Biomarkers, stable carbon isotope, and trace element distribution of source rocks in the Orange Basin, South Africa: implications for paleoenvironmental reconstruction, provenance, and tectonic setting

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Abstract
Aptian to Campanian sediments from the Western offshore to Central Orange Basin were studied by integrating molecular geochemistry, inorganic and isotopic studies to recognize their geochemical characteristics via the reconstruction of the Orange basin’s paleoweathering, paleosalinity, paleovegetation, paleoclimate, and tectonic records. Molecular analyses of both aliphatic and aromatic compounds reveal an input dominantly from a marine source. The source rocks accumulated in a reduced, anoxic, saline water column. Based on various biomarker proxies and vitrinite reflectance data, some samples are thermally mature to produce petroleum, while others are not. According to the V/Ni ratio, samples from the Orange Basin in South Africa are mainly anoxic, with only a few samples ranging from suboxic to anoxic. This is congruent with biomarker and isotope analyses that further indicate the presence of marine-derived source rocks with some terrestrial remains generating hydrocarbons. The investigated sediments are made up of intermediate igneous rocks that have undergone moderate chemical weathering. Geochemical figures on tectonic setting discriminant function diagrams revealed a continental rift of passive margin settings. As a result, the extrapolated crustal processes are directly analogous to the genesis and evolution of the Orange Basin, demonstrating Gondwana’s breaking up and the opening of the Atlantic Ocean Margin.

Keywords Biomarker · Trace element · Stable isotope · Orange basin · Provenance · Tectonic setting

Introduction
During the last thirty years, the South African government has been motivated to explore the Orange Basin due to the discovery of valuable petroleum on the southern Atlantic margins (Jungslager 1999; Hartwig et al. 2012; Adekola et al. 2012). The huge Ihubesi gas reserve off South Africa as well as the Kudu gas field in South Namibia are the result of ongoing hydrocarbon prospecting (PASA 2003). There have been some reports on the geochemical attributes of source rocks from the Orange Basin (Jungslager 1999; Van der Spuy 2003). According to Jungslager (1999) and Van der Spuy (2003), the Orange Basin has primarily three source rock intervals.

Organic geochemistry is an important tool for identifying source rocks and classifying crude oils into families both at the beginning and later stages in oil exploration (Peters et al. 2005; Akinlua et al. 2007a, 2007b; Adekola et al. 2012). A thorough geochemical analysis of source rocks can reveal information about the hydrocarbons they produce (Adekola et al. 2012). The composition and long-term preservation of organic matter deposited in the marine domain throughout the Orange Basin is related to deposition system stacking and, as a result, the depositional systems tracts in which it was deposited (Adekola et al. 2012). Most geochemical analyses rely heavily on data obtained from bitumen extraction. This yields biomarkers from both aliphatic and
studies were integrated to recognize their geochemical char-
molecular geochemistry, inorganic methods and isotopic
unexplored Orange Basin post-rift sequence. In this context,
mineral content, and chemical composition of the vast,
genetic linkage within the source rocks, deposition, thermal
maturation as well as relating their provenance (Peters et al.
2005). Therefore, the quantity, quality and thermal matura-
tion of source rocks are pivotal in petroleum exploration.
In order to answer some questions such as organic matter
origin, depositional condition, thermal maturation, type and
quality of source rocks, researchers ought to work on many
representative samples extending up to the deeper Orange
Basin. In characterizing the source rocks, these conventional
methods may be related to unconventional approaches such
as nuclear magnetic resonance (NMR), Fourier transform
infrared spectroscopy (FTIR), and thermogravimetric analy-

In petroleum exploration, trace elements are also used
to delineate the emergence, depositional environment, ther-
al maturity of organic matter, as well as pathways of oil
movement (Lewan 1984; Akinlua et al. 2015, 2018). Metal
concentration ratios (V/(V + Ni)) is used to identify organic
matters within sediments, such as siliceous versus phos-
phatic shales (Akinlua et al. 2010). The types of organic
matter and depositional environment, according to Lewan
(1984), have a significant impact on the amount of trace ele-
ments in source rocks. As a result, the trace element content
of source rock has become a valuable geochemical tool for
evaluating source rock. The concentration of trace elements
certifies the source rock type (Barwise 1990). A reliable
paleoenvironmental marker, the trace element is not inhib-
ited by maturation and is used to depict depositional age in
source sediments as well as likely time to generate hydro-
carbons. Cumming et al. (2014) determined the depositional
age of source rocks and the timing of petroleum generation
in the Uinta Basin using rhenium–osmium geochronology
(Re-Os). Some research has been conducted on crude oil
and condensates, as well as on the source rock geochemistry
of the South African basin (Van der Spuy et al. 2003).
Vander Spuy et al. (2003; Akinlua et al. 2010) but scarce
inorganic geochemical work undertaken on whole rock sam-
ple. The study of stable carbon isotopes is used to investi-
gate environmental issues that impact organic matter, like
paleoclimatic evolution (Hentschel et al. 2016); provenances
(Thornton and McManus 1994).

The integration of organic and inorganic geochemistry
provides a multiscale perspective that allows researchers
to answer some questions such as origin of organic matter,
genetic linkage within the source rocks, deposition, thermal
maturation, sediment age, type and quality of source rocks,
mineral content, and chemical composition of the vast,
unexplored Orange Basin post-rift sequence. In this context,
molecular geochemistry, inorganic methods and isotopic
studies were integrated to recognize their geochemical char-
acteristics through the reconstruction of the Orange basin’s
paleovegetation and paleoweathering. This approach could
also be adapted to understand certain tectonic elements and
prospericity in other basins in the world. In addition, the
characterization of some representative rock samples for
elementary analysis resulted in a useful environmental and
health implications database.

The geologic setting

The Orange Basin is an offshore passive continental bound-
ary of Southwest Africa’s Atlantic Ocean (Fig. 1; Akinlua
et al. 2011; Jungslager 1999) that is bounded to the north by
the Kudu Arc and to the south by the Agulhas-Columbine
Arc (Fig. 2; Hirsch et al. 2007; Muntingh and Brown 1993).
The basin formed in the late Jurassic-Tertiary period (Brown
1995; Gerrard and Smith 1982; Muntingh 1993). It is located
between latitudes 31–33.5 S and longitudes 16–17 E, stretch-
ing nearly 160,000 km² extending from the continental shelf
toward the deep offshore marine, as shown in Fig. 1 (PASA
2003; Broad et al. 2006).

Orange Basin seems to be larger than the other six (6)
basins in South Africa put together (McMillan 2003). Its
main source is the Orange River, which empties into the
South Atlantic Ocean (Akinlua et al. 2011). Despite the
Orange Basin being South Africa’s largest offshore basin, less
than 40 wells have been drilled, equating to one well
per 4000 Km² (Muntingh 1993). An estimated 43,000 km²
of deep-water license area extends from Namibia’s offshore
southwest volcanic passive margin (Paton et al. 2007) span-
ing from the upper Jurassic to the Holocene (Kuhlmann
et al. 2010). Figure 2 illustrates the basin’s many onshore
provinces, mobile belts, craton, and the Kalahari shield.

Source rock intervals in the Orange Basin are best
explained by tectonostratigraphic events. The tectonic stages
are as follows: late synrift, early post-rift, and drift succe-
sion (Jungslager 1999). These features resemble sedimentary
trenches (Akinlua et al. 2010) made of source rock (Van der
Spuy et al. 2003).

According to petroleum systems, they are also classified
based on individual organic matter content, hydrocarbon
type, and spatial distribution. Within the Orange Basin, three
(3) most qualitative source rock intervals were discovered.
These major source rock intervals are as follows:

i. Haurterivian synrift lacustrine source rocks (Type I)
ii. Pelagic transition sediments from the Barremian to the
Lower Aptian (Type II/III) (Jungslager 1999).
iii. Marine source rocks from the Aptian drift stage (112-
103 Ma)
iv. Cenomanian–Turonian Type II drift marine source
rocks (Vander Spuy et al. 2003).
The Hauterivian synrift source rock is only found in the Orange Basin at the AJ1 well’s half-graben (Barton et al. 1993). The source rock aids in the correlation and reconstruction of the environment up to the South American margins (Paton et al. 2007). Age-wise, Barremian rocks are the second category of source rocks, which is found between the transition–drift tectonic stage in the Aptian anoxic environment (Van der Spuy et al. 2003). It penetrates the AK-half-graben, as evidenced by the AK wells that produce gas. Likewise, the Barremian to Lower Aptian source manifests at OA1 and is oil prone (Jungslager 1999). The source rocks are likely to enrich Namibia’s Kudu gas and the Ibhubesi fields (Kuhlmann et al. 2010).

Finally, within the AK1’s half-graben, the Turonian drift phase source interval appears, presumably producing gas and oil (Van der Spuy et al. 2003). Fluvial and deltaic sandstones with conglomerate from the Paleozoic Karoo section and underlying basement rocks serve as reservoir rocks in the rifting region. Fluvial sandstones and floodplain sediments are found in the drift stage (Jungslager 1999). The Orange Basin contains a variety of play types, including rift plays, which are lacustrine sandstones that trap hydrocarbons from organic-rich claystone. Another significant play is the synrift sediments with drift plays, which include early Cretaceous aeolian sandstone plays, Albian incised valleys, shallow to deep-water structural sediments, and rolling over anticlines (Vander Spuy et al. 2003).

**Sampling and analytic techniques**

Twenty shales were collected from cutting samples of the Orange Basin in four-wells KD-1, KE-1, KF-1, and KH-1 (Fig. 1). The initial geochemical approach began with cleaning, removing oxidized surfaces, followed by crushing and grinding the shale to a fine powder with a pestle and mortar. About 5–10 g of the powdered sample was extracted for 72 h by using Soxhlet apparatus to evaluate extractable organic matter (OM) concentrates as well as the hydrocarbon content of the examined sediments. In a glass jar, 93 percent dichloromethane was mixed with 7 percent methanol before being poured into an empty solvent bottle and thoroughly shaken. A 250-ml conical flask and Soxhlet extractor apparatus
were rinsed with solvent to neutralize any contaminant and then oven-dried. About 150 ml of the solvent was poured into the conical flask, and then alumina was added to avoid bumping and immediate evaporation of the solvent. Copper metal was also added into the conical flask of the solvent to absorb sulfur contained in the shale sample. The conical flask containing the solvent, anti-bump alumina, and Cu was mounted on the Soxhlet extractor, which housed the sample in the thimble and was connected to a condenser for 72 h of mantle heating. The extracted organic matter was separated using liquid column chromatography into saturated hydrocarbons, aromatics, and hetero-NSO fractions, which were then dried at room temperature before being investigated using gas chromatography (GC) or gas chromatography mass spectrometry (GC/MS).

**Molecular approach and isotope method**

The GC and GCMS were used on the aliphatic and aromatics to show the distribution of n-alkane, isoprenoid (Fig. 3a), hopane (Fig. 4a), and sterane (Fig. 5a) as well as some aromatic hydrocarbon fractions (Fig. 6a, b). Saturated fractions were mixed with hexane and analyzed using the gas chromatographs of the Agilent 6890 N series. A gaseous spectrometer FID coupled with an HP-5MS capillary was used for gas chromatography analysis, with intervals of 40 to 300 °C relative to 4 °C per minute, toward 300 °C for 30 min. Similarly, an Agilent V5975B-MSD mass spectrometer outfitted with gas chromatographs and ion sources was adjusted for gas chromatographic mass spectroscopic analysis. By scaling the peak heights of the n-Alkanes, isoprenoids and aromatic hydrocarbon parameters, Table 1; terpane, Table 2; and sterane/diasterane, Table 3 mass fingerprints, biomarker

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**Fig. 2** Geologic setting of southwestern Africa (modified after Hirsch et al. 2009). Illustration shows old cratons enclosing mobile belts that gradually grow during the Damara Orogeny.

**Fig. 3** a: Unimodal mass fragmentogram of m/z 85 representative samples showing isoprenoid and n-alkane distribution. Pr = Pristane and Ph = Phytane, while nC indicate carbon numbers. b: Cross-plots of Pristane/n- C17 against phytane/n- C18 showing organic matter. c: Cross-plots of Pristane/n- C17 against phytane/n- C18 showing organic matter source input, maturation of investigated Orange basin samples (Modified after Connan and Cassou 1980). d: Cross plots of CPI versus Pr/Ph illustrating marine setting (after Meyers and Snowdon 1993). e: Cross-plot of waxiness vs Pr/Ph showing preponderance of more anoxic OM.
imprints were adapted for molecular geochemical identification. Individual compounds were derived based on retention time and compared to previous work’s mass spectrum (Adebanji et al. 2014). The GCMS was performed at the Geology Department, University of Malaya. Peak heights from ion-chromatograms were integrated to calculate aromatic hydrocarbon ratios (Van Aarssen et al. 1999). Agilent ChemStation software was used to process the data collected. For m/z 85, 191, 217 (branched/cyclic) and m/z 178, 184, 192 aromatics, the mass spectrometer was chosen. The bulk stable carbon isotope ($^{13}$C/$^{12}$C) of the whole rock sample was determined using an isotopic mass spectrometry apparatus and the combustion method (Sofer 1980). According to the global standard, the outcome was a delta, represented by the Pee Dee Belemnite (PDB).

**Inorganic geochemical methods**

According to Pi et al. (2013), the whole rock samples were pulverized and digested to examine some major and trace elements.
Fig. 5  
(a): Saturated mass fragmentogram of steranes; m/z 217 for investigated Orange basin shaly samples. 
(b): Triangular plot correlating sterane composition with source input (after Huang and Meinschein 1979). 
(c): Triangular plot correlating sterane composition with environment of deposition (after Huang and Meinschein 1979). 
(d): Cross plot of $C_{27}/(C_{27} + C_{29})$ regular steranes against pristane/phytane ratios illustrating depositional environment settings and source input (Modified after Hossain et al. 2009). 
(e): Cross-plot of two biomarker parameters responsive to thermal maturation source rock samples illustrating early to peak oil maturity of some samples. Modified from Peters and Moldowan (1993).
On a finely crushed sample, an X-ray fluorescing spectrometer (XRF) investigation was carried out using a P-analytical Axios mAX 4 kW sequenced XRF spectrometer. An indestructible wavelength dispersive X-ray fluorescing spectrometer was used to determine major and trace oxides (WDXRF). 0.50 g of samples were placed in a Teflon beaker and dehydrated overnight at 105 °C to determine the concentration of minute traces and rare earth elements. The shales were dampened with milliliters of de-ionized aqueous solution; 5 ml HNO₃ was added and placed on a hotplate at 150 °C just before drying; 10 ml HF was added, followed by 4 ml HClO₄. The solution was heated to 200 °C using

Fig. 6 a (i): Aromatic mass fragmentogram of Phenanthrene (P; m/z 178), Methylphenanthrene (MP; m/z 192). a (ii): Aromatic mass fragmentogram of Phenanthrene (P; m/z 178), plus aromatic Dibenzothiophenes (DBT; m/z 184) for Orange basin samples. b: m/z 184 + 198 + 212 mass peaks for the Orange basin samples where 1 > 4 > 2 + 3 methyldibenzothiophene. c: Plot of 9MP/9MP + 1MP ratio versus aquatic macrophyte n-alkane proxy (Paq) of the examined shaly samples (Modified after Ficken et al. 2000)
a crystalline mush until it was nearly dry. The settled and cooled samples were digested in a fume hood with 10 ml of 5 M HNO₃. The solutions were diluted using de-ionized water in 50-ml volumetric flasks, and ultra-pure water was used to dilute the digested samples up to 100 times. 10 ppm analytic-concentration-standard element solutions were used for calibration, and the detection limit was set at less than one ppb. Trace elements were examined using the Agilent Technologies 7500S-ICP-MS.

