

1 Observations of the Release of Non-Methane 2 Hydrocarbons from Fractured Shale

3 *Roberto Sommariva¹, Robert S. Blake¹, Robert J. Cuss², Rebecca Cordell¹, Jon F. Harrington², Iain*
4 *R. White¹ & Paul S. Monks^{1,*}*

5 ¹Department of Chemistry, University of Leicester, Leicester, UK.

6 ²British Geological Survey (BGS), Nottingham, UK.

7 * To whom correspondence should be addressed (e-mail: P.S.Monks@leicester.ac.uk)

8

9 **Abstract**

10 The organic content of shale has become of commercial interest as a source of hydrocarbons, owing
11 to the development of hydraulic fracturing (“fracking”). While the main focus is on the extraction of
12 methane, shale also contains significant amounts of Non-Methane Hydrocarbons (NMHC). We
13 describe the first real-time observations of the release of NMHC from a fractured shale. Samples
14 from the Bowland-Hodder formation (England) were analysed under different conditions using
15 mass spectrometry with the objective of understanding the dynamic process of gas release upon
16 fracturing of the shale. A wide range of NMHC (alkanes, cycloalkanes, aromatics and bi-cyclic
17 hydrocarbons) are released at ppm or ppb level with temperature and humidity-dependent release
18 rates, which can be rationalised in terms of the physio-chemical characteristics of different
19 hydrocarbons classes. Our results indicate that higher energy inputs (i.e. temperatures) significantly
20 increase the amount of NMHC released from shale, while humidity tends to suppress it;
21 additionally, a large fraction of the gas is released within the first hour after the shale has been
22 fractured. These findings suggest that other hydrocarbons of commercial interest may be extracted
23 from shale and open the possibility to optimise the “fracking” process, improving gas yields and
24 reducing environmental impacts.

25

26 **Introduction**

27 Shale is an abundant type of sedimentary rock comprising silt and clay-sized particles with
28 significant quantities of organic matter. The content of organic matter in shale is typically in the
29 range of 1-3% (and as high as 8%)¹ by weight, but change significantly between different types of
30 shale.² Shales rich in organic matter have long been known as the sources of gas and oil that
31 constitute the “conventional” hydrocarbon reservoirs.^{3,4} Over the past five years, there has been a
32 renewed interest in shales as “unconventional” hydrocarbon reservoirs, especially methane and light
33 alkanes (shale gas), due to a combination of rising oil prices, security of supply (e.g. political
34 instability in certain parts of the world) and improved technology.^{4,5,6} In order to extract oil or gas
35 from shale it is necessary to pervasively fracture the shale formation. This technique, termed
36 hydraulic fracturing (commonly known as “fracking”), consists of drilling a well in the prospective
37 shale units and injecting water under high pressure mixed with sand (~5%) and chemical additives
38 (~0.2%) in order to fracture the rock and stimulate the release of hydrocarbons.^{4,6} Because of the
39 nature of hydraulic fracturing, the release of gas from shale is a dynamic process influenced by the
40 amount of energy transmitted to the rock in the form of changes to stress, pore pressure and
41 temperature.

42 The growth of hydraulic fracturing in recent years has raised several concerns about its
43 environmental impact,^{4,5,7,8} especially with regard to the contamination of ground and surface
44 waters^{4,9} and to the potential triggering of minor earthquakes.^{4,6,7} Shale exploitation also has
45 important implications for air quality and climate change: while much of the atmospheric impact is
46 related to the industrial and transport operations surrounding the extraction of gas,^{10,11} the release of
47 hydrocarbons into the atmosphere from oil and gas extraction activities is well documented¹²⁻¹⁶ and
48 it can lead to the formation of high concentrations of pollutants, such as ozone (>100 parts per
49 billion by volume).^{13,16}

50 In this work, we simulated the pervasive fracturing of a shale specimen and we present a real-time
51 analysis of the release of Non-Methane Hydrocarbon (NMHC) gases from a fractured shale. In

52 recent years, several studies have reported observations of hydrocarbons emissions from extraction
53 of oil and gas (e.g., ^{12,14,15}), but, to our knowledge, this is the first time that the dynamic release of
54 gas from a fractured shale sample has been reported at this level of detail. It must be noted that there
55 are significant differences between our experiments and an actual “fracking” event (as will be
56 discussed in more detail below); there are also large differences in the mineralogical composition
57 and organic content of different shale formations.^{1,2} For these reasons, our results cannot be directly
58 extrapolated to “real world” hydraulic fracturing or to other types of shales; however, they provide a
59 first look into the type of hydrocarbons stored in shale and into the dynamic processes involved in
60 their release when the shale is fractured.

