Polyphase thermal evolution in the Infra-Cambrian Ara Group (South Oman Salt Basin) as deduced by maturity of solid reservoir bitumen

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Abstract

Petrographic and organic geochemical analyses on solid reservoir bitumen from the Late Precambrian to Early Cambrian Ara Group indicate polyphase thermal evolution in the South Oman Salt Basin (SOSB). The Ara Group constitutes a complex petroleum system in the deep subsurface (3–5 km) of interior Oman. Salt diapirs encase isolated, partly highly overpressured carbonate bodies (intra-salt “stringers”) which represent a predominantly self-charging hydrocarbon system. A large number of stringer cores show that reservoir quality is decreased by the presence of solid reservoir bitumen. By using different microscopy techniques, this solid reservoir bitumen has been identified within pores, pore throats and microfractures of the carbonates. Solid bitumen reflectance measurements (BR r) were converted to vitrinite reflectance (VR r), using a new improved calibration. Vitrinite reflectance geothermometry shows that maximum paleo-temperatures have a highly heterogeneous distribution. Paleo-temperatures of 380 °C were obtained from coke-like solid reservoir bitumen, which most likely formed from thermal cracking of oil. In our model, this process is related to hydrothermal fluids, deriving from deeper pre-salt strata of the SOSB, which entered the intra-salt carbonate stringers during times of basement tectonic activity via hydrofractures. This caused the formation of high maturities (“pyrobitumens”) in close vicinity to the fractures and precipitation of “migrabitumens” with increasing distance to the HT source, which is supported by the geochemical composition of the solid reservoir bitumens. The influx of these fluids into the carbonate stringers is considered to represent a major contribution to their strong overpressures.

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1. Introduction

The deep subsurface of interior Oman contains thick evaporite-carbonate sequences of Infra-Cambrian age, known as the Ara Group, forming the
primary petroleum system of the South Oman Salt Basin (SOSB). The Ara Group consists of salt diapirs, which enclose several isolated carbonate bodies at a depth of 3–5 km, known as the intra-salt Ara carbonate “stringer” play. These unusual reservoirs have been proven by Petroleum Development Oman (PDO) in recent times to be profitable exploration targets, but some wells have failed to produce at significant rates due to the reduction of porosity and permeability by solid bitumen (Al-Siyabi, 2005).

In many hydrocarbon provinces the occurrence of solid bitumen represents a major exploration risk, as it strongly decreases reservoir quality. In the SOSB, this solid bitumen occurs mainly in pores and vugs of the Ara carbonate reservoirs, hence, the SOSB, this solid bitumen occurs mainly in pores and vugs of the Ara carbonate reservoirs, hence, according to Lomando (1992), we use the term and vugs of the Ara carbonate reservoirs, hence, the SOSB, this solid bitumen occurs mainly in pores and vugs of the Ara carbonate reservoirs, hence, the precipitation of asphaltenes (Blanc and Connan, 1994). The composition of deasphalted solid reservoir bitumen, which defines a black solid residue, precipitating by secondary alteration processes from oil within a reservoir. The presence of this solid reservoir bitumen is a diagnostic indicator of hydrocarbon generation and migration within a rock unit. According to Rogers et al. (1974) and Blanc and Connan (1994), the most significant processes by which oil alters to solid reservoir bitumen are (1) thermal cracking of oil, (2) gas deasphalting and (3) biodegradation.

Thermal cracking of oil (1) results in the precipitation of solid bitumen from an oil reservoir which is affected by increasing temperature – e.g. if the reservoir is buried deeper. The upper temperature limit for trapped oil before it thermally cracks into gaseous and light hydrocarbons and into a solid residue (pyrobitumen) is around 150 °C at the so-called “oil deadline” (Dahl et al., 1999). However, Horsfield et al. (1992) postulated higher temperatures of 160–190 °C for oil stability. Due to the high thermal stresses, those pyrobitumens have a clear geochemical fingerprint such as a very low HI value (usually less than 80 mg HC/g TOC), a very high $T_{\text{max}}$ (>460 °C) and depletion of polycyclic biomarkers (Blanc and Connan, 1994).

Secondly, solid reservoir bitumen can precipitate by gas deasphalting. Oil accumulations in traps are mostly associated with the occurrence of gas, which can originate from external gas influx into the reservoir. The latter process decreases the average molecular weight of the oil due to gas injection into the oil column, leading to the formation of light oil and to the precipitation of asphaltenes (Blanc and Connan, 1994). The composition of deasphalted solid reservoir bitumens represents a mixture of NSOs, aromatics and asphaltenes (Rogers et al., 1974). In deasphalted reservoirs, solid bitumen mostly occurred in zones which had the best minus-oil poroperm-characteristics, as gas migration is expected to follow the pathway of least resistance (Lomando, 1992). This process can lead to the formation of tar mats as have been reported for the Oseberg oil field in the North Sea (Dahl and Speers, 1986).

Thirdly, biodegradation is the microbial oxidation of crude oil and is controlled by temperature (<80 °C), depth, and the oil–water interface area in relation to the volumes of oil and water and the meteoric water influx (Larter et al., 2003, 2006). The effects of biodegradation are well known such as the degradation of n-alkanes, the loss of isoprenoids (e.g. pristane and phytane, which are consumed by bacteria) and the depletion of aromatic components. At the same time biodegradation leads to the enrichment of NSO compounds within the reservoir, which in turn leads to an increase of the oil viscosity (Wilhelms et al., 2001; Head et al., 2003). These microbial alteration processes result in a decrease of the API gravity of the trapped oil, forming heavy oils and, in places, tar mats (Roadifer, 1987).

In addition, Walters et al. (2006) propose another formation mechanism of solid reservoir bitumen from the Tengiz Field, Kazakhstan, termed reactive polar precipitation. This process forms solid bitumen under reservoir temperatures corresponding to <120 °C by thermal cleavage of labile, non-aromatic sulphur species of the oil. Furthermore, in a temperature range of 100–140 °C and in some settings between 160 and 180 °C, solid reservoir bitumen may form as a by-product by thermochemical sulfate reduction, which is the reaction between aqueous sulfate (from anhydrite dissolution) and petroleum fluids to produce H$_2$S and calcite (Worden et al., 2000; Machel, 2001).

The investigation of solid reservoir bitumen deposits (e.g. tar mats) and its formation mechanisms is of broad economic interest, because the transformation process inside a reservoir has a significant influence on oil composition and quality and on exploration strategies. Therefore, many workers focussed on the geochemical nature of solid reservoir bitumen (Rogers et al., 1974; Curiale, 1986; Landis and Castano, 1995; Littke et al., 1996; Hwang et al., 1998; Hue et al., 2000) and also on its influence on reservoir quality (Dixon et al., 1989; Lomando, 1992). Based on petrographic tech-
niques, the first generic classification of solid bitumens by Abraham (1948) has been revised by Jacob (1989). He subdivided solid bitumens ("migrabitumen") by their optical reflectance, fluorescence intensity, micro-solubility, micro-flowpoint and density into the maceral subgroups asphaltenes and imposonites ("pyrobitumen" after Landis and Castaño, 1995), which in turn are differentiated into the macerals epi-, meso- and cata-imposonites. These pyrobitumens are characterized by their insolubility in CHCl₃ (and immersion oil), a non-fluorescent appearance and a solid bitumen reflectance (BRₙ) exceeding ~0.7%, the latter criterion indicating elevated thermal maturity.