Result and discussion

Molecular properties and organic matter as a source of input

Normal alkane containing pristane and phytanes

The fragmentogram of some of the samples studied, such as KD1-2250 and KH1-4232, contain low-to-moderate humps. Though, the n-alkanes extend further than C₃₁, the humpy
Table 1 n-Alkanes/isoprenoids and Aromatic hydrocarbon parameters for the Orange Basin sediments; The relative number of \( nC_{27}, nC_{29}, nC_{31} \) alkanes and their ratios

| Well depth (m) | Age          | Seismic units | \( Pr/Pr_{n-C_{17}} \) | \( Pr/n-C_{17} \) | Ph/n-C_{18} | WI | TAR | OEP | CPI | DBT/P | DMP | Paq | 9MP/9MP+1MP | MPI | Pwax |
|---------------|--------------|---------------|--------------------------|-------------------|-------------|-----|-----|-----|-----|-------|-----|-----|-------------|-----|-------|
| KE1-1250      | Campanian    | C5            | 0.11                     | 0.07              | 14           | 1.1 | 0.22| 0.68| 0.83| 0.25  | 5.60| 0.79| 0.54        | 0.77| 0.36  |
| KE1-1480      | Lower Campanian | C5             | 0.15                     | 0.1               | 16           | 1.03| 0.13| 0.67| 0.8  | 0.00  | 5.20| 0.87| 0.67        | 1.30| 0.26  |
| KD1-1650      | Coniacian    | C3            | 0.12                     | 0.11              | 8.67         | 0.88| 0.18| 0.65| 0.73| 0.20  | 5.20| 0.73| 0.94        | 0.86| 0.41  |
| KF1-1565      | Santonian    | C4            | 0.5                      | 0.33              | 20           | 8.46| 2.2 | 0.91| 0.98| 0.07  | 1.10| 0.81| 0.65        | 0.57| 0.32  |
| KD1-1900      | Coniacian    | C3            | 0.11                     | 0.08              | 11.43        | 0.44| 0.07| 0.44| 0.64 | 0.00  | 6.7  | 0.67| 0.00        | 0.67| 0.44  |
| KD1-2250      | Upper Turonian | C3            | 0.23                     | 0.33              | 5.75         | 0.78| 0.26| 0.73| 0.8  | 0.03  | 4.60| 0.81| 0.17        | 0.59| 0.34  |
| KE1-2970      | Upper Turonian | C3            | 0.44                     | 0.36              | 3.6           | 2.73| 1.04| 0.93| 1    | 0.07  | 6.7  | 0.67| 0.00        | 0.67| 0.48  |
| KE1-3110      | Upper Cenomanian | C2           | 0.58                     | 0.52              | 4.8          | 3.9  | 1.04| 0.75| 0.84 | 0.05  | 0.25| 0.79| 0.52        | 0.60| 0.37  |
| KE1-3340      | Upper Cenomanian | C2           | 0.25                     | 0.12              | 11           | 0.56| 0.08| 0.82| 0.96| 0.01  | 4.60| 0.88| 0.59        | 1.92| 0.22  |
| KH1-1250      | Campanian    | C5            | 0.84                     | 18.17             | 0.94         | 2.75| 1.27| 0.23| 1.01| 1.03  | 0.50| 0.84| 0.59        | 1.07| 0.29  |
| KE1-1480      | Lower Campanian | C5            | 0.91                     | 68.00             | 1.13         | 4.50| 2.25| 0.70| 1.00| 0.00  | 5.20| 0.87| 0.67        | 1.30| 0.26  |
| KD1-1650      | Coniacian    | C3            | 0.88                     | 16.29             | 1.30         | 2.60| 1.18| 2.14| 0.57| 0.05  | 4.60| 0.85| 0.51        | 0.73| 0.32  |
| KF1-1565      | Santonian    | C4            | 0.21                     | 0.75              | 1.30         | 3.71| 1.73| 2.75| 0.38| 50    | 0.86| 0.86| 0.31        | 0.56| 0.28  |
| KD1-1900      | Coniacian    | C3            | 0.96                     | 53.50             | 1.33         | 1.60| 1.33| 2.00| 0.50| 36.37 | 45.45| 18.18| 0.58        | 1.11|       |
| KD1-2250      | Upper Turonian | C3            | 0.84                     | 12.88             | 0.83         | 1.43| 0.71| 2.50| 0.63| 47.62 | 33.33| 19.05| 0.58        |       |       |
| KE1-2970      | Upper Turonian | C3            | 0.47                     | 2.39              | 1.09         | 1.47| 0.90| 2.75| 0.61| 45.56 | 37.87| 16.57| 1.02        | 0.68|       |
| KH1-3080      | Upper Cenomanian | C2           | 0.48                     | 3.86              | 1.09         | 2.67| 1.33| 4.14| 0.43| 53.7  | 33.33| 12.96| 0.60        | 0.80|       |
| KE1-3110      | Upper Cenomanian | C2           | 0.25                     | 2.00              | 1.56         | 4.55| 1.79| 6.00| 1.00| 61.54 | 28.21| 10.25| 0.68        | 0.56|       |
| KD1-3120      | Upper Albian  | C2            | 0.85                     | 19.33             | 1.14         | 1.81| 0.96| 3.33| 0.33| 50.25 | 34.67| 15.08| 0.59        | 0.87|       |
| KF1-3305      | Lower Cenomanian | C2           | 0.25                     | 2.00              | 1.70         | 5.10| 2.43| 6.00| 0.33| 58.06 | 32.26| 9.68  | 0.74        | 1.01|       |
| KE1-3340      | Upper Albian  | C2            | 0.88                     | 30.50             | 1.31         | 3.40| 1.62| 4.25| 0.25| 54.84 | 32.26| 12.9 | 0.60        | 0.79|       |
| KH1-3350      | Mid Cenomanian | C2            | 0.85                     | 20.00             | 2.15         | 5.38| 2.39| 3.50| 0.75| 53.85 | 30.77| 15.38| 0.88        | 0.90|       |
characteristics of some samples indicate low biodegradation (Volkman 1986). The fragmentograms show unimodal distributions of n-alkane and isoprenoids, additionally, low-to-intermediate-weight compounds predominate (n-C16-n-C26) (Fig. 3a), with high Ph peak illustrating reducing peaks as the number of n-alkane carbon atoms increases (Fig. 3a). In view of these characteristics, a marine carbonate source is more likely to contain algal-derived organic matter (Fig. 3b, d). Based on this data combined with Pr/n-C17 against Pr/Ph cross plot (Fig. 3b), oils are expected to generate and expel from marine carbonate source rock (Fig. 3d). Low-to-moderate-weight compounds with remarkable + n-C26 carbon atoms yield waxiness indexes ranging from 0.44 to 8.46 and values of the CPI range from 0.73 to 1.15 (Table 1). This evaluation is typical of marine shales with mixed algae that have terrestrial organic matter inputs (Fig. 3c, e). Comparison of Pr/n-C17 vs Ph/n-C18 in cross plots (Fig. 3c) show that algae-reducing environments predominate. These source rocks were genetically obtained via the same carbonate-rich lithofacies accumulated from a reducing to an oxidizing setting signifying primitive deposition of marine with mixed organic remains under reducing anoxic settings of the source rocks (Fig. 3b, d). Pr/Ph ratios range from 0.10 to 0.58, indicating a high aquatic contribution (Lijmbach 1975) accumulating under anoxia (Makeen et al. 2015). The ratio of Pristane to Phytanes is commonly used to depict paleoxy-genation settings (Escober et al. 2011), which is higher with greater thermal maturation (Connan and Cassou 1980) and more terrestrial remains. Similarly, as salinity increases, Pr/ Ph ratio falls (Peters et al. 2005). Lesser Pr/Ph (0.10–0.58), higher Ph/n-C18 (2.56–20), and moderate C.P.I. (0.64–1.15) under anoxic, saline water column with some terrestrial input is the source of rock on the western coast, according to the extracts (Fig. 3d, e; Peters et al. 2005; Bechtel et al. 2012). Comparison of Pr/n-C17 vs Ph/n-C18 in cross-plots (Fig. 3c) shows that algae-reducing environments predominate. These source rocks were derived genetically from the same carbonate-rich lithofacies that accumulated from a reducing to an oxidizing environment. Under the reducing anoxic settings of the source rocks, primitive deposition of marine with mixed organic remains occurred. Based on this data combined with Pr/n-C17 against Pr/Ph cross-plot (Fig. 3b), hydrocarbons are expected to generate and expel from marine carbonate source rock.

Terpanes

Tricyclic terpanes found in source rock samples were used to characterize the rocks, correlate oils and extracts, and determine thermal maturation (Zumberge 1987; Peters et al. 2005). The extent of anoxic in mixed sediments is defined by C22T vs C21T, C24T vs C23T, C25T vs C26T, and C24Tet/ C26T ratios (Table 2; Zumberge et al. 2005; El Diasty et al. 2010).
Table 2: m/z 191 Terpane hydrocarbon parameters for the Orange Basin sediments

| Well depth (m) | Age | Seismic units | C29/C30- A | C29NH/C30- B | C29Ts/C29H- C | T28/(T28 + T29)- D | C30/(C30 + M30)- E | C31S/(C31S + C31R)- F | C31R/C30- G | G/C30- H | M30/C30- I | DH30/C30- J | ol/C30H- K | Ts/Tm- L | Ts/(Ts + Tm)- M | ETR- N | 22S/(22S + 22R)C31H- O | C32S/(S + R)- P | C24Tet/C26T- Q | C23/C24T- R | C23/C24Tet- S | C19/C23- T | C22/C21- U | C21T/C23T- V | C24/C23- W | C25T/C26T- X | C26T/C25T- Y | C35/C34- Z |
|----------------|-----|---------------|-----------|-------------|--------------|---------------------|---------------------|---------------------|--------------|------|----------|----------|-------------|---------|-------|--------------------|------|------------------|----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| KE1-1250 Campanian | C5 | 0.17 | 0.70 | 0.36 | 0.85 | 0.32 | 0.24 | 0.17 | 0.14 | 0.13 | 0.34 |
| KE1-1480 Lower Campanian | C5 | 0.25 | 0.70 | 0.52 | 0.38 | 0.24 | 0.22 | 0.25 | 0.10 | 0.18 | 1.35 |
| KD1-1650 Coniacian | C3 | 0.08 | 0.49 | 0.39 | 0.33 | 0.35 | 0.21 | 0.09 | 0.14 | 0.07 | 0.10 |
| KD1-1900 Santonian | C3 | 0.26 | 1.01 | 0.55 | 0.64 | 0.75 | 0.47 | 0.18 | 0.19 | 0.23 | 0.82 |
| KE1-2290 Coniacian | C3 | 0.11 | 0.62 | 0.33 | 0.37 | 0.50 | 0.43 | 0.31 | 0.14 | 0.04 | 0.41 |
| KE1-2360 Upper Turonian | C2 | 0.17 | 0.72 | 0.29 | 0.45 | 0.82 | 0.79 | 0.32 | 0.13 | 0.26 | 0.26 |
| KE1-2800 Upper Cenomanian | C2 | 0.06 | 0.48 | 0.61 | 0.80 | 0.56 | 0.35 | 0.14 | 0.26 | 0.05 | 0.41 |
| KD1-3100 Lower Cenomanian | C2 | 0.33 | 0.62 | 0.61 | 0.49 | 0.80 | 0.61 | 0.31 | 0.29 | 0.13 | 0.28 |
| KD1-3510 Coniacian | C2 | 0.35 | 0.96 | 0.29 | 0.29 | 0.55 | 0.55 | 0.19 | 0.23 | 0.23 | 0.10 |
| KE1-3740 Upper Albian | C2 | 0.07 | 0.74 | 0.11 | 0.45 | 0.1 | 0.58 | 0.37 | 0.06 | 0.06 | 0.40 |
| KE1-4230 Upper Turonian | C2 | 0.21 | 0.79 | 0.13 | 0.49 | 0.88 | 0.56 | 0.11 | 0.14 | 0.08 | 0.10 |
| KE1-4440 Upper Aptian | C2 | 0.22 | 0.77 | 0.59 | 0.38 | 0.87 | 0.65 | 0.23 | 0.13 | 0.15 | 0.09 |