61

62 **Experimental**

63 A shale specimen was collected from a part of the Bowland-Hodder formation in Lancashire (north-
64 western England), which is currently under consideration for commercial exploitation.¹ The
65 specimen was collected from a stream bed, meaning that the material was exposed by stream
66 erosion of the stream in recent times (in geological terms). Shale of this kind has a thin (~1 cm)
67 “skin” of oxidized material, below which the material is similar to deep borehole material. The
68 diffusion rate of gas through the shale at ambient temperature (see below) suggests that only a small
69 fraction of the gas content will have been lost during the exposure period. Using stream samples is
70 not the ideal sampling method, which would be drilling deep boreholes and taking well preserved
71 shale cores; however, that is an expensive procedure and core material was not available for this
72 work.

73 The specimen weighted 17.7 kg, with an average carbon, sulphur and water content were 2.87%,
74 1.84% and 3.9% by weight, respectively. Cylindrical core samples (C2, B1, D1, D2, see Table 1) of
75 54 mm diameter x 25 mm height and ~127 g mass, were prepared at the British Geological Survey
76 (Nottingham, UK) and rectangular samples of various sizes were produced at the Department of
77 Geology (University of Leicester, UK) from the shale specimen. All these samples were taken from

78 below the weathered “skin” of the specimen and sealed in air-tight polythene envelopes until ready
79 for analysis.

80 In order to achieve a pervasive fracturing of the rock, the shale samples were placed inside an open-
81 top aluminium box (12 x 10 x 2 cm), which was sealed in a Tedlar bag. A manual press was then
82 used to crush the sample inside the bag, taking care of not piercing the bag in the process. The
83 crushed sample was then transferred in a desiccator containing a cast iron vessel (a domestic
84 mortar), placed on a temperature controlled hot plate. The mortar acted as a heat sink to help bring
85 the crushed sample up to the desired temperature as quickly as possible. A Kin-Tek 419M
86 calibration unit (Ecoscientific Ltd., UK) fitted with a humidity generator supplied a stream of high
87 purity nitrogen (400 sccm; N6.0 grade, BOC gases).

88 Prior to each experiment, all materials were cleaned with de-ionised water in an ultrasonic bath,
89 washed with hexane and rinsed again in de-ionised water. The mortar was then placed into the
90 desiccator and allowed to dry overnight while flushing with 150 sccm of high purity nitrogen.

91 During the transfer of the crushed shale samples from the Tedlar bag into the desiccator, the flow of
92 nitrogen was increased from 150 sccm to 4000 sccm, in order to minimise contamination by
93 laboratory air for the brief period in which the desiccator lid was lifted.

94 Each experiment had a duration between 60 and 240 minutes, depending on the sample, the
95 conditions and the instruments used. The first five minutes of measurements were rejected to enable
96 the sample to reach the desired temperature/humidity and to exclude contamination by laboratory
97 air. Table 1 lists the experiments discussed in the main text, with the details of the shale sample and
98 the conditions used in each experiment. All samples were analysed using mass spectrometric
99 techniques: details of the instruments, calibrations and methods, as well as preparation of the
100 samples, are described in the Supporting Information.

