An unconventional Neoproterozoic – Early Cambrian source rock interval in southern Oman: Implications for oil and gas generation

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ABSTRACT

The Neoproterozoic – Early Cambrian Ara intra-salt petroleum system in Oman has been the subject of several studies since the early 1990s, not least because of the exploration success that has accompanied the emergence of the play. As one of the oldest known commercial hydrocarbon systems, the properties of the source organic matter have been of particular interest. The Ara intra-salt hydrocarbon system consists of the Al Shomou Silicilyte, a rock which is composed of pure microcrystalline silica, and carbonate colloquially known as “stringers”. Both occur as slabs encased in the Ara salt. In the case of the Silicilyte, the slabs can be shown to act both as source rock and reservoir. However, in the case of the carbonate stringers, the association is more ambiguous. A set of rock and oil samples have been selected from different wells penetrating the silicilyte and carbonate stringer plays to better characterize and understand these systems.

As far as the sedimentary organic matter is concerned, the Al Shomou Silicilyte domain has an average Total Organic Carbon (TOC) of approximately 4 wt.%. The carbonate-prone domains exhibit rare organic-rich lithofacies (TOC of approximately 2 wt.%) and additional intra-salt shales (TOC of approximately 4 wt.%). The organic matter present in both the Silicilyte and carbonate plays is associated with a hypersaline and anoxic depositional environment, rich in sulfur, and showing very similar chemical signatures (bulk composition, elemental analysis, biomarker content, $\delta^{13}$C). The organic matter associated with these sequences is characterized by an unusual “asphaltenic” nature. Compared to classical fossil organic matter taken at an equivalent maturity level, the organic matter found in the intra-salt silicilyte, shales or carbonates releases a large amount of solvent soluble material, which is very rich in Nitrogen-Sulfur-Oxygen (NSO) compounds, implying a standard Type II-S kerogen. However, the organic matter differs from this classic characterization of kerogen (solvent insoluble) in that a large proportion appears to be a sulfur-rich “soluble” kerogen, which has not been previously described. Independent geochemical parameters (Rock-Eval analysis, kinetic parameters) seem to be consistent with this hypothesis. The thermal maturity of the whole set of samples examined places them in the oil window. Moreover, Thermochemical Sulfate Reduction (TSR) did not occur in these samples. As far as the soluble part is concerned, differences in the molecular (significant molecular variations for norhopanes, secobenzohopanes, carotane, X compounds, thianes, thiolanes) and sulfur isotopic composition were demonstrated, and are assumed to reflect subtle variations in depositional settings between Silicilyte and carbonate stringers.

The specific properties of this unconventional organic matter has to be accounted for in the thermal modeling of oil and gas generation. Although the kinetic distribution for kerogen cracking is close to that of a Type II-S kerogen, it is slightly more mono-energetic. A compositional 2-D basin modeling (Temis 2D) was performed on a cross-section through the South Oman Salt Basin, using specific kinetic parameters measured on this unconventional Neoproterozoic – Early Cambrian kerogen (based on a linear grouping of insoluble kerogen and NSO like “soluble kerogen” kinetic parameters). The gas-to-oil ratio GOR prediction was improved within the silicilyte, when compared to the use of classical parameters assigned to Type II-S kerogen.
Finally, the microcrystalline silica mineral matrix of the silicilyte plays is proposed to play a major role in the composition of the fluid, which is expelled and produced by imposing a strong geochromatographic effect on fluids and the retention of polar compounds. The preferential release of aliphatics would lead to the production of oils exhibiting a strong condensate character. This effect has to be considered when modeling the actual composition of the movable fluid in the silicilyte. The significance of the geochromatographic effect is yet to be quantified, but according to available observations, we suggest that this geochromatographic effect could explain the observed API gravity difference between oils produced from silicilyte and carbonate plays.

**INTRODUCTION**

The Neoproterozoic to Cambrian petroleum systems of the Sultanate of Oman comprise some of the oldest known source rocks and reservoirs of commercial hydrocarbon significance (Grantham, 1986, Grantham et al., 1988; Terken et al., 2001). The chronology of exploration, successfully conducted by Petroleum Development Oman (PDO) over 27 years, has been described by Al-Siyabi (2005). The basins developed within the interior of Oman during the Neoproterozoic and Early Cambrian include the South Oman Salt Basin, Al Ghaba and Fahud Salt basins (Figure 1). As further described by Amthor et al. (2005), the Al Shomou Silicilyte play found in South Oman Salt Basin, in particular, is truly enigmatic, having no direct analogues for such a combined source rock and reservoir. The unique geologic configuration of the South Oman Salt Basin has meant that part of these salt-encased, ca. 550 million year-old petroleum systems (Bowring et al., 2007) have just only entered the oil window. This has also provided an unprecedented opportunity to study a Neoproterozoic – Cambrian source rock still undergoing transformation, and the details of an organic assemblage that has remained in what is essentially a closed system.

The Ara Group is part of the late Neoproterozoic to Early Cambrian Huqf Supergroup (Hughes-Clarke, 1988; Amthor et al., 2003) (Figure 2). The geologic setting for this basin is covered in some detail in Al-Siyabi (2005) with a detailed description of the sedimentological setting provided by Schröder et al. (2003, 2005) and Amthor et al. (2005). Fundamentally for the burial history, it is known that the NE-SW trending basin underwent rapid subsidence during deposition of the sediments comprising the Ara Group. Maximum burial temperatures for the South Oman Salt Basin were reached during the deposition of the overlying Haima Supergroup from the Middle Cambrian to Early Silurian (based on Apatite Fission Track data – Visser, 1991; Terken et al., 2001). Halokinesis would have been ongoing throughout this progressive burial. The onset of tilting of the basin from the late Paleozoic and erosion in the Cretaceous resulted in dissolution of the salt from the eastern flank of the salt basin and remigration of intra-salt or pre-salt hydrocarbons into post-salt traps along the eastern edge of the Ara salt basins.

Within the intra-salt of the South Oman Salt Basin, two types of plays were identified: the Al Shomou Silicilyte slabs and the carbonate “stringers” (Figure 1). These two types of lithofacies are probably coeval and correspond to different settings in the basin (Figure 2, Amthor et al., 2005; Al-Siyabi, 2005). The Silicilyte is comprised of finely laminated 80–90% microcrystalline silica, which may represent a deepwater facies setting (Amthor et al., 2005). It is assumed that the silicilyte was deposited in basinal settings between carbonate platforms (Figures 3 and 4) (Gelin et al., 1999). Occasional shaly layers were deposited in both environments. In particular, the Silicilyte is stratigraphically encased by two distinctive organic-rich shales. The ‘U’ Shale is found at the base of the silicilyte and the Thuleilat Shale at the top (Figure 2). Figure 5 presents the geochemical logs for a relatively shallow example of the two shale units occurring at the base and the top of the silicilyte sequence. Total organic contents of all units average 3–4% wt. % TOC (Total Organic Carbon) but the ‘U’ and Thuleilat shales often reach values of up to 10 wt. % TOC. These shales are characterized by a high gamma-ray response, which clearly defines the lower and upper limits of the silicilyte and shows their comparable organic matter richness as source rocks. The logs indicate a high production index (PI: S1 over S1 + S2) for the silicilyte and a high Hydrogen Index (HI: S2 over TOC) throughout all the sequence (Figure 5).
Figure 1: Map of southern Oman showing the location of the main salt basins during deposition of the Ara Group (modified from Amthor et al., 2005). The silicilyte, shale and carbonate samples used for this study are from the Athel Formation and carbonate stringers.
A model for the carbonate deposition including a single depositional sequence with evaporites at the Precambrian (Ediacaran) – Cambrian boundary (ca. 542 Ma) was developed by Schröder et al. (2003, 2005). Slabs of silicilyte and carbonates embedded in the Ara salt are currently the focus of ongoing exploration in southern Oman.

As stated above, it has been assumed that salt movement, which led to the formation of embedded intra-salt traps, occurred prior to hydrocarbon expulsion. This implies that these plays are self-charged (Nederlof et al., 1997, Hartstra et al., 1996; Alixant et al., 1998). The source potential of the silicilyte plays has been previously demonstrated (Nederlof et al., 1997), but the source of hydrocarbons for the carbonate stringers has been questioned. Therefore a pre-salt charge in some of the stringers cannot be excluded (Al-Siyabi, 2005).

This paper seeks to review and summarize the data gained by studying the organic matter associated with the silicilyte and carbonate stringers petroleum systems. The ultimate objective is to tentatively

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**Figure 2:** Generalized stratigraphic column for Neoproterozoic and Early Cambrian strata of the South Oman Salt Basin (from Amthor et al., 2005). Lithostratigraphic and major sequences within the carbonate and evaporite cycles of the Ara Group (from Amthor et al., 2005 and Al-Siyabi, 2005).
Neoproterozoic - Cambrian petroleum system, South Oman Salt Basin

Basinal Carbonates
Halite/Evaporites
Silicilyte
Shale
Salt
Platform Carbonates

Restricted, marine-fed intra-cratonic basin
Open-marine

Mesozoic clastics
Amin/Haradh/Karim
Undifferentiated
Ara Salt
Dhahaban
Haradh/Karim
Haushi
Stages
Natih
Khub
Haushi

A0-A4
A0-A3

Intra-basinal Highs
Eastern Flank

Sea level

Figure 3: Schematic cross-section across southern Oman (after Gelin et al., 1999) showing the structural geometry, the main intervals of interest and the fields corresponding to the samples investigated in this study. For location of section (AA') see Figure 1.

Figure 4: Deposition model of silicilyte and carbonate plays (modified from Gelin et al., 1999 and from Amthor et al., 2005). The intra-salt southern Oman Athel Silicilyte was deposited in basinal settings between carbonate platforms in an extensive stratified water column of varying depth. The water column is characterized by (1) an oxic surface water implying a high organic and inorganic productivity, and (2) an anoxic deeper water implying a high bacterial activity probably related to the formation of silicilyte (Amthor et al., 2005).
develop predictive geochemical concepts for assessing the charge mechanism in the intra-salt prospects at a regional scale in southern Oman. A detailed study of the stratigraphic distribution of the sedimentary organic matter in the silicilyte and stringers areas has been performed. The ‘U’ shale interval encountered at the base of the silicilyte was also investigated. However, the second shale interval found stratigraphically above the silicilyte, the Thuleilat Shale (Alixant et al., 1998; Amthor et al., 2005; Grosjean et al., 2009), was not included in this study. The approach used includes Rock-Eval 6 (RE6) on bulk rock, extracted rock and non-extractable organic matter (“kerogen”), elemental analysis (EA) and isotopic analysis ($\delta^{13}$C and $\delta^{34}$S) of rock extracts and kerogens. In addition, for rock extracts and oils, the chemical characterization, gas chromatography and mass spectrometry analyses of the saturated and aromatic hydrocarbon fractions are performed.