| Well depth (m) | Age | Seismic units | C24Tet/C26T- Q | C23/C24T- R | C23/C24Tet- S | C19/C23- T | C22/C21- U | C21T/C23T- V | C24/C23- W | C25T/C26T- X | C26T/C25T- Y | C35/C34- Z |
|----------------|-----|---------------|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| KE1-1250 Campanian | C5 | 0.08 | 0.67 | 0.67 | 0.52 | 0.44 | 1.09 | 0.60 | 0.25 | 2.50 | 0.82 | 0.82 |
| KE1-1480 Lower Campanian | C5 | 0.57 | 0.65 | 0.38 | 0.49 | 1.54 | 1.29 | 0.87 | 0.24 | 0.43 | 0.24 | 0.40 |
| KD1-1650 Coniacian | C3 | 0.48 | 0.22 | 0.55 | 0.59 | 0.25 | 1.75 | 1.36 | 0.83 | 0.40 | 0.34 | 0.30 |
| KD1-1900 Santonian | C3 | 0.40 | 0.77 | 0.47 | 0.52 | 0.67 | 1.15 | 1.50 | 0.80 | 0.14 | 0.14 | 0.15 |
| KE1-2290 Coniacian | C3 | 0.39 | 0.64 | 0.43 | 0.45 | 0.63 | 1.69 | 2.30 | 0.39 | 0.23 | 0.28 | 0.23 |
| KE1-2360 Upper Turonian | C2 | 0.24 | 0.55 | 0.48 | 0.45 | 1.22 | 2.53 | 2.41 | 0.04 | 0.41 | 0.41 | 0.40 |
| KE1-2800 Upper Cenomanian | C2 | 0.31 | 0.51 | 0.57 | 0.10 | 1.50 | 1.50 | 0.15 | 1.69 | 0.14 | 0.77 | 0.77 |
| KD1-3100 Lower Cenomanian | C2 | 0.29 | 0.71 | 0.53 | 0.59 | 1.00 | 1.90 | 0.00 | 0.83 | 0.50 | 0.60 | 0.64 |
| KD1-3510 Coniacian | C2 | 0.24 | 0.72 | 0.43 | 0.45 | 0.59 | 1.50 | 1.50 | 0.21 | 0.14 | 0.14 | 0.15 |
| KE1-3740 Upper Albian | C2 | 0.34 | 0.48 | 0.56 | 0.29 | 1.27 | 2.43 | 2.41 | 0.10 | 0.23 | 0.23 | 0.23 |
| KE1-4230 Upper Turonian | C2 | 0.49 | 0.60 | 0.58 | 0.53 | 1.69 | 2.18 | 0.00 | 0.90 | 0.32 | 0.40 | 0.73 |
Table 3  m/z 217 Sterane hydrocarbon parameters for the Orange Basin sediments

| Sample name | Age       | Unit | AA    | BB    | CC    | DD     | EE    | FF    | GG    | HH    | H     | J     | KK    | LL    | MM    |
|-------------|-----------|------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| KE1-1250    | Campanian | C5   | 15.22 | 21.01 | 63.77 | 0.72   | 0.28  | 0.12  | 0.34  | 0.24  | 0.19  | 0.09  | 0.96  | 0.75  | 4.19  |
| KE1-1480    | Lower Campanian | C5 | 24.21 | 23.16 | 52.63 | 0.68   | 0.32  | 0.15  | 0.34  | 0.46  | 0.32  | 0.32  | 0.91  | 0.69  | 2.17  |
| KD1-1650    | Coniacian | C3   | 32.32 | 24.25 | 43.43 | 0.61   | 0.39  | 0.31  | 0.34  | 0.74  | 0.43  | 0.40  | 0.86  | 0.64  | 1.34  |
| KF1-1565    | Santonian | C4   | 28.00 | 24.80 | 47.20 | 0.62   | 0.38  | 0.25  | 0.34  | 0.59  | 0.37  | 0.44  | 1.08  | 0.66  | 1.69  |
| KD1-1900    | Coniacian | C3   | 27.50 | 24.50 | 48.00 | 0.70   | 0.30  | 0.28  | 0.34  | 0.57  | 0.36  | 0.34  | 0.91  | 0.66  | 1.75  |
| KD1-2250    | Upper Turonian | C3  | 22.49 | 22.04 | 55.47 | 0.74   | 0.26  | 0.16  | 0.34  | 0.41  | 0.29  | 0.17  | 0.96  | 0.72  | 2.47  |
| KE1-2970    | Upper Turonian | C3 | 25.00 | 18.48 | 56.52 | 0.66   | 0.34  | 0.33  | 0.34  | 0.44  | 0.31  | 0.31  | 0.86  | 0.75  | 2.26  |
| KHI-3080    | Upper Cenomanian | C2 | 24.27 | 19.34 | 53.04 | 0.61   | 0.29  | 0.34  | 0.52  | 0.34  | 0.41  | 0.83  | 0.73  | 1.92  |
| KE1-3110    | Upper Cenomanian | C2 | 19.07 | 27.84 | 53.09 | 0.67   | 0.33  | 0.16  | 0.34  | 0.36  | 0.26  | 0.35  | 0.94  | 0.66  | 2.78  |
| KFI-3305    | Lower Cenomanian | C2 | 24.27 | 35.92 | 39.81 | 0.49   | 0.51  | 0.27  | 0.34  | 0.61  | 0.38  | 0.68  | 0.79  | 0.53  | 1.64  |
| KHI-3350    | Mid Cenomanian | C2 | 28.12 | 36.46 | 35.42 | 0.52   | 0.48  | 0.37  | 0.34  | 0.79  | 0.44  | 0.54  | 0.62  | 0.49  | 1.26  |
| KHI-3510    | Mid Cenomanian | C2 | 44.00 | 34.00 | 22.00 | 0.41   | 0.59  | 0.51  | 0.34  | 2.00  | 0.67  | 1.18  | 0.42  | 0.39  | 0.50  |
| KD1-3120    | Upper Albian | C2 | 26.65 | 23.41 | 49.94 | 0.74   | 0.26  | 0.28  | 0.34  | 0.53  | 0.35  | 0.28  | 0.94  | 0.68  | 1.87  |
| KEI-3340    | Upper Albian | C2 | 29.17 | 19.72 | 51.11 | 0.69   | 0.31  | 0.34  | 0.34  | 0.57  | 0.36  | 0.42  | 0.93  | 0.72  | 1.75  |
| KHI-4232    | Upper Albian | C2 | 31.34 | 26.87 | 41.79 | 0.57   | 0.43  | 0.32  | 0.48  | 0.75  | 0.43  | 0.52  | 0.84  | 0.61  | 1.33  |
| KEI-4105    | Upper Aptian   | C2 | 33.56 | 22.82 | 43.62 | 0.54   | 0.46  | 0.39  | 0.47  | 0.77  | 0.43  | 0.68  | 0.61  | 0.66  | 1.30  |

R27%- AA; R28%- BB; R29%- CC; 29∞∞∞S/(29∞∞∞S + 29∞∞∞R)- DD; 29∞∞∞S/(29∞∞∞S + 29∞∞∞R)- EE; 29∞∞∞S/(20S + 20R)- FF; 29∞∞∞S/(29∞∞∞S + 29∞∞∞R)- GG; R27/R29- HH; R27/(R27 + R29)- II; C29 diaS/R29- JJ; Sterane/hopane-KK; C29/(C28 + C29)- LL; R29/R27- MM; C29 diaS/R29- JJ
Similarly, increasing marine source input are featured by cross-plots, as shown in Fig. 4b, c. Hopanoids (Fig. 4a) were made up of C_{29} norhopane, C_{30} hopane, some C_{31}–C_{35} homohopananes, Gic/C_{30}, and Tm. In all samples, C_{30} hopane predominates over C_{29} norhopane, as shown in Fig. 4a and Table 2, except for KH1-1565, which has a C_{29} norhopane/C_{30} hopane ratio of 1.01. This single sample was taken from an organic-rich carbonate evaporite rock (Zumberge 1984; Connan et al. 1986; Peters et al. 2005). C_{30}H has a higher proportion than C_{29}NH (C_{29}-norhopane/C_{30}H ratio of less than 1) characterizing abundant clay materials in the rocks (Gurgey 1999), as confirmed by C_{29} diasterane/R_{29} with 87 percent of analyzed samples greater than 0.2, indicating a suboxic deposition condition (Makeen et al. 2015; Moldovan et al. 1994; Peters et al. 2005). Thus, extracts have moderate-to-high amounts of pentacyclic and tricyclic terpane with less tetracyclic as determined by C_{24}Tet/ C_{26}T ranging between 0.67 and 2.27; C_{23}T/C_{24}T ranging between 1.24 and 2.50, indicating reasonable terrestrial matter contributions (Fig. 4b). The high preponderance of C_{23}T over C_{24}T (C_{23}T/C_{24}T) 1.15–2.50 confirms microbial action within the examined samples, indicating a dysoxic environment. Furthermore, tricyclic terpane ratios based on the number of carbon atoms have been identified as a means of better understanding source input (Peters et al. 2005). The existence of average to high C_{24}T/C_{23}T values ranging from 0.40 to 0.87 indicates the presence of both marine and terrestrial matter (Marynowski et al. 2000). C_{21}/C_{23}T less than 0.5 indicates that the rock came from the sea (Quihua et al. 2011). The C_{27}T/C_{29}T ratio in the examined samples ranges from 0.10 to 0.50, with only one sample having 1.86 (KD1-2245). The source rocks were formed in a marine anoxic environment with terrestrial input (Fig. 4b). The ratio of C_{26}T to C_{25}T was modified to distinguish between bacterial and terrestrial plant matter (Volk et al. 2005). Low-to-medium C_{24}T/C_{23}T values range from 0.57 to 1.67 in this shaly sediment, with 87 percent greater than 0.9 signifying a mixture of algal and bacterial organic materials making up slightly terrestrial input (Volk et al. 2005). A high C_{26}T versus C_{25}T ratio, a low–medium C_{24}T/C_{23}T ratio, and a low-to-medium C_{27}T/C_{25}T ratio indicate lacustrine mix prilmal matter (Aquino et al. 1989; Krufe et al. 1990; Peters et al. 2005; Volk et al. 2005; Makeen et al. 2015). Some carbon isotope results support this as well (Fig. 13). The C_{31}-22R/C_{30}H ratio is primarily high, exceeding 0.25 in the marine environment and falling below 0.25 in the lacustrine environment of deposition (Peters et al. 2005). C_{11}-22R/ C_{30}H for investigated shales is between 0.21 and 0.46, with carbonate and shaly marine source input accounting for 80% of examined samples and lacustrine influence accounting for 20% (Fig. 4c; Peters et al. 2005).

Furthermore, aromatic fractions show low levels of aromatic compounds in some samples, indicating that the source rock depositional environment is marine (Radke et al. 2000). Lower DBT/P ratios indicate the incorporation of reducing primal sulfate matter (Hughes et al. 1995). Less DBT vs. P (Table 1) suggests algae with a minor terrestrial organic input. Gammacerane is present in all the shales studied, though in trace amounts in some (Table 2). It is made by reducing tetrahymanol (Venkatesan 1989). Tetrahymanol is produced by bacterivorous ciliates that live in the intervening oxic and anoxic realms of a high saline aqua layer separated by a less saline upper stratified aqua column (Ten Haven et al. 1988). Gammacerane is primarily used to calculate salinity in stratified water columns and is thought to be a marker of anoxic photic zones (Adebani et al. 2015). The investigated G_{30} vs C_{30} ratio is between 0.05 and 0.24 (Table 2), indicating the presence of saline in the stratified aqueous column via the sedimentation of lower and upper post-rift deposits in the Orange Basin. Furthermore, G_{30}/C_{30} indicates that the paleoxygenation condition of sediment accumulation was decreasing, as supported by Pr/Ph values of less than 0.8, even though the source rocks have freshwater lacustrine influences (Fig. 4c).

Steranes

Relative sterane richness is a significant quality shift in OM’s biological origin that distinguishes source distinctness while distributing cholesterol from organisms (Fig. 5b, c). C_{29} sterane is abundant in terrestrial land plants, whereas animals and aquatic plants are primarily composed of sterols of C_{27} molecular weight, followed by C_{28} sterols. Sterane C_{27} is primarily found in algae, while Sterane C_{29} is found in higher terrestrial plants. Limnic conditions are characterized by low C_{28} sterol concentrations (Volkman 1986). Similarly, micro-algae and cyanobacteria are good sources of C_{29} sterols. The analyzed shales contain more C_{29} sterols (22.00–63.77 percent) than C_{27} (15.22–44.00 percent) and C_{28} (18.48–36.46 percent) steranes, implying abundant terrestrial input as opposed to planktonic bacterial to algae organic matter, as shown by the regular steranes triangular plot (Fig. 5b). In other words, except for KH1-3510, which is “L” type, the regular sterane is an anti-“L” type that is predominantly found in land plants (C_{27}/C_{29} < 1). It should be noted that the dominance of C_{29} in planktonic land plant input is relatively much higher in KE1-1250 (63.77 percent) and in KH1-3510 (22 percent). A tri-plot of the C_{27}, C_{28}, and C_{29} distributions indicates the type of primal matter as mixed marine–terrigenous source inputs (Fig. 5b, c). The relatively low sterane vs hopane ratio (Table 3) distinguishes terrestrial or microbial rework matters (Tissot and Welte 1984). Steroids and hopanoid constituents differ between organisms; differences in sterane versus hopane allow only a qualitative evaluation of eukaryotes and prokaryotes’ source
inputs (Peters et al. 2005; Seifert and Moldowan 1978). Pr/Ph and C_{29}/(C_{27} + C_{29}) R values range from 0.10–0.58 to 0.19–0.67, respectively, indicating that anoxic primate matter predominates in terrestrial/coastal anoxic environments (Fig. 5d). Furthermore, most samples have a highly anoxic paleoxygenation condition, with Pr/Ph values less than or equal to 0.58 (Table 1).

According to Phenanthrenes, the source input index also provides information on the origin of marine organic matter (Fig. 6a). The Paq index supports this claim, which is defined as the absolute input of aquatic macrophytes as well as higher terrigenous remains (Ficken et al. 2000). Paq values less than 0.1 indicate unmixed terrigenous matter, while Paq values between 0.1 and 0.4 indicate abundant emergent plant contribution, and Paq values between 0.4 and 1 indicate abundant contributions of emergent macrophytes and submerged plant remains under anoxic conditions (Fig. 6c). There is a high concentration of marine inputs as indicated by Paq from 0.7 to 0.94 (Table 1). Furthermore, a measure of methyl dibenzo thiophene isomers (MDBT) in the Orange basin source rocks varies as follows: 1 ˃ 4 ˃ 2 + 3 methyl dibenzo thiophene (Fig. 6b) synonymous to carbonate to shaly organofacies (Hughes et al. 1995). In addition, the peak distribution of methylphenanthrenes (9 1 2 3; Fig. 6a (i)) and the predominance of 9-methylphenanthrene (9MP) over its isomers suggests that organofacies originated from marine input (Budzinski et al. 1995; Escobar et al. 2011). Most samples contain dimethylphenanthrenes and dibenzo thiophene dimethylated duplicates. Based on aromatic biomarker analyses, the studied source rocks were accumulated in reduced anoxic carbonate settings. In conclusion, biomarker analysis reveals that the well “K” sediments studied are genetically derived from the coastal marine environment as Pr vs Ph values ranging from 0.10 to 0.58 support this, indicating marine anoxic conditions (Fig. 3b; Taohua et al. 2018). These source rocks contain a significant number of algae and microbial marine primate matter, as well as some mixed organic remains deposited in a more reducing environment (Fig. 3c).