101 In order to observe the release of NMHC from the crushed samples in real-time, the fast analytical
102 speed of quantitative chemical ionisation offered by Proton-Transfer-Reaction Time-of-Flight Mass-
103 Spectrometry (PTR-TOF-MS)¹⁷⁻¹⁹ was employed. However, the PTR technique is not sensitive to

104 some classes of compounds,^{18,20} so the identification of the whole range of hydrocarbons found in
105 the shale samples was carried out using Thermal-Desorption Gas-Chromatography Mass-
106 Spectrometry (TD-GC-MS).²¹ Linear and branched alkanes (C₅-C₁₂), aromatics (C₈-C₁₂) and mono-
107 and bi-cyclic hydrocarbons were detected in all samples at ppm (μmol/mol) or ppb (nmol/mol)
108 level; carbon disulphide (CS₂) was also detected in all samples. The complete list of NMHC
109 identified by TD-GC-MS is shown in Table SI-1.

110 The TD-GC-MS has high selectivity, but a much lower sampling frequency than the PTR-TOF-MS
111 (1 hour vs. 1 minute) and therefore it does not allow to follow the release of NMHC from fractured
112 shale samples in real-time. For this reason, much of the following discussion will be focused on the
113 larger NMHC (≥C₅), as measured by PTR-TOF-MS.

114 Aromatic compounds are easily identifiable by PTR-TOF-MS, although isomers cannot be
115 distinguished.²⁰ Alkanes, however, are known to fragment^{22,23} even with soft-ionization techniques
116 such as proton-transfer, characteristically losing successive methylene groups (-CH₂). When
117 sampling complex hydrocarbon mixtures, this results in mass spectra where a given mass channel
118 include the parent ion of an alkane ([M-1]⁺) plus contributions from isobaric branched isomers and
119 methylene loss from heavier acyclic alkanes. We employed a simple deconvolution model
120 (described in detail in the Supporting Information) based upon the similarities of the fragmentation
121 patterns of aliphatic compounds^{22,23} to determine the PTR-TOF-MS sensitivities for selected *m/z*
122 channels and calculate the concentrations of ≥C₅ alkanes released from crushed shale.

123 All data were background-subtracted, using spectra taken before and after each experiment; the
124 PTR-TOF-MS spectra were normalized to 1 million counts of the hydronium ion (H₃O⁺, *m/z* = 19),
125 thus ensuring that the analysis of the data was not influenced by contamination from ambient air or
126 by variations in the humidity of the sample (which may change the H₃O⁺ ion count and therefore
127 the sensitivity of the instrument).

128

129 **Results and Discussion**

130 The release of NMHC from a ~200 g shale sample (A4-6, see Table 1) was observed over a period
131 of 24 hours under different conditions. At first, the sample was uncrushed and kept at ambient
132 temperature (~23 °C); after 6 hours, temperature was increased to ~75 °C; finally, after
133 approximately 12 hours, the sample was crushed and observed again at high temperature (~80 °C,
134 similar to rock temperature at ~3.2 km of depth). The time-series for selected NMHC are shown in
135 Figure 1. The results show that, if the shale is uncrushed at ambient temperature, very little NMHC
136 are released. Raising the temperature increases the release of NMHC by a factor of 5 to 10. When
137 the rock is crushed, NMHC release increases by an additional factor of 4 to 8, even after almost 12
138 hours spent at high temperature. The observed behaviour indicates that most of the hydrocarbon
139 mass is trapped inside the shale and cannot be released simply by volatilization at high temperature
140 (see Supporting Video).

141 The data in Figure 1 also show that the release rates of gases from an uncrushed shale above room
142 temperature slowly decrease with time, except for heavier aromatics ($\geq C_9$), whose release rates are
143 almost constant. After the shale has been crushed the release rates of all NMHC show a sharp
144 decrease. The pattern of gas release post-crushing suggests that different NMHC are stored in the
145 shale and released from it by different mechanisms, depending on their mode of storage.

