

Carbazoles and benzocarbazoles confirm migration of leaked petroleum through caprocks and overlaying formations of Valhall Well 2/8-8 in the North Sea

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Abstract A wildcat may not result in a petroleum prospect; however, it may indicate potential need for frontier exploration, since petroleum could leak into economic accumulations. Carbazoles and benzocarbazoles are nitrogen compounds in petroleum and can be employed to explicitly explain migration direction and distance of leaking petroleum. The hypothesis of this study is that the mechanism of the reaction involving the attraction of carbazoles to clay minerals on the matrix of the walls along their migration pathways determines the isomer that is preferentially attached to the mineral matrix. The objectives of this study are (a) to produce a profile for carbazoles and benzocarbazoles ratios in the cap rock overlying the reservoir, (b) to compare carbazole and benzocarbazole ratios to 20S/(20S + 20R) $\alpha\alpha\alpha C_{29}$ Sterane maturity ratios (c) to infer migration direction from the carbazoles and benzocarbazoles ratio. Samples used were side wall cores and drill cuttings of water-based mud drilling. The EOM (extractable organic matter) from various formations overlying the reservoir was obtained using Soxtherm Automatic Equipment. The TPH (total petroleum hydrocarbon) was obtained from the EOM by using a precleaned isolate C_{18} 500 mg / 3 mL column, eluted with hexane, while the polars were eluted with dichloromethane. Fractionation into saturates and aromatics was done using a silver nitrate–silica gel

column. The profiles of 1,8/1,3 and 1,8/2,4 dimethyl carbazoles and the benzocarbazoles ratios show a vertical gradient of decreasing ratio with increasing vertical distance from the reservoir. This corroborates the %VRo equivalent of 20S/(20S + 20R) $\alpha\alpha\alpha C_{29}$ Sterane and the carbazole ratios infer vertical migration of leaked petroleum.

Keywords Migration · Geochromatography · Leakage · North Sea · Valhall

1 Introduction

Migration of petroleum is a major process that makes up the petroleum system concept, and it explains the charging of reservoirs and the occurrence of a potential prospect (Krooss et al. 1991; Larter and Aplin 1995; Larter et al. 2000). When petroleum is generated, it is expelled and undergoes primary migration from the source rock to the carrier pathway, then commences secondary migration through the carrier pathway to the trap, where it is accumulated and may undergo tertiary migration if leakage occurs (Aplin and Larter 2005; Aplin et al. 2003; Clarke and Cleverly 1991; Clayton and Dando 1996; Ingram et al. 1997; Hao et al. 2015; Noble et al. 1997). Carbazoles and benzocarbazoles are nitrogen-containing compounds in petroleum and have been used for migration studies (Allan et al. 1996; Dorbon et al. 1984; Li et al. 1995), such as delineating migration distance and migration direction (Li et al. 1995, 1997; Larter et al. 1996).

Larter et al. (2000) carried out a core flood study, and at the breakthrough of the injected petroleum (crude oil) from the outlet, the core was sliced and each piece extracted. The extracted petroleum from the core showed that the first extracts from the core slices closest to the breakthrough outlet were lighter in color (orange). The color of

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subsequently extracted samples was progressively darker than the initial petroleum sample. This change in color implied a higher concentration of the carbazoles and benzocarbazoles in the later slices (Larter et al. 2000; Mohamed and Heinz Wilkes 2002). Larter et al. (2000) showed that the concentration of the carbazole and benzocarbazole were that of increasing trend with the increasing volume of petroleum extracted from the core after the core flood.

Larter et al. (2000) described the gradual removal of carbazoles and benzocarbazoles from the migrating petroleum through their attachment to the mineral matrix of the walls of their migration pathway during the core flood as “geochromatography.” This process entails the separation of compounds based on the polarity and affinity of the migrating compounds for the stationary phase, which in this case is the core sample (siltstone) (Bennett et al. 2002, 2004).

