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Note

Rapid offline isotopic characterisation of hydrocarbon gases generated by micro scale sealed vessel pyrolysis

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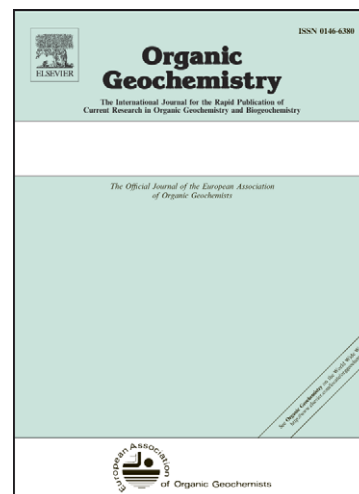
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1 **Rapid offline isotopic characterisation of hydrocarbon gases generated by**  
2 **micro scale sealed vessel pyrolysis**

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12  
13 **Abstract**

14 The method of offline coupling of micro scale sealed vessel pyrolysis (MSSV-Py) and  
15 gas chromatography-isotopic ratio mass spectrometry (GC-IRMS) was developed using  
16 a purpose built gas sampling device. The sampling device allows multiple GC and GC-  
17 IRMS injections to quantify the molecular composition and isotopic evolution of  
18 hydrocarbon gases ( $n$ -C<sub>1</sub> to  $n$ -C<sub>5</sub>) generated by artificial maturation of sedimentary  
19 organic matter. Individual MSSV tubes were introduced into the gas sampling device,  
20 which was then evacuated to remove air and filled with helium at atmospheric pressure.  
21 The tube was crushed using a plunger after which the device was heated at 120 °C for 1  
22 min to thermally mobilize and equilibrate the generated gas products. Aliquots of the  
23 gas phase were sampled using a gas tight syringe and analysed via GC-FID and GC-  
24 IRMS. Hydrocarbon gas yields using this technique have been calculated and compared

25 with those obtained previously by online MSSV pyrolysis of the same samples under  
26 the same conditions. The major objective of this study was to investigate the potential  
27 isotopic fractionation of generated gaseous hydrocarbons within the gas sampling  
28 device as a function of time and temperature. For this purpose several tests using a  
29 standard gas mixture have been performed on the GC-IRMS. The analyses showed no  
30 isotopic fractionation of C<sub>1-5</sub> hydrocarbons within 1 hour, minor  $\delta^{13}\text{C}$  enrichment after 5  
31 hours, and significant enrichment after 22 hours for all the compounds at a temperature  
32 of 120 °C.

33  
34 *Keywords*

35 micro scale sealed vessel pyrolysis, artificial maturation, stable isotopes,  $\delta^{13}\text{C}$ , methane,  
36 hydrocarbon gas, isotopic fractionation

## 38 **1. Introduction**

39 The formation of petroleum (oil and gas) cannot be extrapolated from  
40 geochemical data derived from naturally occurring basins (Michels et al., 2002). In  
41 order to overcome the limitations of natural samples, artificial maturation experiments  
42 using analytical pyrolysis techniques have been employed to simulate the formation of  
43 gases (Michels et al., 2002; Dieckmann et al., 2006). The study of  $\delta^{13}\text{C}$  of the  
44 hydrocarbon (HC) gases, particularly when combined with compositional data, is of  
45 great importance to evaluate natural gas resources (Boreham et al., 1998). A range of  
46 analytical pyrolysis techniques, coupled with online or offline gas chromatography-  
47 mass spectrometry (GC-MS), have been used to characterise organic macromolecules  
48 and simulate geochemical reactions over laboratory timescales. Micro scale sealed

49 vessel pyrolysis (MSSV-Py) involves heating small quantities of sample (typically 0.1–  
50 10 mg) enclosed within glass tubes under controlled temperature (e.g. 250–350 °C) and  
51 time (e.g. hours to days) conditions (Horsfield et al., 1989). However, this approach  
52 does not allow replicate analyses from a single run of a sample required to obtain  
53 reliable quantitative and stable isotopic compositions. Here we report the development  
54 of offline MSSV-Py that enables multiple injections on GC and GC-IRMS in order to  
55 measure the molecular composition and stable isotopic values of HC gases (C<sub>1</sub>–C<sub>5</sub>)  
56 generated by artificial maturation of sedimentary organic matter.