146 To better understand the dynamics of the gas release, several shale samples (Table 1) were crushed
147 and analysed by PTR-TOF-MS under a range of conditions (hot/cold, dry/humid) in real-time.
148 Figure 2 shows the time-series of selected compounds for a typical set of experiments. The amount
149 of gas released is higher (2-5 times) when the rock is crushed in dry air than when it is crushed in
150 humid air (50-60% RH); it is also much higher (~10 times) at high temperature (70-80 °C,
151 comparable to *in-situ* values) than at ambient temperature (23-25 °C). Under all conditions, the
152 maximum concentrations of all NMHC were observed within 30-45 minutes after the rock had been
153 crushed (Figure 2). The total amount of gas per unit mass of shale released during the first ~2 hours
154 after the rock was crushed is shown in Table 2; most of the NMHC mass is constituted of alkanes
155 and cycloalkanes (tens to hundreds of ppm/g) followed by bicycloalkanes (hundreds to thousands of

156 ppb/g) and aromatics (hundreds of ppb/g or less). Note that the numbers shown in Table 2 do not
157 represent the total content of gas in the shale samples but only the fraction released within the time
158 window of the experiments.

159 Analysis of the PTR-TOF-MS data using piecewise regression analysis on all samples (Table 1)
160 indicates that the release of gases from a shale occurs on two timescales (Figure 3): an initial “fast”
161 release ($1\text{-}5\text{ s}^{-1}$), during the first 20-40 minutes after the shale has been crushed, followed by a
162 secondary “slow” release ($0.5\text{-}2\text{ s}^{-1}$), comparable to that from the uncrushed shale (Figure 1). It can
163 be hypothesized that the initial release involves gas stored in the nanometre-scale pores of the
164 shale,^{24,25} which is quickly released when the shale is crushed. As Figure 3 shows, the initial release
165 rates are typically faster for alkanes, cycloalkanes and bi-cyclic hydrocarbons, which are more
166 volatile than aromatics and thus released promptly upon fracturing of the shale. The initial release
167 of the more volatile NMHC is faster at low temperature and high humidity, which may be caused by
168 expansion of the clay minerals owing to swelling under these conditions.

169 In contrast, the release rates of aromatics are very similar during both the initial and the secondary
170 release, suggesting that these species are adsorbed on the mineral surface and need additional
171 energy to be released. Since the presence of water interferes with the desorption of the molecules,
172 this would explain why the release of aromatics is stimulated at higher temperature and suppressed
173 at higher humidity (Figure 3).

174 Our observations show consistent patterns but also significant variability among the samples
175 (Figure 3), despite being taken from the same shale specimen. The variability is due to several
176 factors, including of natural heterogeneity of the rock,² the technical difficulty of achieving
177 consistent fracturing of the samples in the laboratory, the differences in temperature between the
178 surface and the bulk of the samples and the variation in the natural moisture content of the shale
179 itself. It must be noted that the laboratory fracturing process described above differs from the actual
180 “fracking” process in several respects: hydraulic fracturing occurs at depths of hundreds to
181 thousands of meters where pressure is of the order of tens MPa.^{1,4} As explained above, the specimen

182 was a surface outcrop and it is likely that the changes in humidity, temperature and pressure as the
183 rock surfaced over a period of thousands of years caused the partial or total loss of some of the
184 more weakly bound gases. Additionally, the specimen was collected from a stream bed and
185 therefore, it had remained submerged in water for a long period of time (of the order of hundreds of
186 years): the external part of the specimen was carefully excluded from the analysis and the specimen
187 was dry when it was analysed, but the geological history of the specimen might have affected its gas
188 content both in terms of composition and in terms of quantity. Another important point is that
189 hydraulic fracturing uses a mixture of water, sand and additives injected at high pressure to crush
190 the rock:⁴ it is distinctively different from the mechanical fracturing used in this study, although it is
191 unclear whether this might have influenced the results.

192 Our results give insight, for the first time, into the time-dependent release of NMHC from a shale
193 deemed suitable for “fracking”.¹ It is clear that further studies, ideally using deep borehole cores,
194 will be necessary to properly address the issues raised by the differences between laboratory
195 fracturing and “real world fracking”.

196 Methane and light alkanes constitute the main impetus behind the commercial exploitation of
197 shale,^{4,6,26} but there are many other hydrocarbons in shale which are released during the “fracking”
198 process: some of these may be of commercial interest²⁶ if their retrieval can be made economically
199 viable. The release of most NMHC peaks within 45-60 minutes after the shale is crushed (Figure 2):
200 if not extracted rapidly, this fraction of shale gas may be lost, reducing the economic output and
201 resulting in potential contamination of ground and surface waters and the atmosphere.