The biological and geological isomers for carbazoles and benzocarbazole, which are non-hydrocarbon biomarkers, are yet to be identified as a function of maturity (Clegg et al. 1998; Li et al. 1997), unlike the petroleum biomarkers such as $\alpha\alpha\alpha C_{29}$ Steranes and the S and R isomers, which are geological and biological isomers and can be used to express maturity. Clegg et al. (1998) explained that carbazoles and benzocarbazoles generated from source rock could have existed in particular ratios that bear no relationship with shielded/exposed isomers; however, molecular mechanics data (Clegg et al. 1998), indicate that benzo(a)carbazole (shielded) is less stable than benzo(c)carbazole (exposed), and this observation was also made by Larter et al. (2000). Yamamoto (1992) observed enrichment of the nitrogen-masked isomers to nitrogen-exposed isomers in crudes oil rather than in rock extracts. However, mechanistic postulation in organic reaction mechanisms in Fig. 1 (Sykes 1985) show that during migration, the chemistry of the ring-system permits delocalization of electrons, which render the shielded carbazoles (1,8 dimethyl carbazole) more reactive compared to the exposed isomer (2,4 dimethyl carbazole) (Fig. 1). The shielded carbazoles (1,8 dimethyl carbazole) are preferentially attached to the mineral matrix on the wall of their migration pathway, resulting in their removal from the migrating petroleum (Table 1).

In this study, the reservoir oils and extracts from the cap rock formation ranging from 4200 ft (1.2 km) to 8300 ft (2.4 km) of Valhall Well 2/8-8 were examined for possible leakage, and the carbazole and benzocarbazole in the oils and extracts were examined for migration influenced fractionation. The carbazole and benzocarbazole isomer ratios were compared with the S/S + R $\alpha\alpha\alpha C_{29}$ Sterane for evidence of maturity influence fractionation. The descriptive lithology of Valhall Well 2/8-8 was modelled using Zetaware Genesis version 4.8.

2 Geological structure and the location of Valhall field

The Valhall oil field is located on the Norwegian Continental Shelf, and it is currently the most southerly located of all the producing Norwegian Chalk fields in the southern part of the Central Graben (Leonard and Munns 1987). The well under study is Well 2/8-8, and its coordinates are $56^{\circ}16'49.81N$ and $03^{\circ}24'12.71'E$ (Fig. 2). The Valhall oil field is the largest in the greater Ekofisk area (Munns 1985). The field is located on a broad Northwest–Southeast oriented elongated uplifted (anticlinal) feature called the Lindesnes Ridge. The crestal path of the Valhall structure is flat lying due to basal Tertiary erosion (Munns 1985). Tectonic events towards the end of the Cretaceous led to the compressional tectonic in the Valhall area, resulting in reverse movement of the faults (Lindesnes fault), thus creating uplift areas that had been basin. This structural inversion of the Lower Cretaceous in the Valhall field began in the Turonian time and marked the first impressions of the Valhall anticlinal structure (Ali and Alcock 1992). The Upper reservoir section (Tor Formation) thinned out and became absent in parts of the Valhall Structure. Maximum inversion in the Valhall area occurred in the Paleocene. However, Chalks of Danian age were present in other fields but were missing in Valhall field due to earlier uplift. The Late Cretaceous—Early Paleocene uplift and the subsequent formation of the Valhall structure resulted in faulting and local fractures, which occurred in the crestal part of the field.

2.1 Petroleum system of Valhall field

The petroleum system that charges the Valhall oil field is part of the Mandal—Ekofisk (!) petroleum system of the North Sea. The charging source is identified as Kimmeridge Clay dated Middle Volgian in age with vitrinite reflectance values of $0.57\% VR_o - 0.67\% VR_o$ underlying the Valhall structure (Dore and Jensen 1996; Goff 1983; Leonard and Munns 1987; Munns 1985; Scotchman et al. 1998). The generation of oil within the Valhall catchment area is recorded to have commenced by Middle to Late Miocene in the basinal area to the northeast of the structure, while hydrocarbon generation began below Valhall structure about 2 million years ago in the Pleistocene. Leonard and Munns (1987) identified the main migratory pathways as faults and extensive networks of fractures. These are the main pathways by which emplacement of hydrocarbon could have occurred into the reservoirs. The sealing cap rock is of Paleocene strata, which consists of the Balder, Sele, and Lista formations. The Lista Formation has sand grain volume of 35% and second sand bearing shale in the Paleocene.