The standard method to determine thermal maturity of a given stratigraphic level in a sedimentary basin is by means of vitrinite reflectance (VRₙ) measurements. However, marine carbonates and pre-Devonian rocks commonly do not contain vitrinite but may have a significant amount of solid bitumen associated with generated hydrocarbons. Jacob (1989) has shown that there exists a strong correlation of VRₙ and BRₙ, which is:

\[ VR_n = 0.618 \cdot BR_n + 0.4 \]  

The use of BRₙ as a thermal maturity indicator was also established by Landis and Castaño (1995), who have measured a large number of samples, containing particles of vitrinite and solid bitumen. Their results show a linear correlation between BRₙ and VRₙ in the range of ~0.5BRₙ. The correlation equation is

\[ VR_n = (BR_n + 0.41)/1.09 \]  

Barker and Bone (1995) reported seven criteria to differentiate vitrinite from solid bitumen, one of which is its morphology and texture. In detail, Landis and Castaño (1995) showed that the degree of thermal maturation is directly associated with the solid bitumen microtexture. They differentiated a "homogenous" type with a uniform BRₙ, a "granular" type showing BRₙ heterogeneity and "coked" solid bitumen. At the same thermal maturation level, the "granular" type reveals a lower reflectance compared to the "homogenous" type, whereas the "coke"-like type develops if solid bitumen undergoes high temperatures such as due to burial or contact metamorphism (Khavari-Khorosani and Murchison, 1978; Goodarzi et al., 1992; Hwang et al., 1998). This "coked" solid bitumen exhibits a strong optical anisotropy, high BRₙ-values (well in excess of 1% according to Hwang et al., 1998) and appears either as a mosaic optical texture, suggesting an asphaltene-rich precursor, or a flow-like texture, which may originate from deasphalted heavy oils (Nandi et al., 1978). As a result, the coexistence of these types within one sample would reveal a broad reflectance range and a high standard deviation. The occurrence of different generations of solid bitumen reflectance within a sample may indicate several migration episodes (Gentzis and Goodarzi, 1990).

In general, solid reservoir bitumen precipitates out of oil within the reservoir and, therefore, it can be regarded as a reservoir-altering cement which plugs pores, intercrystalline porosity, pore throats and fractures at all dimensions from complete pore occlusion to grain-coating "skins". The shape of solid reservoir bitumen then reflects the shape of the available open pore space because it is a non-crystalline material, resulting in a significant reduction of pore throat size and permeability, respectively, and consequently in reservoir quality (Lomando, 1992).

The purpose of our study is to characterize solid reservoir bitumen from the intra-salt Ara carbonate stringer reservoirs of the SOSB and its implications for the thermal evolution of the Ara Group by means of geochemical analyses, petrographic techniques and correlated maturity analysis.

2. Geological setting

The study area is in the most southwestern part of the SOSB, which represents one of three salt basins constituting the deep subsurface of interior Oman (Fig. 1). The Ara Salt forms part of a restricted Infra-Cambrian salt basin system which stretches from the Arabian Shield to central Iran and probably further east (Mates and Conway Morris, 1990). The formation of the SOSB started with the sedimentation of the Huqf Supergroup from the Neoproterozoic until the Early Cambrian above a crystalline basement (Gorin et al., 1982), showing radiometric ages of 870–740 Ma (Hughes Clarke, 1988). The Huqf Supergroup consists of four groups, which mainly consist of continental clastics and marine deposits (Fig. 1). Solid reservoir bitumen-plugged cores studied in this paper derive from the Ara Group, which spans the Pre-Cambrian/Cambrian boundary (Fig. 1) (Amthor et al., 2003).

During Infra-Cambrian times, rapid subsidence of the SOSB controlled evaporite to carbonate
sedimentation of the Ara Group (Mattes and Conway Morris, 1990), which is represented by at least six third-order cycles of presently 3–4 km thickness. Ara Salt sedimentation occurred at very shallow water depths, followed by the deposition of 20–250 m thick partly isolated carbonate platforms with bioherms (thrombolites) and laminites during transgressive periods (Fig. 2) (Mattes and Conway Morris, 1990; Amthor et al., 2005; Al-Siyabi, 2005). These carbonates form the main reservoir facies of the Ara Group petroleum system (Schröder et al., 2005). The subsurface stratigraphic nomenclature of the Ara Group is shown in Fig. 2.

During seawater highstands, prolific oil source rocks have been formed in the deeper (some hundreds of meters) and periodically anaerobic to dysaerobic parts of the basin. Density stratification of seawater allowed preservation of a sufficient amount of organic material in the bottom layers as high productivity of algal material in the upper water layers was present (Mattes and Conway Morris, 1990). Sulphate deposits are 10–20 m thick, forming transition zones from halite to carbonate (floor anhydrite) and from carbonate to halite (roof anhydrite).

In the Middle Cambrian, the marine facies of the Ara Group was superseded by the continental deposition of the Haima clastics, which form pronounced “pods” due to periods of salt movement (see cross section in Fig. 1). The differential loading (“downbuilding”) of these clastics onto the mobile substrate of the Ara Salt caused strong halokinesis, which had a large impact on the structural style and the hydrocarbon trapping potential of the Ara carbonate stringer play.

The stringer cores show intense diagenetic modifications like extensive cementation by halite and solid bitumen (Al-Siyabi, 2005). In addition, Schoenherr et al. (in press) show that solid bitumen occurs at grain boundaries and intracrystalline microcracks in the Ara Salt in close vicinity to the carbonate stringer reservoirs. They propose that this solid
bitumen has been formed out of oil, which penetrated the salt as the oil pressure in the stringers reached the capillary entry pressure in the pore throats of the Ara Salt, causing a diffuse dilatancy. The overpressure generation in the majority of the Ara carbonate stringers results most likely from conversion of kerogen to oil and gas, compaction and mineral transformation (gypsum to anhydrite) (Mattes and Conway Morris, 1990).

The presence of source rocks in the Ara Group was proven by numerous well penetrations and shows a patchy distribution (Visser, 1991). Grantham (1986) has shown that crude oil of the South Oman (“type A”) is characterized by a predominance of C29 iso- and normal-steranes and stated that these derive from a variety of algae in the Late Pre-Cambrian–Early Cambrian source rocks. Using biomarker analysis, Terken et al. (2001) subdivided three end-members of the Huqf oil family (derived from Neoproterozoic–Early Cambrian source rocks). One of these has been generated within the intra-salt carbonate stringers from mature high-quality Type I/II marine source rocks during the early Cambrian to Ordovician as a result of maximum burial temperatures due to the deposition of the thick Haima clastics (Visser, 1991; Terken et al., 2001). Recent geochemical analyses also suggest contributions of pre-Ara Group oil charge in some of the carbonate stringers (Al-Siyabi, 2005). As source rocks in Oman had a principally oil-prone signature, some of the gas occurrences in the SOSB may be interpreted as a by-product of thermal cracking of formerly trapped oil in the respective reservoirs or source rocks (Terken et al., 2001). The present-day temperature profile of the SOSB corresponds to a geothermal gradient of 18–20 °C/km (unpublished PDO data).

