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Assessment of kerogen types and source rock potential of Lower Jurassic successions in the Mandawa Basin, SE Tanzania

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ABSTRACT

Variability in organic matter types and quality of source rock intervals across evolving rift-basins has been the focus of previous studies, which have shown that due to dynamic sedimentary regimes and water depths such source intervals occur sporadically and restricted to specific stratigraphic horizons. Such heterogeneous settings require detailed geochemical analysis to document variations in source quality. This study presents a comprehensive geochemical analysis of source rock intervals in Lower Jurassic successions (Mbuo, Nondwa and Mihambia Formations) in the Mandawa Basin, on-shore Tanzania, in order to constrain organic matter types and quality. Organic matter richness was measured by Total Organic Carbon (TOC) analysis, while quality and thermal maturity of organic matter was assessed by programmed pyrolysis, complemented by organic carbon isotope analysis ($\delta^{13}C_{org}$) of sediment samples collected from outcrops, cores, and cuttings samples. TOC and programmed pyrolysis datasets from existing literature were synthesized in this study to better understand organic matter quality and thermal maturity evolution on regional scale. These data were examined in relation to paleogeography to gain insight into the factors regulating the distribution of organic matter quality within the Mandawa Basin.

Average TOC contents in Lower Jurassic sediments fluctuate from 0.31 to 4.83 wt% with an average of 1.4 wt%, whereas, kerogen yield (S2) and hydrogen index (HI) remain generally low, with values ranging from 0.01 to 8.6 (mg HC/g rock) with an average (0.92 mg HC/g rock) as well as from 2 to 233 (mg HC/g TOC) with an average of 46 (mg HC/g TOC), respectively. Organic matter is composed mainly of type III (gas prone) to IV (inert) kerogens with lesser admixture of type II-III kerogen (oil-gas prone), which have been deeply buried and undergone a wider range of thermal diagenesis, from early to overmature stage. The δ^{13} Corg isotopic composition of organic matter is consistent with kerogen typing, indicating terrestrial organic matter with a heavier signature during sea level low stands. Upon marine incursions δ^{13} Corg shifts to isotopically more depleted marine organic matter. This implies that the investigated source intervals have poor to fair source potential. Only a few intervals of limited thickness in the Upper Mbuo, Nondwa, and Mihambia Formations of the Mita Gamma-1 and East Lika-1 wells, as well as in the Lower Mbuo Formation in the Mbuo-1 well, have been locally enriched. The enrichment is attributed to periodic marine ingressions that have persisted since the Pliensbachian period and suggests the presence of oil generation potential.

A comparison of TOC and programmed pyrolysis borehole data from this study to those compiled from literature in a paleogeographical context reveals high spatial variability. The southeastern and northwestern parts of the study area have the highest source potential, indicating high organic matter productivity in the dysoxic to anoxic water column, which promoted the preservation of organic matter. In contrast, the eastern and western parts generally show low source potential, indicating degraded organic matter and significant terrestrial influxes from emergent land that were deposited in shallow, mixed oxygenated water with low to moderate organic matter productivity.

1. Introduction

Programmed pyrolysis is the standard and most widely used technique for screening petroleum generation and thermal maturity of source rock (Espitalie et al., 1977, Espitalié et al., 1984; Peters, 1986; Lafargue et al., 1998; Dembicki, 2009; Hart and Steen, 2015). Analysis is carried out on a small fraction of samples (~50 mg) and provides a quick evaluation of organic matter (OM) richness via the total organic carbon content (TOC), OM-types (Hydrogen Index) and level of thermal maturity (Tmax) of a source rock. These parameters are commonly reported

in geochemical logs (parameter *vs.* depth), which are useful for mapping the stratigraphic extent of source beds as well as identifying areas where petroleum can accumulate (Peters, 1986; Bordenave et al., 1993; Peters and Cassa, 1994; Dembicki, 2009; Hart and Steen, 2015). This information is crucial for evaluating the petroleum generative potential of a prospective area, and thus programmed pyrolysis is considered as an important guiding tool in petroleum exploration.

Programmed pyrolysis is routinely carried on rock samples collected either from outcrops or core, sidewall core or cuttings samples obtained during drilling to analyze source rock potential. Samples obtained from

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outcropping may be weathered or incomplete for the entire source section and thus problematic or even unsuitable for geochemical analysis (Littke et al., 1991; Bordenave et al., 1993; Ruebsam et al., 2018). Coring is expensive and rarely performed on source intervals, thus making cuttings samples or occasionally side wall core (SWC) more common to evaluate source rock intervals (Bordenave et al., 1993). SWCs collected from stratigraphically well defined geological successions may potentially suffer from small sample size and thus may not be representative of entire source intervals. Cuttings represent a composite samples of rock fragments taken over 3-5m intervals of sedimentary successions, and may be easily impregnated by drill fluid or affected by caving and hence will not provide accurate lithological information at high resolution (Busch et al., 1987; Bordenave et al., 1993; Serra, 2003). As result, limited geochemical analysis on cuttings or sidewall core samples can mislead in evaluation of source quality and quantity. Therefore, sufficient sampling is often required to assess the source potential in a particular area whereby cutting samples taken over a (5-10m) depth interval may still be suitable in non-source regions or in monotonous sedimentary sequences. However, in intervals where source rocks, particularly those of limited extent, are expected, geochemical sampling can be supplemented by geophysical wireline logs, to allow quasi-continuous analysis of source intervals at a higher resolution (~15 cm) and determination of their thickness (Brosse et al., 1988; Passey et al., 1990; Bordenave et al., 1993; Serra, 2003; Godfray and Seetharamaiah, 2019; Gama and Schwark, 2023b).

Lower Jurassic successions that form syn-rift sedimentary packages in the Mandawa Basin consist of three distinct formations (Mbuo, Nondwa, and Mihambia Formations) that are entirely made up by siliclastic, evaporite and carbonate facies. The stratigraphic and lateral distribution of organic matter types and quality of source rock intervals have been poorly investigated due to the limitation in number of wells

drilled, degree of weathering and halokinesis, and incompleteness of outcropping sections (Alconsult and TPDC, 1997; TPDC, 2003; Corelab and TPDC, 2009; Hudson, 2010; McCabe, 2021). Most of the previous geochemical studies were based on a few cuttings/sidewall samples from the sediment of the Nondwa and Mbuo Formations collected from scattered wells (Kagya, 1996; Godfray and Seetharamaiah, 2019; McCabe, 2021). No attempt has been made to constrain the source rock potential in the Mihambia Formation sediment. As a result, both stratigraphic and lateral variability in source qualities with respect to facies changes in the heterolithic Pindiro Group to date have been poorly documented.

This study aimed at constraining organic matter types and quality of source intervals in the Lower Jurassic sediment successions encountered in the Mita Gamma-1, East Lika-1, and Mbuo-1 wells, as well as in the Nondwa evaporitic sequence outcropping in the Mandawa Basin. This was achieved through TOC, programmed pyrolysis, and carbon isotope analysis of cuttings, cores, and outcropping samples.