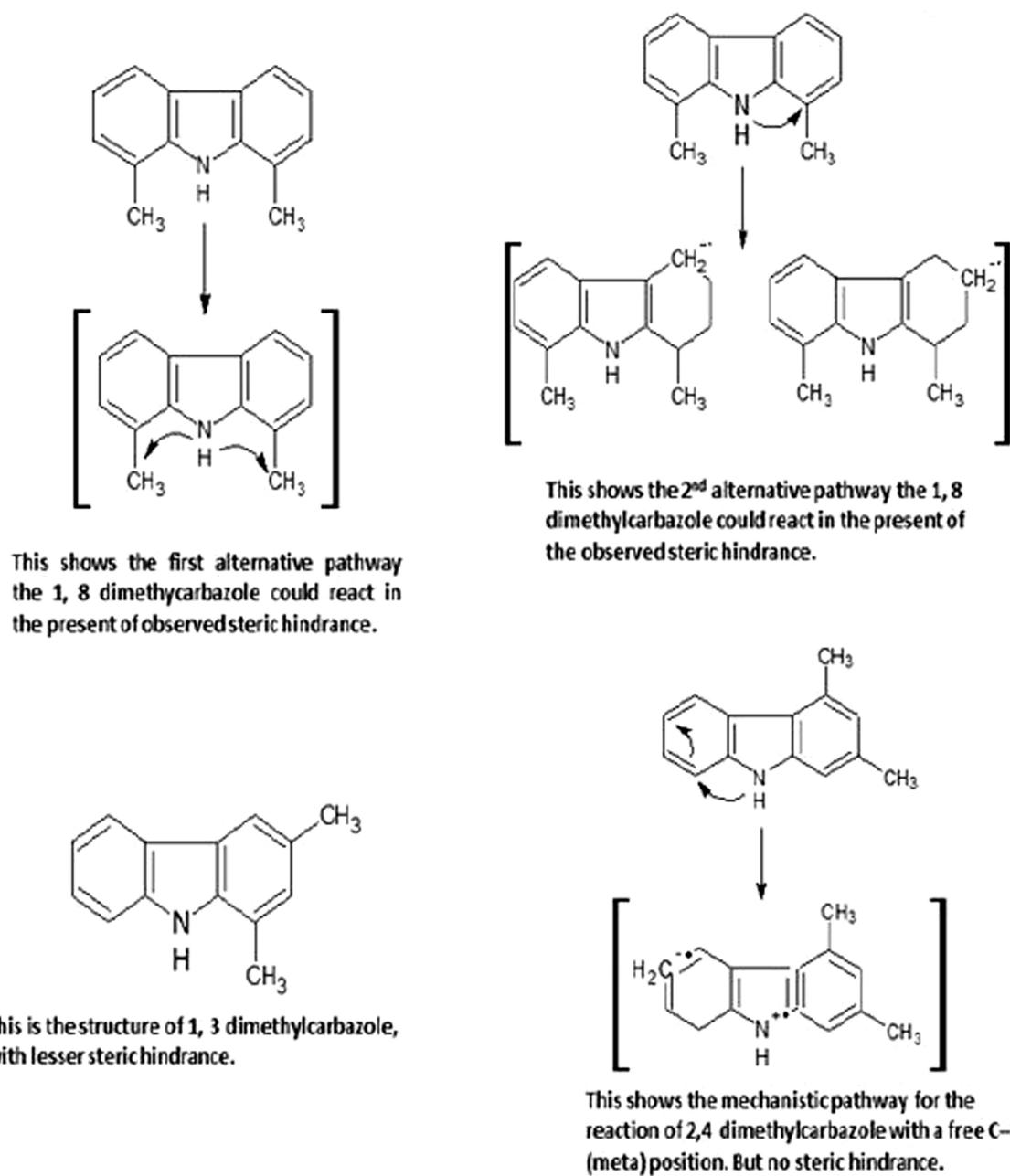


Fig. 1 Structures and mechanistic pathway for reactivity of dimethylcarbazole and benzocarbazole with mineral surfaces of migrating pathways of petroleum

It is described as more of a barrier in function than a seal (Evans et al. 2003).

3 Materials and methods

3.1 Sampling and EOM extraction

Water base mud drilled cuttings were obtained from BP-Amoco via Res Lab Norway for Valhall well 2/8-8. Samples were carefully selected and washed on a sieve