In the first section, the organic matter properties are described. These show that the Neoproterozoic to Early Cambrian kerogen in southern Oman is specific and different from many others known in the world. To confirm our geochemical hypothesis, and to constrain the proposed charge mechanism, 2-D basin modeling simulations along a cross-section passing through the silicilyte plays were performed.

In the second section, the retention role likely played by the silica matrix of the silicilyte is explained using bulk (Rock-Eval (RE 6), Saturates-Aromatics-resins-Asphaltenes (SARA) fractionation) and molecular (aromatics, organosulfur compounds (OSC)) compositional analyses and is further tentatively demonstrated using a laboratory experimental retention test. This retention or geochromatographic effect could explain the API gravity variation observed between oils produced by two adjacent wells corresponding to a silicilyte reservoir (API = 47°, 49.3% of C$_{15}$-) and a carbonate reservoir (API = 37°, 31% of C$_{15}$-).

**MATERIALS AND METHODS**

52 rock-samples ranging in drilling depth from 1,180 to 4,838 m and six oils ranging from 3,771 to 4,807 m were selected in the silicilyte and carbonate plays (Figure 1) according to their differences in produced fluid properties and in maturity. Table 1 summarizes the background information of these selected samples, and detailed information are presented in the Appendix. Figure 6 shows the
Figure 6: Simplified experimental protocol. See Appendix for details of analytical procedure.

Table 1
Background information on silicilyte, shale, carbonate rock samples and oils from South Oman Salt Basin selected for this study

| Plays   | Selected Samples | Sample number and nature | Current Depth (m) | RE6 TOC Range (%) | API |
|---------|------------------|--------------------------|-------------------|--------------------|-----|
| Silicilyte | Silicilyte       | 14 cores                 | 1,177–4,426       | 1.9–5.7            |     |
|          | Basal shales     | 1 core                   | 2,907.5           | 10.3               |     |
|          | Silicilyte       | 5 produced oils          | 3,771–4,410       | 45°–50°            |     |
| Carbonate | Carbonate stringers | 32 cores              | 2,832–4,138       | 0.01–4.5           |     |
|          | Intra-Salt shales | 5 cuttings              | 3,660–3,682       | 3.6–4.7            |     |
|          | Carbonate stringers | 1 oil                   | 4,807             | 37°                |     |

main steps of the analytical approach applied to rock and crude oil samples. The complete analytical procedure and the associated analytical data are described in the Appendix.

The rock samples were crushed and extracted using dichloromethane (DCM). The Total Organic Carbon (TOC) was measured on bulk rocks (RB) and extracted rocks (RD) using Rock-Eval 6 (RE6). Sulfur was removed from the rock extracts by elution on a copper-filled column. Then the rock extracts as well as the crude oils were fractionated using thin layer chromatography (TLC) into saturates, aromatics and polars (NSO compounds) using cyclohexane as eluent. The resulting saturates and aromatics fractions were analyzed using Gas Chromatography/Flame Ionisation Detector (GC/FID) and Gas Chromatography/Mass Spectrometry (GC/MS). The aromatic fractions of DCM rock extracts and crude oils were also analyzed according to the number of condensed aromatic rings by normal phase liquid chromatography. Four fractions were identified corresponding respectively to mono-aromatics, di-aromatics, tri-aromatics and poly-aromatics. Bulk isotope measurements ($\delta^{13}$C and $\delta^{34}$S expressed in ‰) were carried out on an Isotopic Ratio Mass Spectrometer (IR-MS). Kerogen isolation was performed on the DCM extracted rocks. Then the RE6, elemental, $\delta^{13}$C and $\delta^{34}$S analyses were performed on kerogens.

**IDENTIFICATION AND CHARACTERIZATION OF SOURCE ROCK**

**Total Organic Carbon**

Table 1 summarizes the organic content range of the samples set. Except for the majority of carbonate samples, the samples are organic-rich. As shown in Figure 7, the carbonate samples are associated with a very low organic content. Both the carbonate and silicilyte rocks have a variable and high
soluble organic content ranging from respectively 25 to 100% of the total organic content. These high recovery levels probably correspond to reservoired fluid in the case of low TOC carbonate stringers core samples. However, some carbonate stringer samples exhibit a higher organic content (> 1%) and a high soluble organic content and could be regarded as having a similar response to extraction than the silicilyte samples. Silicilyte and shale samples exhibit a high organic content and can be considered as source rock samples. Moreover, they are also characterized by a high soluble organic content ranging from 10–80%. Thus, four organic-rich levels have been distinguished: (1) for the Silicilyte plays: a silicilyte lithofacies (TOC = c. 4%) and a basal shaly interval (‘U’ Shale; TOC = c. 10%), and (2) for the Carbonate-prone domain: an intra-salt shale interval (TOC = c. 4%) and specific carbonate intervals (TOC = c. 2%). Irrespective of lithofacies, this organic matter is rich in sulfur with a weight content ranging from 5–11% (Table 2).

**Maturity**

In the case of the silicilyte lithofacies (Table 2), two groups of samples can be distinguished on the basis of “insoluble kerogen” parameters sensitive to differences in maturity in H/C ratio (about 1 compared to 0.6), Hydrogen Index HI (about 530 compared to 120 mg Hydrocarbons / g TOC) and temperature (about 420° against 445°C) at the maximum of S2 peak (T max). A plot of HI against T max (Figure 8) shows that the thermal evolution of this silicilyte series is consistent with a Type II-S kerogen (represented by the kerogen of the Monterey Formation; A. Huc, unpublished data) and that this thermal evolution clearly distinguishes this organic matter from the Type II kerogen reference represented by Western European Lower Toarcian Shale (W.E.L.T.S.). The shale and carbonate kerogens are located in the first part of the thermal trend as the immature group of silicilyte kerogens (Table 2, Figure 8).

**Isotopic Data**

The carbon isotopic signature of the insoluble kerogens is very light (Table 2). This very light carbon isotopic value is characteristic of oils sourced from the Huqf source rock of Neoproterozoic – Early Cambrian age (Terken et al., 2001). They are probably related to the strong negative excursions of δ13C, which have been recognized worldwide in both organic matter and carbonates within the basal Vendian, uppermost Vendian and Early Cambrian (Hsü et al., 1985; Knoll et al., 1986; Magaritz et al., 1986; Kaufman et al., 1991; Burns and Matter, 1993; Narbonne et al., 1994; Loosveld et al., 1996; Kimura et al., 1997). Based on recent studies on the Ara Group, Amthor et al. (2003) and Le Guerroué et al. (2006) demonstrated the correlation between significant environmental changes coincides with the Precambrian (Ediacaran) – Cambrian boundary and the negative excursion in the carbon isotopic signature.

### Table 2

Characterization of the OM properties of the silicilyte, shale and carbonate rock samples from South Oman Salt Basin

| Plays            | Selected Samples | Bulk Rock | Insoluble OM | Soluble OM |
|------------------|------------------|-----------|--------------|------------|
|                   |                  | TOC %     | HI mg HC/g TOC | T max °C | HI/C | O/C °100 | S wt. % | δ13C % | EOM mg/gC (a) | NSO % |
| Silicilyte        | Immature silicilyte | 1.4–5.0 | 388–670 (b) | 415–430 | 0.99–1.27 | 5.32–8.03 | 5.7–11.3 | -35.2–37.8 | 507–840 | 43.1–77.4 |
|                   | Mature silicilyte | 1.8–5.6 | 57–189 (b) | 430–460 | 0.57–0.65 | 4.4–7.2 | 9–11.2 | -37.2–37.7 | 104–250 | 8.1–20.8 |
|                   | Basal shales     | 10.3     | 547 (b) | 428 | 1.15 | 7.85 | 10.1 | -37.3 | 332.3 | 69.3 |
| Carbonate         | Carbonate stringers B* | 1.5–4.5 | 306–670 | 421–440 | 0.98–1.04 | 3.0–4.37 | 6.8–7.1 | -35.6 | 330–830 | 51.5–70.3 |
|                   | Carbonate stringers A* | 0.01–1.2 | 170–884 | 413–438 | 0.95–1.11 | 6.8 | 5 | -35.2–35.4 | 283–1000 | 20.5–75 |
|                   | Intra-salt shales | 3.5–4.7 | 281–389 | 421–427 | 0.95–1.02 | nd (c) | nd | -35.6–38.4 | 312.1 | 52.1–58.0 |

Note: A and B correspond to two different carbonate stringers population; (a) average range; (b) mode reservoir; (c) nd, not determined.
As previously described, the soluble organic content is significant within the silicilyte and shale source rocks. This extractable organic matter content is dramatically higher than that found within classical source rocks as shown in Figure 9, which compares the solvent soluble OM of southern Oman samples with those of the Toarcian shales of the Paris Basin (Type II kerogen) and the Miocene Monterey Formation (Type II-S kerogen) (Huc, unpublished data; Orr, 1986). These samples encompassed the whole range of maturity. Even with a high organic content, the soluble organic content stays very low (<20%). The diagram shows a difference of an order of magnitude between these reference series and the carbonate, shale and silicilyte samples of southern Oman. Accordingly, we suggest that this southern Oman organic matter, which includes an unusually highly soluble fraction cannot be accommodated by the conventional paradigm describing the sedimentary organic matter contained in a source rock with a

**Figure 7:** Organic matter content in terms of TOC (%) and EOM (%) of the silicilyte, shale and carbonate rock samples from South Oman Salt Basin selected for this study. Except for the majority of carbonate samples (TOC <1%), the shale and silicilyte samples are organic-rich (TOC ranged from 1.9–10.3%) and considered as potential source rocks.

**Figure 8:** Plot of Rock-Eval pyrolysis $T_{max}$ versus Hydrogen Index (HI) for the source rock samples showing the similarity between the insoluble kerogen of South Oman Salt Basin and a Type II-S kerogen (represented by the kerogen of the Monterey Formation).

**Figure 9:** Comparison of organic matter content in terms of TOC (%) and EOM (%) between the potential silicilyte, shale and carbonate source rocks and conventional Type II and Type II-S source rocks. Silicilyte and shale source rock samples from South Oman Salt Basin selected for this study are characterized by a highly soluble organic matter (from 10–80%).
predominance of solvent insoluble organic matter – the kerogen (Durand, 1980) – and a subordinate extractable bitumen; the latter increasing subsequently as a result of the thermal cracking of kerogen. This unusual feature is confirmed by other independent data:

- The bulk composition of C$_{14+}$ solvent extracts of the potential source rock is characterized by a high NSO content (at least 40%). The C$_{14+}$ extracts of silicilyte source rocks exhibit an increase of saturates and disappearance of NSOs as a function of maturity. The C$_{14+}$ extracts in carbonate reservoirs are enriched in saturates.