Maturation of organic matter

This expands on the extent to which OM is intensely heated and transformed into petroleum. The molecular specification for the ratio and distribution of biomarkers has been modified to investigate the degree of thermal maturation (Gogoi et al. 2021). To investigate the thermal maturation of the shaly sediments, a few molecular maturation determinants, such as the C_{29}ββ/(ββ + αα) ratio, the C_{32}22S/(22S + 22R) ratio, and the M_{30}/H_{30} plus methylphenanthrene indices (MPI), were adapted (Table 1).

The sterane isomerization model is widely accepted as an OM maturity guide (Seifert and Moldowan 1978; Xujiuan et al. 2016). C_{29} αααR/ (αββR + 29αααR) ratios in examined shales range from 0.41 to 0.74 (Table 3), a ratio of C_{29}αααS/(20S + 20R) varies from 0.10 to 0.51. C_{32} 22S/(22S + 22R) hopane ratios (0.44–0.82) demonstrated that an equilibrium had been reached and that the shales were mature for hydrocarbon generation (Seifert and Moldowan 1986). With increasing thermal maturation, these fractions increase (Adekola et al. 2012). In the source rocks, the maximum C_{29}αααS/(20S + 20R) values are 0.51 or less. These values propose that some of the examined shales are thermally mature to generate hydrocarbons, while others are immature (Fig. 5e). The mortane versus hopane (M_{30}/H_{30}) reduces with rising thermic maturation between 0.8 for the immature extract and 0.15–0.05 matured sediments (Mackenzie et al. 1980; Peters et al. 2005). M_{30}/H_{30} examined is from 0.14 to 1.00. KD1-1900 is immature, with an M_{30}/H_{30} ratio of no more than 1.00.

C_{29}diasterane versus regular steranes were also suitable for detecting OM thermal maturity. Diasteranes are formed by the transformation of sterols, and diagenesis, as well as catagenesis, making them more balanced than steranes at higher maturation (Peters and Moldowan 1993; Peters et al. 2005). C_{29}diasterane/29αααR ranges from 0.09 to 1.18, indicating that most shales are mature enough for hydrocarbon generation. Other biomarker maturity parameters are Ts vs (Ts + Tm), C_{32}22S/(22S + 22R), M_{30}/H_{30}, the 20S/(20S + 20R), and C_{29}ββ/(ββ + αα) (Mackenzie et al. 1980; Waples & Machihara 1991). Source input and thermal maturity of OM are represented by these ratios. This is based on OM source input and maturity in the case of T_{s} vs (T_{s} + T_{m}) and T_{s} vs T_{m} (Peters and Moldowan 1993). T_{m} is unstable during the catagenesis of hydrocarbon generations; as a result, T_{s} versus T_{m} increases with maturity (Seifert and Moldowan 1978). In the analyzed shales, the T_{s}/ (T_{s} + T_{m}) is from 0.09 to 0.57 (immature to early maturity).

The Ph/n-C_{18} and Pr/n-C_{17} are homogeneous reflecting similar interpretations as for low-to-high thermal maturity (Fig. 3c). In comparison with other biomarker maturity parameters (Fig. 5e) and vitrinite reflectance measurements, the methylphenanthrenes index (Table 1; Radke and Welte 1983; Radke et al. 1982) yielded computed reflectance of vitrinite (VRc percent) ranging from 0.58 to 1.39. (Table 1). Despite inconsistencies in somethermal maturity parameters, the general trend in sample maturity is that, it increases with depth across each respective well. This disparity in maturation is attributed to the Orange basin’s intricate infilling evolution and mixing.

Elemental concentrations and distributions

The genesis, conservation, accumulation, and paleoenvironmental setting of organic materials are significantly influenced by their bulk inorganic composition (Mohialdeen and Raza 2013; Shu et al. 2013; Jia et al. 2013; Moosavirad et al. 2011). Tables 4 and 5 summarize the
| Sample depth | Age Unit | SiO2 | Al2O3 | Fe2O3 | CaO | MgO | MnO | K2O | Na2O | SO3 | ZrO2 | TiO2 | Rb2O | SrO | BaO | P2O5 | CuO |
|--------------|----------|------|-------|-------|-----|-----|-----|-----|-----|-----|------|------|------|-----|-----|------|-----|
| KFI 820      | Lower Campanian | 51.014 | 12.328 | 11.536 | 8.947 | 3.702 | 0.181 | 1.877 | 3.669 | 1.846 | 0.042 | 1.233 | 0.035 | 0.052 | 0.432 | 0.211 | 0.019 |
| K-EI 1250    | Campanian | 56.558 | 14.35 | 11.55 | 4.378 | 3.673 | 1.45 | 1.877 | 2.757 | 1.206 | 0.044 | 1.246 | 0.04 | 0.069 | 0.618 | 0.349 | 0.027 |
| K-D1 1250    | Santonian | 53.734 | 13.536 | 11.422 | 7.816 | 3.816 | 1.45 | 1.365 | 2.381 | 1.123 | 0.052 | 1.256 | 0.021 | 0.088 | 0.618 | 0.349 | 0.027 |
| K-DI 1385    | Lower Campanian | 54.737 | 14.61 | 13.355 | 2.573 | 3.367 | 0.145 | 1.84 | 3.861 | 0.681 | 0.045 | 1.268 | 0.032 | 0.067 | 0.618 | 0.349 | 0.027 |
| K-HI-1500    | Coniacian | 57.314 | 14.436 | 10.502 | 3.702 | 2.816 | 0.077 | 2.28 | 2.309 | 1.182 | 0.056 | 1.304 | 0.05 | 0.088 | 0.618 | 0.349 | 0.027 |
| K-E1 1480    | Lower Campanian | 52.656 | 13.332 | 11.28 | 11.81 | 3.151 | 0.141 | 1.84 | 2.043 | 1.839 | 0.041 | 1.176 | 0.032 | 0.051 | 0.044 | 0.209 | 0.028 |
| K-D1 1650    | Coniacian | 54.575 | 14.766 | 10.865 | 8.956 | 2.28 | 0.118 | 2.217 | 1.613 | 2.347 | 0.048 | 1.112 | 0.051 | 0.049 | 0.073 | 0.378 | - |
| K-FI 1565    | Santonian | 55.703 | 14.384 | 10.865 | 5.123 | 3.119 | 0.099 | 2.162 | 2.381 | 1.346 | 0.046 | 1.27 | 0.024 | 0.043 | 0.057 | 0.191 | 0.013 |
| K-DI 1900    | Coniacian | 58.979 | 17.243 | 9.603 | 2.528 | 2.222 | 0.051 | 2.674 | 1.738 | 0.681 | 0.049 | 1.167 | 0.032 | 0.056 | 0.191 | 0.013 |
| K-DI-2250    | Upper Turonian | 60.26 | 17.473 | 9.172 | 2.016 | 2.043 | 0.08 | 2.309 | 2.564 | 1.375 | 0.05 | 1.116 | 0.057 | 0.073 | 0.191 | 0.013 |
| K-EI 2970    | Upper Turonian | 63.305 | 16.078 | 7.744 | 2.687 | 1.927 | 0.126 | 2.391 | 1.888 | 1.346 | 0.046 | 1.256 | 0.032 | 0.056 | 0.191 | 0.013 |
| K-HI 3080    | Upper Cenomanian | 58.481 | 16.826 | 9.741 | 1.846 | 2.238 | 0.064 | 2.672 | 2.098 | 2.401 | 0.046 | 1.107 | 0.074 | 0.024 | 0.435 | 0.17 | 0.028 |
| K-HI 3350    | Upper Cenomanian | 62.19 | 15.343 | 7.971 | 4.916 | 1.969 | 0.083 | 2.28 | 2.381 | 1.346 | 0.046 | 1.27 | 0.024 | 0.043 | 0.057 | 0.191 | 0.013 |
| K-E1 3340    | Upper Albian | 59.511 | 16.756 | 10.56 | 2.07 | 2.173 | 0.083 | 2.391 | 1.888 | 2.33 | 0.043 | 1.167 | 0.032 | 0.056 | 0.191 | 0.013 |
| K-HI-4232   | Upper Albian | 60.712 | 16.902 | 9.14 | 1.286 | 2.032 | 0.054 | 2.391 | 1.888 | 1.228 | 0.047 | 1.256 | 0.032 | 0.056 | 0.191 | 0.013 |
| K-E1-4105   | Upper Aptian | 61.445 | 16.532 | 9.689 | 2.279 | 2.222 | 0.054 | 2.391 | 1.888 | 2.33 | 0.043 | 1.167 | 0.032 | 0.056 | 0.191 | 0.013 |
| K-HI-4232   | Upper Albian | 60.712 | 16.902 | 9.14 | 1.286 | 2.032 | 0.054 | 2.391 | 1.888 | 1.228 | 0.047 | 1.256 | 0.032 | 0.056 | 0.191 | 0.013 |

| Sample depth | Age Unit | Al/Si | Ti/Al | Al/K | Sr/Ba | Sr/Cu | Fe/Al | Al/Ti | K2O/Al2O3 | K2O/Na2O | Si/Al | Rb/Sr | C-values | ICV | CIA |
|--------------|----------|-------|-------|------|-------|-------|-------|-------|------------|-----------|-------|-------|-----------|-----|-----|
| KFI 820      | Lower Campanian | 0.242 | 0.242 | 6.568 | 0.120 | 2.737 | 0.936 | 9.998 | 0.152 | 0.512 | 4.138 | 0.673 | 0.603 | 2.564 | 45.964 |
| K-EI 1250    | Campanian | 0.254 | 0.254 | 6.568 | 0.120 | 2.737 | 0.936 | 9.998 | 0.152 | 0.512 | 4.138 | 0.673 | 0.603 | 2.564 | 45.964 |
| K-D1 1385    | Lower Campanian | 0.267 | 0.267 | 6.568 | 0.120 | 2.737 | 0.936 | 9.998 | 0.152 | 0.512 | 4.138 | 0.673 | 0.603 | 2.564 | 45.964 |
| K-HI-1500    | Coniacian | 0.269 | 0.269 | 6.568 | 0.120 | 2.737 | 0.936 | 9.998 | 0.152 | 0.512 | 4.138 | 0.673 | 0.603 | 2.564 | 45.964 |
inorganic geochemical outcome within the examined shales, which includes major and trace oxides with applicable geochemical ratios.

### Major/trace element

Major elements are commonly found in greater than 1% of major ores. These oxides were investigated using ICP-MS and XRF equipment (Roy and Roser 2013; Peters et al. 2005). SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, MgO, K$_2$O, Na$_2$O, SO$_3$, TiO$_2$ have average compositions of 58.20 percent, 15.65 percent, 10.10 percent, 3.92 percent, 2.50 percent, 2.44 percent, 2.33 percent, 1.83 percent, and 1.04 percent, respectively. Less than 1 percent is the average concentration of other major oxides, such as Rb$_2$O, Zr$_2$O, Sr$_2$O$_5$, P$_2$O$_5$, BaO, CuO, and MnO. The major oxide have high SiO$_2$ and Al$_2$O$_3$, indicating a quartz and clay mineral predominance, as expected in siliciclastic deposits. Al/Si ratios ranging from 0.242 to 0.293 are extremely low, with an average of 0.269, implying that Si comes from sources other than clay minerals (Fu et al. 2011). High SiO$_2$ and Al$_2$O$_3$ elements demonstrate detrital matter source input (Ross and Bustin 2009), which is supported by titanium (Ti) oxide at a level of about 1.04 (Table 4) because Ti coexists within terrestrial remains as well as coarse-grained matter influenced under higher energy conditions (Ross and Bustin 2009; Calvert et al. 1996). In the studied shales, iron oxide Fe$_2$O$_3$ is the third most prevalent element (averaging 10.10wt%), and it is usually found in association with Fe sulfides (pyrites and marcasite). Its abundance was detected under petrographic observation as pyrite. The major oxide bivariate scatter plots by Herron (1988) are shown in Fig. 9c; this geochemically classified the investigated Orange Basin samples as shales as demonstrated by the various well lithologic descriptions. The average CaO concentration of 3.92 indicates a calcium-rich environment of deposition (marine setting) toward the depocenter of the Orange basin. Phosphorus, another type of major oxide, was also discovered within the block K, Cretaceous shales (Table 4). The observed shales have a moderate phosphorus amount ranging from 0.127 to 0.378, implying a source of organic matter that is mixed and a reducing sedimentation environment (Shu et al. 2013). Paleoxygenation conditions as determined by biomarker distribution also support this (Table 1). Phosphorus (P) detection in sediments indicates some level of nutrient derivation for biological production (algal growth) under reducing conditions that favor organic matter conservation (Van Cappellen and Ingall 1994; Ingall and Jahnke 1994).