TOC and programmed pyrolysis data of source rock intervals compiled from the literature (Alconsult and TPDC, 1997; Corelab and TPDC, 2009; McCabe, 2021) were synthesized in this study to better understand how organic matter quality and thermal maturity evolution may be inferred from sediment of other wells (Mandawa-7, Mbate-1, Mihambia-1, Kizimbani-1) not sampled in this study. To further gain insight into factors that regulated organic matter quality distribution during Early Jurassic times in the Mandawa Basin, we examined TOC and programmed pyrolysis data in relation to paleogeography.

2. Geological and stratigraphy setting

The onshore Mandawa Basin (Fig. 1) is one amongst many East African Coastal Basins that evolved in response to the break-up of

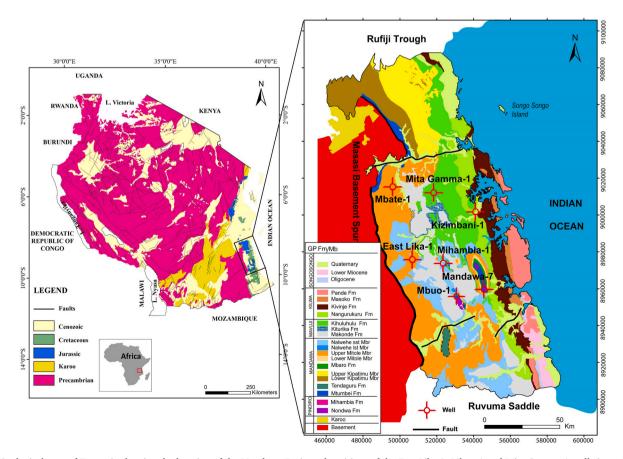


Fig. 1. Geological map of Tanzania showing the location of the Mandawa Basin and positions of the East Lika-1, Mbuo-1 and Mita-Gamma-1 wells investigated as well as Mandawa-7, Mihambia-1, Kizimbani-1 and Mbate-1 wells (adapted from Pinna et al., 2008; Hudson, 2010; Barth et al., 2016).

Gondwana and the drifting of Madagascar during the early Mesozoic era. The Basin is bound to the South by the East-West trending basement high of the Ruvuma saddle, to the North by the Rufiji Trough, to the West by the border fault of the Neoproterozoic Masasi basement spur and covers an area of approximately 15,000 km² (Gama and Schwark, 2023a and references therein).

Early Mesozoic, sedimentation was mainly influenced by tectonics, fluctuations in sea level, and climate (Kent, 1972; Kapilima, 2003; Abay et al., 2019; Caracciolo et al., 2020; Gama and Schwark, 2023b). During the Permo-Triassic era, clastic sedimentation with periodic marine incursions was predominant in the NNE-SSW intracratonic basins (Wopfner, 1994; Mpanda, 1997; Kapilima, 2003; Magohe, 2019; Kiswaka et al., 2023). This was followed by further subsidence and marine ingression during the Toarcian (~180 Ma), which resulted in restricted marine conditions and extensive deposition of evaporites (Geiger, 2004; Geiger and Schweigert, 2006; McCabe, 2021; Mshiu et al., 2022; Gama and Schwark, 2023a). A shift from rifting to drifting occurred around 170 Ma, resulting in the opening of the western Somali and Mozambique Basins. As a result, Madagascar started to drift southward along the N-S trending transform fault of the Davie Fracture Zone (Eagles and König, 2008; Gaina et al., 2013). Seafloor spreading between Madagascar and Africa is believed to have ceased around 120 Ma due to the onset of strike-slip motion between Madagascar and India (Eagles and König, 2008; Reeves, 2018; Fossum, 2019; Fossum et al., 2019).

As a result of the Gondwana breakup, sediment accumulation was mainly marine, coastal, and partly terrestrial, and it persisted into the Neogene period. This resulted in a stratigraphic sequence of five groups listed chronologically as Pindiro, Mandawa, Mavuji, Kilwa, and Songosongo (Hudson, 2010; Fossum et al., 2019). This study focuses on the Lower Jurassic successions (Pindiro Group) that constitute the Mbuo, Nondwa, and Mihambia Formations (Hudson, 2010; Gama and Schwark, 2023a).

The Mbuo Formation rests unconformably on the Precambrian basement and is overlain by the Nondwa Formation. The formation has only been encountered in the subsurface with thickness ranging from 140m to 1770m. The entire succession is mostly composed of thinly interbedded shales, siltstones and coarser to conglomeritic sandstones, with occasional thin limestone beds. The formation is subdivided into two members, the lower member consists of sandstones with siltclaystones and occasional salt-clays while the upper member is mainly made up by thick claystones with alternating thin dolomite beds and occasional thin sandstone beds (Stratadata, 2006; Corelab and TPDC, 2009; Hudson and Nicholas, 2014; Gama and Schwark, 2023a). Strata were deposited in a wide range of depositional environments from alluvial, to fluvial and lacustrine. The Nondwa Formation overlies the Mbuo Formation and is overlain by the Mihambia Formation. It is one of the oldest outcropping sedimentary units in the Mandawa Basin and that comprises thick blocky units of halite interbedded with thinly interbedded anhydrites, shales and carbonates (Stratadata, 2006; Quinton and Copestake, 2007; Corelab and TPDC, 2009; Mshiu et al., 2022). It was deposited in a shallow restricted marine embayment. The true thickness of this formation is difficult to establish in surface outcrops due to salt diapirism and varies greatly in the subsurface from 58 m to 2802 m (Stratadata, 2006; Quinton and Copestake, 2007; Corelab and TPDC, 2009; Hudson and Nicholas, 2014; Mshiu et al., 2022).

The Mihambia Formation lies on the Nondwa Formation and is overlain by the Mtumbei Formation (Stratadata, 2006; Quinton and Copestake, 2007; Corelab and TPDC, 2009; Hudson and Nicholas, 2014). The entire succession consists mainly of clastic with minor carbonates deposited in a shallow marine setting (Alconsult and TPDC, 1997; Quinton and Copestake, 2007; Corelab and TPDC, 2009; Gama and Schwark, 2023a). Mihambia Formation occurs in the subsurface with variable thicknesses ranging from 247 m to 598 m.

3. Materials and methods

3.1. Drill cuttings, core and outcrop sampling and logging

A drill cuttings and core sampling campaign was conducted for three selected boreholes that penetrate Lower Jurassic sediments in the Mandawa Basin. This work took place at the TPDC core repository facility located in Dar es Salaam, Tanzania. Additionally, outcrop sampling and documentation of the Lower Jurassic section was carried out in Mandawa village, located in the Kilwa district, where the Nondwa evaporitic sequence has been exposed due to salt diapirism. A total of 185 drill cuttings, 25 core samples, and 10 outcrop samples were collected during this campaign. The sediment lithotypes documented during sampling were used to reconstruct lithological columns, as shown in Figs. 2–4 and outlined in section 3.2 TOC and programmed pyrolysis analysis (HAWK®).

