Real-time 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.[1,2] Hydraulic fracturing, commonly known as "fracking", is the process used to release and extract hydrocarbons from shale formations. While commercial interest in shale exploitation is focused on the extraction of methane and light alkanes, shale also contains significant amounts of non-methane hydrocarbons (NMHC). To date, there have not been studies characterizing the range and quantities of NMHC released from fractured shale and the physio-chemical dynamics of the fracturing process at petrological level is unknown. Here we describe the first real-time observations of the release and evolution of NMHC from the fracturing of shale. Samples of shale, extracted from the Bowland-Hodder formation in England, were fractured and analysed under different conditions of temperature and humidity using mass spectrometric techniques. A wide range of NMHC (alkanes, cycloalkanes, aromatics and bi-cyclic hydrocarbons) are released at ppm/ppb level from fractured shale with temperature and humidity-dependent release rates. The measured release rates of NMHC can be rationalised in terms of the physio-chemical characteristics of the different hydrocarbons classes. Our results indicate that higher energy inputs (i.e. higher temperatures) significantly increase the amounts of NMHC released from shale, while higher humidity tends to suppress the release of gases; additionally, we found that most of the shale gas is released within the first 45 minutes 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, using an NMHC fingerprint as a proxy of the potential to improve gas yield and to reduce the environmental impacts.

Introduction

Shale is an abundant type of sedimentary rock made of compacted silt and clay that often includes economically significant quantities of organic matter. The content of organic matter is typically in the range of 1-3% (and as high as 8%)[4] by weight. This material is considered crucial in the formation of hydrocarbon deposits that constitute conventional oil and gas reservoirs (hydrocarbon source rock). The hydrocarbon content of shale gas has recently become of high commercial interest, as a combination of rising oil prices, security of supply (e.g. because of political instability in certain parts of the world) and improved technology have made these non-conventional sources of hydrocarbons economically viable[1,2]. In order to extract oil or gas from shale it is necessary to pervasively fracture the rock. This technique, termed hydraulic fracturing ("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[2].

The growth of hydraulic fracturing in recent years has raised several concerns regarding its

environmental impact[1,2,3]; however, most of the attention has been focused on the contamination of ground and surface waters and on the potential to cause minor earthquakes[2,3]. The implications of shale exploitation for air quality and climate change have not received much attention and a detailed study of the gas release process during the fracture of the rock has yet to be done.

Emissions from oil and gas wells are well characterized[5,6,7,8] but natural gas reservoirs are distinctly different from gas shales. 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. We examine, for the first time, the pervasive fracturing of a shale and present a real-time chemical analysis of the release of non-methane hydrocarbon (NMHC) gases from a fractured shale.

Methodology

A shale specimen (Figure 1) was collected from a part of the Bowland-Hodder formation in Lancashire (north-western England), currently under consideration for commercial exploitation[4]. The sample (average carbon, sulphur and water content 2.87%, 1.84% and 3.9% by weight, respectively) was collected from freshly exposed outcrop material, but can be considered representative of the shale at depth. Cores were carefully subsampled from the shale specimen and analysed in the laboratory by mass spectrometry. In order to observe the release of gases in real-time, the fast analytical speed of quantitative chemical ionisation offered by Proton-Transfer-Reaction Time-of-Flight Mass-Spectrometry (PTR-TOF-MS)[9,10,11] was employed. Species identification was carried out using Thermal-Desorption Gas-Chromatography Mass-Spectrometry (TD-GC-MS). Details of the instruments, calibrations and methods, as well as preparation of the samples, are described in the Supplementary Information. The analytical techniques employed in this work are not sensitive to some classes of compounds: in particular, methane and short-chain alkanes ($\leq C_5$), which are some of the most commercially important hydrocarbons in shale, are not detectable by PTR-TOF-MS[10,12]. Consequently, much of the following discussion will be focused on the larger Non-Methane Hydrocarbons ($\geq C_5$).