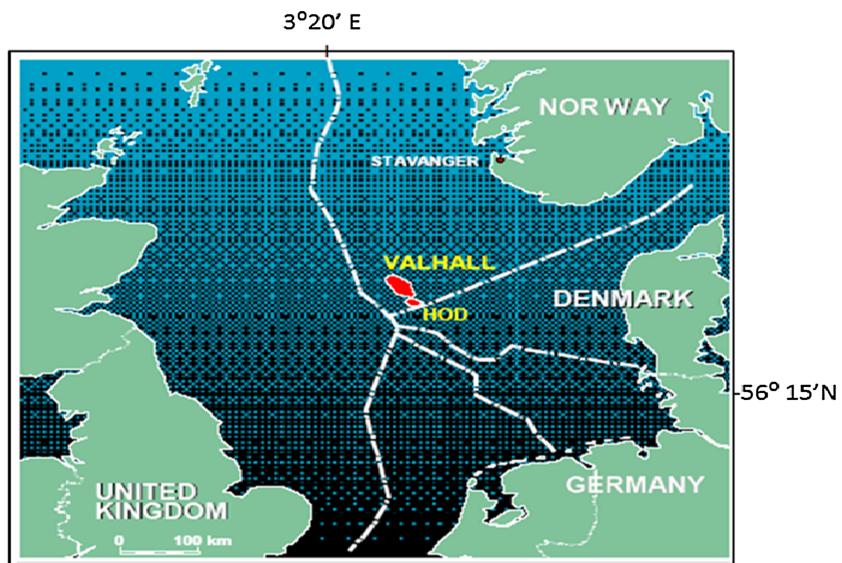
with a mesh size of 0.5 mm (500 µm). The EOM (extractable organic matter) was extracted from the dried and pulverized samples using DCM: MeOH (Dichloromethane: Methanol) ratio of 9:1 with Soxtherm Automatic equipment. The total petroleum hydrocarbon (TPH), which comprises the aliphatic hydrocarbons and the aromatic hydrocarbons, was obtained from the EOM that was extracted from the drill cuttings and the oil sample from the reservoir formation of Well 2/8-8 with a preclean isolate C₁₈ 500 mg / 3 mL column (supplied by Kinesis England). The TPH was obtained by eluting with hexane

Table 1 Ratios of dimethylcarbazoles, benzocarbazoles and %VR equivalents

Depth (ft)	1,8/1,3 Dimethylcarbazole ratio	1,8/2,4 Dimethylcarbazole ratio	a/c benzocarbazole ratio	%VR equivalent
4200	0.41	1.21	0.50	ND
4700	0.58	1.09	0.37	0.55
4800	0.55	1.19	0.30	0.63
4900	0.59	1.53	0.22	0.58
4920	0.57	1.24	0.26	ND
5000	0.60	1.55	0.30	ND
5300	0.71	1.58	0.29	0.63
5800	0.69	1.13	1.06	0.57
6120	0.61	1.52	0.85	0.51
6300	0.77	3.50	3.01	0.56
6700	0.65	1.41	0.90	0.57
7000	0.70	1.70	0.60	0.55
7200	0.62	1.52	0.83	0.5
7400	0.66	1.43	0.82	0.58
7700	0.96	2.27	0.44	0.56
7800	1.05	2.17	0.97	0.5
7900	1.15	2.00	0.86	0.59
7990	1.06	2.60	1.28	0.58
8100	0.90	2.27	1.56	0.59
8300	0.46	1.04	0.78	0.59

ND Not determined

Fig. 2 Map showing the location of Valhall Oil Field, North Sea. Modified from Barkved et al. (2003)



(5 mL), and the polar fraction was eluted with dichloromethane (5 mL). The polar fractions were collected in 10 mL vials. The total hydrocarbon was fractionated into the aliphatic and aromatic hydrocarbon fractions using preclean isolate C₁₈ 500 mg / 3 mL silver nitrate–silica column (Bennett et al. 1996; Bennett and Larter 2000a, b;

Bowler et al. 1997). The aliphatic fraction was eluted with hexane (5 mL), while the aromatic fraction was eluted with 5 mL of Dichloromethane (DCM). The carbazole, which is the pyrrolic nitrogen compound, was obtained from the polar fraction through by GC–MS analysis of the polar fraction.

3.2 Hydrocarbon and polar fraction analysis

The GC, GC–MS analysis for the saturated and polar fractions of the rock extracts and reservoir oils were carried out on an HP 5890 GC fitted with a split/splitless injector. The temperature program used was 50 °C for 2 min, then ramped at 4 °C per minute to 300 °C, at which it was held for 20 min. The column used was a HP–5, 30 m long with internal diameter of 0.25 mm and a film thickness of 0.25 microns, supplied by HP currently known as Agilent UK. Hydrogen gas was used as the carrier gas with a flow of 2 mL/min.

The GC–MS analysis was performed using HP 5890 II GC with a split/splitless injector linked to a HP 5972MSD with electron voltage of 70 eV, filament current of 160 °C, a multiple voltage 1600 V and interface temperature 300 °C. An HP Vectra PC chemstation computer in both full scan and selected ion mode controlled the acquisition. The sample (1 µL) in DCM was injected by an HP 7673 auto sampler and the split opened after 1 min. Separation was performed on a fused silica capillary column (30 m × 0.25 mm i.d.) coated with 0.25 µm, 5% Phenylmethylsilicone (HP–5). The integration of peaks was done using the RTE integrator.