3.2. TOC analysis and programmed pyrolysis (HAWK)

A total of 98 samples from Lower Jurassic sediments samples were used for TOC analysis and programmed pyrolysis. These samples included 42 cuttings samples from three boreholes, 17 core samples from Mbuo sediments in the Mbuo well and 8 Nondwa outcrop samples. For each of these samples, approximately 50 mg of powdered and homogenized aliquots were subjected to programmed pyrolysis. The latter was conducted using a Wildcat Technologies Hydrocarbon Analyzer workstation (HAWK®) following the standard protocol described in Maende (2017). HAWK analysis is compatible to the Rock Eval methodology (Lafargue et al., 1998) as demonstrated by Birdwell et al. (2017). Programmed pyrolysis delivers multiple parameters for organic matter characterization (e.g. Hart and Steen, 2015) including: S1 (quantity of free hydrocarbons expressed as mgHC/g of rock), S2 (hydrocarbon generative potential expressed as mgHC/g of rock), hydrogen index (HI) (quantity of hydrocarbons generated from the kerogen relative to TOC and expressed as mgHC/g TOC), oxygen index (OI) (quantity of carbon dioxide generated from the kerogen relative to TOC and expressed as mgCO2/g TOC), Tmax (temperature of maximum pyrolysate yield expressed in $^{\circ}\text{C}),$ TOC amount of organic matter expressed in wt% and carbonate carbon expressed in wt%.

3.3. Stable carbon isotopes analysis of organic matter (δ^{13} Corg)

A total of 215 samples of Upper Pliensbachian to Middle Toarcian age were subjected to $\delta^{13} Corg$ analysis for bulk organic carbon, carried out on decarbonized sample material. Prior to analysis, well homogenous powdered samples were treated with hydrochloric acid (HCL, 10% and 25%) to remove inorganic (carbonate -and dolomite-bound) carbon, thereafter sample were washed and neutralized with deionized water and dried in an oven at 40 $^{\circ} C$ for 48h.

Between 20 and 40 mg of decarbonated sample material were weighed into tin capsules and subjected to $\delta^{13}\text{Corg}$ analysis. Stable carbon isotope analysis was performed using a Thermo Instruments Delta V isotope ratio mass spectrometer coupled to a Thermo Instruments Flash EA via a Thermo Instruments Conflow III interface. Carbon isotope ratios are expressed in conventional delta notation: $\delta^{13}\text{C}$ (‰) = [(Rsample - Rstandard)/Rstandard - 1] \times 1000, where R is the ratio of $^{13}\text{C}/^{12}\text{C}$ of the sample and of the V-PDB standard for carbon. Reproducibility and accuracy were monitored by replicate standard and sample analysis and were better than 0.1‰.

4. Results

4.1. Downhole variation in organic matter quality and quantity of three wells based on cutting samples

Variation in OM content and quality of the sediments from three

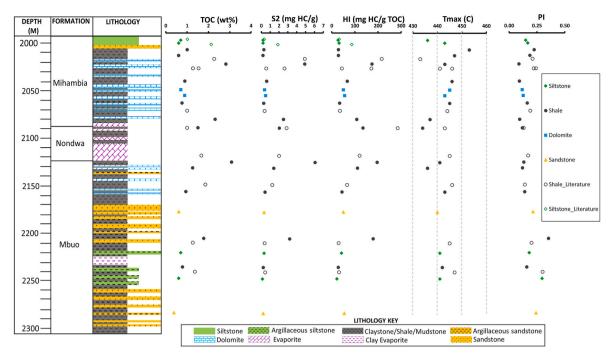


Fig. 2. Downhole variation in total organic carbon (TOC), kerogen yield (S2), Hydrogen Index (HI), Tmax and Production Index (PI) of cuttings samples in sediments from the Mita Gamma-1 well.

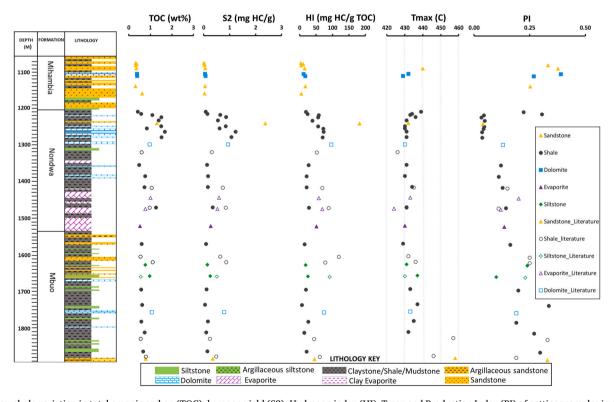


Fig. 3. Downhole variation in total organic carbon (TOC), kerogen yield (S2), Hydrogen index (HI), Tmax and Production Index (PI) of cuttings samples in sediments from the East Lika-1 well.

boreholes investigated are shown in Figs. 2–4. Most of the data indicate that organic matter content and quality determined on the cutting samples varies substantially along stratigraphy (Figs. 2–4). In general, organic matter contents in sediment samples from three wells range from 0.31 to 3.08 wt% with an average of 0.97 wt%, whereas kerogen yield (S2) and HI are generally low, varying from 0.01 to 6.07 (mg HC/

g) with an average 0.64 for S2 and 4 to 220 (mg HC/g TOC) with average 45 (mg HC/g TOC) for HI, respectively. Variation occurred in organic matter contents and quality of cuttings samples from the three wells.

TOC contents in the sediments of Mita Gamma-1 well fluctuate along stratigraphy, they range from 0.38 to 3.08 wt% with average of 1.1 wt%, whereas S2 and HI values are generally low; they vary from 0.13 to 6.07

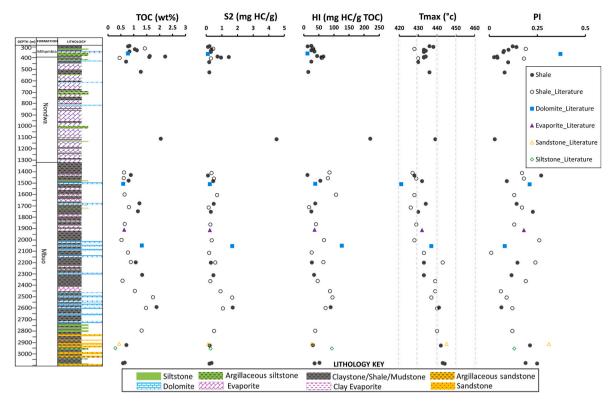


Fig. 4. Downhole variation in total organic carbon (TOC), kerogen yield (S2), Hydrogen index (HI), Tmax and Production Index (PI) of cuttings samples in sediments from the Mbuo-1 well.

(mg HC/g) with an average 1.17 (mg HC/g) and 22 to 196 (mg HC/g TOC) with an average of 72 (mg HC/g TOC), respectively. Sediment samples from the Upper Nondwa and Mihambia Formations in the Mita Gamma-1 well have fair to good petroleum potential whereas, sediment samples from the Mbuo Formation generally exhibit poor source potential. TOC, S2, HI analyzed in the sediments of the East Lika-1 well are generally low, TOC content ranges from 0.31 to 1.67 wt% with an average of 0.75 wt%, whereas S2 varies from 0.01 to 1.23 (mg HC/g) with an average of 0.28 and HI ranges from 4 to 73 (mg HC/g TOC) with an average of 27, respectively. Sediment samples of the Upper Nondwa in the East Lika-1 well exhibit fair source rock potential as opposed to poor source potential in the Mihambia, Lower Nondwa, and Mbuo Formations. While TOC in the sediment of the Mbuo-1 well varies from 0.58 to 2.21 wt% with an average of 1.16 wt%, the S2 fluctuates from 0.11 to 4.49 (mg HC/g) with an average of 0.65 (mg HC/g) and HI values range from 12 to 220 (mg HC/g TOC) with an average of 52 (mg HC/g TOC). Shale samples in the Lower Mbuo Formation show fair source rock potential as opposed to poor potential shown by Nondwa and Mihambia Formations.

