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

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Abstract

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

Introduction

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

The growth of hydraulic fracturing in recent years has raised several concerns about its environmental impact,[4,5,7,8] especially with regard to the contamination of ground and surface waters[4,9] and to the potential triggering of minor earthquakes.[4,6,7] Shale exploitation also has important implications for air quality and climate change: while much of the atmospheric impact is related to the industrial and transport operations surrounding the extraction of gas,[10,11] the release of hydrocarbons into the atmosphere from oil and gas extraction activities is well documented[12-16] and it can lead to the formation of high concentrations of pollutants, such as ozone (>100 parts per billion by volume).[13,16]

In this work, we simulated the pervasive fracturing of a shale specimen and we present a real-time 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 (C_5-C_{12}), aromatics (C_8-C_{12}) and mono-

107   and bi-cyclic hydrocarbons were detected in all samples at ppm (μmol/mol) or ppb (nmol/mol)

108   level; carbon disulphide (CS_2) 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 ($\geq C_5$), 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 (–CH_2). 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 $\geq C_5$ alkanes released from crushed shale.

123   All data were background-substracted, using spectra taken before and after each experiment; the

124   PTR-TOF-MS spectra were normalized to 1 million counts of the hydronium ion (H_3O^+, *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 H_3O^+ ion count and therefore

127   the sensitivity of the instrument).

128

129   **Results and Discussion**

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

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

To better understand the dynamics of the gas release, several shale samples (Table 1) were crushed and analysed by PTR-TOF-MS under a range of conditions (hot/cold, dry/humid) in real-time. Figure 2 shows the time-series of selected compounds for a typical set of experiments. The amount of gas released is higher (2-5 times) when the rock is crushed in dry air than when it is crushed in humid air (50-60% RH); it is also much higher (~10 times) at high temperature (70-80 ºC, comparable to *in-situ* values) than at ambient temperature (23-25 ºC). Under all conditions, the maximum concentrations of all NMHC were observed within 30-45 minutes after the rock had been crushed (Figure 2). The total amount of gas per unit mass of shale released during the first ~2 hours after the rock was crushed is shown in Table 2; most of the NMHC mass is constituted of alkanes 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 (1-5 s^{-1}), during the first 20-40 minutes after the shale has been crushed, followed by a

162 secondary "slow" release (0.5-2 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 interest[26] 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

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

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297

298 **Tables**

299

Sample ID	Sample Mass (g)	Sample Status	Temperature (ºC)	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 ºC: temperature increased to 75 ºC 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

306

	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.
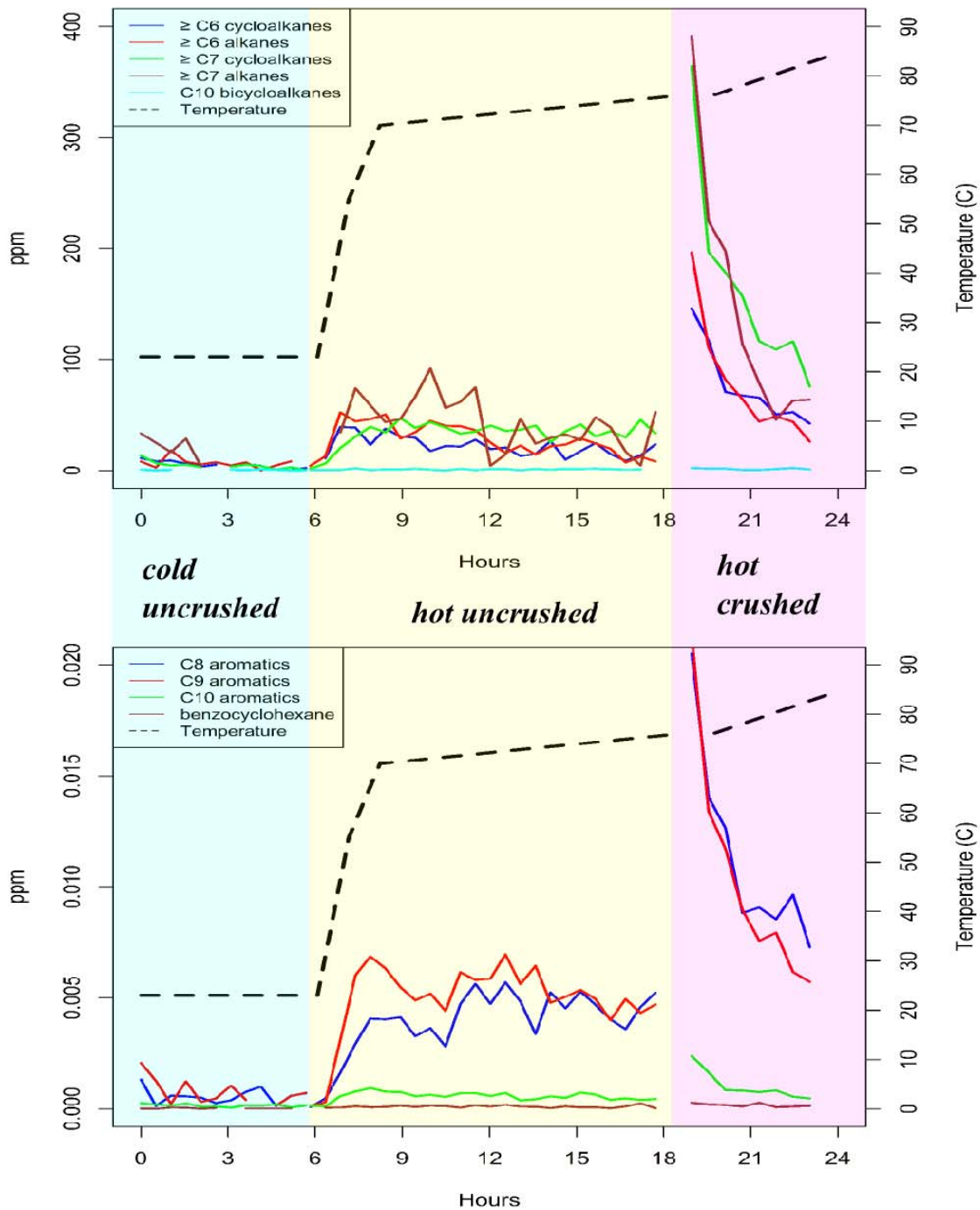
312