Gas chromatographic analysis[12] made it possible to identify the most important NMHC observed by PTR-TOF-MS upon shale fracturing: linear and branched alkanes (C_5-C_{12}), aromatics (C_8-C_{12}) and mono- and bi-cyclic hydrocarbons were detected in all samples at ppm (µmol/mol) / ppb (nmol/mol) level. Carbon disulphide (CS_2) was also detected in all samples. The complete list of NMHC identified by TD-GC-MS is shown in Table SI-2. Aromatic compounds are easily identifiable by PTR-TOF-MS, although isomers cannot be distinguished[12]. Alkanes, however, are known to fragment[14,15] even with soft-ionization techniques such as proton-transfer, characteristically losing successive methylene groups ($-CH_2$). A mass channel associated with the parent ion ($[M-1]^+$) of a straight chain alkane is given here to represent contributions from isobaric branched isomers and methylene loss from heavier acyclic alkanes. Using this approach, described in more detail in the Supplementary Information, it was possible to follow the release of selected NMHC from fractured shale samples in real-time.

Results and Discussion

The release of NMHC from a ~200 g shale sample (A4-6, see Table SI-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,

comparable to *in situ* values). The time-series for selected NMHC are shown in Figure 2. 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 Figure 1 and Supplementary Video).

The data in Figure 2 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 SI-1) were crushed and analysed by PTR-TOF-MS under a range of conditions (hot/cold, dry/humid) in real-time. Figure 3 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) 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 3).

Analysis of the PTR-TOF-MS data using piecewise regression analysis suggests that the release of gases from a shale occurs on two timescales (Figure 4).: an initial “fast” release (1-5 s^{-1}), during the first 20-40 minutes after the shale has been crushed, followed by a secondary “slow” release (0.5-2 s^{-1}), comparable to that from the uncrushed shale (Figure 2). It can be speculated that the initial release involves gas stored in the nanometre-scale pores of the shale[16,17], which is quickly released when the shale is crushed. As Figure 4 shows, the initial release rates are typically faster for alkanes, cycloalkanes and bi-cyclic hydrocarbons, which are more volatile than aromatics and thus released promptly upon fracturing of the shale. The initial release of the more volatile NMHC is faster at low temperature and high humidity, which may be caused by expansion of the clay minerals owing to swelling under these conditions.

In contrast, the release rates of aromatics are very similar during both the initial and the secondary release, suggesting that these species are adsorbed on the mineral surface and need additional energy to be released. Since the presence of water interferes with the desorption of the molecules, this would explain why the release of aromatics is stimulated at higher temperature and suppressed at higher humidity (Figure 4).

Our observations show consistent patterns but also significant variability among the samples, despite being part of the same shale. This may be because of the natural heterogeneity of the rock, the technical difficulty of achieving consistent fracturing of the samples, the temperature differences between the surface and the bulk of the samples and the variation in the natural moisture content of the shale itself.

Our results give insight, for the first time, into the time-dependent release of NMHC from a shale deemed suitable for “fracking”. While methane and light alkanes constitute the main impetus behind the commercial exploitation of shale, many NMHC are found in shale and released during the “fracking” process: some of these may be of commercial interest if their retrieval can be made economically viable.

We also found that the release of most NMHC peaks within 45 minutes after the shale is crushed (Figure 3): if not extracted rapidly, this fraction of shale gas will be lost, reducing the economic output and resulting in potential contamination of ground and surface waters and the atmosphere during the initial stimulation process.

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

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Acknowledgements We would like to thank Dr Nick Riley and Ed Hough for their support and collection of the shale specimen and staff from both the National Geological Records Centre of the British Geological Survey and the Department of Geology at the University of Leicester for help with the preparation of the samples. We are grateful to Prof Sarah Davies (Department of Geology, University of Leicester) for her comments and suggestions.