3. Methodology

3.1. Microscopy

All samples have been studied by reflected and transmitted light microscopy. For reflected light microscopy 2×2 cm-sized blocks were cut using a diamond saw, and polished using a non-crystallizing colloidal silica suspension. Transmitted light microscopy was performed on polished thin sections which are 3 cm wide, 5 cm long and ~30 μm thick. In addition, selected samples have been investigated by scanning electron microscopy, performed on a Zeiss DSM-962. For this, small slabs with an area of ~10×10 mm and ~5 mm thickness were cut out of a solid bitumen-rich reservoir area of the carbonate core using a diamond saw. The rectangular prism was then carefully broken perpendicular to the long side and the obtained broken surface was then coated with gold to differentiate carbon-rich phases during EDX-measurements.

3.2. Solid bitumen reflectance (BRr, %)

Mean random solid bitumen reflectance (BRr, %) measurements were carried out by two different
methods – using a conventional photometer system, and by grey value determination (discussed in the next two sections).

3.2.1. BRr (%) measured by photometer

Solid bitumen reflectance measurements have been carried out on the polished carbonate blocks mentioned above (2 × 2 cm in size) under reflected light using a Zeiss microphotometric system, which was calibrated by a Zeiss yttrium–aluminium–garnet standard ($R = 0.889\%$) or by a Zeiss Cubic Zirconia standard ($R = 3.125\%$). The photometer was provided with a pinhole aperture to read a spot with a diameter of 5 μm on the sample surface at a wavelength of 546 nm, using a 40×/0.85 n.a. lens in oil immersion ($n_e = 1.518$). Moreover, solid bitumen from the pure Ara Salt interval sample B9 was enriched by dissolution of the salt in de-ionized water. After drying, polished mounts of solid bitumen concentrate were prepared for reflectance measurement.

3.2.2. BRr (%) calculated by grey values

Maturity analysis requires a sufficient number (~50) of reflectance measurements on vitrinite or solid bitumen particles to provide reliable data. Reflected light microscopy revealed that some of the SOSB samples contain solid bitumen particles, which are too fine-grained (less than ~5 μm) to apply the conventional method described in 3.2.1. In those samples, we measured the grey values (value of brightness) of the solid reservoir bitumens. For this method a Zeiss Axioplan microscope was interfaced with a Zeiss Axio digital camera and a desktop computer. The calibration was applied with five standards at 10 V for a 40×/0.85 n.a. lens under immersion oil ($n_e = 1.518$). For every standard approximately 60 areas (rectangles) with different amounts of pixels (range: 70–2600 pixel/area) have been measured, from which the grey value was determined by averaging. An equation, which converts the average grey value to BRr (%), was then obtained as the regression equation from the plot of average grey value versus the reflectance of each standard.

Standards used for calibration with corresponding reflectance (%) are:

- Leuko-Saphir: 0.592
- Yttrium–aluminium–garnet: 0.889
- Gadolinium–gallium–garnet: 1.714
- Cubic zirconia: 3.125
- Silicium-carbid: 7.84

3.3. TOC content and Rock-Eval pyrolysis

The assessment of the carbon content was performed with a LECO multiphase C/H/H2O analyser (RC-412). This instrument operates in a non-isothermal mode with continuous recording of CO2 release during oxidation, thus permitting the determination of inorganic and organic carbon in a single analytical run. All analyses were performed in duplicate and the results were averaged.

Rock-Eval analysis was performed with a Rock-Eval II DELSI INC. instrument. Approximately 100 mg of the powdered rock are pyrolysed in a helium atmosphere in the absence of oxygen. Firstly, the sample is rapidly heated to 300 °C and remains exposed to this temperature for 3–4 min. Subsequently pyrolysis proceeds in a temperature-programmed fashion by heating the rock powder to 550 °C at a heating rate of 25 °C/min. The volatiles released from the rock sample by thermal desorption (S1 peak) and thermal cracking (S2 peak) are detected by a flame-ionisation detector (FID). The carbon dioxide produced during decomposition of the organic matter (S3 peak) is detected by means of a thermal conductivity detector (TCD). The detector signals are integrated and quantified by comparison with a “Humble” standard (Posidonia shale).

3.4. Solvent extracts and gas chromatography

About ten grams of the pulverised samples were placed in cellulose thimbles, covered with pre-treated glass wool and subjected to Soxhlet extraction at 60 °C for 48 h using a solvent mixture of acetone, chloroform and methanol (47:30:23 v/v) in order to ensure optimum extraction of bitumen in the samples. In addition, the porous steel discs that acted as fluid reservoirs during thermal degradation experiments were also extracted at 45 °C for 48 h using dichloromethane. Finely split copper plate (2 cm2) activated with HCl was used to scavenge elemental sulphur during extraction. Various extracts were concentrated using a rotating vapour evaporator at room temperature and pressure of 220–250 mbar, transferred to 8 ml glass bottles using the solvent used for extraction, and allowed to evaporate to dryness in a vented hood. This was followed by fractionation using silica gel col-
umn chromatography with columns prepared by activating about 2 g of Baker silica gel in a glass column for 24 h at 200 °C. Each extract was introduced onto a column and progressively eluted into six fractions ranging from aliphatics to polars. Solvents used for elution ranged from 5 ml of n-pentane for the aliphatic fraction to 5 ml of methanol for the polar fraction. Samples were concentrated to 100 μl followed by gas chromatographic (GC) analysis. The methanol fraction was further derivatised after concentration to 1 ml. This was mixed with a BF3 solution (50:50 v/v), homogenised, and placed in a sand bath at 70 °C for 2 h. After cooling, water and diethylether (50:50 v/v) were added to the mixture yielding two phases that could be separated. The less dense phase containing methyl esters of saturated fatty acids was skimmed with a pipette and concentrated to 100 μl for GC analysis. Concentrated extract volumes ranging from 0.2 to 0.5 μl were injected into a GC 8332 (ZB 5 column, 30 m long, 0.25 mm id, 0.25 μl m ft) equipped with an on-column injector and a FID. The GC was kept at the initial temperature of 60 °C for 3 min, then heated to 300 °C at 3 °C/min and held at this final temperature for 20 min.

4. Results

4.1. Occurrence and distribution of solid reservoir bitumen in the Ara Group

4.1.1. Regional occurrence
Solid reservoir bitumen is very common in the Ara Group. The solid reservoir bitumen-bearing Ara carbonates we studied come from two areas in the southwestern most part of the SOSB, namely the Greater Birba Area and the Greater Harweel Area. Their geographic centres are approx. 80 km apart (see Fig. 1). Plugs of core have been sampled randomly from 13 wells in a depth range of 3000–5500 m over a broad range of different stringer intervals (A1C–A4C) and from different carbonate facies (Table 1). Initially, 92 samples from the Ara carbonate cores were investigated, from which 87 samples contain solid reservoir bitumen, showing its widespread spatial occurrence in the Ara Group over a depth range of around 2500 m. A sample set of 47 carbonates and 1 salt sample has been chosen (see Table 1), which contains a large amount of solid reservoir bitumen, enabling the study of its petrographic and geochemical character and its optical reflectance.

4.1.2. Mesostructures of solid reservoir bitumen-bearing Ara cores
Solid reservoir bitumen has been found in various Ara carbonate facies (Table 1). Macroscopically, the carbonate cores show that solid reservoir bitumen occurs as black cement which occludes and lines pores (Fig. 3a). Other cores show abundant solid reservoir bitumen-plugged fractures and thin laminae (Fig. 3b) and in some cases solid reservoir bitumen causes a homogeneous dark colour of the carbonates (Fig. 3c). Occasionally, solid reservoir bitumen has been observed in cores of pure Ara Salt intervals (Fig. 3d).

