the Potiguar Basin

99   (30) that migrated from deeper sources to shallower reservoirs (31). Here, measured Δ_{18}

100   temperatures range from 157-221°C and exceed current reservoir temperatures (66-106°C; Table

101   S2). This is consistent with vertical migration of gases from hotter sources to cooler reservoirs

102   (3). We note that some source rocks in the Potiguar Basin near where samples were collected

103   have experienced sufficient burial temperatures to reach a vitrinite reflectance of 2.7%, within

104   the range observed for the Haynesville and Marcellus shale gas source rocks (1.7-3.1%; Table

105   S3) and consistent with the high-temperature (>150-160°C; 2-4) 'dry gas zone' in which oil is

106   hypothesized to crack to gas (3). Thus, the Δ_{18} temperatures from Potiguar Basin methane (157-

107   221°C) are compatible with the thermal history of some source rocks in the region. Additionally,

108   a positive correlation exists between the Δ_{18} temperatures and $\delta^{13}C$ values (32) of Potiguar Basin

109   gases (Fig. 2; p-value=0.008) with a slope, 5.3°C/‰ (±2.2; 1σ), within error of some theoretical

110   estimates, 8.8°C/‰ (20, 22) and 9.4°C/‰ (20, 23). This relationship is expected because earlier-

111   generated methane is thought to form at lower temperatures with lower $\delta^{13}C$ values than methane

112   formed later at higher temperatures (2, 3, 15, 23). The Potiguar Basin samples raise the issue that

113   mixing of gases with differing $\delta^{13}C$ and δD values can result in Δ_{18} values that are not simply

114   weighted averages of the endmembers (19, 20). However, in this specific case (and for the shale

115   gases), $\delta^{13}C$ and δD values do not span a sufficiently large range for mixing between samples to

116   result in Δ_{18}–based temperatures different (within analytical uncertainty) from the actual average

117   formation temperatures of the mixtures (Fig. S2; *20*).

118   The data discussed above are consistent with the interpretation that Δ_{18} values of

119   thermogenic methane reflect isotopic equilibrium at the temperature of methane formation and

120   that the 'closure temperature' above which Δ_{18} values can freely re-equilibrate is ~>200°C in

121   geological environments because: (i) Experimentally generated methane yields Δ_{18} values within

122   error of formation temperatures (Fig. 1A). (ii) All Δ_{18} temperatures from natural samples are

123   geologically reasonable formation temperatures (*1-4, 10*). (iii) Haynesville Shale Δ_{18}

124   temperatures are within uncertainty of current and modeled maximum burial temperatures (Fig.

125   1A,B). (iv) Haynesville and Marcellus Shale Δ_{18} temperatures are within error of independently

126   modeled gas-formation temperatures. (v) Haynesville and Marcellus Shale Δ_{18} temperatures

127   overlap despite the differing thermal histories of each system (the Marcellus Shale cooled by

128   >100°C after gas generation). This would not be expected if Δ_{18} temperatures represent closure

129   temperatures and thus reset during cooling of the host rocks. And (vi), Potiguar Basin Δ_{18}

130   temperatures and $\delta^{13}C$ values are positively correlated (Fig. 2), with a slope within error of

131   theoretical predictions.

132   The agreement between the Haynesville and Marcellus Shale methane Δ_{18} temperatures

133   and modeled formation temperatures demonstrates that relatively simple gas generation models

134   are accurate when the thermal histories of the source rocks are constrained. The formation

135   temperatures of the Potiguar Basin gases are challenging to constrain with such models due to

136   gas migration, which obscures the location and timing of gas formation. Previously, these gases

137   were interpreted to have been co-generated with oils (*30*) and thus below ~160°C (*2-4*). This

138   disagreement between our data and published interpretations inspired us to examine a range of

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139   gas-formation models (*20*) for the Potiguar Basin samples (Fig. 3). All models presented are in

140   common use and constrained by similar gas chemistry data (*20*); however many disagree with

141   each other and together predict a range of over 170°C for gas formation (Fig. 3). The Δ_{18}

142   temperatures allow these models to be independently evaluated, rejecting some (e.g., low-

143   temperature gas generation solely from kerogen) and narrowing the permitted interpretations.

144   Specifically, methane in the Potiguar Basin could have formed via the mixing of gases produced

145   by low-temperature (~<150-180°C) kerogen breakdown with gases generated from higher-

146   temperature (~>150-160°C) oil breakdown, consistent with the models of (*23*) and (*27*). This

147   scenario requires a specific set of mixing components to generate the observed formation

148   temperatures, $C_1/\Sigma C_{1-5}$ values (Table S2), and correlation between Δ_{18} temperatures and methane

149    $\delta^{13}C$ values. Alternatively, the model of (*10*), which is the only model presented to incorporate

150   the importance of water in gas formation, is consistent with the Δ_{18} temperatures and $C_1/\Sigma C_{1-5}$

151   values (<85%; Table S2) for the Potiguar Basin gases. This may indicate that water should be

152   considered in models of methane formation. Although the gas generation temperatures derived

153   from the breakdown of refractory kerogen, as in the model of (*27*), appear compatible with the

154   Δ_{18} temperatures (Fig. 3), this organic source dominantly generates methane (*27*) and thus cannot

155   be the sole source of gas to the system due to the high concentration of C_{2-5} alkanes in the gases

156   (<85% $C_1/\Sigma C_{1-5}$; Table S2).