Most of the shale samples that are enriched in organic content (TOC ≥ 1 wt %) and with sufficient S2 yield and HI occur in a few localized intervals. These have been encountered in the sediments of Upper Mbuo, Nondwa, and Mihambia Formations in the Mita Gamma-1 and East Lika-1 wells, as well as in the Lower Mbuo Formation in the Mbuo-1 well. Other intervals containing shale, carbonate, evaporite, siltstone and sandstone samples are not enriched (TOC <0.5 wt %) and hence they do not show any enrichment in HI values due to lower S2. Production indices (PI) in source facies (anything not sandstone) fluctuate along stratigraphy with values ranging from (0.03–0.3), unless affected by drilling additives. OM-rich source facies give PI values of only <0.05 (in the East Lika-1 well), <0.1 for Mbuo-1 well (note deeper burial and maturity), Mita Gamma-1 <0.15 (note moderately higher maturity). Consequently, thermal maturity is too low to allow for major petroleum generation and expulsion. Shale samples from sediment that are

enriched in TOC, S2 and HI from all three wells generally show lower PI of <0.25. It appears that both a higher PI (>0.25) and a general trend increasing with depth occurs in sandstone, dolomite and few shale intervals. Hereby, PI increases for well-suited samples from 0.04 to 0.20 in the Mbuo-1 well over a depth of 400–3000 m. In the Mita Gamma-1 well there no increase in PI for source facies, as demonstrated by PI values around 0.10 over a depth range of only 200 m (2000-2200 m). In the East Lika-1 well, organic facies give PI values of 0.04 at 1200 m to approximately 0.25 at 1800 m depth. High porosity and permeability samples (siltstone, dolomite and sandstone) do not exhibit high PI due to low S2 (kerogen-lean). In contrast, high PI values observed over the depths of 2250, 2285, 2178m in the sediments from the Mita Gamma-1 well, and at the depths of 1080-1145, 1890m in the sediments from the East Lika-1 well, and at 350 and 2910m depth from the Mbuo-1 well sediments are attributed to drilling additives. Tmax values for source facies samples with sufficient S2 from all three wells range from 428 to 477 °C. In the East Lika-1 well, they range from 429 to 477 °C with an average 436 °C, whereas in the Mita Gamma-1 well they range from 434 to 453 °C with an average 442 and in the Mbuo-1 well they range from 428 to 435 °C with an average 442 °C. Generally, there is a faint downhole increase in the thermal maturity trend observed in all three wells. Sediment samples from the Mihambia Formation over a depth range 2008-2030 m in the Mita Gamma-1, 1220-1240 m in the East Lika-1, and in 300-550 m in the Mbuo-1 wells show an inverse maturity trend (higher Tmax at a shallower depth). Samples from the Upper Mihambia and Nondwa Formation show moderate generative potential in all three wells, whereas the Lower Mbuo Formation exhibits source rock potential in the Mbuo-1 well only.

4.2. Downhole variation in organic matter quality and quantity of core samples

Variation in OM contents and quality of core samples investigated in the sediment of Mbuo-1 well covering a 12m interval of sedimentary successions are shown in Fig. 5. Generally, both organic matter content and quality vary along the cored section (Fig. 5). TOC values range from 1.42 to 4.83 wt% with an average value of 3.1 wt%. S2 and HI values are generally low, only three samples over a depth range of 2808.8-2809.9 m of the cored section show enrichment with an average S2 and HI of 8.24 (mg HC/g) and 193 (mg HC/g TOC), respectively. Tmax in core samples from the Mbuo-1 well is generally higher compared to cuttings samples in the same well/intervals. Values generally range from 445 to 450 °C, suggesting that Tmax determined from the cuttings samples may be suppressed (Supplement table 1). PI values of core samples vary dramatically along the sedimentary successions of the cored section with average values for source facies of about 0.06, whereas siltstone and sandstones may show higher PI (>0.25) due to impregnation with drill additives. Shale and siltstone over a depth range 2807-2813 exhibit PI values ranging from 0.06 to 0.25 due to low S2 content (organic lean facies). In contrast, three organically enriched shale samples over a depth range of 2808–2809 m possess a very low PI (<0.05), indicative of true petroleum generation potential, as shales are less affected by mud invasion. A comparison of TOC, S2, and HI values in the Mbuo well-1 core samples, averaged over a 5-m interval of the sedimentary successions, to those of cutting samples in the same well revealed compatible results, indicating that shale samples are only enriched to source quality within short sediment intervals in the Mbuo-1 well.

4.3. Variation in organic matter quality and quantity of a Nondwa outcrop section

Variation in OM contents and quality for Nondwa outcrop sediment samples investigated are shown in Fig. 5. It appears that both organic matter contents and quality vary with respect to lithofacies, with shale lithology being more organically enriched than gypsiferous shale (Fig. 5). Within shale the lithology, organic carbon content and quality increase, for example, over a depth interval of 3.8-5.8 m in an outcropping section conforming an internal variability of organic matter in heterolithic successions. Almost all shale samples are enriched in organic carbon (TOC ≥ 1 wt%) and poorly enriched in S2 yield and HI value. TOC in the Nondwa outcropping section ranges from 1.70 to 4.62 wt% with an average of 2.64 wt%, whereas S2 yield and HI values are generally low across the outcropping section. Only two samples located at 4.26-4.96 m and one sample located at 11.3m show enrichment with respect to other samples. S2 and HI values in these intervals are 1.58 (mg HC/g rock) and 51 (mg HC/g TOC) and 6.58 (mg HC/g rock) and 142 mg HC/g TOC, respectively.