Point count analysis over the whole length of stringer core A1C from well Minassa-I1H1 revealed that the vertical distribution of solid reservoir bitumen shows an increasing trend with depth. However, its occurrence is almost unpredictable at the scale of meters (Fig. 4). Quantity and occurrence of solid reservoir bitumen within the Ara Group are most likely not simply related to depth but vary slightly with facies. For example, carbonates with an initially high porosity, such as the reef-constituting thrombolites, are in places completely plugged by solid reservoir bitumen.

4.1.3. Microstructures of solid reservoir bitumen
The microstructure of solid reservoir bitumen in the Ara Group sediments has been characterized by transmitted and reflected light microscopy (under immersion oil) and scanning electron microscopy. Transmitted light microscopy shows that solid reservoir bitumen occurs as a black opaque material, in places completely occluding the porosity of the carbonates (Fig. 5a), although it is rarely found to plug all available porosity in most of the samples. Typically, solid reservoir bitumen partially fills the pores as a meniscus-shaped cement, which coats pore walls and plugs the pore throats of the carbonates (Fig. 5b–d), thus interrupting the pore connectivity. Additionally, most samples reveal intracrystalline angular-shaped particles of solid reservoir bitumen, which are finely dispersed within carbonate grains (Fig. 5e). In some cases, thin and straight-shaped microfractures are completely filled by solid reservoir bitumen (Fig. 5f). “Coke” texture of solid reservoir bitumen has been detected under reflected light over a vertical length of ~20 m in stringer A3C of well Fayrouz-I1H1. This “coke” is characterized by a bright reflective appearance with a strong anisotropy and a massive granular structure with
Table 1
Solid bitumen reflectance of Ara Group samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wellname</th>
<th>Depth</th>
<th>Strata</th>
<th>P</th>
<th>Facies</th>
<th>BRr (%)</th>
<th>Stdev</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_01</td>
<td>Ajeeb-1H1</td>
<td>4532.00</td>
<td>A2C</td>
<td></td>
<td>Cuttings: slope/basinal mudstones</td>
<td>1.27</td>
<td>0.05</td>
<td>10</td>
</tr>
<tr>
<td>P_02</td>
<td>Ajeeb-1H1</td>
<td>4588.00</td>
<td>A2C</td>
<td></td>
<td>Cuttings: slope/basinal mudstones</td>
<td>1.28</td>
<td>0.06</td>
<td>50</td>
</tr>
<tr>
<td>O_85</td>
<td>Birba-2</td>
<td>2857.04</td>
<td>A4C</td>
<td>OP</td>
<td>Offshore transition zone</td>
<td>0.35</td>
<td>0.08</td>
<td>18</td>
</tr>
<tr>
<td>O_80</td>
<td>Birba-4</td>
<td>2911.75</td>
<td>A4C</td>
<td>OP</td>
<td>Offshore transition zone</td>
<td>0.40</td>
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<td>26</td>
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<td>O_03</td>
<td>Birba-5</td>
<td>3008.00</td>
<td>A4C</td>
<td>OP</td>
<td>Peritidal carbonate</td>
<td>0.47</td>
<td>0.10</td>
<td>26</td>
</tr>
<tr>
<td>B_09</td>
<td>Birba North-1H1</td>
<td>3674.00</td>
<td>–</td>
<td>–</td>
<td>Salt</td>
<td>0.35</td>
<td>0.05</td>
<td>50</td>
</tr>
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<td>O_71</td>
<td>Birba North-1H1</td>
<td>3789.22</td>
<td>A3C</td>
<td>NP</td>
<td>Open marine thrombolites</td>
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<td>0.09</td>
<td>67</td>
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<td>O_73</td>
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<td>4201.36</td>
<td>A2C</td>
<td>NP</td>
<td>Grainstone shoals or isolated sandsheets</td>
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<td>0.03</td>
<td>59</td>
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<td>O_04</td>
<td>Dafaq-1H1</td>
<td>5117.82</td>
<td>A2C</td>
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<td>Peritidal carbonate</td>
<td>0.80</td>
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<td>O_05</td>
<td>Dafaq-1H1</td>
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<td>A2C</td>
<td>OP</td>
<td>Slope/basin turbidites</td>
<td>0.93</td>
<td>0.13</td>
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<td>5137.82</td>
<td>A2C</td>
<td>OP</td>
<td>Slope/basinal mudstones</td>
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<td>P_03</td>
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<td>5141.60</td>
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<td>Microbial bound mudstones</td>
<td>1.01</td>
<td>0.03</td>
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<td>4217.70</td>
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<td>4219.54</td>
<td>A3C</td>
<td>OP</td>
<td>Slope/basinal mudstones</td>
<td>3.44</td>
<td>1.41</td>
<td>158</td>
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<td>Fayrouz-1H1</td>
<td>4221.56</td>
<td>A3C</td>
<td>OP</td>
<td>Slope/basinal mudstones</td>
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<td>0.53</td>
<td>10</td>
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<td>P_05</td>
<td>Fayrouz-1H1</td>
<td>4225.80</td>
<td>A3C</td>
<td>OP</td>
<td>Slope/basinal mudstones</td>
<td>5.80</td>
<td>1.60</td>
<td>50</td>
</tr>
<tr>
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<td>4501.32</td>
<td>A2C</td>
<td>NP</td>
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<td>OP</td>
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<tr>
<td>P_09</td>
<td>Lahan-1H1</td>
<td>4092.00</td>
<td>–</td>
<td>–</td>
<td>Cuttings from 4271 m</td>
<td>0.85</td>
<td>0.04</td>
<td>17</td>
</tr>
<tr>
<td>P_10</td>
<td>Lahan-1H1</td>
<td>4200.00</td>
<td>?</td>
<td></td>
<td>to 4297 m</td>
<td>1.40</td>
<td>0.24</td>
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<tr>
<td>O_56</td>
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<td>A1C</td>
<td>OP</td>
<td>Disrupted thrombolite</td>
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<td>Slope/basinal mudstones</td>
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<td>50</td>
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<td>O_63</td>
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<td>A2C</td>
<td>OP</td>
<td>Peloidal packstone</td>
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<td>Reef-1H1</td>
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<td>A3C</td>
<td>OP</td>
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</tbody>
</table>
abundant fissures. Typically, this coke-like solid reservoir bitumen reveals a vesicle-like (ceno-spheric) fabric (Fig. 5g). Solid reservoir bitumen was also observed in the salt intervals, which surround the carbonate stringers. Using transmitted light microscopy, thin brownish “skins” of solid reservoir bitumen cover intracrystalline microcracks and grain boundaries of the salt (Fig. 5h).

4.2. Solid bitumen reflectance (BR_r, %)

Solid bitumen reflectance (BR_r, %) has been measured on 48 samples which come from different stringer intervals of the Ara Group (see Table 1). The use of grey values to calculate BR_r has been applied on particles which are too small to measure with the pinhole aperture of a calibrated photometer. A simple validation of BR_r-values obtained by grey values has been applied by measuring some samples with both methods (Fig. 6). The results show a close approximation to a linear trend.

The results of the BR_r measurements are presented in Fig. 7, and reveal a very heterogeneous distribution of BR_r-values in different stringers at the same depth levels and over vertical lengths within a single Ara carbonate stringer. It is highlighted for stringer A1C of well Minassa-1H1. The BR_r-values of nine samples from well Minassa-1H1 show differences of up to 0.5% BR_r within ~60 m of vertical distance (see Fig. 7).