### Table 4 (continued)

| Sample        | Age Unit   | Al/Si | Ti/Al | AIr | Sr/Ba | Sr/Cu | Fe/Al | Al/Ti | K$_2$O/Al$_2$O$_3$ | K$_2$O/Na$_2$O | Si/Al | Rb/Sr | C-values | ICV | CIA   |
|---------------|------------|-------|-------|-----|-------|-------|-------|-------|---------------------|----------------|-------|-------|----------|-----|-------|
| K-HI 3080     | Upper Cenomanian | 0.288 | 0.061 | 6.297 | 0.055 | 0.857 | 16.400 | 0.159 | 3.476                | 3.083          | 71.777 |
| KEI 3110      | Upper Cenomanian | 0.247 | 0.058 | 6.539 | 0.057 | 0.944 | 16.724 | 0.151 | 1.274                | 3.083          | 71.456 |
| KFI-3305      | Lower Cenomanian | 0.293 | 0.057 | 6.815 | 0.063 | 1.094 | 17.124 | 0.151 | 1.278                | 3.411          | 70.075 |
| K-HI 3350     | Mid Cenomanian  | 0.266 | 0.051 | 5.238 | 0.034 | 0.657 | 16.095 | 0.147 | 3.671                | 3.057          | 70.956 |
| K-HI 3510     | Mid Cenomanian  | 0.247 | 0.049 | 6.020 | 0.032 | 0.532 | 16.311 | 0.166 | 0.790                | 3.498          | 66.771 |
| KDI 3120      | Upper Albian    | 0.286 | 0.050 | 6.073 | 0.034 | 0.450 | 19.816 | 0.165 | 1.788                | 3.706          | 74.110 |
| K-EI 3340     | Upper Albian    | 0.278 | 0.055 | 5.597 | 0.245 | 0.541 | 18.948 | 0.191 | 1.453                | 3.592          | 71.500 |
| KHI-4232      | Upper Albian    | 0.269 | 0.050 | 5.853 | 0.062 | 0.541 | 18.686 | 0.171 | 1.960                | 3.717          | 70.956 |
| K-EI-4105     | Upper Aptian    | 0.269 | 0.057 | 6.049 | 0.373 | 1.631 | 15.641 | 0.155 | 1.140                | 3.735          | 64.724 |

### Total

| Sample        | Age Unit   | Al/Si | Ti/Al | AIr | Sr/Ba | Sr/Cu | Fe/Al | Al/Ti | K$_2$O/Al$_2$O$_3$ | K$_2$O/Na$_2$O | Si/Al | Rb/Sr | C-values | ICV | CIA   |
|---------------|------------|-------|-------|-----|-------|-------|-------|-------|---------------------|----------------|-------|-------|----------|-----|-------|
| Total         |            | 5.374 | 1.346 | 6.490 | 0.373 | 1.631 | 15.641 | 0.155 | 1.140                | 3.735          | 64.724 |
Table 5  Trace elements composition of the shales of the Orange Basin (ppb)

| Sample depth | Age    | Unit  | Be   | V    | Cr   | Mn   | Co   | Ni   | Cu   | Zn   | As   | Se   | Mo   | Cd   | Hg   | Pb   | Ni/Co | V/Ni | Mo/Ni | V/(V + Ni) | Co/Ni |
|--------------|--------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|-------|------|-------|-------------|-------|
| KFI 820      | Lower Campanian | C5    | 75.090 | 68.070 | 73.990 | 73.980 | 75.050 | 73.650 | 40.620 | 36.690 | 86.290 | 76.590 | 73.860 | 87.280 | 73.100 | 0.981  | 0.924 | 1.040 | 0.480       | 1.019 |
| K-EI 1250    | Campanian    | C5    | 4.620  | 248.100 | 96.450 | 1952.000 | 60.180 | 107.000 | 123.400 | 433.700 | 17.590 | 24.140 | 12.120 | 0.580  | 1.990  | 1525.000 | 2.319 | 0.113 | 0.699 | 0.557       |
| K-D1 1570    | Santonian    | C4    | 5.990  | 150.800 | 1282.000 | 2230.000 | 60.180 | 112.700 | 146.700 | 206.300 | 18.470 | 14.630 | 7.490  | 0.520  | 30.440 | 7046.000 | 1.338 | 0.066 | 0.572 | 0.354       |
| KFI 1385     | Lower Campanian | C5    | 5.990  | 150.800 | 1282.000 | 2230.000 | 60.180 | 112.700 | 146.700 | 206.300 | 18.470 | 14.630 | 7.490  | 0.520  | 30.440 | 7046.000 | 1.338 | 0.066 | 0.572 | 0.354       |
| KHI-1500     | Coniacian    | C3    | 29.220 | 27.680 | 28.900 | 38.230 | 30.520 | 35.400 | 36.510 | 23.390 | 35.980 | 29.510 | 30.020 | 83.060 | 45.900 | 1.160  | 0.782 | 0.439 | 0.862       |
| K-DI 1650    | Coniacian    | C5    | 0.850  | 3.600  | 6.500  | 1.210 | −0.140 | −0.210 | 0.350  | −13.820 | −14.300 | −22.620 | −0.670 | −0.170 | 1.500  | −17.143 | 3.190  | 1.062 | 0.667 |
| K-KI 2970    | Upper Turonian | C3    | 5.460  | 251.400 | 368.600 | 4873.000 | 116.900 | 196.300 | 252.100 | 110.400 | 269.300 | 1.281  | 0.049  | 0.730  | 0.424  | 0.919  |
| K-HI 3080    | Upper Cenomanian | C2    | 5.960  | 409.700 | 242.900 | 1439.000 | 86.920 | 151.500 | 183.500 | 93.230  | 23.060  | 2.066  | 1.376  | 0.037  | 0.714  | 0.549  |
| K-HI 3350    | Mid Cenomanian | C2    | 6.180  | 194.100 | 271.100 | 1347.000 | 71.920 | 148.600 | 138.900 | 152.700 | 20.830  | 16.280 | 12.120 | 0.600  | 24.400  | 0.798  |
| K-E1 3510    | Mid Cenomanian | C2    | 5.990  | 204.500 | 271.100 | 1347.000 | 71.920 | 148.600 | 138.900 | 152.700 | 20.830  | 16.280 | 12.120 | 0.600  | 24.400  | 0.798  |
| KFI-3305     | Lower Cenomanian | C2    | 5.990  | 204.500 | 271.100 | 1347.000 | 71.920 | 148.600 | 138.900 | 152.700 | 20.830  | 16.280 | 12.120 | 0.600  | 24.400  | 0.798  |
| K-HI 3510    | Mid Cenomanian | C2    | 6.180  | 194.100 | 271.100 | 1347.000 | 71.920 | 148.600 | 138.900 | 152.700 | 20.830  | 16.280 | 12.120 | 0.600  | 24.400  | 0.798  |
| K-DI 3120    | Upper Albian | C2    | 5.970  | 5.050  | 90.370 | 3988.000 | 111.700 | 191.200 | 233.900 | 150.700 | −10.740 | −0.040 | 0.026  | 0.000  | 0.026  |
| K-E1 3340    | Upper Albian | C2    | 5.400  | 769.900 | 324.900 | 4882.000 | 124.800 | 204.300 | 254.800 | 114.500 | 36.330  | 28.260 | 19.890 | 0.570  | 67.490  | 3.768  |
| K-HI 4232    | Upper Albian | C2    | 6.460  | 301.600 | 234.700 | 2789.000 | 71.180 | 166.500 | 179.000 | 115.700 | 32.640  | 27.450 | 26.650 | 0.460  | 46.620  | 0.811  |
| K-E1 4105    | Upper Aptian | C2    | 5.970  | 5.050  | 90.370 | 3988.000 | 111.700 | 191.200 | 233.900 | 150.700 | −10.740 | −0.040 | 0.026  | 0.000  | 0.026  |
| Total Average |       |       | 341.420 | 4428.480 | 4444.450 | 41,494.640 | 1465.460 | 2470.600 | 2812.260 | 2373.580 | 456.040 | 712.350 | 482.970 | 272.820 | 708.820 | 16,604.420 | 17.071 | 221.424 | 222.223 | 2074.732 | 73.273 | 123.530 | 140.613 | 118.679 | 22.802 | 35.618 | 24.149 | 13.641 | 35.441 | 830.221 |
as well as paleoclimates and tectonic restructuring are determined using major and trace elements (Makeen et al. 2015a; Mohialdeen and Raza 2013; Shu et al. 2013; Jia et al. 2013; Moosavirad et al. 2011; Tribovillard et al. 2005). Cretaceous sediments from the Orange Basin were analyzed using ICP-MS to determine the trace element composition of some post-rift rocks. There are 113,169.94 parts per billion of iron (Fe), followed by aluminum (30,008 ppb), manganese Mn (2,074.73 ppb), and lead (Pb) (830.22 ppb). Among the trace elements found in OM (biophile), the most abundant is chromium Cr, with a concentration of 222.22 parts per billion (ppb) followed by vanadium (221.42 ppb), then nickel (123.53 ppb), cobalt (73.27 ppb), and molybdenum (24.15 ppb) are the least. It is common to analyze source rocks for Ni and V to determine their depositional conditions, oil sources, migration pathways, hydrocarbon maturity, and crude oil classification (Akinlua et al. 2007a, 2007b; Frankenberger et al. 1994; Lewan 1984; Barwise 1990). They are metalloporphyrin complexes that are biophilic in nature incorporated into organic matter or formed during sedimentation (Akinlua et al. 2007a, 2007b; Akinlua et al. 2015). When it comes to identifying oil families, Ni and V are excellent choices (Akinlua et al. 2015; Frankenberger et al. 1994). V/Ni concentrations are similar in all examined shales, and they are genetically related, as shown in Fig. 7a. Vanadium concentrations are lower in KF1-820, KD1-2250, KE1-4105, KH1-1500, and KD1-3120 due to migration. Our findings confirmed that all samples came from the same rock which also affirmed (Akinlua et al. 2018; Fig. 7a).

**Paleoenvironmental setting during OM sedimentation**

Inorganic geochemical parameters can be used to track physiochemical changes as they occur during sedimentation. Several paleoxygenation sensitive elements, such as V, Ni, Cu, Cr, Mo, and Mn, have been found to be good indicators of paleoredox settings (Adebaji et al. 2014; Mc Manus et al. 1999).

**Vanadium (V) vs Nickel (Ni) ratio** The ratios of redox-sensitive elements like V and Ni reveal information about anoxia and deposited matter (Pi et al. 2013; Adebaji et al. 2014). Mostly, sediments contain a comparable amount of these biophile (Lewan 1984). The primary determinants of paleoxygenation conditions during deposition are V and Ni (Galarraga et al. 2008; Bechtel et al. 2001). In this manner, V versus Ni, V versus Cr, and Ni versus Co (Table 5) are sensory indicators of paleoredox settings that differentiate oxic, dysoxic, and anoxic deposits (Galarraga et al. 2008; Akinlua et al. 2017; Hakimi et al. 2015). In a marine environment that ranges from suboxic to anoxic, the amount of vanadium (V) is greater than the amount of nickel (Ni) (Barwise 1990). Vanadium concentrations that are on average higher than nickel concentrations indicate a preponderance of alternating suboxic to anoxic conditions in the area under investigation (Fig. 7b).

Higher V vs Ni ratios indicate marine OM input, while lower V versus Ni ratios indicate terrestrial matters (Akinlua et al. 2018; Galarraga et al. 2008; Akinlua et al. 2007a; Lewan 1984). A greater than one V versus Ni ratio indicates a declining marine environment, whereas a ratio of less than one indicates a terrestrial or mixed source (Akinlua et al. 2015; Vander Spuy et al. 2003).

The proven source rock assemblage of Late Aptian age was determined to be terrestrial, with an average V/Ni of 0.026 (Table 5); this contradicts some reports that Aptian shales are anoxic (Hirsch et al. 2009; Paton et al. 2008; vander Spuy et al. 2003; Herbin et al. 1987). Furthermore, 86 percent of its Cenomanian–Turonian source rocks are marine-derived, while only 14 percent show some mixing (Fig. 7b; Table 5). Co/Ni is adapted to distinguish samples from marine and lacustrine environments in order to

![Fig. 7](image-url)
differentiate the source rocks into their appropriate origins. The investigated shales have Co/Ni ratios ranging from 0.428 to 1.019 (Table 5). Lacustrine samples have Co/Ni values ranging from 0.79 to 1.07 (Akinlua et al. 2018), accounting for up to 25% of the total rock examined (Table 5). Marine-derived source rocks, on the other hand, have a Co/Ni ratio of less than 0.79, accounting for up to 75% of the sample (Table 5). The V/Ni ratios of some inferred Albian succession source rocks range from 0.641 to 3.768, while Campanian source rocks have V/Ni ratios of 0.981 to 1.873. In general, the investigated shaly samples are primarily of marine origin (Fig. 7a, b), with 75% of the samples being anoxic, and only KF1-820, KH1-1500, KD1-2250, KD1-3120, and KE1-4105 having a V/Ni ratio of less than 1. This suggests that the terrestrial remains in these few samples are insignificant, and that marine organic matter is more prevalent in all the samples.

\[ \text{V/ (V + Ni) fraction} \]

V/ (V + Ni) values greater than 0.5 were found in 75% of the tested samples, indicating reduced bottom water conditions, while 25 percent have values less than 0.5, indicating a dysoxic to anoxic setting of the organic matter (Akinlua et al. 2016). Similarly, V/ (V + Ni) ratios more than 0.84, between 0.54–0.82, and 0.46–0.60, indicates anoxic, eutoxic, and anoxic to dysoxic conditions respectively (Chen et al. 2018; Akinlua et al. 2015). The average V/ (V + Ni) fraction for all investigated shales is 0.56, indicating anoxic to dysoxic and mostly anoxic conditions.

**Stable isotope of carbon**

Bulk carbon isotope data also distinguishes the varying depositional conditions of organic matter as either marine or mixed matter and depicts the genetic relationship that exists within source rocks (Collisten and Wavrek 1996; Sofer 1984).

According to Sofer (1984), bulk δ13C saturates as well as δ13C aromatic fractions were also utilized to distinguish rock extracts environment (Fig. 8a). δ13C saturate and δ13C aromatic fractions range from -22.29 to -12.24 and -21.38 to -12.4, respectively, with a mean variable 13C signature ranging from -21.84 to -12.32. (Table 6). Source rocks from marine versus terrigenous depositional settings were also distinguished using the canonical variable (CV). CV less than 0.47 denotes marine matters, while CV greater than 0.47 denotes terrestrial plant input (Al-Khafaji et al. 2020; El Diasty et al. 2016; Sofer 1984). The source rocks were derived from the sea, as indicated by the CV range of −8.83 to −2.72 in the extracts under investigation (Table 6). This is consistent with biomarker interpretations and trace elemental properties.

According to Sofer (1984) plots, these δ13C saturated and aromatic fractions were primarily marine-derived (Fig. 8a). As a result, the investigated source rocks are classified as marine source dominated and mixed marine setting with some terrestrial matters. The δ13C of marine organic matter ranges from −22 to slightly less than −20. Mixed marine organic matter following the C₄ pathways, on the other hand,
ranges from slightly below −12 to up to −18. (Fig. 8a, b). As a result, approximately 57 percent of the samples examined are marine-influenced, while 43 percent are mixed derived via the C4 path. This is also consistent with inorganic geochemistry findings.

Correlation analysis using statistics

For the purpose of describing the geochemical processes that affected the studied shales, the geochemical data was subjected to a Pearson correlation analysis. The Pearson correlation matrix for the investigated shales is shown in Table 7. Except for Al2O3 and K2O, SiO2 having negative correlation with all the major oxides, as shown by the matrix (Fe2O3, CaO, MgO, MnO, Na2O, TiO2). Quartz is the primary source of silica because SiO2 has a negative correlation with all the major oxides (Abubakar et al. 2021, 2019; Sonfack et al. 2021; Ahmad and Chandra 2013). The fact that SiO2 is positively correlated with Al2O3 and K2O indicates that clay mineral is a secondary source of silica (Nagarajan et al. 2017). Al2O3 has a significant negative correlation with Fe2O3, CaO, MgO, MnO, Na2O, TiO2, and P2O5, indicating that it is dissociated from clay minerals (Abubakar et al. 2021). The decomposition of K-feldspars could be a source of kaolin minerals, based on the strong positive relationship between Al2O3 and K2O (Abubakar et al. 2019). Fe2O3 exhibits a strong positive relationship with CaO, MgO, MnO, Na2O, TiO2, and P2O5, implying that these elements are associated with heavy mineral fractions (Sonfack et al. 2021). CaO has a good association with MgO, MnO, Na2O, TiO2, and P2O5, indicating that it is related to carbonate minerals (Nagarajan et al. 2017). In contrast to other major oxides, CaO has a negative correlation, particularly SiO2, Al2O3, Fe2O3, and K2O, signifying that carbonate minerals are the primary source of Ca (calcite), with no influence from detrital sources (Bessa et al. 2021). As indicated by K-feldspar and plagioclase products in the studied shales, chemical weathering is responsible for the negative correlation between both K2O and Na2O (Nagarajan et al. 2017).