4 Results and discussion

The maturity of formations overlaying the reservoir of Valhall well 2/8-8, as obtained from the completion well report, ranged from 0.32%VRo to 0.43%VRo correspondingly from 4200 ft (1.2 km) to 8300 ft (2.4 km) at the reservoir–caprock interface. This observation infers that the formations above the reservoir were not matured enough to generate hydrocarbons, as generation and expulsion occurs at about 0.6%VRo–1.0%VRo (Zhang et al. 2013). It also indicates that petroleum found in the sections above the reservoir is not indigenous, hence could have migrated from the reservoir into the formation overlying the reservoir (Nordgard Bolas and Hemanrud 2002).

4.1 Sterane isomerization ratio

The sterane isomerization ratio was calculated using the sterane maturity formula ($S/S + R \alpha\alpha\alpha C_{29}\text{Sterane}$), and this was then converted to %VRo equivalent (percent vitrinite reflectance equivalent) (Zumberge 1987). The profile of the %VRo equivalent, derived from the extracts in the formations ranging from the reservoir–caprock interface at 8300 ft (2.4 km) to the most shallow depth at 4200 ft (1.2 km), shows a consistent trend (Fig. 3), inferring that the petroleum observed in the formations above the reservoir–caprock is similar in terms of maturity to petroleum in

the reservoir and that petroleum in the formations could have leaked from the reservoir. The %VRo value varies between 0.5%VRo and 0.6%VRo for both the petroleum in the formations and that of reservoir oils (Fig. 3). The constant and consistent %VRo values infer recent and fast leakage of petroleum across formations from the reservoir. A paleo leakage is indicated by a significant step change in %VRo value (Fig. 4).

4.2 Dimethyl carbazole ratios

The profiles of dimethylcarbazole ratios of 1,8/1,3 dimethylcarbazole and 1,8/2,4 dimethylcarbazole were observed to decrease with vertical migration distance away from the reservoir. The mechanistic postulation in the organic reaction mechanism could be employed to explain the observed trend. The 1,8 dimethylcarbazole (shielded isomer) has the capability to delocalize the electrons from the nitrogen into the benzene ring and to activate other carbon sites, enhancing reactivity at other carbon sites and resulting in the 1,8 dimethylcarbazole becoming most reactive of the isomers (Fig. 1). During migration, the 1,8 dimethyl carbazole is preferentially attached to the clay mineral matrix on the wall of their migration pathway, resulting in the removal of 1,8 dimethyl carbazole from the migrating petroleum. Hence the 1,8/1,3 and 1,8/2,4 dimethylcarbazole ratios decrease with distance. Clegg et al. (1998) confirmed that enrichment of the shielded dimethyl carbazoles such as 1,8 dimethyl carbazole was not observed in their study. Their observation conforms to the result obtained in this study.

The 1,3 dimethylcarbazole is more attractive compared to the 2,4 dimethycarbazole based on mechanistic postulation in organic reaction mechanism, hence the profile of the 1,8/2,4 dimethylcarbazoles also follow the same trend as the 1,8/1,3 dimethylcarbazoles (Fig. 5), which decreases vertically with distance from the reservoir–cap rock interface (2.4 km) to the most shallow formation (1.2 km).

4.3 The profile of the benzo(a)carbazole/benzo(c)carbazole ratio

The profile of the benzo(a)carbazole/benzo(c)carbazole ratio also show a decreasing trend with increasing vertical distance from the reservoir. The benzo(a)carbazole has little steric hindrance, and this results in delocalization of the lone electrons on the nitrogen into the benzene ring system, activating alternative carbon sites within the ring system. The benzo(c)carbazole has no steric hindrance, so it preferentially uses the lone pair nitrogen electrons for bonding with the clay mineral surfaces. The results from this study show preferential depletion of benzo(a)carbazole