The BR_r-values of all samples do not show a linear depth-thermal maturity trend in the Ara Group. The lowest BR_r values have been measured on samples from different stringer intervals of the Greater Birba Area and from those samples revealing two (maturity-related) generations of solid reservoir bitumen such as sample O-19 from well Sakhiya-1H1, sample O-22 from well Shujairat-1H1, and sample O-11 from Fayrouz-1H1 (see Fig. 5g). Coke-like solid reservoir bitumen has been found only in stringer A3C of well Fayrouz-1H1, where the highest reflectance in the study area has been recorded (3.5–5.8% BR_r).

As shown in Fig. 5g, some samples contain two types of solid reservoir bitumen, distinguishable by their microstructure and reflectance. A number of samples from stringer A3C of well Fayrouz-1H1 show high reflective (coke-like) and moderate reflective (flow-like) solid reservoir bitumen types at a depth of around 4220 m (Fig. 8a). Two types of solid reservoir bitumen were also identified in
sample O-19: one moderate reflective phase which fills thin microfractures, and a low reflective phase occurring as intra- and intercrystalline particles with a clear spherical shape (Fig. 8b).

4.3. Organic geochemical analyses

4.3.1. Organic carbon content and Rock-Eval pyrolysis

Total organic carbon (TOC) was measured on 19 samples and ranged from 0.5 to 17.8 wt.% (Table 2). Values greater than 3% occur in samples containing solid reservoir bitumen-plugged macropores and mm-wide solid reservoir bitumen-filled fractures (Fig. 5a and 5f). Regionally, the highest TOC values occur in coke-bearing samples O-10 and O-11 from well Fayrouz-1H1. Most samples contain only low percentages of organic carbon (less than 2% or even 0.5%), but these values are nevertheless high enough to cause a black staining of the carbonates. This is due to the fact that a thin “carpet” of solid bitumen often surrounds mineral grains. The results of the Rock-Eval pyrolysis are summarized in Table 2.

Care should be taken with respect to S3 peaks and calculated oxygen indices since it is well-known that in carbonate-rich lithologies CO2 is generated in Rock-Eval analyses not only from organic matter but also from carbonates (Peters, 1986). In a plot of HI versus OI (Fig. 9) it becomes evident that HI values are highly variable, ranging from almost 0 to 700. As none of the samples contains significant
Fig. 5. Micrographs of solid reservoir bitumen-associated microstructures of Ara Group samples. (a) Black solid reservoir bitumen occupies complete pore space of sample O-10 (transmitted light, crossed nicols). (b) Solid reservoir bitumen occurs as black meniscus-shaped cement in otherwise open pores in sample O-32 (transmitted light, crossed nicols). The SEM image from the same sample shows a smooth cover of solid reservoir bitumen at the pore wall. (c) Granular solid reservoir bitumen fills small pores between “dog tooth” dolomite cements in sample O-18 (reflected light under immersion oil). (d) SEM image of a broken piece of sample O-16 shows intergranular dark solid reservoir bitumen between euhedral dolomite rhombohedrons. (e) Intracrystalline solid reservoir bitumen exhibiting angular shape within dolomite cement of sample O-07 (reflected light under immersion oil). (f) The SEM image of a thin section of sample O-06 shows that solid bitumen-plugged microfractures have an angular shape and force through calcite (Cc) and anhydrite (An), and incorporate angular dolomite (Dol) fragments in the lower centre. EDX analysis of dark solid reservoir bitumen in the fracture reveals a high amount of carbon. (g) Coke-like solid reservoir bitumen of sample O-10, showing bright reflectance and a massive granular mosaic texture with cenospheric textures in the centre; note intragranular low reflective solid reservoir bitumen with a flow-like texture, which is finely dispersed around the “coke” (reflected light under immersion oil). (h) Thin section of Ara Salt sample B-09 scanned in transmitted light (see Fig. 3d) shows that solid reservoir bitumen covers grain boundaries and intragranular microcracks (micrograph upper left taken under transmitted light).
amounts of primary organic matter, the differences have to be attributed to variable composition of the solid reservoir bitumen. Lowest HI values were found for the samples from well Fayrouz-1H1, which contain coke-like solid reservoir bitumen, as well as for the sample from Qashoob-1H1 and Ghafeer-4H1. Highest HI values characterize samples from the wells Ghafeer-3H1, Minassa-1H1 and Shujairat-1H1. It should be noted, however, that variability is significant, even over short distances. For example, different carbonate stringers from the same well can be characterized by vastly different HI values.

Reasons for these differences become evident if HI is plotted vs. solid bitumen reflectance (Fig. 10). With increasing reflectance, HI decreases, although there is some scatter for samples with low reflectance values. Because solid bitumen reflectance is considered to be a function of temperature and heating rate, samples with low HI values can be regarded as “overmature” and those with high HI values as “immature” or “marginally mature” bitumen. The latter has a significant residual hydrocarbon generation potential, although the characteristics of hydrocarbons generated, i.e. oil or gas, from solid reservoir bitumen are not yet well understood. HI values appear quite high for some of the solid reservoir bitumen. However, it should be noted that most of the S2 peak measured to calculate HI is more similar to soluble bitumen than to kerogen (see below). Accordingly, “real” HI values would be even lower than those measured here and PI values would be higher.

In contrast to solid bitumen reflectance, another widely used maturation parameter, $T_{\text{max}}$ (see Table 2), has only a limited validity in this sample series, showing only a weak correlation with HI, BR, r or depth. This is due to the fact, that some samples have two S2 peaks, one of them being released at low temperatures of about 350 °C. Geochemically, this material is probably more similar to bitumen (soluble organic matter) than the rest of the kerogen (insoluble organic matter). If it would be added to the S1 rather than S2 peak, much higher PI values would result (see Table 2), which would better represent the impregnated nature of the sequence. The unusual character of some S2 peaks is shown in Fig. 11.

Furthermore, a test sample (O-32) was subjected to solvent extraction with dichloromethane and...
subsequently analyzed by Rock-Eval pyrolysis. As expected, the total S1 peak disappeared almost completely. In addition, the S2 peak was reduced to less than 25% of the original value, indicating that the S2 "kerogen" has to be regarded as "bitumen" in this case.

4.3.2. Solvent extracts and molecular data

Eighteen samples were extracted and percentages of aliphatic hydrocarbons, aromatic hydrocarbons and NSO compounds were determined. Extract yields were generally high, ranging from about 0.5 to greater than 6 wt.% (TOC-normalized, Table 3). Highest values were established for samples O-07 of well Fayrouz-1H1 and O-06 of well Dafaq-1H1. Correlation of extract yields and BRr is poor, although most samples with high BRr are low in extract yield. The relative proportion of compound groups was plotted from the 18 samples extracted plus data from 11 samples provided by Petroleum Development Oman. Fig. 12 shows that the data vary extensively, although many samples are characterized by a ratio of aliphatic over aromatic hydrocarbons of about 1.5.

However, the relative contribution of NSO compounds ranges from close to 0% to 70%, indicating a highly variable geochemical composition. Very low NSO contributions were found in samples from stringer A2C of Fayrouz-1H1, and also in Dafaq-1H1. Highest NSO contributions were found in sample O-19 from well Sakhiya-1H1. Aromatic hydrocarbons seem to be enriched in the Birba-5H1 samples.