57

## 58 **2. Experimental**

### 59 *2.1. Kerogen sample*

60 Kerogen was isolated from Hovea-3 well core from the basal Kockatea Shale,  
61 Perth Basin Western Australia at 978.3–978.4 m, which is a representative of the  
62 Sapropelic Interval, Hovea Member. The uppermost Permian interval of the Hovea  
63 Member consists of inertinitic kerogen (Intertinitic Interval) whereas the Lower Triassic  
64 Sapropelic Interval contains Type II algal-rich kerogen (Thomas and Barber, 2004;  
65 Thomas et al., 2004; Grice et al., 2005, 2007). The sampled kerogen contained 61%  
66 total organic carbon (TOC) and yielded Rock-Eval Hydrogen Index (624 mg/g TOC),  
67 Oxygen Index (22 mg/g TOC) and a T<sub>max</sub> at 428 °C.

68

### 69 *2.2. MSSV-Py*

70 Artificial maturation experiments were performed using the principles of MSSV-  
71 Py (Horsfield et al., 1989). Aliquots of kerogen (0.87 and 2.75 mg) were loaded into  
72 MSSV glass capillary tubes (5 cm x 5 mm i.d.), the void volume was filled with

73 thermally pre-cleaned (400 °C overnight) glass beads (60–80 mesh) and the tubes were  
74 flame sealed. The MSSV tubes were heated in an Al block at 300 °C. The temperature  
75 was increased at 0.7 °C/min and the tubes were removed from the heating block at 389  
76 °C and 415 °C, representing kerogen transformation ratios (TR) of 0.3 and 0.7,  
77 respectively (Horsfield and di Primio, 2010). The method developed (see below) was  
78 then applied to determine the gas yields of the artificially matured Kockatea shale  
79 samples for comparison with previously published results from the same samples and  
80 under the same conditions using online MSSV-Py (Horsfield and di Primio, 2010).

81

### 82 *2.3. Offline gas sampling*

83 The apparatus and procedure for offline sampling of the generated HC gases is  
84 shown in Fig. 1. The individual MSSV tubes were placed between the side port and  
85 main chamber of the gas sampler. The device was evacuated for 5 minutes by  
86 connecting the side port of the sampler to a vacuum line using a custom Swagelok  
87 fitting. The device was then filled with helium at atmospheric pressure after which the  
88 MSSV tube was crushed by winding down the threaded glass stopcock. The main  
89 chamber of the sampling device containing the crushed sample was heated to 120 °C by  
90 inserting through a vacant injector port of a Hewlett Packard 5890 GC oven. After  
91 cooling to ambient temperature the gaseous products released were sampled using a gas-  
92 tight syringe and analysed by GC and GC-IRMS.

93

### 94 *2.4. GC and GC-IRMS analyses*

95 GC analysis of  $n$ -C<sub>1</sub> to  $n$ -C<sub>5</sub> HC gases was performed using a Hewlett Packard  
96 5890 gas chromatograph equipped with a HP-PlotQ column (30 m x 0.32 mm i.d.; film

97 thickness 20  $\mu\text{m}$ ). Helium carrier gas was used at a constant pressure of 16 psi and a  
98 split ratio of 20:1. The GC oven temperature was held at 200  $^{\circ}\text{C}$  to achieve optimum  
99 separation of gases and the flame ionisation detector at 250  $^{\circ}\text{C}$ . A gas standard  
100 consisting of  $\text{C}_{1-5}$  hydrocarbons (Table 1) was used to confirm baseline resolution of the  
101 individual components and to check linearity, reproducibility and detection limits for  
102 GC analysis. Calibration curves for quantitation of individual compounds were  
103 developed by performing multiple injections of different volumes of the gas standard  
104 from gas sampling bags filled at known pressure (1 atm). Peak areas were plotted as a  
105 function of the number of moles of each component, calculated from the ideal gas law  
106 ( $PV = nRT$ ); where P is the partial pressure of the gas, V is the volume of gas injected,  
107 and T is the laboratory temperature (22  $^{\circ}\text{C}$ ). The calibration was repeated every 3 days  
108 to ensure stability and reproducibility. The yields ( $\mu\text{g/g}$  sample) of generated HC gases  
109 from the Kockatea shale kerogen were calculated by injecting a 200  $\mu\text{l}$  aliquot from the  
110 gas sampling device (total volume 1.6 ml) at known internal pressure (1 atm).

111 The carbon isotope analysis of the generated gases was performed using a  
112 Micromass IsoPrime isotope ratio monitoring-mass spectrometer (irm-MS) interfaced to  
113 a Hewlett Packard HP 6890 gas chromatograph (GC) with a GS-Carbon plot column  
114 (30 m x 0.32 mm i.d x 3  $\mu\text{m}$  film thickness). The GC oven was initially held at 70  $^{\circ}\text{C}$  for  
115 1 min, heated at rate of 20  $^{\circ}\text{C}/\text{min}$  to 250  $^{\circ}\text{C}$ , and held for 5 min. Helium was used as  
116 carrier gas. Analyses were performed using two different sized gas loops (250  $\mu\text{l}$  and  
117 500  $\mu\text{l}$ ) with a split ratio of 20:1. Stable carbon isotopic compositions are expressed in  
118 ‰ (parts per thousand) relative to the international carbon isotope reference material  
119 Vienna Pee Dee Belemnite (VPDB).