Fig. 3 Profile of the %VR equivalent obtained from sterane isomerization values

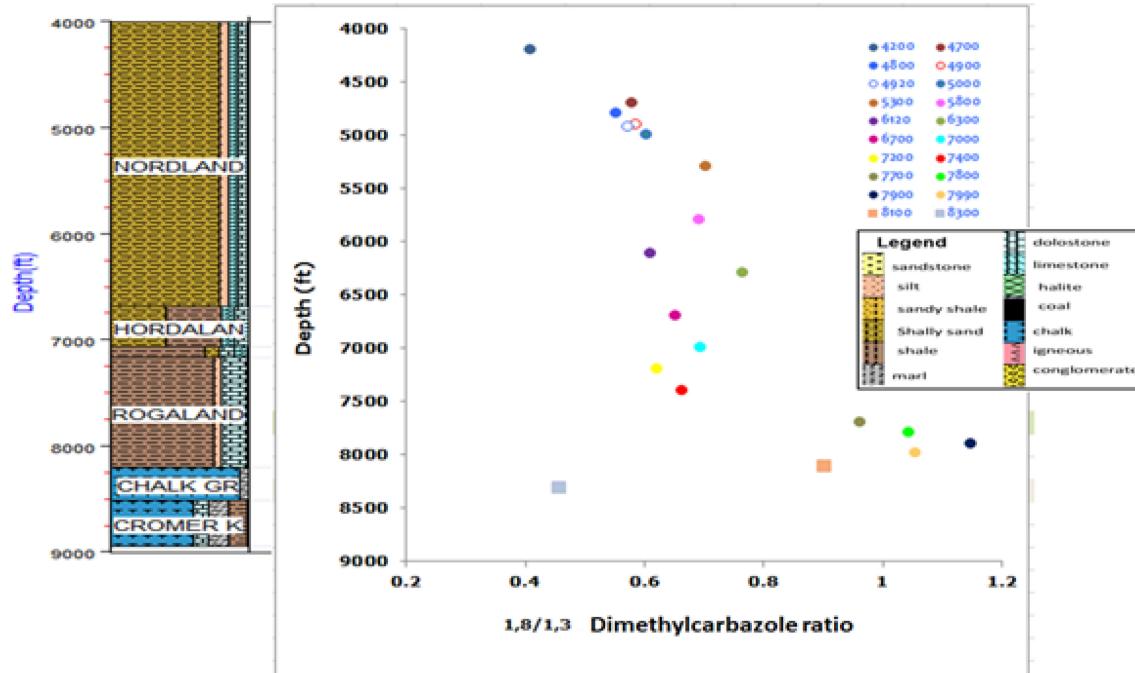
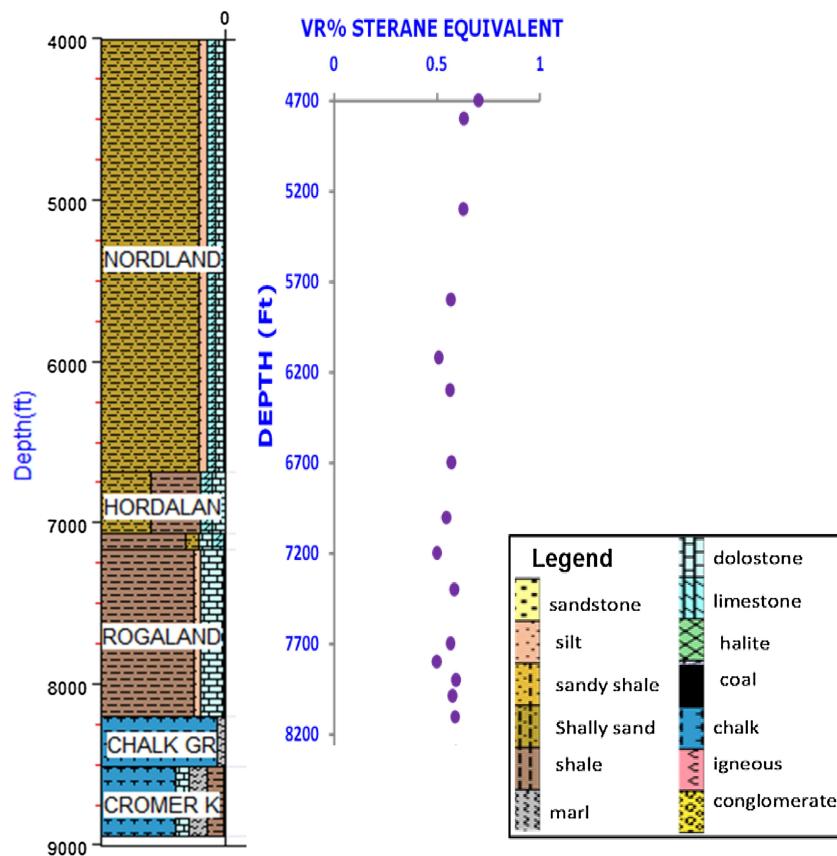


Fig. 4 Profile of 1,8/1,3 dimethylcarbazoles

relative to benzo(c)carbazole and the ratio continuously decreases with the distance from the reservoir–caprock interface (Fig. 6). Larter et al. (2000) also observed the

decrease in the benzo(a)carbazole/benzo(c)carbazole ratio during the core flood study. Clegg et al. (1998) mentioned lesser stability of benzo(a)carbazole based on molecular