Figures

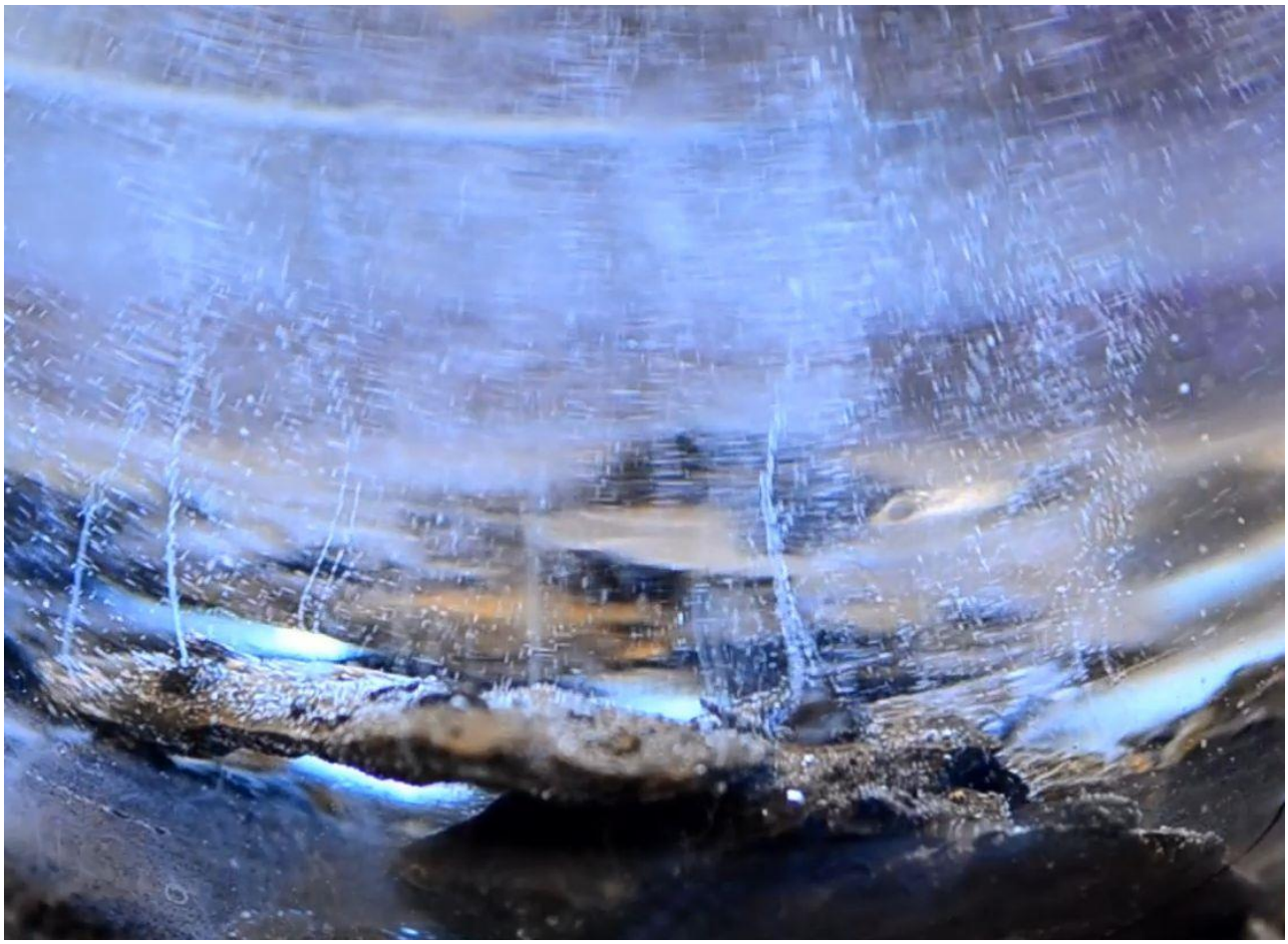

Figure 1. Sample of Bowland-Hodder shale releasing gas. The shale sample is in a heated paraffin bath, with bubbles showing the release of gas from the rock. In contrast, samples of Callovo-Oxfordian claystone, which does not contain natural gas, placed in a similar bath do not show formation of bubbles. A corresponding movie clip is provided in the Supplementary Video.