- The considered organic matter exhibits a very specific behavior using RE pyrolysis. Usually, in RE pyrolysis, the S2 peak characterizes the residual petroleum potential, which corresponds to the amount of hydrocarbons (HC) resulting from thermal cracking of kerogen. However, the comparison of measured RE curves obtained on bulk source rocks and extracted rocks shows that a substantial part of S2 peak belongs to an extractable high molecular weight organic matter. This difference in S2 peak distinguishes this organic matter from the conventional properties of most known organic matter pointing to a bias due to the solvent extract in bulk rocks. This phenomenon is clearly apparent in the immature silicilyte samples as displayed in Figure 11. This is exemplified by the comparison of the HI difference between rock and insoluble kerogen in the different lithofacies (shale, silicilyte and carbonate) of southern Oman and from the Monterey Formation, belonging to a Type II-S kerogen and assumed to be the most comparable one to the southern Oman organic matter (Figure 12). This observation emphasizes the ambiguous character of this southern Oman organic matter. A large part of the extractable organic matter behaves like kerogen under classical pyrolysis conditions.
This specific property together with the higher amount of extractable organic matter exhibited by these southern Oman samples suggests that we are dealing with an unconventional type II-S kerogen constituted of an insoluble kerogen and an NSO-like “soluble kerogen”. The occurrence of this NSO-like “soluble kerogen” in the source/reservoir rock will interfere with the conventional assessment of the “potentially recoverable” oil.

ENVIRONMENT OF DEPOSITION, MATURITY ASSESSMENT AND THERMAL HISTORY

Geochemical Aspect

Biomarkers

The gas chromatogram profiles and biomarker distribution are displayed in Figures 13, 14 and 15 respectively. Table 3 compares the different geochemical parameters of the extractable bitumen from the different lithologies. The saturated HC distributions show overall high similarities, however, minor differences can be identified. Apart from the mature silicilyte rock extracts, the samples are characterized by a large carbon range (up to C40) and a high abundance of isoprenoids and polycyclic biomarkers. The gas chromatograms (Figure 13) exhibit a relatively immature character for these samples and often a relatively important unresolved complex mixture (UCM). In contrast, the polycyclic biomarkers are nearly absent in the mature silicilyte rock extracts and the pristane (Pr) and phytane (Ph) content is very low.

According to the distribution of polycyclic biomarkers and isoprenoids in the saturates (Figures 13–15, Table 3), the depositional environment of the organic matter in the silicilyte and carbonate plays is likely to have been hypersaline (presence of gammacerane and 21-norcholestane, which is identified only in silicilyte samples) and anoxic (predominance of the C_{35} extended hopanes over the C_{34} extended hopanes, low Pr/Ph).

The saturated HC in these extracts exhibit some unusual features:

- wide distribution of X-branched compounds, which is tentatively attributed to extinct heterotrophic bacteria (Thiel et al., 1999; Höld et al., 1999). This series, which is especially abundant in the silicilyte samples, occurs in the C_{13}-C_{28} range and its most abundant

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members are in the C_{16}-C_{24} range (Figure 13);
- C_{29} sterane predominance previously interpreted as the result of the contribution of some form of primitive algae in the Neoproterozoic source rocks (Grantham, 1986) and a noticeable occurrence of C_{26} steranes. The 21-norcholestan e, usually assigned to a hypersaline environment (Guzman-Vega and Moldowan, 1998), is only identified in the silicilyte samples;
- high C_{29}αβ hopane content;
- substantial amount of C_{23} and C_{24} tricyclic terpanes (Figure 14).

In the silicilyte lithofacies, another relevant aspect deduced from saturates is the change related to thermal maturity. The difference in n-alkane distribution patterns, the decrease in the isoprenoids/n-alkanes ratio (Figure 13), the decrease in biomarker concentration (Figures 14 and 15), the increase of saturates and aromatics maturity parameters (Table 3) in addition to the dramatic decrease in HI and the increase in T_{max} (of S2 peak) values (Table 2) clearly reflect the presence of two distinct maturity groups in these samples.

### Table 3
Comparison of geochemical parameters of soluble OM of the silicilyte, shale and carbonate rock extracts and produced oils. Qualitative and quantitative presence of biomarkers

| Soluble OM of Rocks | Silicilyte Plays | Carbonate Plays | Crude Oils |
|---------------------|------------------|-----------------|------------|
|                     | Immature | Mature | | Immature | Mature | A | B | Immature | Mature | A | B |
| **Saturates**       |          |       | |          |       | |          | |          |       | | |
| Monomethyl alkanes  | xx (major C_{20}-C_{24}) | x | (x) | x | (major C_{20}-C_{24}) | x | (major C_{20}-C_{24}) |
| 21-norcholestan e   | x       | -     | - | - | - | - | - | - | - |
| 25-28-30-trisnor17-hopane | xx | - | xx | x | - | - | - | - | - |
| 28, 30-dinor17-hopane | xx | - | xx | x | - | - | - | - | - |
| 25nor17-hopane      | x       | -     | x | (x) | - | - | - | - | - |
| gammacerane         | xx      | -     | x | x | x | xx | xx | x | x |
| carotane            | x       | -     | - | - | x | xx | - | - | - |
| Pr/Ph               | 0.3–0.4 | 0.5–0.6 | 0.36 | 0.36–0.62 | 0.3–0.4 | 0.2–0.45 | 0.57–0.89 | 0.5 | na |
| steranes % C_{29}/C_{27}-C_{29} | 23-12-65 | 35-17-48 | 36-14-50 | 22-11-67 | C_{29}>60% | 23-10-67 | na | na |
| C_{29} steranes: 20S/20R+20S | 0.50–0.53 | 0.38–0.54 | 0.48–0.54 | 0.52 | 0.50 | 0.56 | 0.40–0.50 | - | - |
| [αα/ββ] | 0.38–0.62 | 0.39–0.57 | 0.42 | 0.50 | 0.60 | 0.60 | 0.59–0.62 | - | - |
| Ts (Ts/Ts+Tm)       | (0.20–0.47) | (0.55–0.92) | (0.39) | (0.48–0.59) | (0.28) | (0.3–0.49) | - | (0.2) |
| C_{35}/C_{34}       | 1.25–2.85 | 0.53–1.5 | 1.21 | 1.36-1.49 | 1.7 | 1.59–1.93 | - | 1.87 |
| **Aromatics**       |          |       | |          |       | |          | |          |       | | |
| Secobenzohopanes diaromatics | x | - | - | - | x | xx | - | x |
| Monooaromatic derived from lanostane | x | - | - | - | x | xx | - | x |
| MAS-TAS              | x       | -     | x | x | na | - | - | - | - |
| MP                   | 1.1     | 1.6-2.1 | 0.7-1.3 | 0.9 | 1.6-2.4 | 2.0 | na | na |
| Thianes, Thiolanes   | x       | x | - | - | - | - | - | x | - |
| DBT                  | x       | xx | x | x | x | x | x | - | x |
| DBT index            | 1.2–1.3 | 2.9–3.4 | 1.3–1.6 | 2.0 | 2.4–3.1 | 2.6 | na | na |
| Thiadiamondoids      | -       | -     | - | - | - | - | - | na | - |
| NSO wt. %            | 43–77   | 8–20  | 69.3 | 39.7–58 | 25.7–31.8 | 23.6–75.7 | 0.7–6.5 | 22.3 |
| Organic Sulfur       |          |       | |          |       | |          | |          |       | | |
| wt. %               | 3–7.6   | 1.2–3.1 | 6.1 | 4.49–4.65 | na | na | 1.25–1.86 | 0.95 |
| δ^{34}S_{w}          | 13.5–16.5 | 13.3–15.7 | 13.5–16.5 | 13.5–16.5 | 13.5–16.5 | 13.5–16.5 | 13.5–16.5 | 13.5–16.5 |

Biomarker presence in sample: (a) na: not analyzed; - absent; (x) detected; x present; xx abundant
Neoproterozoic - Cambrian petroleum system, South Oman Salt Basin

Figure 13: Gas chromatograms/Flame ionization detector (GC/FID) showing the C₁₄+ saturate distributions for the silicilyte, shale and carbonate (population A and B) extracts from southern Oman plays. The saturated HC distributions show overall high similarities (presence of X-branched compounds, biomarkers, relatively important unresolved complex mixture (UCM)). However minor differences can be identified: (1) a wide distribution of X-branched compounds in the C₁₃–C₂₈ range (most abundant members are in the C₁₆–C₂₄ range) especially abundant in the silicilyte samples, (2) a decrease in the isoprenoids/n-alkanes ratio and in biomarker concentration as a function of maturity in the silicilyte samples.
Figure 14: MRM chromatograms (M$^+ \rightarrow m/z$ 191) showing the C23-C35 hopane distributions for the silicilyte, shale and carbonate (population A and B) C$_{14}$ saturate extracts from southern Oman plays. The hopane distributions (carbon number and relative intensity shown) show overall high similarities: presence of C$_{29}\alpha\beta$ hopane, C$_{23}$ and C$_{24}$ tricyclic terpanes, gammacerane and predominance of the C$_{35}$ extended hopanes over the C$_{34}$ extended hopanes. 25 norhopanes are only present in silicilyte samples.
Figure 15: MRM chromatograms ($M^+ \rightarrow m/z$ 217) showing the C21-C29 sterane distributions for the silicilyte, shale and carbonate (population A and B) C14+ saturate extracts from southern Oman plays. The sterane distributions (carbon number and relative intensity shown) show overall a C29 sterane predominance. 21-norcholestanol is only detected in silicilyte samples.
Moreover, for all the samples, the biomarker ratios classically used for maturity assessment seem to indicate a high maturity (sterane isomerizations and \( \alpha\beta \) hopanes isomerization nearly completed) (Table 3). However, it is known that \( 20S / (20S + 20R) \) and especially \( \beta\beta / (\beta\beta + \alpha\alpha) \) sterane ratios can be affected for samples from hypersaline sources leading to imprinting immature samples with a “thermally mature signature” (Ten Haven et al., 1986).

According to the classification of Radke (1987), the thermal maturity level deduced from parameters based on aromatics (MPI: Methyl Phenanthrene Index and DBTI: Dibenzothiophene index) (Table 3) is relatively low and compatible with the early stage/peak of oil window similarly to what has been deduced from the maturity assessment based on saturated biomarkers as well as on RE6 data.