Distribution of silica content

The mineralogical content of shales, particularly the calcitic content, as well as the quartz content, regulates fracture growth (Ding et al. 2012; Jarvie 2012). These shales range from 51.01 to 63.31 percent silica content (Table 4), with the Upper Turonian KE1-2970 having the highest silica content. Al2O3 has a remarkable range of 12.33–17.85 percent, whereas CaO is generally low, ranging from 1.29 to 11.81%. This shales’ mineralogy is silica dominant, as determined by radiolarian and planktonic tests (Davies 1970). As a result of the presence of reasonable clastic (silica and some carbonates) in the investigated shales, it becomes hard and brittle, allowing it to possibly expel hydrocarbons.
### Table 7: 2-tailed Pearson correlation matrix for the major elements

|       | SiO2 | Al2O3 | Fe2O3  | CaO   | MgO   | MnO   | K2O   | Na2O  | SO3   | Cl    | ZrO2  | TiO2  | Rb2O  | SrO   | BaO   | P2O5  | CuO   |
|-------|------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SiO2  | 1    |       |        |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Al2O3 | .767* | 1     |        |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| Fe2O3 | -.826** | -.518* | 1     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| CaO   | -.746** | -.800** | .409  | 1     |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
| MgO   | -.845** | -.802** | .799** | .577** | 1     |       |       |       |       |       |       |       |       |       |       |       |       |       |
| MnO   | -.882** | -.843** | .772** | .763** | .843** | 1     |       |       |       |       |       |       |       |       |       |       |       |       |
| K2O   | .741** | .851** | -.643** | -.715** | -.816** | -.809** | 1     |       |       |       |       |       |       |       |       |       |       |       |
| Na2O  | -.509* | -.609** | .444* | .094  | .670** | .490* | -.505* | 1     |       |       |       |       |       |       |       |       |       |       |
| SO3   | .050  | .233  | -.184 | .128  | -.179 | -.124 | .092  | -.560* | 1     |       |       |       |       |       |       |       |       |       |
| Cl    | -.362 | -.358 | .289  | -.108 | .366  | .233  | -.207 | .890** | -.599** | 1     |       |       |       |       |       |       |       |       |       |
| ZrO2  | .220  | .051  | -.323 | -.150 | -.282 | -.260 | .074  | .049  | .035  | .219  | 1     |       |       |       |       |       |       |       |
| TiO2  | -.754** | -.526* | .773** | .533* | .809** | .659** | -.688** | .264  | .184  | .031  | -.119 | 1     |       |       |       |       |       |       |
| Rb2O  | .583* | .774** | -.467* | -.676** | -.689** | -.694** | .927** | -.396 | .032  | -.072 | .088  | -.548** | 1     |       |       |       |       |       |
| SrO   | -.685** | -.801** | .302  | .896** | .482* | .710* | -.633** | .218  | .041  | .053  | -.119 | .307  | -.623** | 1     |       |       |       |       |
| BaO   | .130  | -.013 | -.344 | -.225 | -.226 | -.241 | .265  | .351  | -.332 | .539  | .100  | -.576** | .216  | .140  | 1     |       |       |       |
| P2O5  | -.542* | -.368 | .441  | .629** | .211  | .486* | -.406  | -.180 | .260  | -.188 | -.009 | .408  | -.317 | .611** | -.256 | 1     |       |       |
| CuO   | -.200 | -.048 | .365  | .080  | .060  | .160  | -.076 | .004  | -.179 | .049  | -.608 | -.215 | .051  | .111  | .195  | .088  | 1     |       |

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)
Provenance

Using the obtained SiO₂, geochemical proxies from the examined shales determine the origin of sediments, which can be grouped based on mafic, intermediate, and feldspar content (Armstrong-Altrin 2009). All evaluated samples fall within the compositional field of intermediate igneous rocks, as shown by the plot Al₂O₃/TiO₂ vs SiO₂ in Fig. 9a. Similarly, K₂O/Al₂O₃ ratios can be used to identify the parent matter of muddy rocks. Samples with a K₂O/Al₂O₃ ratio of less than 0.4 show little alkali feldspar, whereas shales with values greater than 0.5 show abundant alkali feldspar in proportion to some other minerals within the shales (Cox et al. 1995). The presence of a small amount of K₂O/Al₂O₃ values (0.126–0.191) in the examined shales indicates a low granitic composition in the source area. Furthermore, Al₂O₃/TiO₂ accurately depicts the genesis of source rock (Andersson et al. 2004; Hayashi et al. 1997; Garcia et al. 1994). Whenever Al₂O₃/TiO₂ ratio is 3–8wt percent, it refers to mafic igneous rock, 8–21wt percent denotes an intermediate source origin, and 21–70wt percent denotes feldspar-dominated igneous rock. For the shale samples examined, the Al₂O₃/TiO₂ ratios ranged from 9.998 to 20.311 (Table 4), indicating that the sediments were formed by intermediate igneous rocks (Fig. 9a). It is worth noting that all the computations and illustrative plots performed confirm the origins of Orange Basin shales from Intermediate Igneous rocks, as Zr/Ti plots (Fig. 9b). The major oxide bivariate scatter plots by Herron (1988) are shown in Fig. 9c; geochemically classifying the investigated Orange Basin samples as shales as observed on hand specimen and some lithologic descriptions. Similarly, the major elements discrimination diagram (Fig. 9d) plotted the shales within the intermediate igneous field.

Paleoweathering conditions and sediment maturity

Alkali and alkali earth metal concentrations in rocks determine the degree of weathering in sediments (Nesbitt and Young 1982). Weathering indices are calculated using the following formulas: i) The chemical index of alterations (CIA) and ii) chemical variability index (ICV) as initiated by Nesbitt and Young (1982).

Fig. 9 a: Al₂O₃/TiO₂ vs SiO₂ plot for the Orange Basin sediments. b: Scatter diagram of Zircon against Titanium oxides of the shales in Orange Basin (after Hayashi et al. 1997). c: Geochemical classification of the shales, Orange Basin (after Herron, 1988). d: Discriminant function figure of the major elements showing provenance of the shales (Roser and Korsch 1988)
Rb₂O/SrO and SiO₂/Al₂O₃ ratios were also calculated to assess the textural and compositional maturity of the Orange Basin shale.

\[
\text{ICV} = \frac{(K_2O + Fe_2O_3 + Na_2O + CaO + MgO + MnO) \times 100}{'Al_2O_3'}
\]

\[
\text{CIA} = \left(\frac{Al_2O_3}{[Al_2O_3 + CaO + K_2O + Na_2O]}\right) \times 100 \quad \text{(Nesbitt and Young 1982)}
\]

It is worth noting that SiO₂ vs Al₂O₃ ratio of 3 indicates basic igneous rocks, while a ratio of 5 reveals acidic rocks (Cox et al. 1995). In clastic sediments, these ratios are higher than 5, indicating high maturity, while below the SiO₂/Al₂O₃ ratio indicates immaturity (Abubakar et al. 2021; Hernández-Hinojosa et al. 2018; Cox et al. 1995). The calculated SiO₂/Al₂O₃ ratios range from 3.41 to 4.14, indicating that the investigated sediments are texturally immature (Table 4).

Similarly, an average ICV index greater than 0.85 denotes a typical rock-forming mineral, while less than 0.85 denotes alteration product. Sediment ICV values is from 1.07 to 2.56, with an average of 1.55, signifying weathering activities within the study area (Table 4). Furthermore, ICV versus CIA (Fig. 10) demonstrates that all the original matter analyzed shales plotted above the Post Archean Australia Shales (PAAS) ICV index of about 0.85, indicating immaturity in the composition as well as relatively mild weathering of original source materials (Hernández-Hinojosa et al. 2018).

Another calculation that explains the level of weathering within the source area is the CIA (Nesbitt and Young 1982). Thus, calculated CIA average value is 64.72, oscillating between 45.93 and 74.41 (Table 4), attesting the weathering effect around the parent aggregates (Fig. 10).

Because Sr^{2+} easily leaches out of terrestrial inputs, the Rb₂O/SrO fraction is also used to investigate weathering processes (McLennan et al. 1993). The examined shales have mean Rb^+/Sr^2+ values ranging from 2.10 to 0.32 above the mean upper continental crust (UCC) value of 0.32, implying some level of weathering activity, as demonstrated by other computations.

**Paleosalinity**

Sr^{2+} and Ba are useful paleosalinity index metals (Wang 1996; Deng and Qian 1993; Liu et al. 1984). They have been significantly modified to depict both seawater and freshwater imprints (Moradi et al. 2016). A high Sr/Ba ratio indicates a high level of salinity, whereas a low Sr/Ba ratio indicates a low level of salinity (Deng and Qian 1993).

Less than 0.20 Sr/Ba ratio indicates freshwater, and more than 0.5 indicates marine water influence (Li et al. 2020; Wei and Algeo 2020). Values ranging from 0.2 to 0.5 indicate a brackish water environment, but caution should be exercised when generalizing the Sr/Ba ratio. The Sr/Ba ratio in the investigated shales ranges between 0.032 and 1.160 (Table 4). In general, 40 percent of the studied shales were derived from seawater, 25 percent from brackish waters, and 35 percent from freshwater settings. The V/Ni vs Sr/Ba cross-plots (Fig. 11b) illustrate relatively low-to-moderate saline stratification as compatible with the varying marine to freshwater influences (0.032–1.160). Due to the low gammacerane index (Fig. 11a; Table 2), stratification during deposition of most samples was minimal signifying low salinity (Peters et al. 2005; Sinninghe Damste et al. 1995).

**Paleovegetation and paleoclimatic evolution**

Proxy wax (P_{wax}), proxy aqueous (P_{aq}), and average chain length (ACL) biomarker identifiers are best suited for...
reconstructing paleovegetation and paleoclimates (He et al. 2019; Ortiz et al. 2013). Pwax deals with the concentration of waxy hydrocarbons derived from higher plants (Zheng et al. 2007). These proxies, specifically n-C23/(n-C27 + n-C31) ratios, measure the comparable amount of Sphagnum species to terrigenous remains to represent the water level within sediments (Andersson et al. 2011). According to He et al. 2019, n-C23/(n-C27 + n-C31) value greater than 0.2 indicates a predominance of sphagnum in a wet environment, as demonstrated by ranges of the analyzed sediments from 0.71 to 5.60. This analysis is supported by Paq values (Table 1), which indicate the contributions of emergent and submerged plants, as well as P_wax values. A humid environment with abundant C27 n-alkanes promotes the growth of woody vegetative cover. Herbaceous remains, on the other hand, are rich in n-C31 and thrive in a dry, warm environment. Even though we are dealing with the dominantly marine-influenced matter as proved by low terrigenous aquatic ratio ranging between 0.07 and 2 (Table 1). The relative number of nC27, nC29, nC31 alkanes is adapted to categorize terrigenous remains as grasses dominated or predominantly from deciduous trees or conifers. Abundant %C31 shows grasses input (Maffei 1996), while the preponderance of %C27 shows more deciduous trees (Ortiz et al. 2010). The predominance of conifers is increasing in n-C29 (Schwark et al. 2002). Woody vegetation is associated with a humid climate that contains more C27 alkanes, while herb shrubs thrive in the warm, droughty season (Vegas et al. 2010). A tri-plot of n-alkane %C27, %C29, and %C31 shows a predominance of C27 n-alkanes (Fig. 12), confirming humid paleovegetative climatic cover. It was determined by Lopez-Dias et al. (2013) that woody and herbaceous higher plants contributed to the paleoclimate in different proportions by adapting to the n-C27/n-C31 ratio. n-C27/ n-C31 ratio ranges between 2.00 and 14.00 (Table 1), which corresponds to our more humid climatic phase of deciduous tree growth.

Terrigenous input and paleoclimatic settings are constructed using a variety of major and trace elements (Liang et al. 2018; Li et al. 2020). Paleoclimatic reconstruction in the Orange Basin is largely based on C-values. This shows that warm, humid sediments have higher Fe, Mn, Ni, Cr, V, and Co concentration, while arid emplaced deposits are blessed with higher Ca, Mg, Sr, Ba elements.

$$C-value = \frac{\Sigma (Fe + Mn + Ni + Cr + V + Co)}{\Sigma (Ca + Mg + Sr + Ba + K + Na)}$$

part per million (Li et al. 2020). This means the greater the C-values, the more humid while lower C-values connote arid paleoclimate. C-value above 0.8 shows humid nature, 0.6–0.8 signifies a semi-humid climate, and 0.4–0.6 connote semiarid to semi-humid paleoclimatic settings. On the other hand, semiarid paleoclimates have C-values that spans from 0.2 to 0.4 (Cao et al. 2012; Qui et al. 2015), and below 0.2 refers to arid paleoclimates. The shales of the Orange basin have C-values ranging from 0.60 to 1.34 (Table 4) signifying semi-humid to humid paleoclimatic conditions. The Sr/Cu values were adopted to depict the paleoclimatic setting when terrestrial organofacies were emplaced (Liu & Zhou 2007; Moradi et al. 2016; Li et al. 2020). Low Sr/Cu ratios are associated with humid climates, also, the higher the values, the more aridity it is (Liu & Zhou, 2007). Sr vs Cu index ranging from 1.5 to 5 represents warm–humid climate, whereas ratios above 5 connote hot, dry climatic conditions (Han et al. 2020). The investigated shaly sediments are within the warm, humid climatic condition as the Sr/Cu ratio is averagely up to 1.63, ranging from 0.857 to 2.737 (Table 4). The inorganic calculations on the paleoclimate settings of the Orange Basin are therefore tied to the biomarker proxies.
Using a stable isotope of carbon as a determinant of sediment settings and paleoclimate is hard to decrypt. δ¹³C variability is predominant than observed between macerals of the exact succession; as such, these differences are not from changes in organic matter composition only (Jingjing et al. 2020). A good correlation of maceral indices exists between δ¹³C and the vegetation index. The vegetation index (VI) computes the maceral constituent ratio (Calder et al. 1991), which is supported by δ¹³C and other data (Table 6; Fig. 8b). Therefore, $VI = \frac{TEL + FUS + SFU + SUB + RES}{DEN + INT + ALG + LPD + SPO + CUT}$.