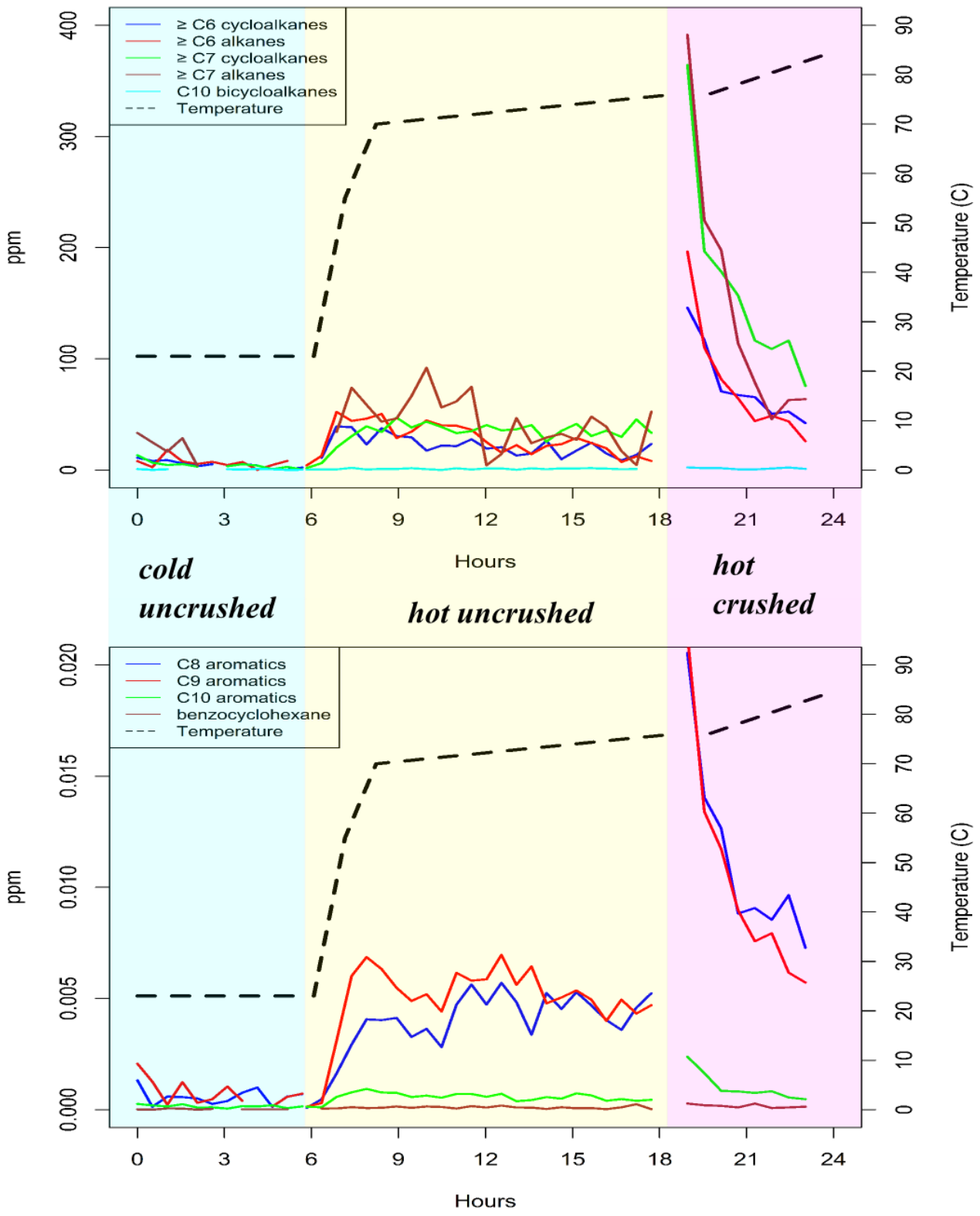

Figure 2. Time-series of selected NMHC released from a shale sample. The sample (A4-6, see Table SI-1) weighted 207-215 g and was observed over a period of 24 hours under different conditions: (shaded cyan) uncrushed at 23 ºC; (shaded yellow) uncrushed at 75 ºC; (shaded magenta) crushed at 80 ºC.