More information was derived from the study of aliphatic hydrocarbons by gas chromatography (GC). Three examples of GC-traces are shown in Fig. 7. Depth versus solid bitumen reflectance plot of 48 Ara samples; values are shown in Table 1. The same symbol shape but different fillings differentiate the stringer intervals (A1C–A4C) for the individual wells. The diagram shows a heterogeneous distribution of BRr-values in the Ara Group, even within a single stringer (differences can be up to ~0.5% BRr within 30 m vertical distance as in Minassa-1H1). Note that the exceptionally high reflectance values (3.5–5.8% BRr) of the coke-like samples from A3C stringer of well Fayrouz-1H1 are not shown in the diagram (see Fig. 8a). Arrows point to the lower reflective solid reservoir bitumen generation of sample O-10 from Fayrouz-1H1 illustrated in Fig. 8a and of sample O-19 from Sakhiya-1H1 illustrated in Fig. 8b.
Fig. 13 and basic ratios are summarized in Table 3. All samples have in common that pristane/phytane ratios are low, varying between 0.36 and 0.65. These low values are usually explained to be characteristic for carbonate rather than clastic source rocks deposited in highly anoxic depositional conditions (Peters et al., 2005).

Furthermore, CPI-3 values are usually lower than 1, which refer to the ratio of odd over even numbered \( n \)-alkanes for the range between \( C_{27} \) and \( C_{29} \) (Peters et al., 2005). Such low values can only be expected for material derived from source rocks, with no contribution from higher land plant waxes, which is consistent with the pre-Devonian age of the investigated sequence.

Higher values were observed for the odd/even ratio for hydrocarbons in the range of \( C_{23} - C_{25} \), often varying between 1.1 and 1.2. These numbers are found as CPI-1 in Table 3. These elevated values suggest that in addition to algal material, some macrophytes living in the water may have contributed to the initial plant material of the source rock. In summary, the similarity with respect to CPI-1, CPI-3 and pristane/phytane values suggests that one common source rock generated the oil from which the solid reservoir bitumen derived.

Furthermore, the gas chromatograms show a pattern of short-chain hydrocarbons clearly dominating over long-chain hydrocarbons. This is quantified by the high to very high CPI-6 values in the samples. Such values are usually regarded as being typical for oils derived from mature or highly mature source rocks (Peters et al., 2005). Lowest values characteristic of a somewhat lower maturity were found in samples from well Dafaq-1H1 (sample O-05) and well Fayrouz-1H1 (sample O-07) and coincide with moderate solid bitumen reflectance values of 0.93% and 0.80%, respectively.

Finally, several samples show gas chromatograms with a significant hump below the peaks (Fig. 13a and 13b). This hump characterizes an unresolved mixture of hydrocarbons which represents a significant part of the extractable organic matter. High ratios of “hump area” over “peak area” were found for samples from stringer A3C of Fayrouz-1H1 (coke-like solid reservoir bitumen).
and stringer A2C of Shujairat-1H1, whereas the hump is relatively small in Birba-5H1 samples (Fig. 13c).

5. Interpretation and discussion

In the following we discuss the origin and the formation mechanisms of solid reservoir bitumen in the Ara Group sediments by integration of organic geochemical analyses and microstructure-correlated maturity analyses. The results confirm that the formation of solid reservoir bitumen in the Ara Group cannot be simply explained by “normal” burial conditions. Furthermore, we present an improved calibration to calculate vitrinite reflectance from solid bitumen reflectance by the use of previously published data.

5.1. Origin of solid reservoir bitumen

Geochemical analyses revealed that the solid reservoir bitumen of the Ara Group derives from a

<table>
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<tr>
<th>Table 2</th>
<th>Summary of Rock-Eval data of selected Ara carbonates</th>
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<tr>
<td>Sample</td>
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<tr>
<td>O_03 Birba-5</td>
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For comparison with maturity data (Table 1), samples with measured BRr (%) are shaded in bold. Sample O_32 R represents the residual after solvent extraction of sample O_32 with dichloromethane (see text for explanation). * Probably, due to heterogeneity, the TOC value was determined on a non-representative aliquot of O_32. n.d. is not determinable.
carbonate/evaporite source rock, most likely deposited in a highly anoxic environment (Table 3), in good agreement with data of Visser (1991) and Terken et al. (2001) who concluded that the "Huqf oil" mainly derives from the intra-salt carbonate stringers and was already generated by the early Paleozoic.

There is a wide range of different microstructures of solid reservoir bitumen observed in the Ara Group sediments, and few of these are indicative of their precursor material. According to Nandi et al. (1978), the partly observed flow-like texture of solid reservoir bitumen (Figs. 5g and 8a) may suggest that this material originates from deasphalted heavy oil. In the same sample (O-10), one of the most interesting microstructures is represented by the granular mosaic fabric of the coke-like solid reservoir bitumen (Fig. 5g), which has been only detected in stringer A3C of well Fayrouz-1H1. Barker and Bone (1995) concluded that this structure is a characteristic fabric, which forms during short-term high temperature (HT) events. They observed that the proportion of this texture within a carbonate host rock increases towards a basalt dike and that the (locally) cenospheric texture of the pyrobitumen is a result of a sudden and very high temperature alteration which is related to the effects of contact metamorphism due to the intrusion of the basalt dikes (Buchan Rift, Australia). Similar observations were made on thermally metamorphosed coal from the South Sumatra Basin, Indonesia (Amijaya and Littke, 2006).

In the following we adduce reasons which suggest that the contact-metamorphic scenario in the Buchan Rift may partly serve as an analogue for the processes leading to the formation of solid reservoir bitumen in the Ara carbonate stringer play of the SOSB.

5.2. Solid reservoir bitumen as a maturity parameter

The most significant parameter to reconstruct the thermal evolution of the carbonate stringer reservoirs is the BR_r, which shows only a weak correlation with depth (Fig. 7). HI and BR_r values correlate very well (Fig. 10), which is regarded as

Fig. 9. The modified van Krevelen diagram (1951) shows a broad scatter of the organic content quality of the Ara carbonates, which corresponds mainly to a type-I to type-II material. A very low HI is characteristic of coke-bearing samples (Fayrouz-1H1, A3C) and the Qashoob-1H1 sample, whereas the highest HI values derive from Minassa-1H1 and Ghafeer-3H1.
additional evidence that \( BR_r \) can be applied as a valid maturity indicator. The calibrations of Jacob (1989) and Landis and Castaño (1995) have shown a strong linear relationship between \( VR_r \) and \( BR_r \), which allows the conversion of \( BR_r \) to \( VR_r \) by using Eq. (1) or (2) (see above). However, both calibrations differ from each other: The regression equation of Jacob (1989) only includes \( BR_r \) values with a maximum of up to 2.7%. The \( BR_r \) data of the Ara Group have their maximum at 5.8% (sample P-05) and the extrapolation of the values in between would result in much lower \( VR_r \) as compared to values obtained from Eq. (2) of Landis and Castaño (1995). This is related to the fact that the linear relationship between \( VR_r \) and \( BR_r \) is not strictly linear beyond the maximum of \( BR_r \).
trend of the relationship of Landis and Castaño (1995) increases much more with increasing maturity than that of Jacob (1989). For example, the difference of VR$_r$ of the coke-bearing sample P-05 (BR$_r$ = 5.8%) calculated by both equations is around 2.2%, whereby the difference of the low mature solid reservoir bitumen from Minassa-1H1 is only around 0.1% VR$_r$. In order to approach the best-fit regression equation, we combined the datasets of Jacob (1989) and Landis and Castaño (1995) (Fig. 14). With these data points ($n = 82$) the correlation to calculate VR$_r$ from BR$_r$ is then

$$VR_r = \left( BR_r + 0.2443 \right) / 1.0495$$

which can be applied for maturity studies, if solid bitumen is present and vitrinite is lacking.