The detailed comparison of the biomarker distributions from oils and extracts (Table 3) shows that the soluble organic matters extracted from the carbonate stringers and immature silicilytes appear to be genetically different because significant molecular variations for norhopanes, secobenzohopanes, carotane, thianes, thiolenes are observed.

In particular, carotane is present in the carbonates (population A) but not in the shales while demethylated hopanes are detected in the shales but not in the carbonates (population B) or just in traces (population A). In the silicilyte, X compounds and demethylated hopanes (including 21-norcholestanate) are abundant. The presence of dinorhopane and carotane in carbonate extracts (population A) suggests that this organic matter is probably formed by a mixture of organic matter originating from carbonate B population and intra-salt shales present in the carbonate-prone domain. This suggests that intra-salt shale interval, at least partly, has contributed to the charge of these carbonate A reservoirs.

Sulfur isotopic data were obtained on crude oils and rock extracts (Table 3). \( \delta^{34}S \) of silicilyte soluble organic matter ranged from 13.3 to 16.5‰, with the carbonate B one being around 16‰. As far as the shale levels are concerned, the basal shale exhibits the highest \( \delta^{34}S \). The sulfur composition of the silicilyte oils is similar to the one measured on the extracts of the corresponding rock. The carbonate oil is enriched in \( \delta^{34}S \) compared to the silicilyte oils. Furthermore, the significant sulfur isotopic signature difference between the organic and inorganic sulfur species (\( \delta^{34}S \) of anhydrite = + 35‰) as well as the absence of thiadiamondoids, molecules recently proposed by Hanin et al. (2002) as a specific Thermochemical Sulfate Reduction (TSR) marker, in the silicilyte and in the carbonate stringers leads to the conclusion that TSR did not occur in these formations. Therefore the slight differences observed in sulfur isotopic signature between the organic matter from shales, carbonates and silicilyte could be attributed to small variations in depositional environment conditions suggesting that thianes and thiolenes, very abundant in the silicilyte, were probably formed by sulfurization of the organic matter at an early stage of diagenesis. This is also a significant argument in favor of a genetic difference between the organic matter from carbonates and silicilytes because these compounds were neither detected in the carbonate samples nor in the shales samples.

These results therefore lead us to consider three genetically different types of soluble organic matter (shales, carbonates and silicilyte) that occur in the set of investigated samples, all exhibiting a thermal maturity corresponding to an early stage or peak oil window. Furthermore, Grosjean et al. (2009) recently identified an unusual biomarker series: A-norsteranes showing different patterns in carbonate rocks and oils from pre-salt (Nafun Group: Buah, Shuram, Masirah Bay formations) and Athel intra-salt (Ara Group: ‘U’ and Thuleilat shales, Athel Silicilyte) rocks investigated in their work. Thus, with this new discrimination based on the study of the main source rocks present in the Huqf Supergroup, these authors provide evidence of a predominant self-charging mechanism for the carbonate stringer plays.

Diamondoids

The maturity parameters deduced from biomarker distributions (steranes and hopanes, notably) are difficult to interpret for the mature samples because the biomarkers are present in very low concentration in these samples and because these parameters have reached their maximum values (Table 3). They cannot therefore, be used to further discriminate the maturity levels reached by
the different samples. Consequently, the maturity assessment in the mature silicilyte samples was performed using diamandoid hydrocarbons. Diamandoids correspond to a series of cage-like hydrocarbons (condensed cycloalkanes) with a carbon skeleton similar to that of diamond. A maturity parameter based on the isomerisation ratios of methyladamantanes MA (first member of the diamandoid series) was proposed by Chen et al. (1996). The authors showed on a set of natural samples that the MAI % (Methyl Adamantane Index) = 1-MA / (1-MA + 2-MA) measured for oils and source-rocks increases with increasing vitrinite reflectance (Ro) (Chen et al., 1996). According to these results, the MAI values calculated to be around 70% in the case of the oils produced by the most mature reservoirs studied in the set of silicilyte samples correspond to a maturity of about 1.2–1.3% Ro. This suggests that the maturity reached by silicilyte samples is probably equivalent to the onset of secondary cracking affecting only the NSO compounds. Diamandoids were not clearly identified in the carbonate produced oil as well as in silicilyte, shales or carbonate rock extracts.

Numerical Simulation

The basin modeling approach allows the consistency of the basin evolution to be tested with respect to the physical and chemical laws that govern thermal evolution, the maturation of the source rock and the dynamic of the fluids during the history of a sedimentary basin (Vandenbroucke et al., 1999). Different geological and geochemical hypotheses were tested and the comparison of the data allowed the most probable scenario to be predicted, i.e. the one that closely reproduces the observations. Temis 2D software was used for basin modeling (Ungerer et al., 1990; Burrus et al., 1991).

The thermal cracking of the organic compounds was simulated using the kinetic approach proposed by Behar et al. (1992). The approach describes the composition of hydrocarbons as being the result of two main processes:

1. primary cracking of kerogen, where the product composition generated at this stage strongly depends on the organic matter type and its degree of preservation;

2. secondary cracking of the generated products (oil), which governs stages of oil migration and entrapment. This secondary cracking can occur at three different places: (a) in the source rock itself where some of the generated products are retained controlling the composition of the products actually expelled, (b) during migration along drains toward reservoirs. This effect can be enhanced if heavy compounds are adsorbed on the rock minerals along the migration pathways. (c) In the reservoirs under high temperature conditions. In this case, the secondary cracking changes the composition of the entrapped oils and may result in the formation of condensates or as gas and pyrobitumens in the reservoir porosity.

These thermal processes (primary cracking of the kerogen and secondary cracking of oil) are strongly related to the temperature history undergone by the source rock and by the hydrocarbon fluids. In the case of the silicilyte slabs, the overall picture is simplified by the fact that the source rock and the reservoir form a single entity. The segregation of the products during expulsion and migration is not possible in such closed systems. It is thus difficult to estimate the role of secondary versus primary cracking, although the observed composition of the fluids exhibits significant cracking of chemical species of heavy molecular weight.

With respect to the numerical simulation of the thermal cracking, a specific approach has been used to define the kinetic parameters of this unconventional organic matter associated with silicilyte lithofacies. Kinetic data were acquired based on non-isothermal experiments (Rock-Eval type). In order to use the secondary cracking scheme implemented in Temis software (Behar et al., 1992; Behar et al., 1997), the cracking products obtained were separated into 15 different chemical classes. The geological cross-section was constructed in order to include the silicilyte slab corresponding to the most mature samples studied in these plays. The constraints for reconstructing past thermal history of the basin were obtained from apatite fission track measurements (Terken, PDO internal report). The temperature histories inferred from apatite fission track analyses indicated that the period of maximum temperature was younger than 400 Ma (“Hercynian” top Haima and pre Al Khata erosion) and that temperatures above 120°C were reached at this time. In addition, the temperature
data available at different well locations along the regional section were used to calibrate the present-day thermal regime. Based on Apatite Fission Track Analysis (AFTA) data, the heat flow was adjusted in order to consistently reproduce the present-day temperatures and the observed composition of the current fluids. We estimated a spatially constant heat flow, but varying as a function of time: between 400 Ma (period when maximum temperature was reached according to AFTA) and present-day, heat flow decreased by 20 mW/m² at the base of sediments.

**Determination of Kinetic Parameters of the Unconventional Kerogen**

The most immature sample available in the set of silicilyte samples was used for the determination of kinetic parameters of the unconventional “kerogen” made up of an insoluble kerogen and an NSO-like “soluble kerogen”. Based on geochemical data, this kerogen was interpreted as early mature with a transformation ratio estimated to be around 20%.

The global kinetic parameters, corresponding on the one hand to the partial HC potential distributed on a discrete scale of activation energy (Ea) ranging from 38 to 64 Kcal/mole and on the other hand to the frequency factor A (= $1.15 \times 10^{13}$ sec$^{-1}$) of the two parts of this unconventional “kerogen” were determined by Rock-Eval analysis. The activation energy (Ea) histograms resulting for the insoluble kerogen and NSO are displayed in Figure 16. Although the distribution is slightly shifted to lower activation energies for the soluble fraction, the distribution of the global kinetic parameters of the two parts of the kerogen share the same mean for Ea (50 kcal/mole) and are very similar for A (= c. $1.1 \times 10^{13}$ sec$^{-1}$) even if differences exist in terms of petroleum potential (mg HC/gTOC). This similarity between the insoluble kerogen and NSO-like “soluble kerogen” is in agreement with the hypothesis of two very closely related organic materials. According to these data, a reconstruction of the total kerogen kinetics was performed by recombining linearly the parameters of insoluble kerogen and NSO-like “soluble kerogen” with respect to their calculated relative proportions in the rock sample. For the kinetics calculations we considered that NSO-like “soluble kerogen” only corresponds to NSO compounds even if saturated and aromatic HC have been identified in the immature rock extract, and probably correspond to the HC generated by primary cracking of the kerogen (TR of about 20%).

In this respect, the “asphaltenic” kerogen of silicilyte rocks is constituted of 46% of soluble fraction (NSO of soluble organic matter = total extractable organic matter = 549.48 mg/gTOC) and of 54% of insoluble fraction (insoluble kerogen). The data for the compositional kinetics were obtained from open preparative pyrolysis experiments performed on soluble and insoluble kerogens (from 250°C to...)

![Figure 16: Comparison of activation energy distribution (Ea) and the frequency factor (A) calculated for the two parts of the unconventional silicilyte kerogen: (a) for the NSO-like “soluble kerogen” and (b) for the insoluble kerogen.](http://pubs.geoscienceworld.org/geoarabia/article-pdf/14/4/53/5444728/kowalewski.pdf)
to 600°C at 25°C/min) (Vandenbroucke et al., 1988). Figure 17 summarizes the compositional kinetic parameters of this unconventional kerogen, which was then used as input for 2-D basin modeling. The results are presented in lumped groups of chemical species usually identified by standard geochemical analyses: methane to pentane (C\textsubscript{1}-C\textsubscript{5}); condensates (saturates and aromatics C\textsubscript{6}-C\textsubscript{13}) and three oil fractions: heavy saturates (C\textsubscript{14+} n-alkanes and C\textsubscript{14+} iso-cycloalkanes), aromatics (C\textsubscript{14+} aromatics) and products including heteroatoms such as resins and asphaltenes (NSO). These six classes allowed direct comparison between the computed composition of the fluids and the analytical results. When compared to conventional kerogens, (Type I, II, II-S and III), two main attributes can be emphasized: (1) the main activation energy of this unconventional kerogen (E\textsubscript{a} = 50 kcal/mole) is comparable to the main energy values of a sulfur-rich kerogen (i.e. E\textsubscript{a} = c. 49 kcal/mole for type II-S), and (2) the Hydrogen Index HI of the silicilyte kerogen (714,7 HC/g TOC) is higher than the one of Type II-S kerogen (566 mg HC/g TOC). Moreover as previously discussed, the selected silicilyte kerogen sample does not correspond strictly to an immature end member, it might even be possible that the initial potential will be higher and that the type of considered organic matter belongs to a Type I-S kerogen instead of a Type II-S kerogen. This would be consistent with the inferred primitive precursors and referring to the study of an Italian Type I-S kerogen (Lehne and Dieckmann, 2007) will be without consequence on the kinetics behavior described in this paper.