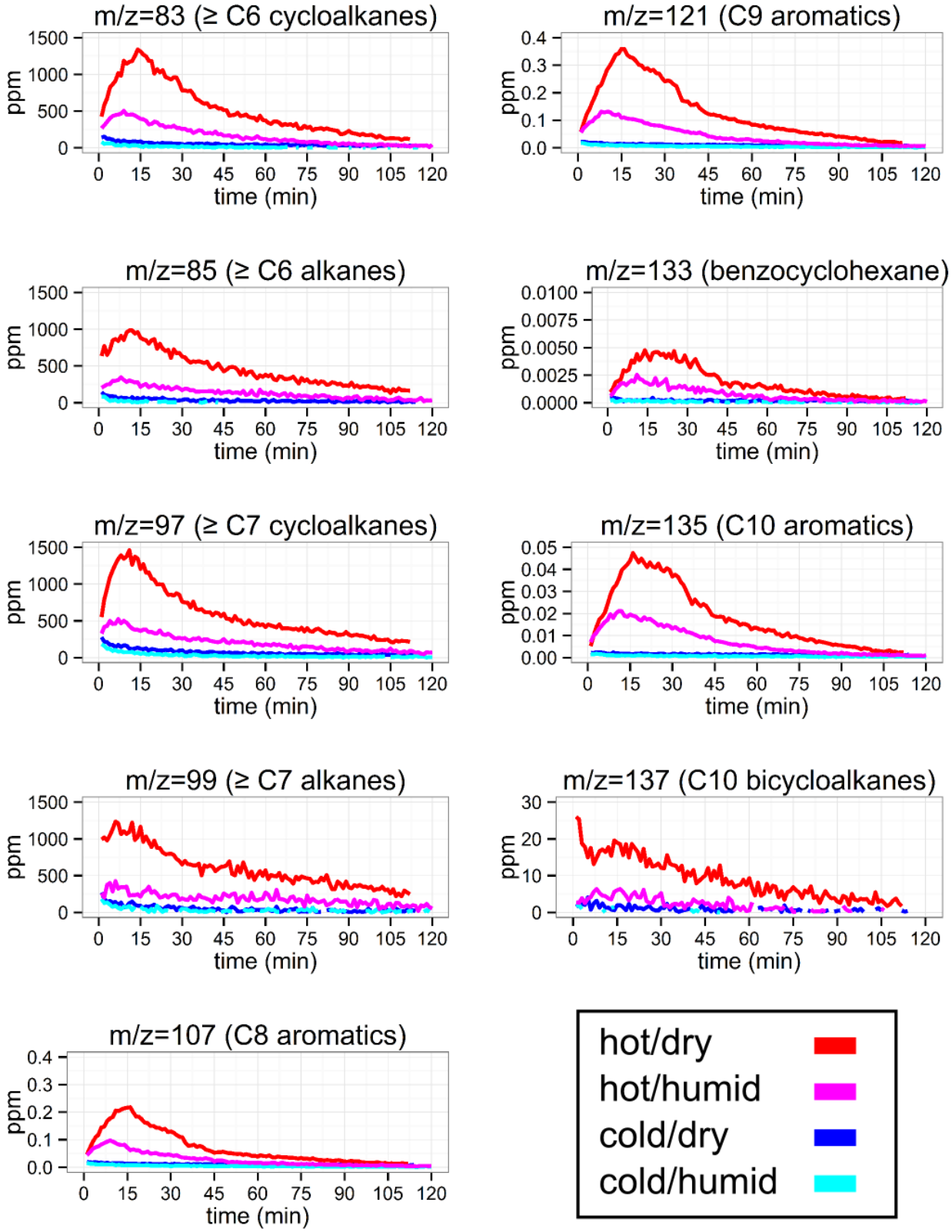

Figure 3. Effect of temperature and humidity on the release of NMHC from shale samples. The shale samples were cylindrical cores (C2, B1, D1, D2, see Table SI-1) weighting 114-118 g. The samples were crushed and placed under hot (70-80 ºC) or cold (23-25 ºC), dry or humid (50-60%) conditions.