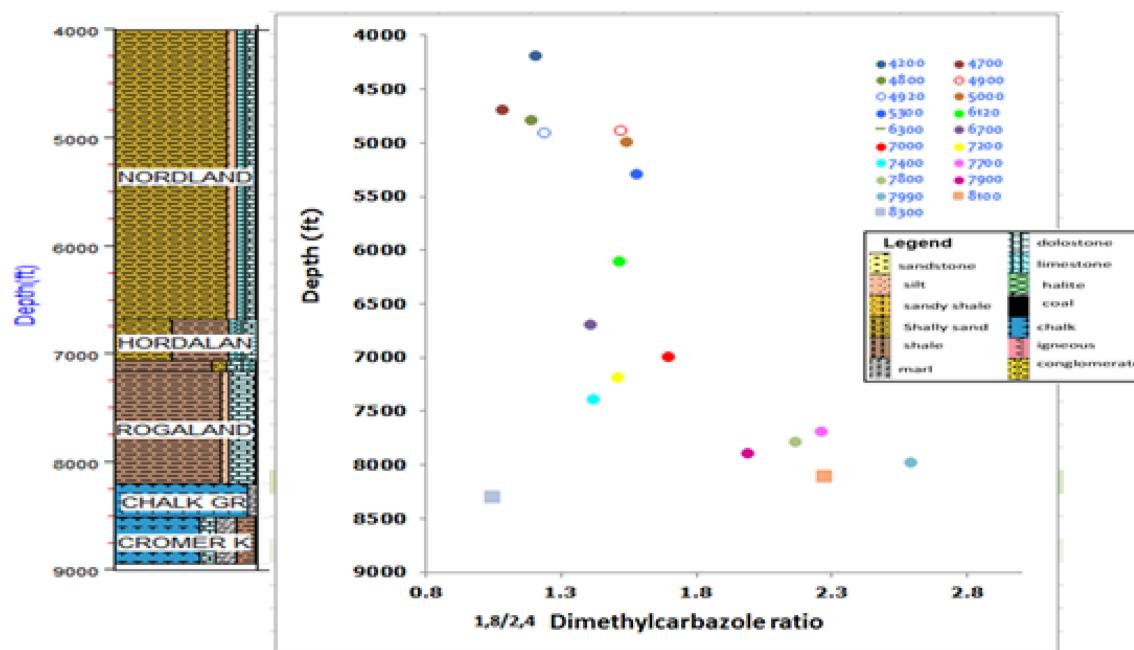


Fig. 5 Profile of 1,8/2,4 dimethylcarbazole

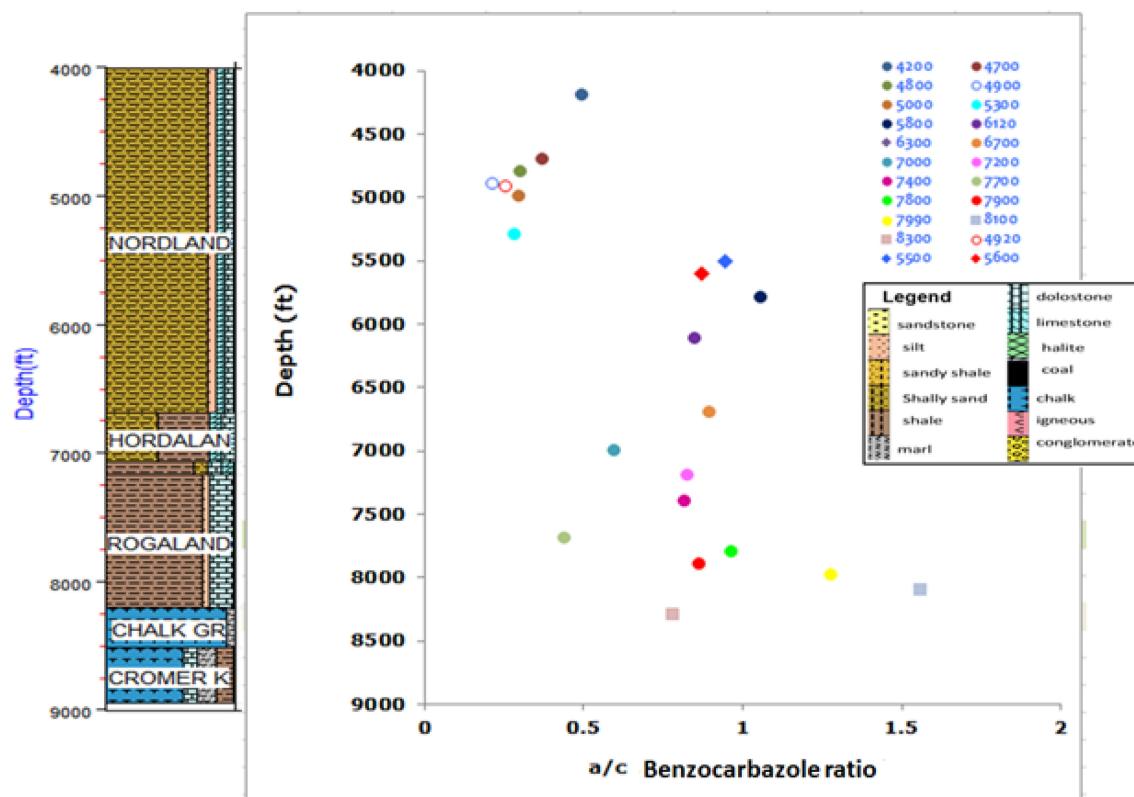


Fig. 6 Profile of a/c benzocarbazoles

mechanics, implying greater reactivity of benzo(a)carbazoles compared to benzo(c)carbazoles.

4.4 Corroborating isomerization ratio and dimethylcarbazoles ratios

The sterane isomerization ratio expressed by $S/S + R\alpha\alpha C_{29}$ sterane was converted into %VR_o equivalent using the equation $\%VR_o = 0.49(20S/20R) + 0.33$, where %VR_o is vitrinite reflectance (Zumberge 1987). The obtained result indicates that the maturity of the hydrocarbon in the formations of Valhall Well 2/8-8 is constant and consistent from the reservoir-cap rock interface (2.4 km) to the most shallow formation (1.2 km). This observation infers that petroleum in the formations originates from the same source (reservoir), which is due to leakage; the observed consistency infers that the leakage is recent and fast. A significant step change in the maturity value will indicate an overprint of an earlier leakage event or a paleo leak, which will have a significantly lower maturity value. Contrary to the trend of the maturity values, the 1,8/1,3 dimethylcarbazole ratio and the 1,8/2,4 dimethylcarbazole ratio show a trend of decreasing values from the reservoir-cap rock interface at 8300 ft (2.4 km) to the most shallow formation at 4000 ft (1.2 km) (Fig. 4). The maturity values are consistent, indicating some petroleum in the formations, while the decreasing dimethyl carbazole ratios indicate a migration phenomenon.

The benzo (a) carbazole and the benzo (c) carbazole were also examined, and the ratio of benzo(a)carbazole/benzo(c)carbazole also shows a similar trend as that of the dimethylcarbazole ratios. Hence, benzo(a)carbazole/benzo(c)carbazole ratio is a reliable tool as a migration indicator (Larter et al. 2000).

