



Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

Phenolic compounds in oil-bearing fluid inclusions: Implications for water-washing and oil migration

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ARTICLE INFO

Article history:

Received 21 June 2017

Received in revised form 15 January 2018

Accepted 2 February 2018

Available online 6 February 2018

Keywords:

Fluid inclusions

Crude oil

Phenol

Carbazole

Water washing

Polar compounds

ABSTRACT

In comparison to genetically related crude oils, oil-bearing fluid inclusions are often relatively enriched in polar compounds. Phenolic, carbazolic and benzocarbazolic compounds, which are part of the polar fraction, are characterised by elevated solubilities in water, rendering them potentially useful indicators for oil migration and entrapment, as well as water-washing of oil-bearing fluid inclusions. These compounds were investigated in a set of crude oils and fluid inclusions, and methods were modified to allow for the direct and simultaneous analysis of phenolic and carbazolic compounds. By avoiding chromatographic column fractionation, this new analytical approach allows for faster analyses and higher throughput. Phenolic and carbazolic compounds were found to be present in all investigated crude oil samples, yet they represent only minor constituents of oil-bearing fluid inclusions. A newly described phenol–cresol index (PCI) is systematically elevated (> 0.7) in oil-bearing fluid inclusions, while crude oils are characterised by significantly lower values (< 0.5). Supported by observations of increasing PCI during progressive water-washing experiments, our data suggest oil–water interaction as a possible reason for the elevated PCI in oil-bearing fluid inclusions. Moreover, some of the phenolic compounds detected in oil-bearing fluid inclusion samples may derive from co-occurring aqueous fluid inclusions, whose simultaneous co-extraction cannot be avoided on this spatial scale. Our study highlights the importance of oil–water interaction in the subsurface and offers new techniques to aid understanding of this commercially relevant phenomenon.

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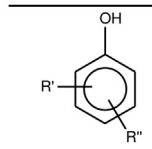
1. Introduction

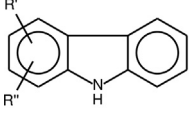
Crude oil is principally composed of aliphatic and aromatic hydrocarbons, with usually lesser amounts of polar compounds, i.e. those containing nitrogen, sulphur, and oxygen (NSO compounds). Yet oils trapped in fluid inclusions are mostly enriched in polar compounds when compared to co-occurring and genetically related crude oils (Karlsen et al., 1993; Nedkvitne et al., 1993; George et al., 1997a; Pang et al., 1998), which has been attributed to an adsorption effect during trapping (Karlsen et al., 1993; George et al., 1997a). Within the polar fraction phenolic, carbazolic and benzocarbazolic compounds (Fig. 1) are of particular interest as they can provide information about primary and secondary migration of crude oils (e.g., Taylor et al., 1997; Galimberti et al., 2000; Bennett et al., 2002; Bastow et al., 2003;

Hallmann et al., 2007). Alkylphenols (and probably many other hydroxylated compounds in crude oils) are thought to principally form through acid catalysed hydroxylation of alkylbenzenes, which takes place in the source rock during petroleum formation (Bastow et al., 2005). Phenolic and carbazolic compounds are relatively resistant to degradation processes in the subsurface (i.e., in the absence of oxygen and light) and only start to degenerate by cracking during late catagenesis. For example, phenolic compounds would produce CH_4 and H_2O due to condensation (Tissot and Welte, 1984). One important aspect of alkylphenols that renders them of particular interest to the field of petroleum geochemistry is their elevated solubility in water. This makes them susceptible to water-washing processes of crude oil (Taylor et al., 2001), and hence turns them into sensitive indicators of oil–water interaction in the subsurface. Oil-bearing fluid inclusions in petroleum reservoirs often co-occur with aqueous fluid inclusions that may have been entrapped during the same inclusion formation events (Dutkiewicz et al., 2003). The aqueous fluid inclusions are often co-analysed during destructive bulk analysis, as it is mostly impos-

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Compounds	R'	R''	<i>m/z</i>
	H	H	94
Phenol	H	H	94
Methylphenol (Cresol)	CH ₃	H	108
Dimethylphenol	CH ₃	CH ₃	122
Ethylphenol	C ₂ H ₅	H	122

	H	H	167
Carbazole	H	H	167
Methylcarbazole	CH ₃	H	181
Dimethylcarbazole	CH ₃	CH ₃	195
Ethylcarbazole	C ₂ H ₅	H	195

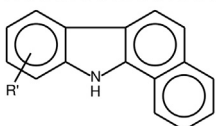
	H		217
Benzocarbazole	H		217
Methylbenzocarbazole	CH ₃		231

Fig. 1. Phenolic, carbazolic, and benzocarbazolic compounds with up to two substituents (R' and R'') and corresponding *m/z* values.

sible to separate them from oil-bearing fluid inclusions of the same generation or in the same mineral grain (George et al., 2012). It is poorly understood to what extent two different types of fluid inclusions with the same migration and entrapment history affect each other during analysis, especially if the different types of fluid inclusions are relatively enriched or depleted in certain compounds. This can lead to unexpected results such as the presence of the polar compound furan in aqueous fluid inclusions (Ruble et al., 1998). Despite the fact that furan has never been reliably detected in fluid inclusions filled with oil and is of low abundance, or absent, in most crude oils.