Kerogen S2-content and HI of enriched shale samples (organofacies) generally show very low production indices \sim 0; this may be due to evaporative loss of volatiles during surface exposure over prolonged time. When TOC, S2, and HI values in Nondwa shale and gypsiferous shale samples taken at depths of 0–5m and 5–10m in outcropping section are averaged at intervals equivalent to cutting samples, the results are comparable to those obtained from the Nondwa cutting samples collected in the Mbuo-1 well. Values for such a comparison are 2.53 wt%

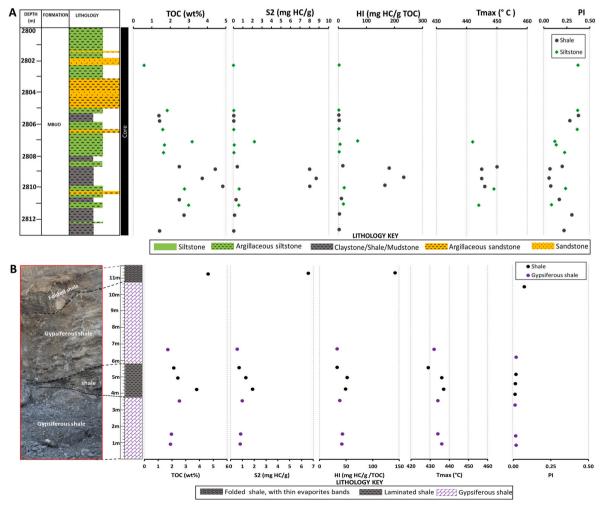


Fig. 5. Variation in TOC, kerogen S2 yield, HI, Tmax, and PI in sediments from: A (Mbuo core), B (outcropping Nondwa evaporitic sequences).

for TOC, 1.16 (mg HC/g rock) for S2, 45 (mg HC/g TOC) for HI versus and 2.82 wt% for TOC, 2.62 (mg HC/g rock) for S2, and 69 (mg HC/g TOC) for HI, respectively. Tmax values determined from outcrop samples generally range from 429 to 437 $^{\circ}\mathrm{C}$ with an average of 434 $^{\circ}\mathrm{C}$, which indicates a maximum burial depth of around 2000–2300m, followed by i.e. 2000-2300 m uplift due salt diapirism.

5. Discussion

5.1. Quality assurance of pyrolysis data

Discussion of organofacies and maturity is based on programmed pyrolysis measurements executed on a few core and outcrop samples but dominantly on cuttings samples, which are prone to alteration, i.e. impregnation with oil-based drilling mud. Hence, data quality assurance is of pivotal importance for interpretation and therefore, the sample suite is differentiated in a suite of best quality samples (termed "organofacies" samples) versus the remainder of the "standard" samples. considered to deliver data of lower suitability for organic geochemical interpretation. Sample quality assurance is based on TOC and S2 content, with samples showing the highest TOC and S2 being considered more reliable (Bordenave et al., 1993); these sample mostly constitute shale lithologies. The remainder of the "standard" samples are important to identify trends along the succession studied and are critically screened for their utility for interpretation. Whereas TOC and HI values of standard samples may reflect primary sample composition, the S1 and PI values are affected and enhanced by mud contamination (Bordenave et al., 1993) to a variable degree, as will be discussed below. Degree of mud contamination is controlled by lithology, with sandstones and siltstones owing to their higher porosity and permeability being more susceptible for mud infiltration. Tmax values exhibit a tendency to be affected by oil-based mud infiltration, which may suppress Tmax values. A threshold of S2 abundance of 1 mg/g TOC here is taken as cutoff value for quality assurance of Tmax values (Supplement table 1), whereas other sources consider a threshold of 2 or even 4 mg/g TOC as appropriate (Bordenave et al., 1993; Peters and Cassa, 1994; Lafargue et al., 1998; Yang and Horsfield, 2020). Utilization of organofacies vs. standard sample data leads to substantial differences in interpretation between both data set, which is discussed in detail below. Above mentioned averaging effects of source quality for cuttings intervals of 3–5 m may explain why individual layers may be more enriched and source prolific as referred to in discussion below when addressing core samples.

5.2. Organic matter types and quality for four different locations

5.2.1. Organic matter quality from cuttings, core and outcrop samples for four different location (3 borehole wells)

The relationship between HI and OI (modified Van Krevelen diagram), S2 and TOC can give indication on the quality of organic matter or kerogen types (Figs. 6 and 7). Most of the cuttings samples from three boreholes analyzed in this study and along with data supplemented from literature have low HI values (<200 mg HC/g TOC) and variable OI values. On a modified Van Krevelen diagram (Fig. 6), almost all samples plot within the kerogen types III to IV fields, with minor populations in mixed types II and III. Generally, for cuttings sediment samples from three wells it appears that HI do not decrease with increasing with thermal maturity (Figs. 3–6). Therefore, minor variation in HI and thus position of the kerogen samples observed in Fig. 6, besides drilling mud alteration, would represent primary compositional differences of the kerogen rather than differences in maturity (Bordenave et al., 1993). Core and outcrop samples plot towards the origin, indicating a higher

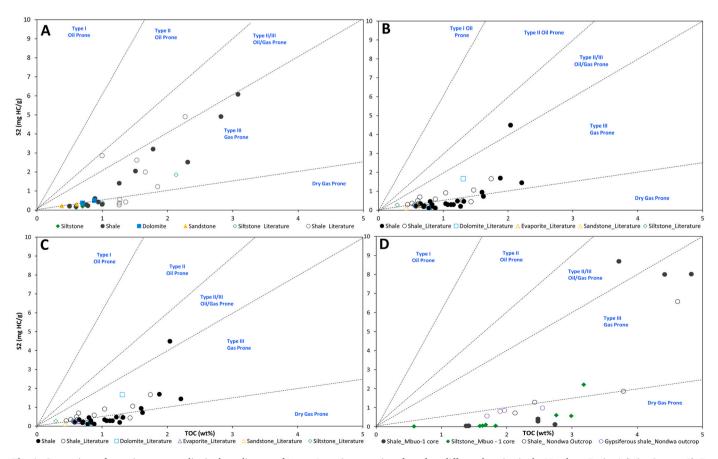


Fig. 6. Comparison of organic matter quality in the sediments of Lower Jurassic successions from four different location in the Mandawa Basin: A (Mita Gamma-1), B (East Lika-1), C (Mbuo-1), D (core and outcrops samples).

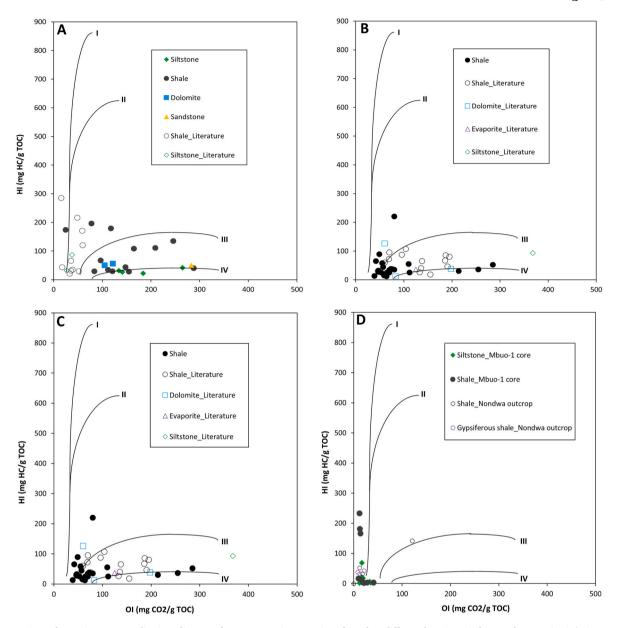


Fig. 7. Comparison of organic matter quality in sediments of Lower Jurassic successions from four different locations in the Mandawa Basin: A (Mita Gamma-1), B (East Lika-1), C (Mbuo-1), D (core and outcrops samples).

and unaltered level of maturity and more refractory composition of organic matter. All sediment samples from the three boreholes show variation in OI, whereas core and outcrop samples plot toward the origin and do not show much variation in OI. The former indicates a differential degree of oxidation in water column, whereas the latter indicates high degree of maturity of the core and outcrop samples. Consequently, the best quality organofacies samples plot in the II/III fields, whereas the standard samples due to both poor preservation during deposition via aerobic degradation and alteration upon drilling show a refractory and oxidized composition. In addition, storage of cuttings due to their large surface area may have affected organic matter by secondary oxidation, which is prone to decrease HI and increase OI (Bordenave et al., 1993; Jarvie et al., 2004). Based on the presence of kerogen III and mixed types of kerogens in the samples, it is evident that most shale samples are primarily gas-prone, while other samples are unsuitable to generate hydrocarbons and very few samples are oil-prone. The TOC vs. S2 binary plot (Fig. 7) reveals a very minor differences in OM composition, with almost all samples scattered in kerogen type-III/IV fields and a minority in the mixed kerogen type II-III. Almost 50% of the cuttings samples as well as core and outcrop samples that have TOC concentration < 1 wt %, exhibit low hydrocarbon source potential.