There is no significant difference in maturity between the hydrocarbon in the reservoir oils and the hydrocarbon from the formations above the reservoir, but the dimethylcarbazole ratio and the benzo(a)carbazole/benzo(c)carbazole ratio show a similar trend of decreasing value with migration over distance covering the formations above the reservoir. This observation is due to the preferential bonding of shielded benzo(a)carbazole and dimethylcarbazole with the mineral surfaces, eventually resulting in lower ratios in the migrating petroleum. This means that the earlier migrating fronts had lesser ratios of dimethylcarbazoles and benzocarbazoles compared to the later migrating fronts closed to the reservoir.

5 Conclusion

The %VR_o (vitrinite reflectance) of the formations studied are between 0.3% and 0.4%, and this is below hydrocarbon generation value of 0.6%–1.0%. It implies that no petroleum was generated from the formations. The %VR_o equivalent of the hydrocarbons indicates the presence of thermogenic hydrocarbon of the same maturity vertically through the formation into the reservoir. This invariably means that the hydrocarbons in the formation are not indigenous to the formation but are migrant hydrocarbon from the reservoir, confirming a leaking caprock, for which the leaked hydrocarbon migrated vertically.

The profiles of the 1,8/1,3 and 1,8/2,4 dimethylcarbazole and benzo(a)carbazole/benzo(c)carbazole ratios show decreasing values with increased distance from the reservoir, confirming vertical migration away from the reservoir.

The consistency of the maturity values and the decreasing gradient of the dimethylcarbazole and benzocarbazole ratios away from the reservoir infer a leaking caprock, for which the leaked petroleum migrated vertically.

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