To date phenol and traces of a methylphenol have only been found in fluid inclusions by using an online crushing method (Ruble et al., 1998), but it remains unknown whether these phenolic compounds were released from fluid inclusions filled with oil, water, or both. There have been no studies focussed on phenolic, carbazolic or benzocarbazolic compounds in oil-bearing fluid inclusions, even though these might reveal crucial information about the dynamics of oil-bearing fluid inclusion formation, i.e. migration, entrapment and water interaction. As oil-bearing fluid inclusions are sometimes considered as “time-capsules” capable of tracing the early biogeochemical evolution of Earth (George et al., 2008, 2009), it is important to increase our understanding of these dynamics.

Phenolic, carbazolic, and benzocarbazolic compounds were investigated in a range of oil-bearing fluid inclusions and crude oils to address the dynamics of fluid inclusion formation for the first time. We also sought to develop new proxies based on these compounds in fluid inclusions, to potentially reveal information about secondary oil migration, a process that has only rarely been discussed (George et al., 2004), and oil-water interactions.

2. Material and methods

2.1. Samples

The studied sample set includes a range of crude oils and fluid inclusion oils from both the Phanerozoic and Precambrian, which have been provided by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (Table 1). These samples were chosen as promising targets for the detection of phenolic, carbazolic and benzocarbazolic compounds because their molecular compositions were already known, as were the relative amounts of their polar fractions.

2.2. Sample preparation

All oil-bearing fluid inclusion samples were described and extracted previously (Table 1), using techniques described in George et al. (2007). The extracted fluid inclusion oils had been stored refrigerated in the dark at the CSIRO North Ryde site. Prior to gas chromatography–mass spectrometry (GC–MS) analyses they were dissolved either in *n*-hexane for analysis at the University of Bremen (for more details see Hallmann et al., 2011), or in dichloromethane (DCM) for analysis at Macquarie University.

2.2.1. Extraction of fresh oil-bearing fluid inclusions

The oil-bearing fluid inclusion samples were originally extracted and analysed up to 22 years ago (Table 1). Because phenolic compounds are photoreactive and volatile, one fresh sample was re-extracted and analysed at Macquarie University to confirm the reproducibility of the data. Specifically, a core sample from drill hole Tirrawarra-1 was extracted and analysed, so as to compare new results with those from the same sample extracted 21 years ago. A 10 g aliquot of pure quartz grains (mineral concentrates) that had been stored at the CSIRO was rinsed with 1 × hexane, 2 × methanol (MeOH) and 3 × DCM. The last DCM rinse was collected as an ‘outside rinse’ and analysed to determine remnant contamination. The quartz grains were then transferred to a solvent-cleaned agate mortar and again checked for contaminants, prior to hand crushing the grains under solvent (DCM:MeOH, 9:1, v:v) to a fine powder. The solvent–powder mixture was extracted by ultrasonic agitation in ca. 20 mL of the same solvent mixture for two cycles of 10 min each. Between extractions, the solution mixture was stirred using a glass rod and left to stand for a few minutes. The supernatants containing any fluid inclusion oil were then collected in a beaker, and the remaining slurry powder was again extracted with 20 mL of DCM for 10 min. The supernatants were combined and reduced in volume on a hot plate (35 °C) until approximately 50 µL remained, and then transferred into micro-volume inserts before GC–MS analysis. Column fractionation of the fluid inclusion oils was not performed for the fresh oil-bearing fluid inclusion sample from Tirrawarra-1 or the other already extracted samples because the yield was very small (< 1 µg/g sample). All the fluid inclusion oil samples were spiked with an internal standard prior to GC–MS analysis: 1 µg of phenol-*d*₆ (99 atom%D, Sigma Aldrich).

2.2.2. Column chromatography of crude oils

Seven crude oils (Table 1) and the NSO-1 standard oil (Weiss et al., 2000) were directly analysed by GC–MS after column chromatography. Fractionation of the crude oils followed the procedure of Bastow et al. (2003), which was used to concentrate and identify phenolic, carbazolic and benzocarbazolic compounds. An activated silica gel column (a glass pipette plugged with a small amount of glass wool and dry packed with ca. 0.6 g activated silica gel) was made uniform by passing 3 bed volumes of hexane through it. About 20 mg of each crude oil was dissolved in ca. 100 µL hexane and adsorbed onto the top of the silica gel. Total hydrocarbons were eluted from the column under gravity with 4 mL hexane/DCM (9:1, v:v) and archived. A phenol/carbazole fraction was then eluted from the column under gravity with 5 mL hexane/diethyl ether (7:3, v:v) and collected in a small beaker. The phenol/carbazole fraction was spiked with an internal standard by adding 1 mL of a hexane solution containing 1 µg of phenol-*d*₆. The fraction was further reduced, using a hot plate, until approximately 50 µL remained, which was then transferred into a microvolume insert before GC–MS analysis. The same unfractionated crude oils were also directly analysed by GC–MS to check if there was any fractionation effect during chromatography that could have resulted in a different distribution of the target compounds.

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