2-D Basin Modeling Results

In a first approach, the comparison of a standard Type II-S kerogen (implemented in Temis as default Type II-S kerogen) and the unconventional kerogen of silicilyte plays was investigated in terms of maturity timing and amount of generated hydrocarbons. For this test, the comparison was performed with a simple set of hypotheses especially assuming a constant heat flow through time applied by using the two sets of compositional parameters associated respectively with standard Type II-S and silicilyte kerogen.

Figure 18 compares the model results of the calculated transformation ratios along a geological cross-section of silicilyte plays. The results show that silicilyte “kerogen” is roughly as reactive as Type II-S kerogen; similar transformation ratios are obtained whatever the kerogen used. However, the silicilyte kerogen might be slightly more reactive than the Type II-S kerogen because the used kinetic parameters are derived from an already slightly mature silicilyte kerogen (TR 20%). Despite this uncertainty, modeling shows that the current-day observed transformation of the kerogen (primary cracking) is consistently acquired during the maximal burial prior to Al Khlata erosion (400 Ma). This means that primary cracking occurred mainly during an initial burial of the source rock at 550–400 Ma. Then, the system was quenched from 400 Ma to present-day.

In our compositional simulations using silicilyte kerogen, we have matched the composition of the producible fluids in most mature wells available in the set of silicilyte samples (Table 4). When different samples were available we took the mean values. The density and GOR values were compared. At low temperature (129°C), the predicted composition of the silicilyte oil is too heavy (NSO and C\textsubscript{14+} aromatic contents too high) with a too few amount of light components (too low GOR) compared to the produced oils. At 150°C, the limit for NSO stability is reached (NSO are nearly absent) but the
Figure 18: Comparison of the predicted transformation ratio (TR) obtained for Type II-S and silicilyte kerogen along a geological cross-section of Silicilyte plays at present-day. For location of section (BB', northwest-southeast) see Figure 1.
GOR remains too low. Increasing the temperature until the correct GOR is reached implies the entire degradation of the NSOs and a very high saturates/aromatics ratio, which do not match with the present-day properties of the produced oils.

In conclusion, although the unusual properties of the studied organic matter made up an insoluble kerogen and an NSO-like “soluble kerogen” were taken into account in the 2-D basin modeling of oil and gas generation to simulate the composition of the most mature producible fluids in the wells penetrating the silicilyte, the predicted GOR remains too low. Other factors have thus to be considered to honour the composition of the actual fluids. In this respect the role of the unusual mineralogy of the reservoirs has been investigated (see below). The computed maximum past temperature reached at this well is about 150°C. The reconstructed thermal history results in an “equivalent vitrinite value” of 1.2% R<sub>0</sub>. This value is consistent with the one previously suggested by geochemical parameters based on diamondoid hydrocarbon ratios. The intensity of secondary cracking implied by this scenario can be considered as medium, including NSOs not entirely destroyed and aromatics slightly degraded.

**PROPERTIES OF PRODUCED FLUIDS**

As reported in Table 1, five oils produced from silicilytes and one from carbonate stringers were investigated. The carbonate oil is heavier (API = 37°, 31% of C<sub>15</sub>-) than the silicilyte oils, which exhibit a condensate character (API > 45° and more than 40% of C<sub>15</sub>-) (Table 5).

For all these oils, the C<sub>14+</sub> fractions are characterized by a low Pr/Ph ratio (0.5–0.89) and a very high content of saturates, which is higher for the silicilyte oils (Table 5). The distributions of the saturates are dominated by C<sub>13</sub>–C<sub>23</sub> hydrocarbons. However, the carbon number range is heavier in carbonate oil (up to C37) compared to the silicilyte distribution (Figure 19). The X-branched compounds are present in a lower proportion in carbonate oil. Biological markers are absent in silicilyte oils and detected in the carbonate oil. The NSO compounds are nearly absent in the silicilyte oils but account for more than 20% in the carbonate oil.

Since silicilyte clearly acts both as source rock and reservoir, the oils are genetically related to the extracts of the associated rocks, which correspond to the most mature group of silicilyte samples. Based on the saturated biomarkers the carbonate oil seems to be similar in terms of origin and maturity to the soluble organic matter found in the carbonate stringers (population B). However, this maturity of carbonate oil seems to be higher when deduced from the study of the aromatics (Table 3).

According to all these observations, the difference in composition (SARA, biomarker concentration) of the carbonate oil and silicilyte oils could be attributed to a lower maturity for the carbonate oil. However, this interpretation is not in agreement with the fact that the two oils belong to two adjacent
reservoirs and that the aromatic parameters indicate a similar maturity for the silicilyte oils and the carbonate oil. Another observation that needs to be explained is a significant depletion in NSO content of the production fluids from the silicilyte when compared to the corresponding source rock extract (from about 15.3% in the extracts to 3.4% in the oils) and a more comparable content for the carbonates (from about 29.3% in the extract to 22.3% in the oil). Since silicilyte is made of pure microcrystalline silica, the property differences, especially the API gravity 37° for carbonate produced oil and 47° for silicilyte produced oil, are tentatively explained by a substantial geochromatography effect in the silicilyte reservoir. In order to investigate this hypothesis, different approaches have been explored. This assumed matrix effect is supported by Rock-Eval pyrolysis evidence. The comparison of RE pyrolysis curves between extracted rock (RD) and the corresponding non-solvent extracted kerogen (Figure 20) displays an unusual increase of the S2b peak from this kerogen (released hydrocarbons by thermal cracking). The occurrence of hydrocarbons, which are released following the destruction of the mineral matrix (involved in the preparation of kerogen; Durand and Niçaise, 1980) suggests a strong retention of HC on the mineral matrix, unable to be released upon the pyrolysis of the total rock.

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The geochemical characterization of the samples shows significant differences in the chemical composition between the produced oils and the extracts of the corresponding source rocks of the silicilyte. The saturates/aromatics ratio increases between the rock extracts (1.3–1.9) and the produced oils (2.1–2.3). The oils are substantially enriched in non-polar compounds compared to the extracts of

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**Table 5**

Comparison of geochemical properties between silicilyte and carbonate produced oils

| Crude oils | Nature   | Depth (m) | °API | C15/C15+ | H/C | Org. S (%) | C14+ Saturates (%) | C14+ Aromatics (%) | NSO (%) | Pr/Ph |
|-----------|----------|-----------|------|----------|-----|------------|-------------------|--------------------|---------|------|
| S1        | silicilyte oil | 3,771–4,195 | 46.5 | 0.87     | 1.88 | 1.31       | 69.1              | 30.2               | 0.7     | 0.63 |
| S2        | silicilyte oil | 3,992–4,344.6 | 45.8 | 0.74     | 1.88 | 1.36       | 66.5              | 32.2               | 1.3     | 0.60 |
| S3        | silicilyte oil | 4,155      | 47   | 0.9      | 1.83 | 1.86       | 59.1              | 37.5               | 3.4     | 0.59 |
| S4        | silicilyte oil | 4,259      | 47   | 0.81     | 1.84 | 1.70       | 57.5              | 37.6               | 4.9     | 0.57 |
| S5        | silicilyte oil | 4,410      | 47   | 0.97     | 1.92 | 1.25       | 53.1              | 40.3               | 6.5     | 0.89 |
| C5        | carbonate oil | 4,807      | 37   | 0.45     | 1.82 | 0.95       | 49.9              | 27.8               | 22.3    | 0.50 |

**Figure 19:** Gas chromatograms/Flame ionization detector (GC/FID) comparing the C14+ saturate distributions for a) the silicilyte (S5) oil and b) the carbonate (C5) oil belonging to two adjacent wells. The distributions of the saturates dominated by C15–C33 HC show 1) a heavier carbon number range for the carbonate oil (up to C37), 2) a lower proportion of X-branched compounds for the carbonate oil and, c) the absence of biological markers for the silicilyte oil.

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the corresponding rocks. This difference is even more pronounced when the more polar NSO compounds are considered (saturates/NSO = 2.5–3.0 for the extracts compared to 50–99 for the produced oils). In fact, the differences between oils and related rock extracts seem to increase as a function of polarity. This again suggests that a selective retention of polar compounds due to a geochromatographic effect (specific retention of polar compounds) on microcrystalline silica dramatically affects the composition of the produced oil from the silicilyte reservoirs. Such a difference in chemical composition is not apparent on the carbonate samples.

The study of organosulfur compounds and aromatic fractions at a molecular level comforts this proposed retention role played by the mineral matrix of the silicilyte. Alkylthianes and alkylthiolanes, sulfur-containing cycles with long alkyl chains, (Schmid et al., 1987) were identified in all silicilyte oils, in the immature as well as in the mature rock extracts. Figure 21 shows the distribution of these sulfides present in silicilyte oils. The mass chromatograms m/z 87 and m/z 101, typical for these compounds, clearly display a succession of repetitive patterns (C_{12} to C_{27}) suggesting the presence of homologous series based on linear skeletons and revealing the presence of a great number of isomers in each pattern. These organosulfur compounds were abundant in the silicilyte oils but occurred only in trace amounts in the extracts of the corresponding source rock suggesting a concentrating effect of compounds exhibiting linear aliphatic skeletons (with non polar properties) in the produced fluids.

Similarly, important differences in the distribution of the aromatics between the silicilyte oils and the extracts of the corresponding source rock were shown using liquid chromatography coupled to UV detection (Figure 22). As far as the UV signal can be considered as proportional to concentration, the difference in the aromatics content increases as a function of the number of aromatic rings, which could be approximately

Figure 20: Rock-Eval pyrolysis curves of extracted rock (RD) and non-solvent extracted kerogen (KB) showing an increase in the amount of heavy molecular weight hydrocarbons (S2b peak) after destruction of the mineral matrix.