202 Since we have analysed only one type of shale, it is reasonable to expect variability in the type and
203 amounts of NMHC released from different shale formations. There is an urgent need for further
204 work to understand the fundamental relationships between gas release, energy input, temperature
205 and humidity. The outcome could lead to opportunities to optimise the “fracking” process, improve
206 its efficiency and reduce the environmental impact.

207

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212 University of Leicester) for her comments and suggestions. The authors declare no competing
213 financial interest.

214

215 **Supporting Information.** Additional information about the shale specimen, including a video
216 showing the release of gas from a heated shale sample, the full list of NMHC identified by gas-
217 chromatographic analysis, details of the deconvolution model used to determine the PTR-TOF-MS
218 sensitivities and typical spectra can be found in the Supporting Information. This material is
219 available free of charge via the Internet at <http://pubs.acs.org/>.

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- 296
- 297

Sample ID	Sample Mass (g)	Sample Status	Temperature (°C)	Relative Humidity (%)
A1-a	80.1	Crushed	50	0
A1-b	80.1	Uncrushed	50	0
	80.1	Crushed	25	0
A1-c	70.1	Crushed	25	0
A1-d	81.3	Crushed	50	60
C2 (†)	118.4	Crushed	80	0
B1 (†)	116.7	Crushed	75-81	52-54
D1 (†)	117.7	Crushed	23	0
D2 (†)	114.4	Crushed	23	49-50
A4-1	127.4	Crushed	80	0
A4-2	216.27	Crushed	80	0
A4-3	242.9	Crushed	80	0
A4-4	251.1	Crushed	80	0
A4-6	215.0	Uncrushed	23	0
	215.0	Uncrushed	23-75 (*)	0
	206.7 (**)	Crushed	75-85	0

300 (†) Cylindrical core samples (54 x 25 mm): the mass before crushing was ~127 g.

301 (*) The experiment started at 23 °C: temperature increased to 75 °C within an hour.

302 (**) Approximately 10 g of the sample were lost during the crushing process.

303

304 **Table 1.** List of samples and experimental conditions.

305

	Hot/Dry (sample C2)	Hot/Humid (sample B1)	Cold/Dry (sample D1)	Cold/Humid (sample D2)
m/z=83 (≥ C6 cycloalkanes)	451914.4	151969.8	43670.17	10698.69
m/z=85 (≥ C6 alkanes)	398684.3	121474.1	28515.1	5912.4
m/z=97 (≥ C7 cycloalkanes)	515792.2	186054.6	63555.1	25678.5
m/z=99 (≥ C7 alkanes)	515527.8	165174.6	41565.1	25848.1
m/z=107 (C8 aromatics)	62.4	25.2	9.1	4.1
m/z=121 (C9 aromatics)	113.5	39.9	9.3	4.6
m/z=133 (benzocyclohexane)	1.6	0.7	0.2	0.1
m/z=135 (C10 aromatics)	15.9	6.7	1.3	0.6
m/z=137 (C10 bicycloalkanes)	7952.6	1774.4	831.5	170.8

307

308 **Table 2.** Total NMHC per unit mass of shale released over a period of 1:50 hours after crushing of
309 the shale sample under different conditions. The shale samples were cylindrical cores (C2, B1, D1,
310 D2, see Table 1) with mass ~127 g before crushing. Units in ppb (nmol/mol) of gas per gram of
311 rock.