TEL = tellocollinites, FUS = fusinite, SFU = semifusinite, SUB = suberinite, RES = resinite, DEN = densinite, INT = inertodetrinite, ALG = alginite, LPD = liptodetrinite, SPO = sporinite, and CUT = cutinite.

Thus, VI (Jingjing et al. 2020) adequately depicts the amount of preserved tissues, degraded tissues, and particulate organic matters present. Almost all less negative δ¹³C values go with the intermediate VI values (Table 6; Fig. 8b). Higher VI connotes woody vegetation, favoring drier and shallow water table (Calder et al. 1991; Calder 1993; Jingjing et al. 2020). Low VI, on the other hand, may indicate a wetter environment, resulting in larger, more microbially diverse herbaceous plants. Therefore, VI and the mean δ¹³C association corroborate that there were fluctuating semidry and wet intervals in the time of Orange Basin sediment amassment (Table 6).

**Tectonic framework restructuring**

The tectonic setting in the Orange basin is well-understood via inorganic major and trace element bivariate plots. Plate tectonics influences the rock chemistry (Peters et al. 2005; Makeen et al. 2015a). Using bulk elemental analyses, bivariate plots of K₂O/Na₂O vs SiO₂ were used to reconstruct the tectonic setting of the Orange basin (Roser and Korsch, 1986). The concentration of K₂O/Na₂O and SiO₂ increases from oceanic island arc settings through active continental boundary settings into passive margins. Most of the investigated shales fall within the passive continental margin, with only two samples falling within the active margin (Fig. 13a). Generally, three types of tectonic settings, according to Verma and Armstrong-Altrin (2013): island or continental arc, continental rift, and collisional configuration. Figure 13b depicts plots within the continental rift indicating the Orange basin shales as a byproduct of the rifted passive margin. A similar tectonic episode is thought to have occurred in West and Central Africa at about the same time as the South American plate opened during the Cretaceous (Genik 1992). The opening of the Atlantic Ocean during the Early Cretaceous Period was the primary cause of the separation of the West African plates (Guiraud and Maurin 1992).
Fig. 13  a: Bivariate plots of K2O/Na2O versus SiO2 showing the tectonic setting of Orange Basin based on investigated shales (adapted after Roser and Korsch 1986). b: Tectonic setting based on discriminant function for the shales of the Orange Basin (after Verma and Armstrong-Altrin 2013)

Conclusions

The depositional environment, lithotype, age and thermal maturity of Cretaceous post-rift sediments from the Orange Basin were revealed by molecular, bulk geochemical, and elemental characterization. Some of the findings are as follows:

I. The unimodal pattern of n-alkane, as well as its components such as Pr vs Ph, Pr/nC17 versus Ph/nC18 cross-plot, Pr/Ph vs C29R/C27R, Pr vs Ph, and C27/(C27 + C29) R, confirms the accumulation of the studied lithofacies in a coastal anoxic environment. To determine the origin of source rock samples, a biomarker with structural similarities to precursor kerogen and biodegradation resistance was used. Based on aliphatic and aromatic compounds, this method revealed that all samples have the same structure. As a result, all the samples were obtained from the same source.

II. Biomarker finger printing is consistent with inorganic trace elements because samples are primarily from the same source rock from the same family of rocks and derived under anoxic to dysoxic conditions. This is supported by a Pr/Ph ratio of less than one, a homohopane distribution, and a V/(V + Ni) ratio. Geochemically, the G/C30 value reflects that the source rock must have been accumulated under reduced conditions, with the sedimentary column consisting of a stratified aqueous column.

III. A wide range of maturation is evident in the samples examined, ranging from immature to late oil generation. Thermal maturity parameters adapted included C3222S/(22S + 22R), C29αααS/(20S + 20R), M30/C30 ratio, C29diasterane/29αααR and the methylphenanthrene index calculated vitrinite reflectance (VRc percent) and measured VRo percent), with 50% of examined samples showing peak oil window (0.676–0.899).

IV. Inorganic trace findings, together with molecular geochemical cross-plots, isotopic δ13C saturate, and δ13C aromatic cross-plots, confirm the marine genetic origins of organic matters with few mixed materials.

V. The majority of the less negative δ13C values are associated with woody vegetation that thrives in lower standing water tables and less wet climatic conditions. Thus, VI and the mean δ13C association support the existence of fluctuating dry and wet intervals during the time of Orange Basin sediment accumulation.

VI. Source rock inputs were differentiated by adapting Paq, TAR, and total amounts of n-C27, n-C29, and n-C31. A long-chain n-alkane in a variable form, particularly n-C27, demonstrates diversity in vegetation and can be used to reconstruct paleoenvironmental evolution; in the dry season, grasses grow, while trees multiply in the rainy season.

VII. Inorganic computations on the paleoclimatic condition of the Orange Basin agree with biomarker proxies and isotopic studies confirming semi-humid to humid paleoclimatic conditions.

VIII. In terms of textural and compositional maturity, shale samples were classified as immature. Tectonic setting discriminant function diagrams showed that the continental rift’s marginal zone was passive. According to this interpretation, the tectonic setting is consist-
ent with the Cretaceous event of West and Central Africa, which separated the South American plate from the West African plate, resulting in the opening of the South Atlantic Ocean and the creation of the Orange Basin.

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Abubakar U, Usman MB, Aliyuda K, Dalha A, Bello AM, Linus LN (2021) Major and trace element geochemistry of the shales of Sekuliyie Formation, Yola Sub-Basin, Northern Benue Trough, Nigeria: implications for provenance, weathering intensity, and tectonic setting. J Sediment Environ. https://doi.org/10.1007/s43217-021-00067-2

Abubakar U, Usman MB, Bello AM, Garba TA, Hassan S (2019) Geochemical and palaeocurrent analysis of the Tertiary Kerri-Kerri Formation in the Gongola Sub-Basin of the Northern Benue Trough North-eastern Nigeria: implications for provenance, tectonic setting and palaeoweathering. SN Appl Sci 1(10):1–11. https://doi.org/10.1007/s42452-019-1196-7

Adebanji KA, Sarki Yandoka BM, Abdullah Ahakegebobi WHIM (2015) Molecular geochemical evaluation of late cretaceous sediments from chad (bornu) basin, NE Nigeria: implications for paleodepositional conditions, source input and thermal maturation. Arab J Geosci 8:1591–1609. https://doi.org/10.1007/s12517-014-1341-y

Adebanji KA, Abdullahu WH, Hakim HI, Babangida MSY, Mustapha KA, Adeyinka OA (2014) Trace elements geochemistry of kerogen in upper cretaceous sediments, Chad (Bornu) Basin, northeast Nigeria: origin and paleo-redox conditions. J Afr Earth Sci. https://doi.org/10.1016/j.jafrearsci.2014.08.014

Adekola SA, Akinlua A, Mangelsdorf K (2012) Organic geochemical evaluation of cretaceous shale samples from the orange Basin, South Africa. Appl Geochem 27:1633–1642. https://doi.org/10.1016/j.applgeochem.2012.03.012

Ahmad I, Chandra R (2013) Geochemistry of loess-paleosol sediments of Kashmir Valley, India: provenance and weathering. J Asian Earth Sci 66:73–89. https://doi.org/10.1016/j.jseaes.2012.12.029

Akinlua A, Adekola SA, Adeyemi AK (2018) Rare earth and trace element geochemistry of Cretaceous kerogens. Arab J Geosci. https://doi.org/10.1007/s12517-018-3900-0

Akinlua A, Olise FS, Akomolafe AO, McCrindle RI (2016) Rare earth element geochemistry of petroleum source rocks from northwestern Niger Delta. Mar Pet Geol. https://doi.org/10.1016/j.marpetgeo.2016.06.023

Akinlua A, Sigedle A, Buthelezi T, Fadipe OA (2015) Trace element geochemistry of crude oils and condensates from South African Basins. Mar Pet Geol 59:286–293. https://doi.org/10.1016/j.marpetgeo.2014.07.023

Akinlua A, Maende A, Adekola SA, Swakamisa O, Fadipe OA, Akinyemi SA (2011) Source rock potential of selected Cretaceous shales, orange Basin, South Africa. Int Geol Rev 53:1508–1521. https://doi.org/10.1080/00206811003755370

Akinlua A, Adekola SA, Swakamisa O, Fadipe OA, Akinyemi SA (2010) Trace element characterization of cretaceous orange Basin hydrocarbon source rocks. Appl Geochem 25(10):1587–1595. https://doi.org/10.1016/j.applgeochem.2010.08.008

Akinlua A, Ajayi TR, Adeleke BB (2007a) Trace elements geochemistry of petroleum source rocks from the Orange Basin, eastern Nigeria: origin and paleo-redox conditions. J Afr Earth Sci. https://doi.org/10.1016/j.jafrearsci.2007.08.014

Akinlua A, Ajayi TR, Adeleke BB (2007b) Trace elements geochemistry of cretaceous orange Basin hydrocarbon source rocks. Appl Geochem 22:555–577. https://doi.org/10.1016/j.applgeochem.2007.08.014

Al-Khafaji AJ, Hakimi HI, Mohialdeen IMJ, Idan RM, Afify WE, Lashin AA (2020) Geochemical characteristics of crude oils and basin modelling of the probable source rocks in the Southern Mesopotamian Basin, South Iraq”. J Petrol Sci Eng. https://doi.org/10.1016/j.petrol.2020.107641

Andersson RA, Kuhl H, Meyers P, Zebib Y, Cripl P, Mörth M (2011) Impacts of paleohydrological changes on n-alkane biomarker compositions of a holocene peat sequence in the eastern European Russian Arctic. Org Geochem 42:1065–1107. https://doi.org/10.1016/j.orggeochem.2011.06.020

Andersson POD, Worden RH, Hodgson DM, Flint S (2004) Provenance evolution and chemotatigraphy of a palaeozoic submarine fancomplex: tanqua karoo basin, South Africa. Mar Petrol Geol 21:555–577. https://doi.org/10.1016/j.marpetgeo.2004.01.004
Aquino Neto FR, Triguis J, Azevedo DA, Rodrigues R, Simonet BRT (1989) Organic geochemistry of geographically unrelated Tasmanites. Org Geochem 18(6):791–803. https://doi.org/10.1016/0146-6380(92)90048-3

Armstrong-Altrin JS (2009) Provenance of sands from cazones, acapulco, and bahia kino beaches, México. Rev. Mex. Rev. Mex. Ciencias Geol 26:764–782. http://www.scielo.org.mx/scielo.php?script=sci_arttext&pid=S1026-8774200600030012

Ayinla HA, Abdullah WH, Makeen YM, Abubakar MB, Jauro A, Sarki Yandoka BM, Zainal Abidin NS (2017) Petrographic and geochemical characterization of the upper cretaceous coal and mudstones of gombe formation, gongola sub-basin, Northern Benue Trough Nigeria: Implication for organic matter preservation, paleo depositional environment and tectonic settings. Int J Coal Geol 180:67–82. https://doi.org/10.1016/j.coal.2017.06.010

Barton KR, Muntingh A, Noble RDP (1993) Geophysical and Geological studies applied to hydrocarbon exploration on the West Coast Margin of South Africa. Extended abstract of the Third International Congress of the Brazilian Geophysical Society, Rio de Janeiro, Brazil. 7-11 1993. Doi: https://https://doi.org/10.9979/2214-4609-pdb.324.1316

Barwise AIG (1990) Role of nickel and vanadium in petroleum classification. Energy Fuels 4:647–652. https://doi.org/10.1021/ef00024a005

Bechtel A, Jia JL, Strobl SA, Sachsenhofer RF, Liu ZJ, Gratzer R, Püttmann W (2012) Palaeoenvironmental conditions during deposition of the Upper Cretaceous oil shale sequences in the Songliao Basin (NE China): Implications from geochemical analysis. Org Geochem 46:76–95. https://doi.org/10.1016/j.orggeochem.2012.02.003

Bechtel A, Gruber W, Sachsenhofer RF, Gratzer R, Püttmann W (2001) Organic geochemical and stable carbon isotopic investigation of coals formed in low-lying and raised mires within the Eastern Alps (Austria). Org Geochem 32(682):1289–1310. https://doi.org/10.1016/S0146-6380(01)00101-2

Bessa AZE, Armstrong-Altrin JS, Fuç GC, Betsi TB, Kelepile J, Ndijugi PD (2021) Mineralogy and geochemistry of the Ngao undaba Crater Lake sediments, northern Cameroon: implications for provenance and trace metals status. Acta Geochimica. https://doi.org/10.1007/s11631-021-00463-5

Broad D, Jungselaeger E, McLachlan I, Roux J (2006) Offshore Mesozoic basins. The Geology of South Africa. Geological Society of South Africa, Johannesburg Council for Geoscience, Pretoria, 553–571

Brown LF (1995) Sequence Stratigraphy in Offshore South African Divergent Basins: An Atlas on Exploration for Cretaceous Lowstand Traps by Soekor (Pty) Ltd, AAPG Studies in Geology 41: AAPG

Budzinski H, Garrigue PH, Connan J, Devillers J, Domine D, Radke M et al (1995) Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. Geochim Cosmochim Acta 59:2043–2056

Calder JH (1993) The evolution of a ground-water-influenced (Westphalian B) peat-forming ecosystem in a piedmont setting: The No. 3 Seam, Springhill Coalfield, Cumberland Basin, Nova Scotia. In: Cobb, J.C., Ceci, C.B. (Eds.), Modern and Ancient Coal-Forming Environments, Geological Society of America Special Paper 286, 153–181

Calder JH, Gibling MR, Mukhopadhyay PK (1991) Peat formation in a Westphalian B peatmoss setting, cumberland basin, nova scotia: implications for the maceral-based interpretation of rheotrophic and raised paleo mires. Bulletin De La Société Géologique De France 162:283–298

Calvert SE, Bustin RM, Ingall ED (1996) Influence of water column anoxia and sediment supply on the burial and preservation of organic carbon in marine shales. Geochim Cosmochim Acta 60:1577–1593

Cao J, Wu M, Chen Y, Hu K, Bian L, Wang L, et al (2012) Trace and rare earth element geochemistry of Jurassic mudstones in the northern Qaidam Basin, northwest China 72 245–252

Chen Z, Simonet BRT, Wang TG, Ni Z, Yuan G, Chang X (2018) Molecular markers, carbon isotopes, and rare earth elements of highly mature reservoir pyrobitumens from Sichuan Basin, southwestern China: Implications for Precambrian-Lower Cambrian petroleum systems. Precambri Res 317:33–55. https://doi.org/10.1016/j.precamres.2018.08.005