Figure 21: GC/MS fragmentograms (m/z 87 and m/z 101) showing the Alkylthiane and Alkylthiolane distributions for the silicilyte oils. The fragmentograms display a succession of repetitive patterns (C_{12} to C_{27}) suggesting the presence of homologous series based on linear skeletons and revealed the presence of a great number of isomers in each pattern.
correlated to the retention time, as illustrated in Figure 22. As the mono- and di-aromatics content stays relatively constant, there is a loss of tri- and polyaromatics content revealed by a lower UV absorbance intensity at the related retention times on the High Pressure Liquid Chromatography (HPLC) profile (Figure 22). The figure clearly points to a substantial relative concentration effect of the less polar compounds (less condensed aromatics) in the silicilyte oil samples compared to the extracts of the corresponding source rock.

All this evidence supports the occurrence of a substantial geochromatographic effect resulting in a selective retention of polar compounds within the particular mineral rock matrix made of microcrystalline quartz (80–90%) (Amthor et al., 2005). It is well known that this type of adsorption phenomena on silica is currently used for oil fractionation in geochemical laboratories where the order of elution is a function of increasing polarity: saturates < aromatics < NSO compounds. However, the experimental conditions do not allow us to quantify the role of the specific surface. This could imply that, in the reservoir, part of the hydrocarbons are not free in the porosity but adsorbed on the silicilyte matrix and, therefore, retained. Such a phenomenon could considerably affect the composition of the produced silicilyte oils by enhancing their condensate-like features (preferential expulsion of aliphatic LMW compounds essentially composed of saturated HC together with thianes and thiolanes which exhibit non polar properties). Therefore, this geochromatographic effect could result in a similarly mature character with a richness in saturates and a depletion in NSO compounds for the silicilyte oils compared to the carbonate oils, inducing a significant increase in the API gravity for the former. The silicilyte oils thus acquire an apparently more mature character via this process although the maturity levels evaluated from molecular parameters deduced from aromatics, notably, seem similar for carbonate and silicilyte oils.

In order to test the difference of retention properties between the silicilyte and the carbonate matrices, a simple laboratory experiment was performed. The carbonate oil (C5), which is apparently poorly affected by the expulsion from its carbonate matrix, was percolated throughout the two considered lithologies. It should be noted that in this preliminary testing operation, the actual specific surface of the percolated mineral support was not considered (i.e. no information on accessible surface versus oil volume or flux). The carbonate and silicilyte rock samples were crushed and extracted using dichloromethane (DCM). Then, the free organic matter matrices were obtained after oxidation and destruction of the residual organic matter of extracted rocks by $\text{H}_2\text{O}_2$ treatment. The complete removal of organic matter was checked by RE analyses which showed no residual organic matter on the mineral matrix.

n-Pentane and then dichloromethane were used as solvents for the elution within a glass mini-column (Pasteur pipette, 10 cm x 4.5 mm i.d.) filled with the same volume of crushed organic-free mineral matrices. Identical experimental conditions and amounts of carbonate oils were used for the two columns. The compositions of the eluted oils were compared to the carbonate and silicilyte produced oils in order to evaluate the retention effect of the mineral matrix. The results of the experimental test are summarized in Figure 23. The carbonate oil fractionated using the silicilyte matrix is significantly enriched in saturates and depleted in NSO compounds. The composition of the oil after elution is, in
fact, close to the one observed for the silicilyte produced oil. In contrast, no significant differences are observed between the initial composition of the carbonate oil and of the fluids recovered after contact with carbonate matrix. The amount of organic material, including at least 90% of NSO compounds retained on the silicilyte matrix, is about three times higher than the one retained on the carbonate matrix. The results of this experiment increase our confidence in the postulated geochromatographic effect as a major process liable to explain the observed differences in API gravity between oils produced from adjacent silicilyte and carbonate reservoirs. It is probable that this effect is greater on immature oils (high content in heavy compounds) and tends to disappear in more mature oils due to the progressive diminution of NSO concentration.

As previously described for the 2-D model run, at a temperature of 150°C, the compositional simulations predicted a GOR as well as a saturates/aromatics ratio that were too low compared to the observed values of the present-day produced fluid (Table 5). With respect to the proposed retention effect, the 2-D modeling was run again by including retention coefficients, assuming that a fraction of the C$_{14}$ polar heavy compounds are adsorbed on the silicilyte matrix and do not contribute to the free produced fluids. Note that even when these species are adsorbed, they are also submitted to thermal cracking and can release lighter free compounds. We tested retention coefficients for the NSO compounds in new simulations by assuming that saturates are not adsorbed (as they are not polar molecules). Using the same parameters as in the previous simulations and an NSO retention of about 80%, the compositional results were improved as shown in Table 6. The numerical modeling results support the contention that retention onto the mineral matrix is likely to contribute significantly in the compositional features of the oil produced from the silicilyte reservoirs.

![Laboratory Experiment](image)

**Figure 23:** Results of the experimental retention test aiming to demonstrate the role of the silicilyte matrix on the expulsion of oils. The carbonate (C5) oil has been percolated throughout two columns (Pasteur pipette) filled by the crushed and organic free silicilyte and carbonate matrices respectively. The results indicate an enrichment in C$_{14}$ saturates and a depletion in NSO compounds of the carbonate oil after percolation on silicilyte matrix.
Four types of organic-rich lithofacies were identified in the set of samples studied in the Neoproterozoic – Early Cambrian Ara intra-salt hydrocarbon system in southern Oman. They include for the Silicilyte plays: (1) a silicilyte lithofacies (TOC = c. 4%), and (2) a basal shaly interval ("U" Shale, TOC = c. 10%); and for the carbonate-prone domain: (3) an intra-salt shale interval (TOC = c. 4%), and (4) specific carbonate intervals (TOC = c. 2%). The accumulation of the sedimentary organic matter present in the carbonate stringers and the silicilyte occurred within a hypersaline and highly anoxic depositional environment, rich in sulfur associated with a strong bacterial activity. Although this organic matter shows very similar chemical signatures (bulk composition, elemental analysis, biomarker content, δ¹³C) characterized by an unusual “asphaltenic” nature, differences can be noted in specific biomarkers and organosulfur compounds. These differences lead us to consider three genetically different types of soluble organic matter respectively associated with shales, carbonates and silicilyte that occur in the set of investigated samples. The organic thermal maturity reached by all the samples is clearly within the oil-window stage.

From our study the oils produced in the silicilyte and carbonates reservoirs are likely to derive from the in situ thermal cracking of an unconventional sulfur-rich kerogen (made up of an insoluble kerogen and an NSO-like “soluble kerogen”). The fluid composition is also most probably influenced by a "geochromatographic retention" on the microcrystalline silica matrix of the silicilyte reservoirs (retention of the C₁₄⁺ polar compounds within the reservoir matrix). This change in composition of organic fluid probably occurred during geological time and/or during production. The modeling results confirm that some secondary cracking and retention must be taken into account to reconcile the maturity level and composition of the observed fluids. The best numerical results were obtained using the specific compositional kinetic parameters of the silicilyte kerogen and implementing a retention coefficient of 80% for the NSO fraction. These two specific features have to be taken into account for any modeling of oil and gas generation in the South Oman Salt Basin.

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APPENDIX: METHODS

Detailed information on the samples used for this study and their associated analytical data are presented in Tables A1 and A2. Figure A1 describes the complete analytical procedure performed on rock and crude oil samples.

Rock Samples

The rock samples were crushed and extracted using dichloromethane (DCM). The Total Organic Carbon (TOC) was measured on bulk rocks (RB) and extracted rocks (RD) using Rock-Eval 6 (RE6). The RE6 pyrolysis was performed using the following temperature program: isotherm 200°C during 5 min., followed by a heating ramp from 200 to 650°C at a rate of 25°C/min. with nitrogen as carrier gas. The classical parameters $T_{\text{max}}$ and Hydrogen Index (HI) were determined.

Soluble Organic Matter

Sulfur was removed from the rock extracts by elution on a copper-filled column. Then the rock extracts as well as the crude oils were fractionated using thin layer chromatography (TLC) into saturates, aromatics and polars (NSO compounds) using cyclohexane as eluent. The resulting saturates and aromatics fractions were analyzed using GC/FID and GC/MS as follows:

GC/FID analysis of saturates and aromatics fractions was performed on a Hewlett-Packard 6890 gas chromatograph equipped with an on-column injector, a FID set at 300°C and a Hewlett-Packard HP-5 fused silica column (30 m x 0.35 mm i.d., 0.25 µm film thickness). Hydrogen was used as carrier gas (2.5 ml/min). The temperature program was from 55 to 300°C at 5°C/min followed by an isothermal at 300°C during 30 min.

GC-MS analyses were carried out on a Varian 3400 gas chromatograph coupled to a Finnigan MAT TSQ 700 mass spectrometer operating in the electron impact mode. Chromatographic separations were performed on a Hewlett-Packard HP5-MS column (30 m x 0.25 mm, 0.1 µm film thickness) using helium (32 cm/s at 40°C) as carrier gas and a temperature program of 55°C (1 min isothermal), 55°C–100°C (10°C min$^{-1}$), 100–300°C (4°C min$^{-1}$), followed by an isothermal at 300°C (30 min). Mass spectra were produced at 70 eV electron energy, using a source temperature set at 180°C.

![Figure A1: Schematic analytical procedure.](http://pubs.geoscienceworld.org/geoarabia/article-pdf/14/4/53/5444728/kowalewski.pdf)
Table A1
Background information and analytical results on rock and oil samples from the silicilyte of South Oman Salt Basin selected for this study

| Plays | Wells | Formation | Nature | IFP ID | Current depth (m) | RE6 TOC (%) | Degree API | Extract mg/g iTOC | Saturates % | Aromatics % | Resins % | Asphaltenes % | NSO % | $\delta^{13}$C (%) |
|-------|-------|-----------|--------|--------|------------------|-------------|------------|------------------|-------------|-------------|----------|---------------|------|------------------|
| W-1   | Silicilyte | core | 159745 | 1,177-1,184 | 3.4 | 648.5 | 6.4 | 16.3 | 56.5 | 20.9 | 77.4 | -37.8 |
| W-2   | Silicilyte | core | 159746 | 2,032-3,035 | 4.4 | 507.2 | 28.0 | 29.1 | 42.6 | 0.5 | 43.1 | -35.2 |
| W-3   | Silicilyte | core | 160413 | 2,687.8 | 2.6 | 530.0 | 23.5 | 29.2 | 44.8 | 2.4 | 47.2 |
| W-4   | Silicilyte | core | 160414 | 2,690.1 | 1.9 | 769.5 | 17.9 | 28.3 | 43.7 | 10.1 | 53.8 |
| W-5   | Silicilyte | core | 160461 | 3,780.9 | 2.6 | 142.3 | 47.1 | 39.3 | 13.2 | 0.4 | 13.6 |
| W-6   | Silicilyte | core | 160462 | 3,793.2 | 1.9 | 162.0 | 51.3 | 38.1 | 10.0 | 0.5 | 10.5 |
| W-7   | Silicilyte | cuttings | 159751 | 3,772-4,000 | 5.7 | 103.9 | 49.2 | 36.8 | 13.2 | 0.9 | 14.1 | -37.2 |
| W-8   | Silicilyte | core | 159770 | 4,133 | 4.5 | 226.3 | 52.0 | 27.2 | 20.8 | nd | 20.8 |
| W-9   | Silicilyte | cuttings | 159772 | 4,145.49 | 3.6 | 249.2 | 49.7 | 31.2 | 19.1 | nd | 19.1 |
| W-10  | Silicilyte | core | 159750 | 4,048-4,344 | 2.0 | 133.5 | 52.2 | 27.3 | 19.5 | 1.1 | 20.5 |
| W-3   | U' shale | core | 159747 | 2,907.5 | 10.3 | 332.3 | 8.6 | 22.1 | 56.0 | 13.3 | 69.3 | -37.3 |
| W-7   | Silicilyte | oils | S1-159225 | 3,771-4,195 | 46.5 | 69.1 | 30.2 | 0.7 | -34.1 |
| W-6   | - | | S2-159224 | 3,992-4,344.6 | 45.8 | 66.5 | 32.2 | 1.3 | -34.2 |
| W-8   | - | | S3-159227 | 4,155 | 47 | 59.1 | 37.5 | 3.4 | -35.5 |
| W-8   | - | | S4-159226 | 4,259 | 47 | 57.5 | 37.6 | 4.9 | -35.6 |
| W-11  | - | | S5-163060 | 4,410 | 47 | 53.1 | 40.3 | 6.5 | -35.8 |