5.3. Paleo-temperature estimation

The VR$_r$ data can in turn be used to estimate peak temperature ($T_{\text{peak}}$) by a calibrated vitrinite reflectance geothermometer (VRG) of Barker and Pawlewicz (1994) to calculate $T_{\text{peak}}$ from VR$_r$. The equations are:

$$T_{\text{peak hydrothermal}} = (\ln(\text{VR}_r) + 1.19)/0.00782$$

$$T_{\text{peak burial}} = (\ln(\text{VR}_r) + 1.68)/0.0124$$

The purpose of using this VRG for our samples is to provide a clue towards maximum temperatures for the burial history of the Ara Group and to compare $T_{\text{peak}}$ from the VRG with the present-day temperatures in the SOSB.

It has been shown that homogenization temperatures ($T_h$) of re-equilibrated (stretched) aqueous
Fluid inclusions (mostly in calcite crystals) can be used to estimate $T_{\text{peak}}$ of sedimentary basins (Barker and Goldstein, 1990; Tobin and Claxton, 2000). In the study of Barker and Goldstein (1990), $T_h$ was compared to present-day temperatures (from wells that are interpreted to be at $T_{\text{peak}}$) and to VR$_r$ of samples from over 30 geologic settings of “normal” burial and geothermal environments. They have demonstrated that $T_h$ strongly correlates with $T_{\text{peak}}$ and VR$_r$ in the range of 59–350 °C and 0.4–4.6%, respectively. For accurate prediction, Barker and Pawlewicz (1994) stated that the regression equations of the $T_h$ versus VR$_r$ plot and hence, $T_{\text{peak}}$ have to be developed for each geologic environment. Consequently, Eqs. (4) and (5) are the result of a split of the dataset of Barker and Goldstein (1990) into hydrothermal and burial heating subsets. On the basis of the Barker and Goldstein (1990) dataset and its subdivision by Barker and Pawlewicz (1994), this seems to be very valid in the case of our study, since there is quite some evidence that hydrothermal rather than normal burial

Fig. 13. Gas chromatograms of aliphatic hydrocarbons of three selected samples. (a) Coke-bearing sample O-10 (Fayrouz-1H1, A3C). (b) Sample O-22, which contains two generations of solid reservoir bitumen (Shujairat-1H1, A2C). (c) Low mature sample O-03 (Birba-5H1, A4C).
events affected the solid reservoir bitumen-impregnated carbonate stringers. By the use of Eq. (4) the maximum paleo-temperature of the “coked” solid reservoir bitumen is in the range of 320–380 °C. Using instead the equation for “normal” deep burial heating by Barker and Pawlewicz (1994) would lead to lower maximum temperatures of 240–280 °C for the coke-like material. However, such temperatures are at least 140 °C higher than present-day (borehole) temperatures (which are at ~100 °C) and cannot explain the occurrence of the low reflective solid reservoir bitumen in stringers nearby. Therefore, the latter approach is discarded. For our purposes, we used the correlation for $T_{\text{peak}}$ estimations due to hydrothermal metamorphism (Eq. (4)), which is considered from the presence of the coke-like solid reservoir bitumen and from the following arguments.

If the calculated paleo-temperatures for all samples are plotted versus depth, it becomes clear that most of the values are significantly higher than present-day (borehole) temperatures of the Ara Group (Fig. 15). The plot reveals a large scatter of $T_{\text{peak}}$ in the Ara Group (compare with Fig. 7), which is valid for the $T_{\text{peak}}$ distribution calculated from samples which derive from same depth intervals – and more significantly from several samples within a single stringer. This is shown by the data points ($n = 9$) from stringer A1C of well Minassa-1H1, which have a $T_{\text{peak}}$ range of 90 °C within 22 m of vertical distance. Similar heterogeneities were also observed for stringer A3C of well Shujairat-1H1, which shows a higher maturity than the more deeply buried stringer A2C.

The different kerogen types and HI values, respectively, support this observation and indicate the overall high variability of the solid reservoir bitumen maturity in the Ara Group (Figs. 9 and 10).

5.4. Model of solid reservoir bitumen formation

In our model we suggest that the conspicuous scatter of maturity ($T_{\text{peak}}$, HI, $T_{\text{max}}$) and geochemical composition with depth is the result of very
local thermal alterations of the solid reservoir bitumen. This was most likely caused by the external entry of hot fluids into the carbonate stringers by a process illustrated in Fig. 16. Gas-rich and/or hydrothermal solutions must have penetrated the thick Ara Salt and the carbonate stringers via a regional hydrofracture system (Fig. 16a), which had evolved under very high fluid pressure conditions. Another possibility may be a very fast ascent of very large fluid batches (so-called “mobile” hydrofractures) from the pre-salt strata through the salt and the carbonate stringers as proposed by Bons (2001) for the formation of meter-wide quartz veins at Poolamacca Station, New South Wales Australia. It can be speculated that the source of these (hydrothermal) fluids is located in the deeper pre-Ara salt strata, e.g. in the basement. 2D and 3D seismic surveys from the Ghaba Salt Basin (see Fig. 1 for location) have proven the presence of a deep-rooted basement-involved fault system, which is dipping very steeply and is in places around 10 km thick (Peters et al., 2003). This so-called Maradi strike-slip fault zone cuts from the basement at around 9 km depths across the whole Ghaba Salt Basin. Although the SOSB is thought to have experienced a slightly different tectonic history than the Ghaba Salt Basin (Loosveld et al., 1996), parts of it may have been affected by similar basement movements as the Ghaba Salt Basin to produce a deep-rooted (hydro)fracture network in the Ara Group as proposed in Fig. 16a. Although highly speculative and lacking evidence, a possible date of such an event may be related to the Maradi fault zone activity during Late Cretaceous times (Filbrandt et al., 2006) or to Oligocene times as the Gulf of Aden rift developed along the south coast of Oman by the reactivation of northeast-southwest trending Pre-Cambrian faults along the eastern margin of the SOSB (Loosveld et al., 1996).
Once a hydrothermal intrusion hits a stringer, the fluids (e.g. methane) expand through the pore network of the dolostones, whereby a local temperature and pressure front develops inside the stringer. The associated heating event caused solid reservoir bitumen to precipitate from the resident oil by (1) thermal cracking along HT-channels as interpreted for the formation of the coke-like solid reservoir bitumen and (2) by gas deasphalting more distant from the HT source where the incoming gas cooled down (Fig. 16b). Evidence for a role of gas in solid reservoir bitumen precipitation is the presence of thermally very mature gas in some stringers. The isotope signature of this gas fits to an origin from deeper, thermally very mature sedimentary rocks (Taylor et al., 2006). The variable geochemical com-