5.3. Comparison of organic matter maturity of four locations in the Mandawa Basin

5.3.1. Organic matter types versus maturity

Thermal maturity is another important factor for source rock evaluation, in addition to organic richness and quality (Espitalie et al., 1977, Espitalié et al., 1984; Peters, 1986; Lafargue et al., 1998; Dembicki, 2009; Yang and Horsfield, 2020). Comparison of the downhole variation of Tmax of cuttings samples from three boreholes, core, and outcrop samples (Figs. 2–5) indicates a wide range of thermal maturity, ranging from onset of to within to the mature stage of the oil window. In this study a Tmax vs. HI binary plot (Fig. 8) was used to evaluate the effect of thermal maturity on organic matter for the sediment of Lower Jurassic successions in the Mandawa Basin. Comparison of the Tmax vs. HI binary plot for four locations in the basin indicates that most of the organo-facies samples are mainly composed of Type III/IV kerogens and

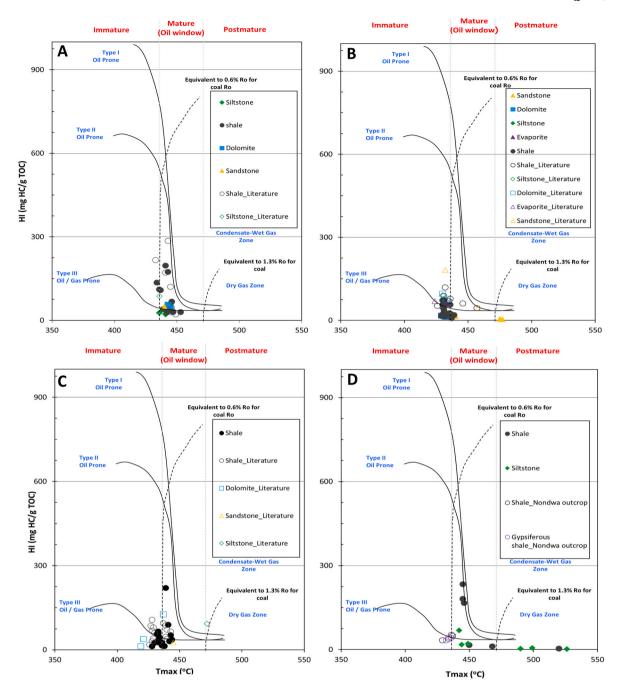


Fig. 8. Comparison of organic matter quality vs. maturity in the sediments of Lower Jurassic successions from four different locations in the Mandawa Basin: A (Mita Gamma-1), B (East Lika-1), C (Mbuo-1), D (Core and outcrops samples).

are within the onset to mature oil window zones with respect to the organic matter level of maturity. An average Tmax for samples analyzed from the sediment of Mita Gamma-1 is 440 $^{\circ}$ C (oil window zone, whereas, in the East Lika-1 and Mbuo-1 wells is 435 $^{\circ}$ C (onset of oil window). Differences in Tmax indicate differences in burial history between the three locations.

In general, sandstone and siltstone of the cuttings samples from the three wells display a higher level of Tmax, possibly due to drilling alteration. Average Tmax of the outcrop samples is 435 $^{\circ}\text{C}$ (onset of oil window), whereas core samples are more mature (450 $^{\circ}\text{C}$) compared to other samples. Comparison of the Tmax values determined from core samples in the sediments of the Mbuo Formation (2002–2014m) to those of cuttings intervals (2800m) in the same well (Mbuo well-1) suggests that the Tmax values of the cuttings sample are suppressed due to oil

impregnation. A comparison of the Tmax of Nondwa sediments from outcrop samples with those from drill holes indicates that outcrop samples have a higher Tmax because of deeper burial. Consequently, we suggest that the outcrop succession was buried approximately 2000–2300 m and then uplifted by salt diapirism.

5.3.2. Quality of organic matter with respect to maturity

Stable carbon isotope ratios are commonly employed to trace the origin and fate of OM, to distinguish between marine and terrestrial plant sources and to identify OM that derived from land plants using the C3 or the C4 photosynthetic pathway (Buchardt et al., 1986; Hollander et al., 1992; Tyson, 1995; Meyers, 2003; Bauersachs et al., 2014). The HI corresponds to the quantity of pyrolyzable organic compounds relative to the total organic carbon in the samples, which is sensitive to maturity

as opposed to the organic carbon isotope signature ($\delta^{13}C_{org}$), which is an indicator of the facies and types of organic matter that within the temperature range of the oil window is not affected by maturity (Bordenave et al., 1993). These two parameters were employed in the $\delta^{13}C_{org}$ vs. HI binary diagram (Fig. 9) in order to assess, if there is variation in the type of organic matter in sediments of Lower Jurassic successions in the Mandawa Basin. Most of the samples displayed in the $\delta^{13}C_{org}$ vs. HI binary diagram (Fig. 9) show two main trends: Lower HI and heavier isotopic composition vs. higher HI and lighter isotopic composition of organic matter (Fig. 9). The $\delta^{13}C_{org}$ vs. HI binary diagram (Fig. 9a,c,d) shows a broad isotopic composition range of -19.6 to -27.2% in samples from Mita Gamma-1, East Lika-1, Mbuo-1, and outcrop sediments, in contrast to the narrow range of -19.8 to -23.5% observed in East Lika-1 sediments (Fig. 9b). $\delta^{13} C_{org}$ variability may indicate changes in the proportion of marine (δ^{13} Corg: 24 to -28% VPDB) vs. terrestrial organic matter (δ^{13} Corg: 22 to -24% VPDB). For the Jurassic sediments, heavier isotopes values indicate terrestrial organic matter, whereas lighter isotopic composition corresponds to marine organic matter (Tyson, 1995). Based on the observed $\delta^{13}C_{org}$ vs. HI data trend (Fig. 9), most of studied sample are predominantly derived from terrigenous organic matter, with only smaller proportions of marine organic matter. Terrestrial-marine transitional samples show mixed OM isotope and quality signatures. We therefore suggest that low HI values with corresponding heavier carbon isotopic composition (δ^{13} Corg: 22 to -24%VPDB) point to depositional systems with high sediment influxes and probably transitioning from fluvial-lacustrine towards lacustrine to restricted marine conditions in an evolving rift basin. In contrast, changes in preservation conditions due to marine ingression resulted in an increase in HI and a shift to lighter isotopic composition. Low HI and intermediate isotopic composition of sediments indicate that organic matter is possibly sourced from a mixed terrestrial-marine environment. The occurrence of organic matter with lighter carbon isotopic composition (δ^{13} Corg: 24 to -28% VPDB) observed in the sediment samples of the Nondwa, Mihambia, and Mbuo Formations in the four locations,

suggest that the Mandawa Basin experienced a short-lived marine incursion over a long time due to rifting, accompanied by an increase in sea level.