312

313 TOC/Abstract Art

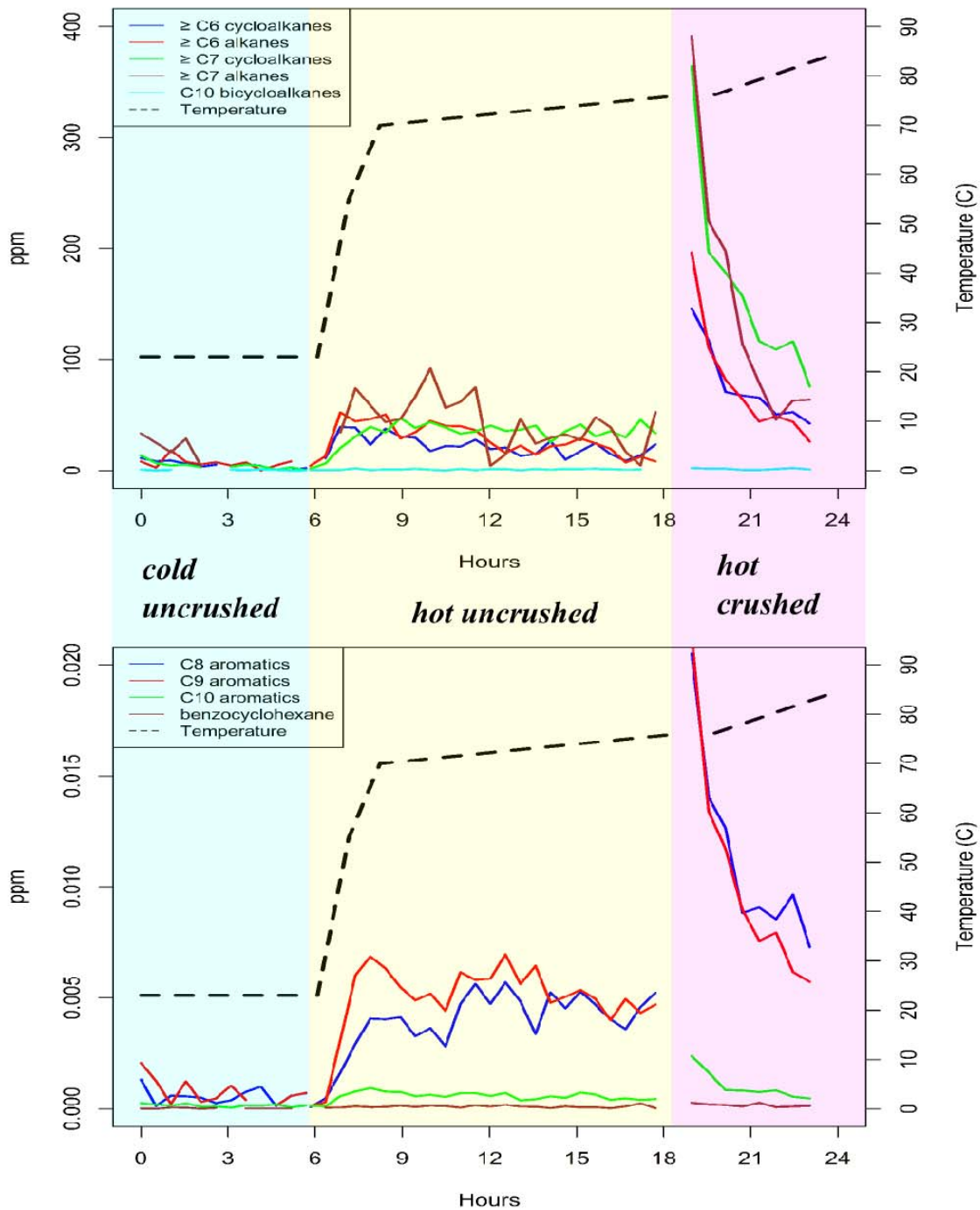
314



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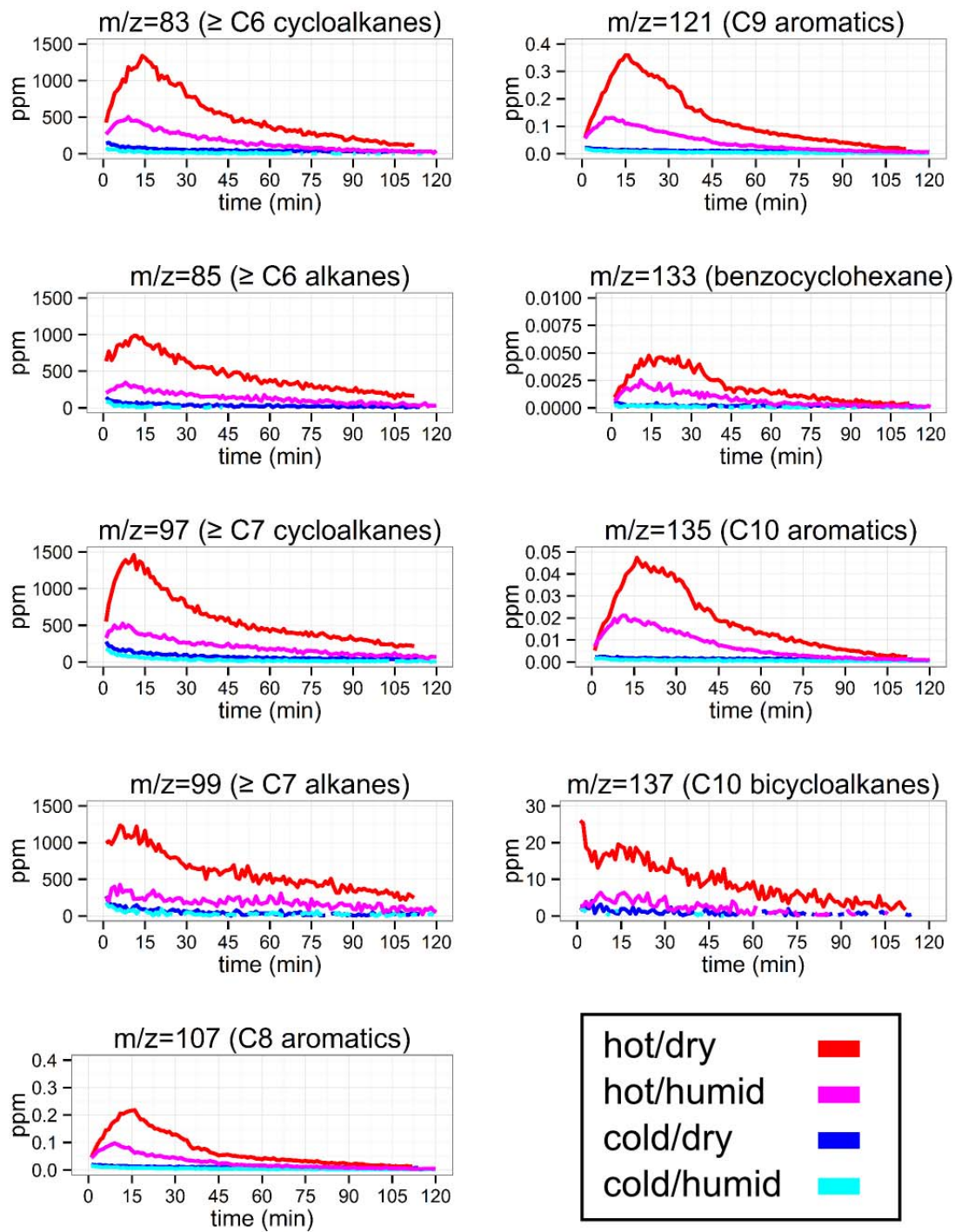
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317



320

321 **Figure 1.** Time-series of selected NMHC released from a shale sample. The sample (A4-6, see
 322 Table 1) weighted 207-215 g and was observed over a period of 24 hours under different conditions:
 323 (shaded cyan) uncrushed at 23 °C; (shaded yellow) uncrushed at 75 °C; (shaded magenta) crushed at
 324 80 °C.