157   Thus, while the addition of Δ_{18} temperatures does not provide a unique interpretation of

158   the origin of the Potiguar Basin gases, it rules out several otherwise plausible interpretations and

159   places specific constraints on the remaining models. Importantly, our results for the Potiguar

160   Basin indicate that the formation environments for methane extend to higher temperatures (and

161   presumably depths) in this system than many models of petroleum genesis predicted (Fig. 3), and

162   supports experimental evidence that significant quantities of methane can be generated at higher

163   temperatures than sometimes appreciated (*33*). This requires that this basin possesses a

164   previously unsuspected 'root' that reached high temperatures at some point in its history,

165   generating high-temperature methane that ascended into shallower reservoirs. Thus, Δ_{18}

166   temperatures not only constrain the conditions and mechanisms of methane formation, but also

167   provide a window into the geological and thermal histories of basins in which methane forms.

168   To examine Δ_{18}-based temperatures from known low-temperature sources of methane, we

169   measured Δ_{18} values from two sources of biogenic gases produced from the biodegradation of oil

170   (Gulf of Mexico). They return Δ_{18} temperatures (34 ± 8 and $48 \pm 8°C$) within error of their

171   current reservoir temperatures (42 and 48°C, respectively; Fig 1A,B; Table S2). We further

172   measured two gases from the Antrim Shale, which has been interpreted as containing a mixture

173   of biogenic gases higher in $C_1/\Sigma C_{1-5}$ and thermogenic gases lower in $C_1/\Sigma C_{1-5}$ (*17*). The sample

174   closer to the biogenic endmember (99.99% $C_1/\Sigma C_{1-5}$) returns a Δ_{18} temperature of 40°C (± 10;

175   1σ), whereas the sample interpreted here to be closer to a thermogenic endmember (88.9%

176    $C_1/\Sigma C_{1-5}$) returns a higher temperature of 115°C ($\pm 12°C$; 1σ). Thus, the natural biogenic gases

177   have Δ_{18} temperatures consistent with their expected formation temperatures, both as pure

178   endmembers and as dominant components of mixtures. We note that preliminary results for

179   methanogens grown in pure culture (*34*) indicate that they can produce methane out of internal

180   isotopic equilibrium. Nevertheless, our measurements of natural biogenic methane indicate that

181   natural environments (at least those investigated to date) permit the attainment of local

182   equilibrium.

183   These results indicate that Δ_{18} values can be used to calculate formation temperatures of

184   methane from both pure and mixed thermogenic and biogenic gas deposits and interrogate

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185 models of gas formation and geological histories of basins. Additionally, if the interpretation of

186 Δ_{18}-based temperatures as formation temperatures is correct, it has implications for our

187 understanding of the chemistry of thermogenic and biogenic methane formation. Specifically, it

188 requires a heretofore unrecognized step for both processes that allows C-H bonds to equilibrate

189 during methane formation. This interpretation is unexpected because $\delta^{13}C$ values of thermogenic

190 and biogenic methane are almost universally considered to be controlled by kinetic-isotope

191 effects rather than equilibrium-thermodynamic effects (*2, 16, 22-24, 35*). This apparent

192 contradiction can be reconciled if reacting methane precursors (e.g., methyl groups) undergo

193 local hydrogen exchange faster than the rate of net methane generation. For thermogenic gases,

194 this could occur via exchange reactions with water (*36*) or catalytic hydrogen exchange on

195 organic macromolecules, mineral surfaces, or transition metals (*11, 37*). For biogenic methane,

196 reversible hydrogen exchange could occur on methane or methane precursors if the pathway for

197 methane formation is partially reversible (*35, 38*). Thus, Δ_{18} measurements may also elucidate

198 chemical and biochemical mechanisms of methane formation.

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262   32. *$\delta = (R/R_{std}-1)x1000$ where $^{13}R=[^{13}C]/[^{12}C]$, $^{D}R=[D]/[H]$, and 'std' denotes the standard to*
263   *which all measurements are referenced (VPDB for carbon and VSMOW for hydrogen*
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338

339   **Figures:**

340   Fig. 1: Comparisons of Δ_{18} temperatures to environmental/formation temperatures. A)

341   Formation/reservoir temperatures vs. Δ_{18} values. The dashed line is the theoretical dependence of

342   Δ_{18} on temperature (*19*). Equilibrated gas data are from (*19*). Temperatures are

343   formation/equilibration temperatures for the pyrolysis and equilibrated samples and current

344   reservoir temperatures for the Haynesville Shale and Gulf of Mexico samples. B) Current

345   reservoir temperatures vs. Δ_{18} temperatures for all natural samples investigated except the

346   Antrim Shale samples, which are excluded because they are a mixture of thermogenic and

347   biogenic gases. The dotted line is a 1:1 line. Uncertainty for well temperatures is estimated to be

348   ~±10°C. Error bars are 1σ.

349

350   Fig. 2: $\delta^{13}C$ values vs. Δ_{18} temperatures for methane from the Potiguar Basin. A positive

351   correlation (*p*-value=0.008) is observed. The gray band is the 95% confidence interval for the

352   linear regression through the data. Error bars are 1σ.

353

354   Fig. 3: Comparison of modeled methane formation temperatures for the Potiguar Basin samples

355   (*10, 15, 20, 23, 27, 39, 40*) to Δ_{18} temperatures. Blue lines indicate gases generated from kerogen

356   breakdown, purple from oil breakdown, red from bitumen breakdown, and green the measured

357   range of Δ_{18} temperatures from the Potiguar Basin.

358

359   **Supplementary Materials**