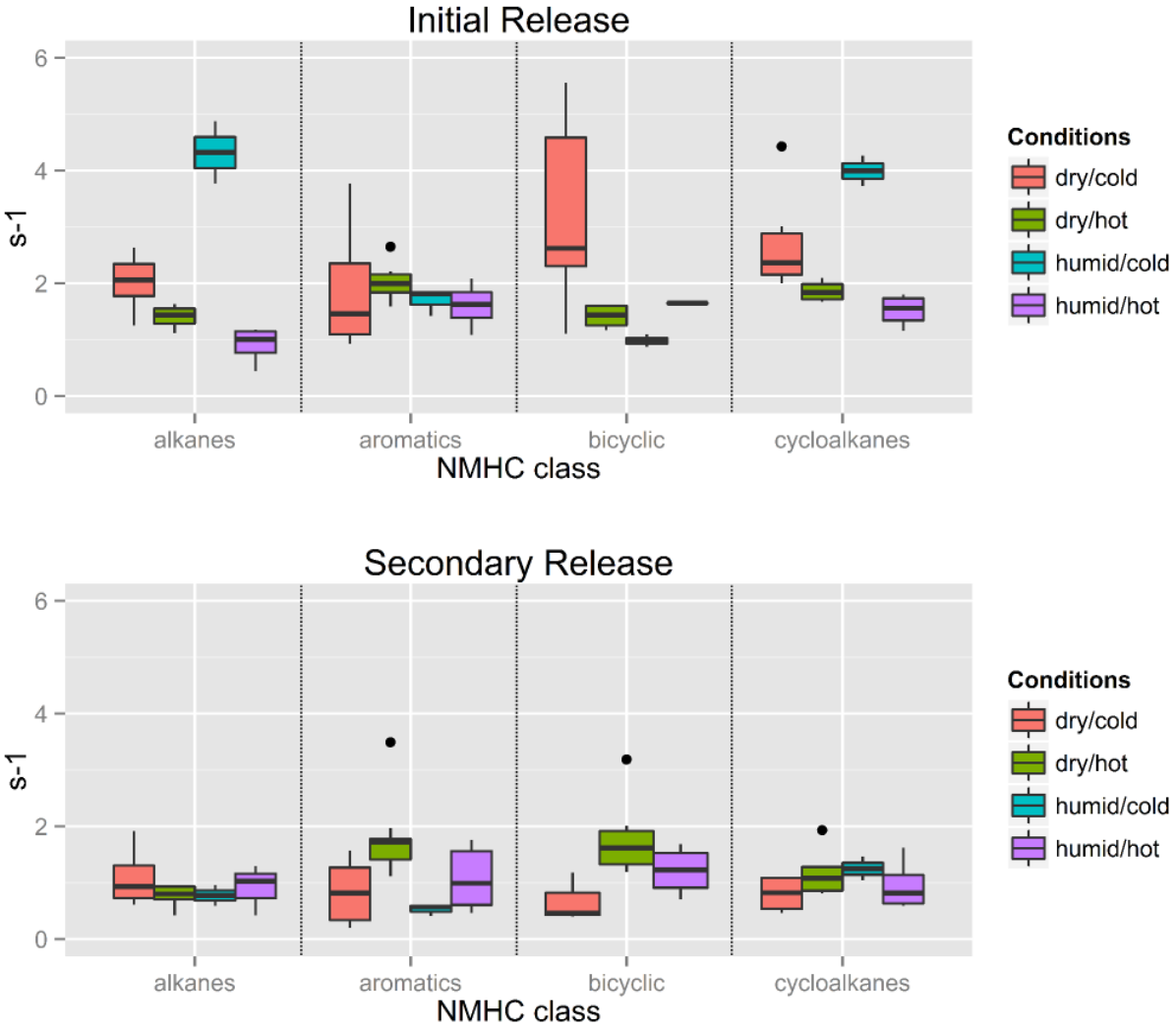

Figure 4. Release rates of NMHC classes from crushed shale samples. Initial (top panel) and secondary (bottom panel) release rates of NMHC classes under different experimental conditions: hot (70-80 ºC) or cold (23-25 ºC), dry or humid (50-60%). All the crushed samples analysed in this work (see Table SI-1) have been taken into account.