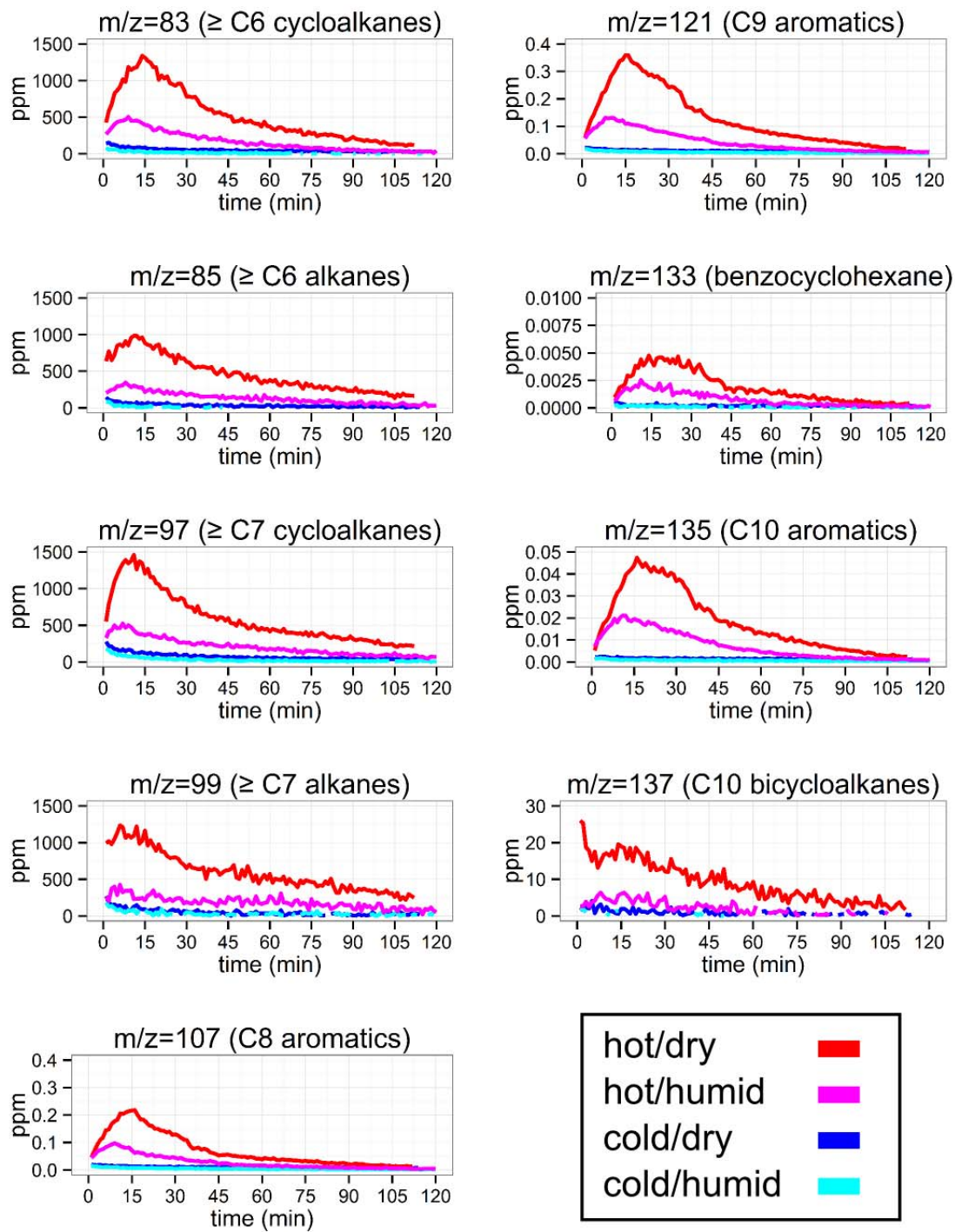313 **TOC/Abstract Art**

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316

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Figures

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 ºC; (shaded yellow) uncrushed at 75 ºC; (shaded magenta) crushed at

324   80 ºC.