5.4. Comparison of organic matter quantity and quality for all wells drilled in the Mandawa Basin

To further understand how petroleum potential, thermal maturity evolution, and paleogeography in the Mandawa Basin evolved, the study integrated data published from other wells drilled in the basin. The TOC and Rock Eval datasets of four wells (Mandawa-7, Mbate-1, Mihambia-1, and Kizimbani-1 wells) collected from either published or unpublished literature (Alconsult and TPDC, 1997; Corelab and TPDC, 2009; McCabe, 2021) were synthesized in this study.

A modified Van Krevelen diagram (Fig. 10a) and TOC vs. total hydrocarbon yield binary plots (Fig. 10b) is used for source, facies and maturity assessment. Three trends of organic matter quality/types could be deduced (Fig. 10a): Recalcitrant (reworked organic matter with variable OI), terrigenous kerogen type-III and aquatic material of kerogen type-II/III in the sediments of Mandawa-7, Mbate-1 and occasionally in sediments from the Mbuo-1, East Lika-1 and Mita Gamma-1 wells. Almost 80% of all sediment samples either generated from this study or compiled from literature show poor generation potential. Samples from sediments of Mandawa-7 and Mbate-1 show goodexcellent source potential and the few samples from the Mita Gamma-1, East Lika-1, and the Mbuo-1 core that show fair to good source potential imply better preservation and a preferentially aquatic marine organic matter deposited upon marine incursions. Core samples from sediment of the Mbuo-1 well have high TOC compared to other samples but they have poor generation potential due to the recalcitrant nature of the organic matter. Comparison of the Tmax vs. HI binary plot (Fig. 11a) from 7 locations indicate that most of the samples are mainly composed of Type II, mixed II/III to III/IV kerogens and with respect to the organic matter level of maturity are within the onset to mature oil window

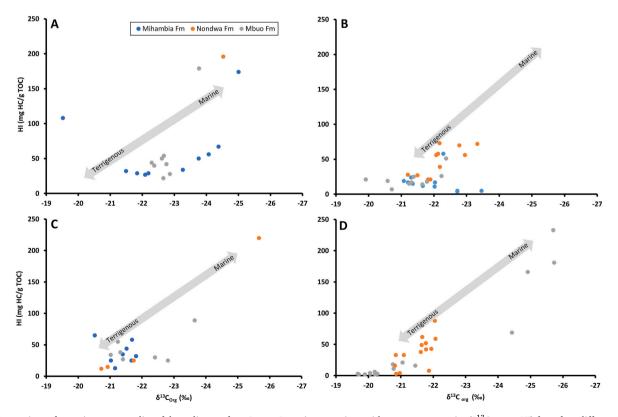


Fig. 9. Comparison of organic matter quality of the sediments from Lower Jurassic successions with respect to maturity (δ^{13} Corg vs. HI) from four different locations in the Mandawa Basin: A (Mita Gamma-1), B (East Lika-1), C (Mbuo-1), D (core and outcrops samples).

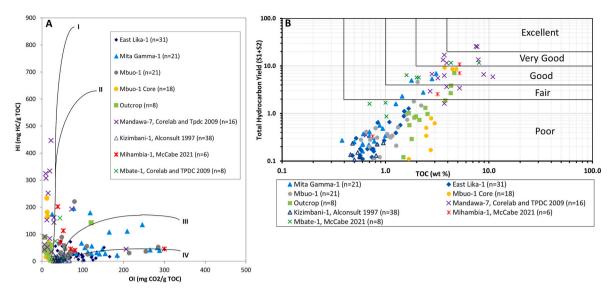


Fig. 10. Comparison of organic matter quality of Lower Jurassic intervals from all wells in the Mandawa Basin using: A (Modified Van Krevelen diagram) and B (TOC versus total hydrocarbon yield). Data from Kizimbani-1, Mihambia-1, Mandawa-7, Mbate-1 wells have been compiled from literature (Alconsult and TPDC, 1997; Corelab and TPDC, 2009; McCabe, 2021).

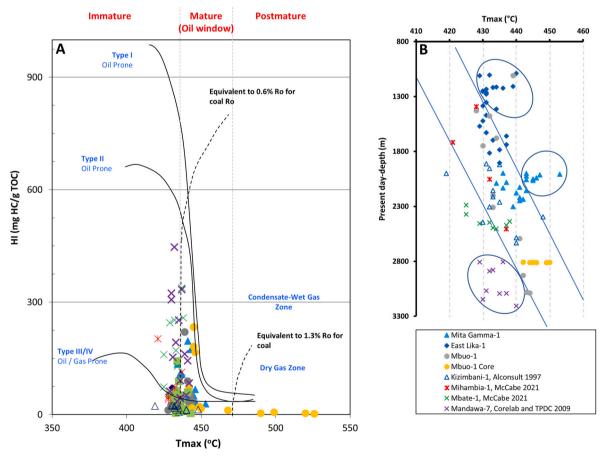


Fig. 11. Comparison of organic matter quality of all wells from the Mandawa Basin using: A (Tmax vs. HI) and B (Tmax vs. present day depth). Data from Kizimbani-1, Mihambia-1, Mandawa-7, Mbate-1 wells have been compiled from literature (Alconsult and TPDC, 1997; Corelab and TPDC, 2009; McCabe, 2021).

zones. This indicates that the Lower Jurassic sediments in the Mandawa Basin have been deeply buried and sediments have undergone thermal alteration, whereby slight differences in Tmax across wells would indicate different burial histories. Deeper burial is evident from the unaltered core samples of the Mbuo Formation in the Mbuo-1 well. There are

obvious differences between HI values from sediments of the Mandawa-7 vs. Mbate-1 wells, and other wells at low maturity that may be due to the sedimentary environment (different types of organic matter).

To further constrain maturity evolution of Lower Jurassic sediments in the Mandawa Basin, Tmax vs. present day depth plots were used

(Fig. 11b). In general, the Tmax data from sediment samples from all wells plotted according to present-day depths show an increasing maturity trend with depths. However, a few sediment samples from the East Lika-1, Mita Gamma-1, and Mandawa-7 wells exhibit inverse maturation trends at a given depth. The two former exhibit Tmax values seemingly too high, whereas the latter exhibits Tmax values too low (Fig. 11b). It is unlikely that an uplift of 1000m is responsible for the elevated Tmax in the East Lika-1 and Mita Gamma-1 wells, since other samples in the wells do not show this unusual trend. Consequently, this study proposes that the anomalously elevated Tmax derive from different types of organic matter (recalcitrant/reworked organic matter or of previously coalified materials) that can be linked to the relative position of deposition sites to the hinterland. During Pliensbachian -Toarcian times, high sediment influxes occurred in the East (Mita-Gamma-1) and West (East Lika-1) of the Mandawa Basin, which allowed deposition of reworked sediment at the basin margin as observed in these two wells. Moreover, Tmax may be suppressed due to the presence of thermally labile kerogen that may show elevated HI and high TOC (Snowdon, 1995), features that are similar to those found in the Nondwa sediment in Mandawa-7 well. Thus, the suppression of Tmax at a depth of 2800-3300m in the Mandawa-7 well sediment is proposed to be caused by oil-prone organic matter (algal type). There is no evidence for this Tmax suppression to be caused by evaporitic thermal retardation since it does not occur in other wells that contain this lithology.