(a) nd: not determined
Table A2
Background information and geochemical results on rock and oil samples from the carbonate-prone domain of South Oman Salt Basin selected for this study

| Plays | Wells | Formation | Nature | IFP ID | Current depth (m) | R6 TOC (%) | Degree API | Extract mg/g iTOC | Saturates % | Aromatics % | Resins % | Asphaltenes % | N50 % | δ13C (‰) |
|-------|-------|-----------|--------|--------|------------------|------------|------------|----------------|-------------|-------------|----------|--------------|-------|-----------|
| W-12  | A3 Anhydrite floater | cuttings | 162377 | 3.660 | 3.7 | 333.1 | 15.5 | 26.5 | 54.9 | 3.1 | 58.0 | -35.6 |
| W-12  | A3 Anhydrite floater | cuttings | 162378 | 3.670 | 3.7 | 357.7 | 17.2 | 27.2 | 49.6 | 6.0 | 55.6 |
| W-12  | A3 Anhydrite floater | cuttings | 162379 | 3.674 | 4.6 | 249.1 | 18.6 | 25.3 | 51.1 | 5.0 | 56.1 | -38.1 |
| W-12  | A3 Anhydrite floater | cuttings | 162380 | 3.678 | 4.1 | 310.6 | 20.1 | 27.8 | 41.2 | 10.9 | 52.1 | -38.4 |
| W-12  | A3 Anhydrite floater | cuttings | 162381 | 3.682 | 4.1 | 462.2 | 17.9 | 26.7 | 42.3 | 13.1 | 55.4 |
| W-13  | A4 Stringer | core | 162429 | 2.906.46 | 0.6 | 899.9 | 29.3 | 25.9 | 40.4 | 4.4 | 44.8 |
| W-13  | A4 Stringer | core | 162400 | 2.912.15 | 0.6 | 867.2 | 28.2 | 23.9 | 44.3 | 3.7 | 48.0 |
| W-13  | A4 Stringer | core | 162401 | 2.930.38 | 0.4 | 780.0 | 26.7 | 29.7 | 41.7 | 1.9 | 43.6 |
| W-13  | A4 Stringer | core | 162422 | 2.936.26 | 0.3 | 715.1 | 24.0 | 27.3 | 45.9 | 2.8 | 48.7 |
| W-13  | A4 Stringer | core | 162423 | 2.944.15 | 0.3 | 604.5 | 23.8 | 24.0 | 49.1 | 3.1 | 52.2 |
| W-13  | A4 Stringer | core | 162444 | 2.947.64 | 0.8 | 476.9 | 47.8 | 31.7 | 18.7 | 1.8 | 20.5 |
| W-13  | A4 Stringer | core | 162445 | 2.950.23 | 1.0 | 506.3 | 27.9 | 21.6 | 44.6 | 5.8 | 50.4 |
| W-12  | A3 Carbonate (A3 C) | core | 162412 | 3.321.35 | 0.6 | 968.5 | 40.5 | 31.6 | 27.2 | 0.7 | 27.9 |
| W-12  | A3 Carbonate (A3 C) | core | 162413 | 3.324.35 | 0.6 | 720.7 | 42.6 | 31.2 | 25.4 | 0.8 | 26.2 | -35.1 |
| W-12  | A3 Carbonate (A3 C) | core | 162414 | 3.328.25 | 0.5 | 970.6 | 43.4 | 29.6 | 26.3 | 0.7 | 27.0 |
| W-12  | A3 Carbonate (A3 C) | core | 162415 | 3.433.6 | 0.5 | 918.9 | 42.4 | 31.9 | 24.9 | 0.8 | 25.7 | -35.4 |
| W-12  | A3 Carbonate (A3 C) | core | 162416 | 3.438.6 | 0.4 | 839.0 | 39.2 | 33.3 | 26.5 | 1.0 | 27.5 | -34.7 |
| W-12  | A3 Carbonate (A3 C) | core | 162417 | 3.443.46 | 0.1 | 1000.0 | 39.8 | 30.0 | 27.7 | 2.5 | 30.2 | -34.2 |
| W-12  | A3 Carbonate (A3 C) | core | 162418 | 3.446.5 | 0.1 | 881.9 | 39.9 | 28.3 | 29.0 | 2.8 | 31.8 | -34.7 |
| W-12  | A3 Carbonate (A3 C) | core | 162419 | 3.448.2 | 0.3 | 745.1 | 40.7 | 30.7 | 27.0 | 1.6 | 28.6 |
| W-12  | A3 Carbonate (A3 C) | core | 162421 | 3.696.67 | 0.3 | 681.7 | 44.2 | 32.2 | 22.0 | 1.6 | 23.6 |
| W-12  | A3 Carbonate (A3 C) | core | 162425 | 4.043.05 | 0.2 | 766.6 | 45.2 | 28.2 | 24.3 | 2.3 | 26.6 |
| W-15  | A3 Carbonate (A3 C) | core | 162427 | 4.060.89 | 0.3 | 750.2 | 43.5 | 30.9 | 23.3 | 2.3 | 25.6 |
| W-15  | A3 Carbonate (A3 C) | core | 162428 | 4.081.03 | 0.4 | 549.2 | 46.0 | 27.1 | 23.5 | 3.3 | 28.8 |
| W-15  | A3 Carbonate (A3 C) | core | 162429 | 4.096.56 | 0.4 | 509.3 | 36.8 | 30.9 | 28.7 | 3.6 | 32.3 |
| W-15  | A3 Carbonate (A3 C) | core | 162430 | 4.107.15 | < 0.1 | 841.5 | 38.7 | 24.8 | 30.1 | 6.4 | 36.5 |
| W-15  | A3 Carbonate (A3 C) | core | 162431 | 4.114.97 | 1 | 566.6 | 42.5 | 34.4 | 21.9 | 1.2 | 23.1 |
| W-15  | A3 Carbonate (A3 C) | core | 162432 | 4.117.27 | < 0.1 | 708.2 | 40.5 | 26.7 | 25.5 | 7.3 | 32.8 |
| W-15  | A3 Carbonate (A3 C) | core | 162433 | 4.124.24 | 0.3 | 262.4 | 40.3 | 28.6 | 26.6 | 4.5 | 31.1 |
| W-15  | A3 Carbonate (A3 C) | core | 162434 | 4.133.95 | 0.5 | 489.0 | 41.2 | 30.7 | 25.8 | 2.3 | 28.1 |
| W-15  | A3 Carbonate (A3 C) | core | 162435 | 4.138.63 | 0.3 | 529.9 | 40.9 | 28.2 | 29.4 | 1.5 | 30.9 |
| W-16  | A4 Stringer | core | 156803 | 2.832.96 | 0.3 | 1000.0 | 26.8 | 28.5 | 44.7 |
| W-17  | A4 Stringer | core | 156852 | 3.007.49 | 0.6 | 874.7 | 12.8 | 11.5 | 25 | 50.7 | 75.7 |
| W-18  | A1 Carbonate (A1C) | core | 156906 | 2.961.74 | 1.2 | 534.9 | 16 | 13.7 | 39 | 31.3 | 70.3 |
| W-19  | Birba Stringer | oil | 156907 | 2.962.3 | 2.2 | 402.0 | 17.5 | 18.2 | 19.8 | 44.5 | 64.3 |
| W-19  | Birba Stringer | oil | 1563061 | 4.807 | 37 | 49.9 | 27.8 | 22.3 | -36.3 |
GC-MS analysis of saturates and aromatics using MRM (Metastable Reaction Monitoring) detection mode was carried out on the VG AUTOSPEC mass spectrometer (Micromass) equipped with an HP 35890 II gas chromatograph using a splitless injector at 320°C, a J&W DB-1 column (60 m x 0.22 mm i.d., 0.25 μm film thickness) and helium as carrier gas. The oven was programmed from 50 to 150°C at 35°C/min, followed by heating at 2°C/min to 320°C and a hold for 30 min. Mass spectra were produced at 70 eV electron energy, using a source temperature set at 300°C and in MRM (Metastable Reaction Monitoring) detection mode over the 50–600 amu range (cycle time 1.1 second).

The aromatic fractions of DCM rock extracts and crude oils were also analyzed according to the number of condensed aromatic rings by normal phase HPLC (VARIAN STAR 9010 pump) on Petrospher B (Chrompack, 250 x 4.6 mm). Four fractions were identified corresponding respectively to monoaromatics, di-aromatics, tri-aromatics and poly-aromatics. The solvent used for isocratic elution was n-hexane and the flow rate was maintained at 1 ml/min. The elution time of each aromatic family was determined using a mixture of reference compounds and the chromatographic column was back-flushed after elution of pyrene. The detection was done by monitoring absorption at 254 nm (Varian 9050 UV detector).

Bulk isotope measurements (δ¹³C and δ³⁴S) were carried out on an isotopic mass spectrometer Isoprime (Micromass). δ¹³C and δ³⁴S measurements are expressed in ‰ with respect to PDB and S2 (silver sulphide) respectively. Replicate analyses were performed on the samples and the accuracy of the instrument was 0.1 ‰ for δ¹³C and 0.8 ‰ for δ³⁴S.