120

### 121 3. Results and discussion

#### 122 3.1. Gas composition and yield

123 The procedure was applied to Kockatea shale kerogen samples, artificially  
124 matured to transformation ratios (TR) of 0.3 and 0.7, to confirm reproducibility and  
125 compare the HC gas yields using the offline technique with those obtained previously  
126 by online MSSV pyrolysis (Horsfield and di Primio, 2010). Excellent reproducibility  
127 was observed for duplicate offline pyrolysis experiments (Table 2). HC gas yield  
128 increased with temperature due to increased conversion of kerogen to volatile products.  
129 However, it is evident that the gas yields from the offline injection method are between  
130 1.6–4.8 times lower than those obtained by online MSSV-Py. This is most likely related  
131 to the different injection conditions employed for each method. Online MSSV-Py  
132 involves crushing the sample tube directly inside a heated injector system (typically 300  
133 °C) under a constant flow of helium. In contrast, the offline approach involves heating  
134 the crushed sample to 120 °C to mobilise and equilibrate the gaseous components within  
135 the sampling device prior to GC analysis. Adsorption of gas products to the exposed  
136 pyrolysed kerogen residue may explain the lower yields. However, no significant  
137 differences in gas yields were observed by adding a known amount of the standard gas  
138 mixture to the device with and without kerogen residue. In addition, heating the main  
139 chamber of the sampling device to higher temperatures (350 °C) after crushing duplicate  
140 MSSV pyrolysed kerogen samples also showed no significant difference in gas  
141 distribution and yields at the higher temperature, indicating minimal, if any, adsorption  
142 to the kerogen residue. We therefore attribute the lower gas yields compared with the  
143 previous online study not to thermal transfer effects but to the absence of He carrier gas  
144 flushing within the offline system.



### 145 3.2. $\delta^{13}\text{C}$ of gaseous hydrocarbons

146 The gas sampling device was filled with the standard gas mixture at atmospheric  
147 pressure to investigate the potential for isotopic fractionation due to temperature and  
148 time. Table 1 shows that no significant isotopic fractionation was observed for any  $\text{C}_{1-5}$   
149 hydrocarbons as a result of the mild heating (120 °C) used to mobilise/equilibrate the  
150 gaseous products within the device. Fig. 2 shows changes in  $\delta^{13}\text{C}$  values for  $\text{C}_{1-4}$   
151 hydrocarbons over a 23 h period using 250  $\mu\text{l}$  and 500  $\mu\text{l}$  gas loops.  $\delta^{13}\text{C}$  values showed  
152 no isotopic fractionation within 1 hour and only minor fractionation to more enriched  
153 values within 5 hours. However, significant fractionation was observed after 22 h. The  
154  $\delta^{13}\text{C}$  values for all the compounds become heavier over time, most likely due to  
155 preferential loss of the isotopically lighter components from the system through the  
156 punctured septa of the gas sampling device. It is recommended that the generated gas  
157 hydrocarbons should be sampled within 1 hour to avoid isotopic alteration.

### 159 4. Conclusions

160 An offline sampling technique coupled to GC and GC-IRMS was developed in  
161 order to determine the gas yields and  $\delta^{13}\text{C}$  values of hydrocarbons ( $\text{C}_{1-5}$ ) generated from  
162 MSSV-Py artificial maturation of kerogen from the Kockatea Shale (Perth Basin, WA).  
163 The HC gas yields using this offline approach were slightly lower than previous results  
164 for the same sample using online MSSV-Py, most likely due to the absence of He  
165 carrier gas flushing within the offline system. GC-IRMS results showed no significant  
166 isotopic fractionation of HC gases within 1 hour of crushing the MSSV sample, nor due  
167 to the mild heating used to mobilise the gaseous components within the sampling  
168 device. This offline sampling technique is rapid and inexpensive, enabling multiple

169 isotopic analyses of gases generated by laboratory maturation. The approach has great  
170 scope for characterising gas formation in sedimentary systems.