Collister JW, Wavrek DA (1996) 13C compositions of saturate and aromatic fractions of lacustrine oils and bitumens: evidence for water column stratification. Org Geochem 24(8–9):913–920. https://doi.org/10.1016/S0146-6380(96)00066-6

Connan J, Bouroullec J, Dessort D, Albrecht P (1986) The microbial input from carbonate-anhydritic facies of a sabkha paleoenvironment from guatemala: a molecular approach. Org Geochem 10:29–50. https://doi.org/10.1016/0146-6380(86)90007-0

Connan J, Cassou AM (1980) Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels. Geochim Cosmochim Acta 44:1–23. https://doi.org/10.1016/0016-7037(80)90173-8

Cox R, Lowe DR, Cullers RL (1995) The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. Geochim Cosmochim Acta 59:2919–2940. https://doi.org/10.1016/0016-7037(95)00185-9

Cumming VM, Selby D, Lillis PG, Lewan MD (2014) Re-Os chronology and Os isotope fingerprinting of petroleum sourced from a Type I lacustrine kerogen: insights from the natural Green River petroleum system in the Uinta Basin and hydrosy pyrolysis experiments. Geochim Cosmochim Acta 138:32–56. https://doi.org/10.1016/j.gca.2014.04.016

Davies JC (1970) Petrology of Cretaceous mowy shale of Wyoming Am. Assoc Petrol Geol Bull 54(3):487–502. https://doi.org/10.1306/5D25C9B3-16C1-11D7-8654000102C1865D

Davies CPN (1997) Unusual biomarker maturation ratio changes through the oil window, a consequence of varied thermal history. Org Geochem 27:537–560. https://doi.org/10.1016/S0146-6380(97)00059-4

Deng HW, Qian K (1993) Analysis on sedimentary geochemistry and environment. Science Technology Press, Gansu, pp 15–85 (in Chinese)

Ding W, Li C, Li C, Xu C, Jiu K, Zeng W et al (2012) Fracture development in shale and its relationship to gas accumulation. Geosci Front 3(1):97–105. https://doi.org/10.1007/s11631-010-00017-3

Escobar M, Márquez I, Inciarte S, Rojas J, Esteves I, Malandrino G (2011) The organic geochemistry of oil seeps from the Sierra de Perijá eastern foothills, Lake Maracaibo Basin, Venezuela. Org Geochem 42:727–738. https://doi.org/10.1016/j.orggeochem.2011.06.005

El Diasty WSh, El Beialy Y, Mahdi AQ, Peters KE (2016) Geochemical characterization of source rocks and oils from northern Iraq: Insights from biomarker and stable carbon isotope investigations. Mar Pet Geol 207:1140–1162. https://doi.org/10.1016/j.marpetgeo.2016.07.019

Ficken KJ, Li B, Swain DL, Eglinton G (2000) An n-alkane proxy for the sedimentary input of submerged/ floating freshwater aquatic macrophytes. Org Geochem 31(7–8):745–749. https://doi.org/10.1016/S0146-6380(00)00081-4

Frankenberger A, Brooks RR, Varela-Alvarez H, Collen JD, Filby RH, Fitzgerald SL (1994) Classification of some New Zealand crude oils and condensates by means of their trace element contents. Appl Geochem 9:65–71. https://doi.org/10.1016/0883-2927(94)90053-1
Ordos Basin, China: Implications for paleo-environment and organic matter accumulation. Mar Pet Geol 111:852–867. https://doi.org/10.1016/j.marpetgeo.2019.09.003

Liang C, Wu J, Jiang Z, Cao Y, Song G (2018) Sedimentary environmental controls on petroleum and organic matter accumulation in the upper fourth member of the Shahejie Formation (Paleogene, Dongying depression, Bohai Bay Basin, China). Int J Coal Geol 186:1–13. https://doi.org/10.1016/j.coal.2017.11.016

Lijmbach GW (1975) On the origin of petroleum: Paper presented at the 9th World Petroleum Congress, Tokyo, Japan, May 1975. https://www.onepetro.org/WPCONGRESS/Proceedings-abstract/WPC09/All-WPC09/WPC-16134/199233

Liu YJ, Cao LM, Li ZL, Wang HN, Chu TQ, Zhang JR (1984) Element geochemistry. Science Press, Beijing, pp 283–372 (in Chinese). https://doi.org/10.1007/s00531-013-0903-7

Liu G, Zhou D (2007) Application of microelements analysis in identifying sedimentary environment taking Qianjiang Formation in the Jiang Han Basin as an example. Pet Geol Exp 29(307–310):314 (in Chinese with English abstract)

Long H, Flemings PB, Germaine JT, Saffer DM (2011) Consolidation and overpressure near the seafloor in the Ursa Basin, Deepwater Gulf of Mexico. Earth Planet Sci Lett 305(1–2):1035–1049. https://doi.org/10.1016/j.epsl.2011.02.007

López-Díaz V, Urbanczyk J, Blanco CG, Borrego AG (2013) Biomarkers as paleoclimate proxies in peatlands in coastal high plains in Asturias. N Spain Int J Coal Geol 116–117:270–280. https://doi.org/10.1016/j.coal.2013.04.006

Mackenzie AS, Patience RL, Maxwell JR, Vandenbroucke M, Durand B (1980) Molecular parameters of maturation in the Toarcian (Aptian-Lower Albian), Orange Basin, Western Offshore, South Africa. AAPG Study Geol 65, 187–197. https://www.sciedirect.com/science/article/abs/pii/0305197896000373

Maffei M (1996) Chemotaxonomic significance of leaf wax n-alkanes in the Umbelliﬂerae, Cruciferae and Leguminosae (Subf. Papilionoideae). Biochemical Systematics and Ecology 24, 531–545. http://www.sciedirect.com/science/article/pii/0305197896000373

Makeen YM, Abdullah WH, Hakimi MH, Hadad YT, Elhassan OMA, Mustapha A (2015) Geochemical characteristics of crude oils, their asphaltene and related organic matter source inputs from Fula oilﬁelds in the Muglad Basin Sudan. Marine Pet Geol 67:816–828. https://doi.org/10.1016/j.marpetgeo.2015.07.001

Makeen YM, Abdullah WH, Hakimi MH (2015a) The origin, type and preservation of organic matter of the Barremian-Aptian organic-rich shales in the Muglad Basin, Southern Sudan, and their relation to paleoenvironmental and paleoclimate conditions. Marine and Petroleum Geology 65, 187–197. https://www.sciedirect.com/science/article/pii/S0264871215000823

Marynowsky L, Narkiewicz M, Grelowski C (2000) Biomarkers as environmental indicators in a carbonate complex, example from the middle to upper devonian, holy cross mountains, Poland. Sediment Geol 137:187–212. https://doi.org/10.1016/S0037-0738(00)00157-3

McLennan SM, Hemming S, McDaniel DK, Hanson GN (1993) Geochemical approaches to sedimentation, provenance, and tectonics. In: In: Johnsson, M.J., Basu, A. (Eds.), Processes Controlling the Composition of Clastic Sediments: Geological Society of America Special Paper, vol. 284, pp. 21–40

McManus J, Berelson WM, Hammond DE, Klinkhammer GP (1999) Barium cycling in the North Pacific: implication for the utility of Ba as a paleoproducitivity and paleoalkalinity proxy. Paleoceanogr Paleoclimatol 14:53–61. https://doi.org/10.1029/1999PA900007

McMillan IK (2003) Foraminiferal-deﬁned biot stratigraphic episodes and sedimentation pattern of the Cretaceous drift succes sion (Early Barremian to Late Maastrichtian) in seven basins on the South African and southern Namibian continental margin. South African Journal of Science, 99(11–12), 537–576. https://hdl.handle.net/10520/EJC97566

Meyers PA, Snowden LR (1993) Types and maturity of organic matter accumulated during Early Cretaceous subsidence of the Exmouth Plateau, Northwest Australia margin. AAPG Stud Geol 37:119–130. SG 37: Source Rocks in a Sequence Stratigraphic Framework. Pub. Id: A033 (1993), 119–130

Mohialdeen IMJ, Raza SM (2013) Inorganic geochemical evidence for the depositional facies associations of the Upper Jurassic Chia Gara Formation in NE Iraq. Arab J Geosci 6:4755–4770. https://doi.org/10.1007/s12517-012-0716-1

Moldowan JM, Peters KE, Carlson RMK, Schoell M, Abu-Alia MA (1994) Di verse applications of petroleum biomarker maturity parameters. Arab J Sci Eng 19:273–298

Moosasirada SM, Janardhanab MR, Sethumadhava MS, Moghadam MR, Shankara M (2011) Geochemistry of lower jurassic shales of the shemshak formation, kerman province, central Iran: provenance, source weathering and tectonic setting. Geochim 71:279–288. https://doi.org/10.1016/j.chemer.2010.10.001

Moradi AV, Sari A, Akkaya P (2016) Geochemistry of the Miocene oil shale (Hançili Formation) in the Çankırı-Çorum basin, central Turkey: Implications for paleoclimatic conditions, source–area weathering, provenance and tectonic setting. Sed Geol 341:289–303. https://doi.org/10.1016/j.sedgeo.2016.05.002

Muntingh A (1993) Geology, Prospects in Orange Basin Offshore Western South-Africa. Oil & Gas Journal, 91(4), 106–109. https://www.ogj.com/home/article/17223488/geoology-prospects-in-orange-basin-offshore-western-south-africa

Muntingh A, Brown JrL (1993) Sequence Stratigraphy of Petroleum Plays, Post-Rift Cretaceous Rocks (Lower Aptian to Upper Maastrichtian), Orange Basin, Western Offshore, South Africa: Chapter 4: Siliciclastic Sequence Stratigraphy: Recent Developments and Weimer P, Posamentier H (1993), 71–98

Nagarajan R, Armstrong-Altrin JS, Kessler FL, Jong J (2017) Petrological and geochemical constraints on provenance, paleoweathering, and tectonic setting of clastic sediments from the Neogene Lambir and Sibuti Formations, northwest Borneo. In Sediment provenance (pp. 123–153). https://www.sciedirect.com/science/article/pii/B9780128033869000071

Neshitt HW, Young GM (1982) Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature 299:715–717. https://doi.org/10.1038/299715a0

Ortiz JE, Torres T, Delgado A, Llamas JF, Soler V, Valle M et al (2010) Palaeoenvironmental changes in the padul basin (Granada, Spain) over the last 1 Ma based on the biomarker content. Palaeogeogr Palaeoclimatol Palaeoecol 298:286–299. https://doi.org/10.1016/j.palaeo.2010.00.003

Ortiz JE, Moreno L, Torres T, Vergas J, Ruiz-Zapata B, Garcia-Cortés A et al (2013) A 220 ka palaeo-environmental reconstruction of the Fuenteúllo maar lake record (Central Spain) using biomarker analysis. Örg Geochem 55:85–97. https://doi.org/10.1016/j.orgeochem.2012.11.012

PASA (2003) Exploration Opportunities in the Deepwater Orange Basin, off the West Coast of South Africa. https://petroleumagemcysa.com/ (accessed 07.09.10)

Paton DA, Di Priomo R, Kuhlmann G, van der Spuy D, Horsfeld B (2007) Insights into the petroleum system evolution of the southern orange basin, South Africa. S Afr J Geol 110(2–3):261–274. https://doi.org/10.2113/gssaj.110.2-3.261

Paton DA, Van der Spuy D, Di Priomo R, Horsfeld B (2008) Tectonically induced adjustment of passive-margin accommodation space; influence on the hydrocarbon potential of the Orange
de Calatrava Volcanic Field, Spain). J Quat Sci 25:1051–1062. https://doi.org/10.1002/jqs.1262

Venkatesan MI (1989) Tetrahymanol: its widespread occurrence and geochemical significance. Geochim Cosmochim Acta 53:3095–3101. https://doi.org/10.1016/0016-7037(89)90190-7

Verma SP, Armstrong-Altrin JS (2013) New multi-dimensional diagrams for tectonic discrimination of silicilastic sediments and their application to precambrian basins. Chem Geol 355:117–133. https://doi.org/10.1016/j.chemgeo.2015.11.011

Volk H, George SC, Middleton H, Schofield S (2005) Geochemical comparison of fluid inclusion and present-day oil accumulations in the Papuan Foreland – evidence for previously unrecognized petroleum source rocks. Org Geochem 36:29–51. https://doi.org/10.1016/j.orggeochem.2004.07.018

Volkman JK (1986) A review of sterol biomarkers for marine and terrigenous organic matter. Org Geochem 9:83–89. https://www.sciencedirect.com/science/article/abs/pii/0146638086900896

Wang AH (1996) Discriminant effect of sedimentary environment by the Sr/Ba ratio of different existing forms. Acta Sedimentol Sin 14:168–173

Waples DW, Machihara T (1991) Biomarkers for Geologists: a practical guide to the application of steranes and triterpanes in petroleum geology. American Association of Petroleum Geologists Methods in Exploration, Tulsa, Oklahoma

Wei W, Algeo TJ (2020) Elemental proxies for paleosalinity analysis of ancient shales and mudrocks. Geochim Cosmochim Acta 287:341–366. https://doi.org/10.1016/j.gca.2019.06.034

Xiujian D, Guangdi L, Changhai G, Zhihong H, Jiangxiu Q, Xuejun L, Pangen W, Zhelong C (2016) Geochemical characterization and depositional environment of source rocks of small fault basin in Erlian Basin, northern China. Mar Pet Geol. https://doi.org/10.1016/j.marpetgeo.2015.11.006

Zheng Y, Zhou W, Meyers PA, Xie S (2007) Lipid biomarkers in the Zoigè- Hongyuan peat deposit: indicators of Holocene climate changes in West China. Org Geochem 38:1927–1940. https://doi.org/10.1016/j.orggeochem.2007.06.012

Zumberge JE (1984) Source rocks of the La Luna (Upper Cretaceous) in the Middle Magdalena Valley, Colombia. In: Palacas, J.G. (Ed.), Geochemistry and Source Rock Potential of Carbonate Rocks. American Association of Petroleum Geologists, Tulsa, OK, pp. 127–133

Zumberge JE (1987) Terpenoid biomarker distributions in low maturity crude oils. Org Geochem 11:479–496. https://doi.org/10.1016/0146-6380(87)90004-0

Zumberge JE, Russell JA, Reid SA (2005) Charging of Elk Hills reservoirs as determined by oil geochemistry. Am Asso Petrol Geol Bull 89:1347–1371. https://doi.org/10.1306/05100504003

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