Fig. 16. Schematic model of HT/HP tectonism, which leads to the formation of solid reservoir bitumen in the Ara Group. (a) Hydrothermal fluids enter the carbonate stringer reservoirs by far-reaching hydrofractures (black), which perhaps originate from deep pre-Ara strata of the SOSB. (b) Schematic illustration of a carbonate stringer, showing that coke-like solid reservoir bitumen is formed close to a hydrofracture by thermal cracking and a deasphalting zone in more distance to the hydrofracture (HT source). The incoming fluids and gases increase the pore pressure in the stringer, which results in a pressure release and dilatancy zone in the Ara Salt, respectively. (c) Schematic illustration showing salt/carbonate interface (see circle in a). When the fracture hits a stringer, the HT/HP fluids (in red) form fractures and a dike and sill system in the carbonate; black circle represents figure (d) Detail view of dike and sill system at the grain-scale (see black circle in c). The influx of the hydrothermal fluids redistributes the oil in the fractures and displaces the oil in pores; black circle represents figure (e) Detail view at the micron-scale. The hot fluids flow through the pore network of the carbonates, which leads to the precipitation of coke-like solid reservoir bitumen near the HT source by thermal cracking and to deasphalting of oil in distance to the hot fluids. The resulting microstructure is solid reservoir bitumen, occurring for example in pore throats as observed in Fig. 5b.
position (NSOs, asphaltenes and aromatics) of most samples (Fig. 12) supports a deasphalted signature of this solid reservoir bitumen (Rogers et al., 1974). The solvent extract data have shown (Table 3) that solid reservoir bitumen was most likely not formed out of biodegraded oil, as the pristane/n-C_{17} ratio and the phytane/n-C_{18} ratio are lower than 1.0 (Peters et al., 2005). However, from our data, it cannot be excluded that “normal” burial heating, which entails thermal cracking of oil into gas and solid reservoir bitumen, has formed some of the solid reservoir bitumen. This may be shown by data points, which cluster around 150°C at a depth of ~4500 m such as Ghafeer-4H1 (A3C and A2C), Fayrouz-1H1 (A2C) and Ma’mour-1H1 (A3C) (Fig. 15) but cannot explain the presence of coke-like pyrobitumen from Fayrouz-1H1 (A3C) and Qashoob-1H1 (A2C) (Fig. 15). Temperatures postulated for oil to gas cracking to occur are at around 150–190°C (Horsfield et al., 1992; Dahl et al., 1999).

The orientation of fractures in the salt is controlled by the in situ state of stress, which was calculated by Schoenherr et al. (in press). They have shown that the difference between the mean principal stresses \( \sigma_1 \) and \( \sigma_3 \) is very low in the salt (<2 MPa). It can be assumed that the stress orientation is most likely not homogeneous throughout the diapir, which results in a very heterogeneous orientation of the hydrofractures (Fig. 16a).

Fig. 16c shows how once the hydrothermal fluids reach a carbonate stringer, hydraulic intrusion fracturing may lead to the formation of a dike-sill system. This causes fractures to grow perpendicular and normal to the lamination of the carbonates, when the injected fluid overcomes the sum of the total normal stress and the tensile strength of the carbonate rock (Mandl, 2005). The resulting rock fabric of this process can be seen in Fig. 3b.

The envisaged HP/HT fluids may have redistributed the hydrocarbons within the stringer, whereby solid reservoir bitumen precipitated at pore throats, in pores and in microfractures (Figs. 16d and e, see Fig. 5f). However, our model does not exclude that the solid reservoir bitumen has been precipitated before the entry of the HT fluids into the Ara carbonates. The model presented in Fig. 16 does not necessarily require gas from external sources for oil deasphalting since the thermal cracking of oil leads not only to solid reservoir bitumen but also to gas generation. Anomalous heavy carbon isotope values for methane in carbonate stringer gases suggest a separate source of dry gas mixing with oil-associated gases in these reservoirs (Taylor et al., 2006).

5.5. Overpressure formation mechanism

Samples from the Greater Birba Area seem to indicate that there are no traces of hydrothermal alteration if samples are compared to those from the Harweel Area. This may be due to the fact that either the respective cored intervals are located a large distance away from a hydrothermal intrusion point or that the Birba stringers were simply not affected by the HT/HP event, which would be in good agreement with their near-hydrostatic state of pore pressure (Table 1). However, the salt which surrounds some of the Birba stringers is partially stained black by solid reservoir bitumen located at intracrystalline microcracks and grain boundaries (Fig. 5h) which indicates that these stringers must have been overpressured in the past. The following mechanism might be responsible for the pressure history in this area.

The influx of focussed high temperature fluids must have caused significant local thermal anomalies in the Ara Group. This process inevitably increased the fluid volume within the carbonate stringers leading to a strong pore pressure pulse, which most likely contributed to their overpressures (Table 1). The overpressures were partly released by the migration of oil from the carbonate stringers into the surrounding Ara Salt as shown by Schoenherr et al. (in press). During this process the oil must have moved preferentially into the grain boundary triple junction tubes of the salt by exceeding the capillary entry pressure, resulting in diffusively dilated zones in the Ara Salt (Fig. 16a and b) as described from the Greater Birba Area.

5.6. Implications for hydrocarbon exploration

One of the most challenging tasks for the hydrocarbon industry in this part of Oman is to map the spatial distribution of solid reservoir bitumen to better predict zones of decreased quality in the reservoirs. The distribution of solid bitumen in the Ara stringer reservoirs seems to be rather localized and not well predictable, although there is a tendency of higher solid reservoir bitumen content in deeper parts of a stringer (Fig. 4). So far, the occurrence of solid reservoir bitumen has not been studied with respect to its spatial distribution.
Nevertheless, Fig. 4 shows that solid reservoir bitumen occurs very heterogeneously over the whole length of stringer A1C of well Minassa-IH1. This may depend on (1) the availability of oil, (2) the orientation of (paleo-) oil–water-contact(s), (3) on facies and (4) on the porosity and permeability distribution, which is directly linked to diagenetic processes pre-dating solid reservoir bitumen formation in the Ara carbonates. However, it can be assumed that the occurrence of solid reservoir bitumen in the Ara carbonates follows the irregular and complex geometry of the hydrofractures and the associated dike- and sill system in the Ara Group. In other words, solid reservoir bitumen occurs where external gas and associated heat entered the stringers. A similar scenario has been described by Lomando (1992) for the West Purt field of the U.S. Gulf Coast, where solid bitumen occurs only in the direct vicinity of a fault, which allowed the external entry of gas into the oil reservoir (gas deasphalting).

6. Conclusions

Organic geochemical analyses revealed that the solid reservoir bitumen in Ara carbonate reservoirs is derived from carbonate/evaporite source rocks. Microstructure-correlated maturity analysis in this study is based on a new calibration for calculating vitrinite reflectance using a combined dataset from the literature for rocks which do not contain vitrinite, such as those in the Infra-Cambrian Ara carbonates of the South Oman Salt Basin. The vitrinite reflectance values were used to calculate paleo-temperatures, which are significantly higher than present-day well temperatures. In most of the intra-salt Ara carbonate stringers, a very heterogeneous distribution of paleo-temperatures and HI values is observed. This is best explained by the close interrelation of the processes of thermal cracking and gas deasphalting within the stringer reservoirs. Coke-like solid reservoir bitumen was locally observed and indicates maximum temperatures of 380 °C most likely originating from hot fluids, which were sourced from deeper pre-Ara Salt strata via a regional hydrofracture system. A lower mature phase of solid reservoir bitumen precipitated from the associated influx and expansion of gas into the oil pool (gas deasphalting) as temperatures re-equilibrated. By this process, the fluid volume of the affected stringers increased, which is considered to be a significant contribution to their strong overpressures.

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