Insoluble Organic Matter

Kerogen isolation was performed using the method proposed by Durand and Nicaise (1980). The destruction of minerals by successive HF and HCl mixtures was performed on the DCM extracted rocks. Then the RE6, elemental, δ¹³C and δ³⁴S analyses were performed on kerogens.

REFERENCES

Alixant, J.L., N. Frewin, P. Nederlof and N. Al Ruwehy 1998. Characterization of the Athel silicilyte source rock/reservoir: Petrophysics meets geochemistry. In Society of Professional well log Analysis, 39th Annual Logging Symposium, May 26th-29th, p. 1-14.

Al-Siyabi, H.A. 2005. Exploration history of the Ara intra-salt carbonate stringers in the South Oman Salt Basin. GeoArabia, v. 10, no. 4, p. 39-72.

Amthor, J.E., J.P. Grotzinger, S. Schröder, S.A. Bowring, J. Ramezani, M.W. Martin and A. Matter 2003. Extinction of ‘Cloudina’ and ‘Namacalathus’ at the Precambrian – Cambrian boundary in Oman. Geology, v. 31, no. 5, p. 431-434.

Amthor, J.E., K. Ramseyer, T. Faulkner and P. Lucas 2005. Stratigraphy and sedimentology of a chert reservoir at the Precambrian – Cambrian Boundary: The Al Shomou Silicilyte, South Oman Salt Basin. GeoArabia, v. 10, no. 2, p. 89-122.

Behar, F., S. Kressman, J.L. Rudkiewicz and M. Vandenbroucke 1992. Experimental simulation in a confined system and kinetic modelling of kerogen and oil cracking. Organic Geochemistry, v. 19, no. 1-3, p. 173-189.

Behar, F., M. Vandenbroucke, Y. Tang and F. Marquis 1997. Thermal cracking of kerogen in open and closed system: Determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. Organic Geochemistry, v. 26, no. 5-6, p. 321-329.

Bowring, S.A., J.P. Grotzinger, D.J. Condon, J. Ramezani, M.J. Newall and P.A. Allen 2007. Geochronologic constraints on the chronostratigraphic framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman. American Journal of Science, v. 307, p.1097-1145.

Burns, S.J. and A. Matter 1993. Carbon isotopic record of the latest Proterozoic from Oman. Eclogae Geologicae Helvetiae, v. 86, no. 2, p. 595-607.

Burrus, J., A. Kuhfuss, B. Doligez and P. Ungerer 1991. Are numerical models useful in reconstructing the migration of hydrocarbons? A discussion based on the northern Viking graben. In W.A. England and A.J. Fleet (Eds.), Petroleum migration. Geological Society, Special publication, v. 59, p. 89-109.
Chen, J.H., J.M. Fu, G.Y. Sheng, D.H. Liu and J.J. Zhang 1996. Diamondoid hydrocarbon ratios: Novel maturity indices for highly mature crude oils. Organic Geochemistry, v. 25, p. 179-190.
Durand, B. and G. Niçaise 1980. Procedures for kerogen isolation. In B. Durand (Ed.), Kerogen, insoluble organic matter from sedimentary rocks. Technip, Paris, p. 35-54.
Gelin, F., N. Frewin, A.Y. Huc, I. Kowalewski and J.E. Amthor 1999. Depositional model for Infracambrian organic matter in South Oman Basin. 39th International Meeting of the European Association of Organic Geochemists, Istanbul, v. 1, p. 389-390.
Granath, P.J. 1986. The occurrence of unusual C27 and C29 sterane predominances in two types of oman crude oil. Organic Geochemistry, v. 9, no. 1, p. 1-10.
Granath, P.J., G.W.M. Lijmbach, J. Posthuma, M.W. Hughes-Clarke and R.J. Willink 1988. Origin of crude oils in Oman. Journal of Petroleum Geology, v. 11, no. 1, p. 61-80.
Grosjean, E., G.D. Love, C. Stalvies, D.A. Fike and R.E. Summons 2009. Origin of petroleum in the Neoproterozoic-Cambrian South Oman Salt Basin. Organic Geochemistry, v. 40, no. 1, p. 87-110.
Guzman-Vega, M.A. and M. Moldowan 1998. 21-norcholestane as hypersaline parameter in worldwide and Mexican oil samples. 6th ALAGO Meeting 1998, Margarita Island, Venezuela.
Hanin, S., P. Adam, I. Kowalewski, A.-Y. Huc, B. Carpentier and P. Albrecht 2002. Bridgehead alkylated 2-thiaadamantanes: novel markers for sulfurisation processes occurring under high thermal stress in deep petroleum reservoirs. Chemical Communications, v. 16, p. 1750-1751.
Hartstra, B., G. Graham and J. Hartsink 1996. The Athel silicilyte play: Status and scope in exploration in Oman, new ideas from old basins. PDO publication, p. 79-86.
Höld, I.N., S. Schouten, J. Jellemse and J.S. Sinninghe Damsté 1999. Origin of free and bound mid-chain methyl alkanes in oils, bitumens and kerogens of the marine, Infracambrian Huqf Formation (Oman). Organic Geochemistry, v. 30, no. 11, p. 1411-1428.
Hsu, K.J., O. Hedi, J.Y. Gao, S. Su, H. Chen and U. Krahenbuhl 1985. “Strangelove ocean” before the Cambrian explosion. Nature, v. 316, p. 809-811.
Hughes-Clarke, M.W. 1988. Stratigraphy and rock unit nomenclature in the oil–producing area of interior Oman. Journal of Petroleum Geology, v. 11, no. 1, p. 5-60.
Kaufman, A.J., J.M. Hayes, A.R. Knoll and G.J.B. Germs 1991. Isotopic composition of carbonates and organic carbon from Upper Proterozoic successions in Namibia: Stratigraphic variation and the effects of diagenesis and metamorphism. Precambrian Research, v. 49, p. 301-327.
Kimura, H., R. Matsumoto, Y. Kakuwa, B. Hamdi and H. Zibartesz 1997. The Vendian-Cambrian δ13C record, North Iran: Evidence for overturning of the ocean before the Cambrian explosion. Earth and Planetary Science Letters, v. 147, p. E1-E7.
Knoll, A.R., J.M. Hayes, A.J. Kaufman, K. Swett and I.B. Lambert 1986. Secular variation in carbon isotopic ratios from Upper Proterozoic successions of Svalbard and East Greenland. Nature, v. 321, p. 832-838.
Le Guerroué, E., P.A. Allen and A. Cozzi 2006. Chemostratigraphic and sedimentological framework of the largest negative carbon isotopic excursion in Earth history: The Neoproterozoic Shuram Formation (Nafun Group, Oman). Precambrian Research, v. 146, p. 68-92.
Lehne, E. and V. Dieckmann 2007. Bulk kinetic parameters and structural moieties of asphaltenes and kerogens from a sulfur-rich source rock sequence and related petroleums. Organic Geochemistry, v. 38, no. 10, p. 1657-1679.
Loosveld, R.J.H., A. Bell and J.J.M. Terken 1996. The tectonic evolution of interior Oman. GeoArabia, v. 1, no. 1, p. 28-51.
Magaritz, M., W.T. Holster and J.L. Kirschvink 1986. Carbon isotope events across the Precambrian-Cambrian boundary on the Siberian platform. Nature, v. 320, p. 258-259.
Narbonne, G.M., A.J. Kaufman and A.R. Knoll 1994. Integrated chemostratigraphy of the Windermere Supergroup, Northern Canada: Implications for Neoproterozoic correlations and early evolution of animals. Geological Society of America Bulletin, v. 106, p. 1281-1292.
Nederlof, P.J.R., J.E. Amthor and A. Bell 1997. The Athel Formation: A unique oil producing source rock in South Oman. 18th International Meeting of the European association of Organic Geochemists, Maastricht, Abstract, v.1, p. 107-108.
Orr, W.L. 1986. Kerogen/asphalene/sulfur relationships in sulfur-rich Monterey oils. Advances in organic Geochemistry 1985. Organic Geochemistry, v. 10, p. 499-516.
Radke, M. 1987. Organic Geochemistry of aromatic hydrocarbons. In J. Brooks and D. Welte (Eds.), Advances in Petroleum Geochemistry. Academic Press, London, v. 2, p. 141-207.
Schmid, J.C., J. Connan and P. Albrecht 1987. Occurrence and geochemical significance of long-chain dialkythiacyclopentanes. Nature, v. 329, p. 54-56.

Schröder, S., B.C. Schreiber, J.E. Amthor and A. Matter 2003. A depositional model for the terminal Neoproterozoic – Early Cambrian Ara Group evaporites in South Oman. Sedimentology, v. 50, p. 879-898.

Schröder, S., J.P. Grozinger, J.E. Amthor and A. Matter 2005. Carbonate deposition and hydrocarbon reservoir development at the Precambrian – Cambrian boundary: The Ara Group in South Oman. Sedimentary Geology, v. 180, p. 1-28.

Ten Haven, H.L., J.W. De Leeuw, T.M. Peakman and J.R. Maxwell 1986. Anomalies in steroid and hopanoid maturity indices. Geochemica et Cosmochemica Acta, v. 50, p. 853-855.

Terken, J.J.M., N.L. Frewin and S.L. Indrelid 2001. Petroleum systems of Oman: Charge timing and risks. American Association of Petroleum Geologist Bulletin, v. 85, no. 10, p. 1817-1845.

Thiel, V., A. Jenish, G. Wörheide, A. Löwenberg, J. Reitner and W. Michaelis 1999. Mid-chain branched alkanoic acids from “living fossil” demosponges: A link to ancient sedimentary lipids? Organic Geochemistry, v. 30, p. 1-14.

Ungerer, P., J. Burrus, B. Doligez, P.-Y. Chenet and F. Bessis 1990. Basin evolution by integrated two-dimensional modeling of heat transfer, fluid flow, hydrocarbon generation, and migration. American Association of Petroleum Geologists Bulletin v. 74, no. 3, p. 309-335.

Vandebroucke, M., F. Behar and J. Espitalié 1988. Characterization of sedimentary organic matter by preparative pyrolysis: Comparison with Rock-Eval pyrolysis and pyrolysis-gas chromatography techniques. Energy & Fuels, v. 2, p. 252-258.

Vandebroucke, M., F. Behar and J.-L. Rudkiewicz 1999. Kinetic modelling of petroleum formation and cracking: Implications from the high pressure/high temperature Elgin field (UK, North Sea). Organic Geochemistry, v. 30, no. 9, p. 1105-1125.

Visser, W. 1991. Burial and thermal history of Proterozoic source rocks in Oman. Precambrian Research, v. 54, no. 1, p. 15-36.

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