326

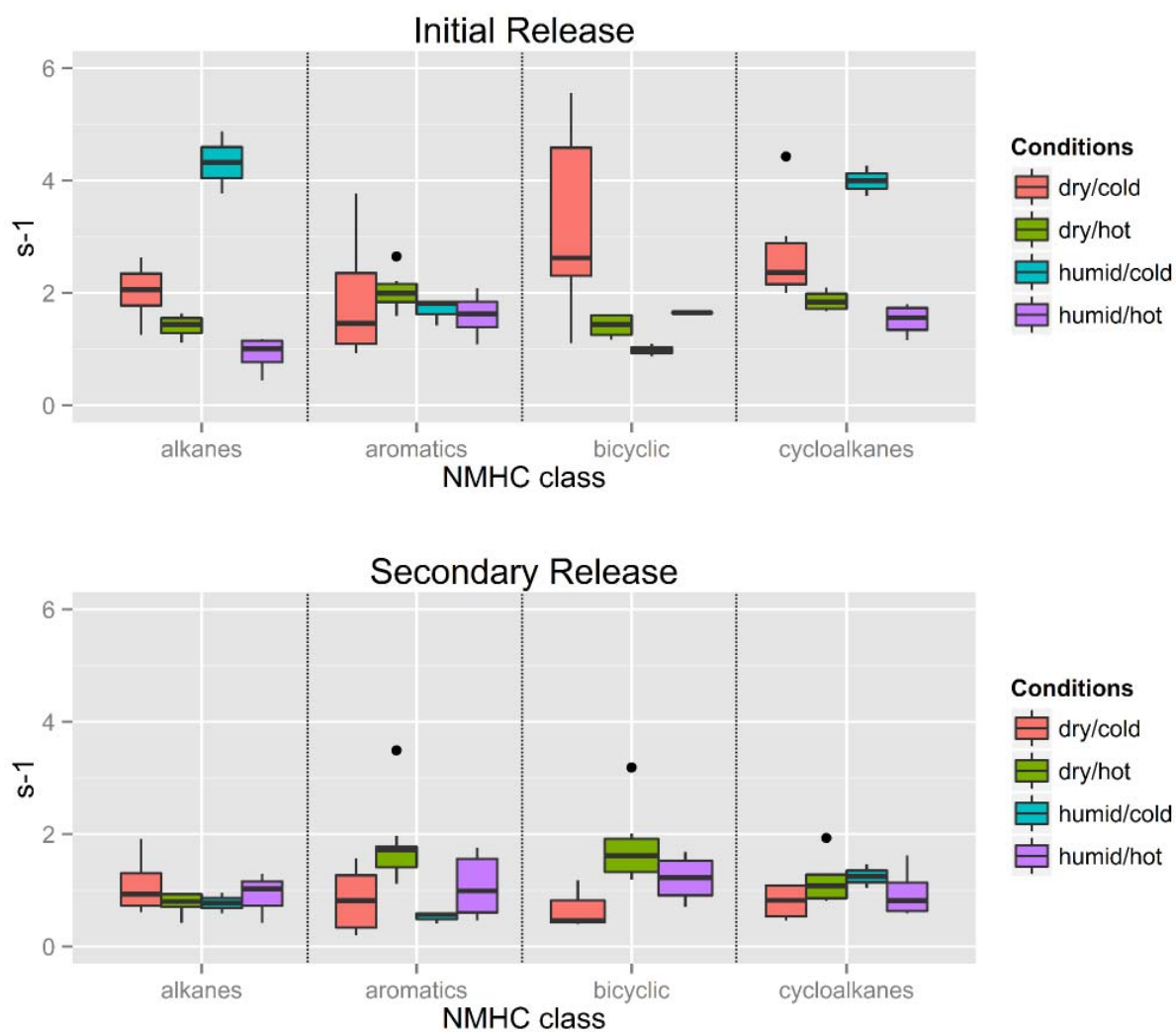
327 **Figure 2.** Effect of temperature and humidity on the release of NMHC from crushed shale samples.

328 The shale samples were cylindrical cores (C2, B1, D1, D2, see Table 1) with mass ~127 g before

329 crushing. The samples were crushed and placed under hot (70-80 °C) or cold (23-25 °C), dry or

330 humid (50-60%) conditions.

331



332

333 **Figure 3.** Initial (top panel) and secondary (bottom panel) release rates of classes of NMHC from
 334 crushed shale samples under different experimental conditions: hot (70-80 °C) or cold (23-25 °C),
 335 dry or humid (50-60%). The bottom and top of the box represent the first and third quartiles, the
 336 whiskers represent the ± 1.5 interquartile range (IQR), the points are the outliers. All the crushed
 337 samples listed in Table 1 have been taken into account.

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