171

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178

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180

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## 211 Tables

212 Table 1. Composition and carbon isotopic values of the standard gas mixture and  
 213 stable carbon isotope measurements of the gases within the sampling device at ambient  
 214 temperature (22 °C) and after heating to 120 °C. Numbers in parentheses are standard  
 215 deviations; superscript indicates the number of replicate analyses.

Component	Mole Fraction (%)	$\delta^{13}\text{C}$ (‰)	22 °C	120 °C
Methane	75.9	-46	-45.6 [0.11] <sup>2</sup>	-45.6 [0.08] <sup>2</sup>
Ethane	9.14	-31.3	-30.9 [0.07] <sup>2</sup>	-30.9 [0.09] <sup>2</sup>
Propane	5.87	-35.1	-35.2 [0.16] <sup>2</sup>	-35.2 [0.18] <sup>2</sup>
<i>iso</i> -Butane	2.97	-29.3	-30.0 [0.21] <sup>2</sup>	-30.0 [0.15] <sup>2</sup>
<i>n</i> -Butane	3.01	-25.2	-25.3 [0.19] <sup>2</sup>	-25.3 [0.22] <sup>2</sup>
<i>iso</i> -Pentane	1.07	-27.1	-23.6 [0.31] <sup>2</sup>	-23.7 [0.26] <sup>2</sup>
<i>n</i> -Pentane	1.05	-23.8		
CO <sub>2</sub>	0.989	-8.2		

217

218

219 Table 2. Comparison of gas yields ( $\mu\text{g/g}$ ) from Kockatea shale kerogen at two different  
 220 transformation ratios (0.3 and 0.7) using offline (this study) and online (Horsfield and di  
 221 Primio, 2010) GC analysis. Duplicate values for the new offline technique are provided.

222

TR 0.3

TR 0.7

Component	Offline	Online	Offline	Online
Methane	1471, 1423	2569	3868, 3978	6334
Ethane	850, 818	1968	2422, 2462	5881
Propane	916, 908	2123	2750, 2806	5837
<i>iso</i> -Butane	242, 220	617	718, 786	1432
<i>n</i> -Butane	424, 406	1462	1862, 1896	4222
<i>iso</i> -Pentane	174, 160	797	616, 644	1777
<i>n</i> -Pentane	244, 214	915	1743, 1761	2977

223

224

225 **Figures**

226

227 Fig. 1. Schematic representation of gas sampling device; (a) Sample loading and

228 evacuation (b) Sample crushing and gas analysis.

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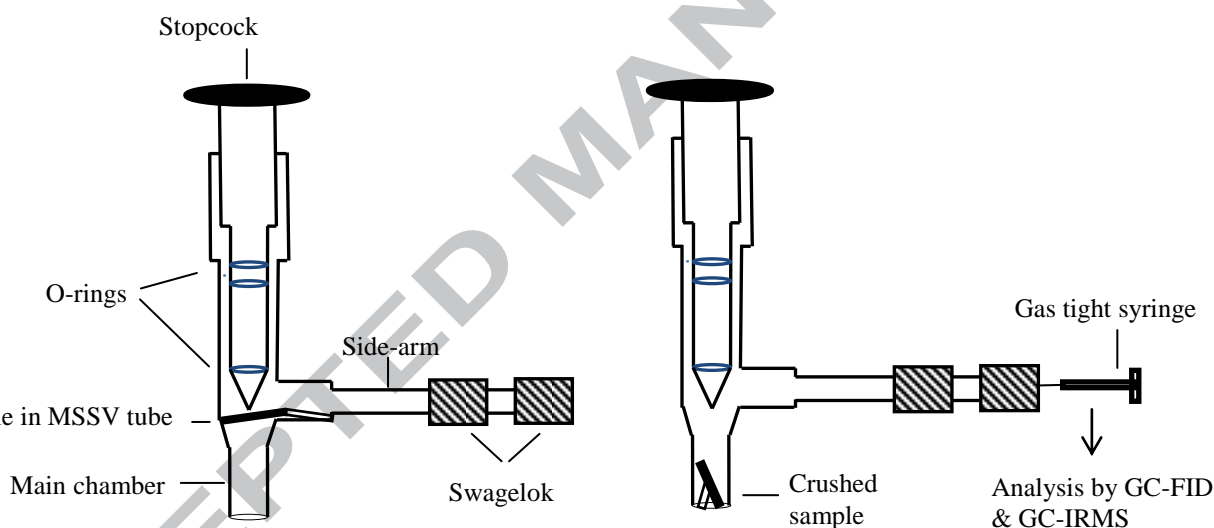
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240 Fig. 2. Stable carbon isotope measurements of HC gases over time using (a) 500  $\mu$ l and241 (b) 250  $\mu$ l gas loops.

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