325

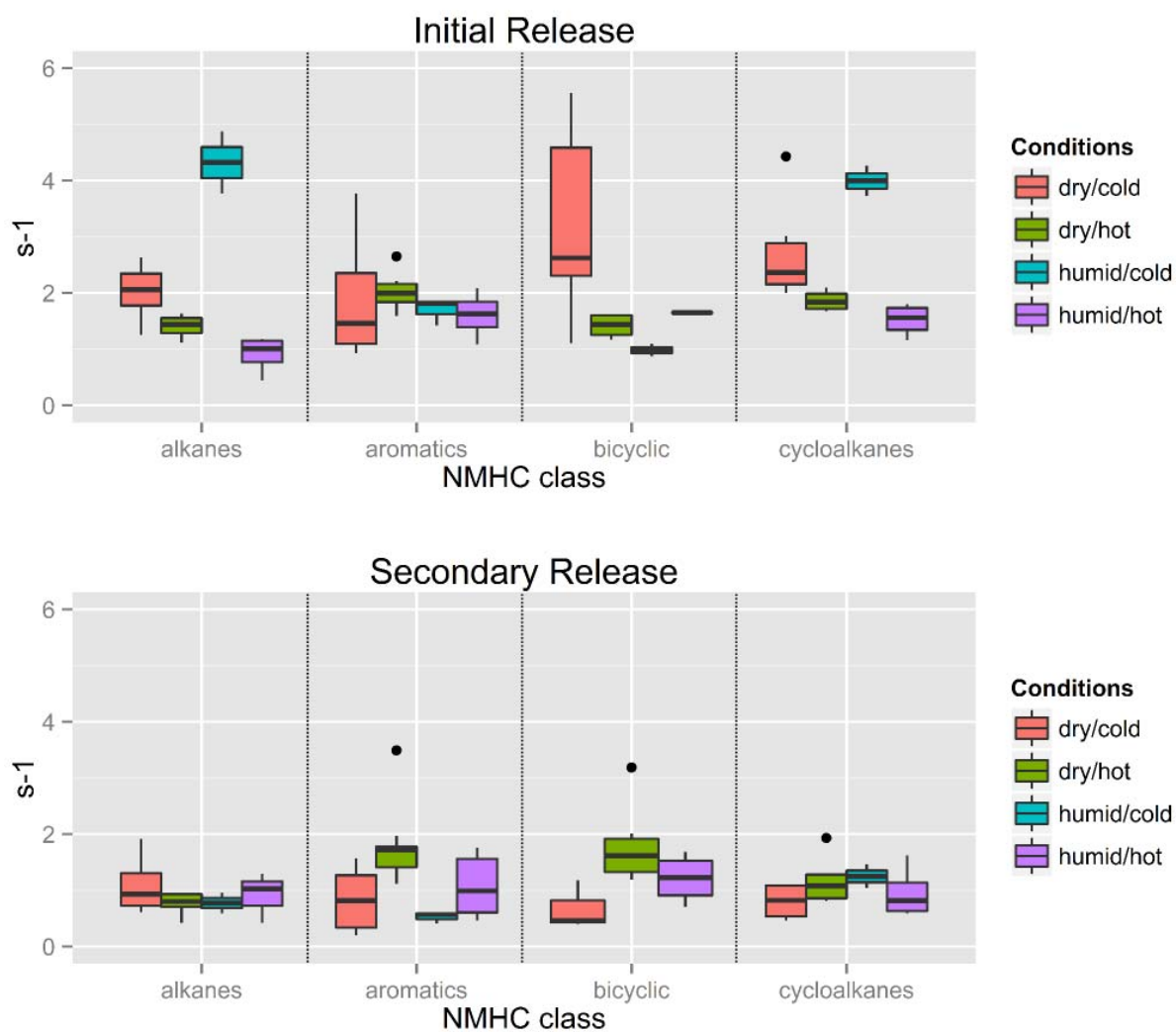326

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

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

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

humid (50-60%) conditions.

331

332

Figure 3. Initial (top panel) and secondary (bottom panel) release rates of classes of NMHC from

crushed shale samples under different experimental conditions: hot (70-80 ºC) or cold (23-25 ºC),

dry or humid (50-60%). The bottom and top of the box represent the first and third quartiles, the

whiskers represent the ±1.5 interquartile range (IQR), the points are the outliers. All the crushed

samples listed in Table 1 have been taken into account.

338