5.5. Palaeogeographical control of source rock source rock potential

Paleogeography is controlled by interaction between tectonic processes, sea level fluctuations, and local climate and will influence sediment accommodation, types, and facies in both marine and continental depositional environments (Herbin et al., 1995; Leanza et al., 2000; Stasiuk and Fowler, 2004; Scotese, 2014; Cao et al., 2017; Gama and Schwark, 2023a). Therefore, spatial and temporal variations in organic matter recorded in sediment archives can be linked with the paleogeographical history of a particular area.

During the Late Triassic to Early Jurassic times, the Mandawa Basin

was a rift basin, which propagated northeast between the Matandu and Mbwemkuru lineaments (Figs. 12 and 13), (Hudson, 2010; for a review see Gama and Schwark, 2023a). This rifting event is attributed to the regional extension between East Africa and Madagascar. The interplay between rifting events, sea level changes and local climate dominated the paleogeographic evolution of the Mandawa Basin. This interaction led to the creation of accommodation space, formation of paleo-highs and regulation of sedimentation patterns in the basin. As result, the southern and central parts of the basin subsided at a much higher rate than the adjacent areas and formed the deepest part of the basin. Other parts of the basin such as at the western (Masasi Basement spur), eastern (Kiswere, Pande and Kizimbani), and southern margin (Ruvuma saddle) remained as structural highs and sourced most of the continental sediment into the basin. To understand the paleogeographical control of source rock potential of Lower Jurassic sediments in the Mandawa Basin, paleogeographical maps for two time slices that constitute the Pliensbachian and the Toarcian were reconstructed with respect to the position of the seven wells that penetrated Lower Jurassic successions in the Mandawa Basin (Figs. 12 and 13). TOC and programmed pyrolysis data from sediments of Lower Jurassic successions from four wells collected from the literature and those from three wells generated in this study were averaged and plotted on the Pliensbachian, respective Toarcian paleogeographic maps (Figs. 12 and 13).

5.5.1. Palaeogeographical control of source rock source rock potential during the Pliensbachian (Mbuo Formation)

The Mandawa Basin during the Pliensbachian was considered to be a small endorheic basin, as the Masasi basement spurs and the Eastern rift high acted as barrier to rivers draining the hinterland from the West and East, thus any established rivers would probably be flowing through the Malagasy trough to the North (McCabe, 2021; Gama and Schwark, 2023a). These two paleo-highs were positioned at the eastern and western basin margin, with two depocenters located in South of the Mbate-1 and Mbuo-1 wells, constituting an important paleogeographical element during Pliensbachian times. Sedimentation was mainly continental to partly marine controlled by variations in sea-level and

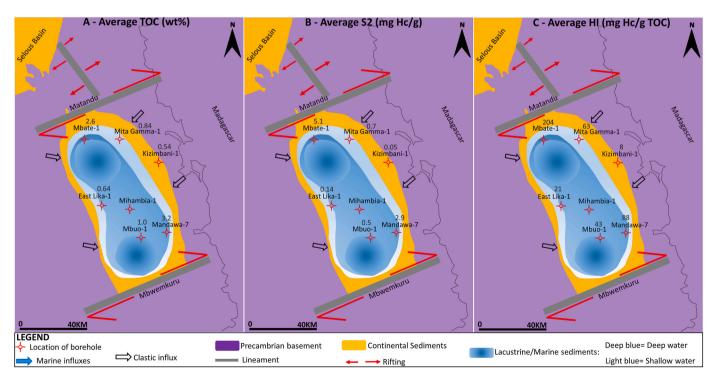


Fig. 12. Comparison of source rock quantity (TOC) and quality (S2, HI) of sediments from 7 wells in Mandawa Basin with respect to paleogeography during the Pliensbachian (Mbuo Formation). Paleogeographical map is adapted from (Hudson and Nicholas, 2014; Mccabe, 2021; Gama and Schwark, 2023a). Data from Kizimbani-1, Mandawa-7, Mbate-1 wells have been compiled from the literature (Alconsult and TPDC, 1997; Corelab and TPDC, 2009; McCabe, 2021).

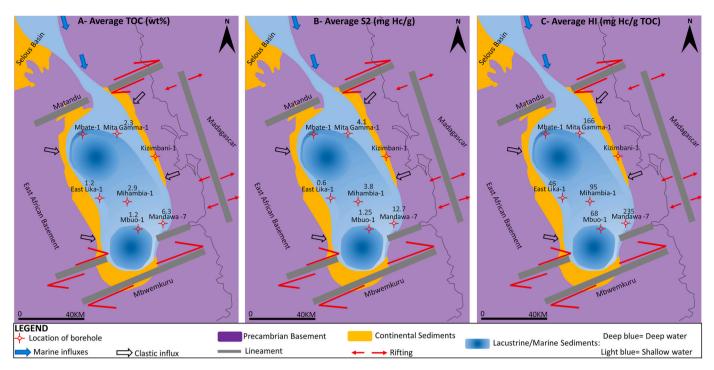


Fig. 13. Comparison of source quantity (TOC) and quality (S2, HI) of sediments from six wells in the Mandawa Basin in relation to paleogeography during the early Toarcian (Nondwa Formation). Paleogeographical map is adapted from (Hudson and Nicholas, 2014; Mccabe, 2021, Gama and Schwark, 2023). Data from Kizimbani-1, Mandawa-7, Mihambia-1 wells have been compiled from the literature (Alconsult and TPDC, 1997; Corelab and TPDC, 2009; McCabe, 2021).

tectonics (Fig. 12). During sea level lowstand, deposition of continental sediments was limited to the basin margins, whereas coastal wetland to lacustrine/evaporitic conditions prevailed in the southern basin centre, which mostly likely was flooded during short-lived sea level highstands. The paleogeographical map indicates that sediment of the Mbuo Formation showed a wide range of depositional environment, ranging from continental, shallow, to deeper lake in dependence of distance to the sediment source area. These differences in depositional conditions would suggest variations in the nature and preservation conditions of organic matter across drill sites. TOC and programmed pyrolysis data in sediments of the Mbuo Formation on the paleogeographic map show relatively elevated values in the northern (Mbate-1 well) and in nouthern (Mandawa -7 and Mbuo -1 wells) parts, and generally lower values (TOC <1 wt%, S2 <1, and HI < 50) in the eastern (Mita Gamma-1, Kizimbani-1) and western (East Lika-1) parts of the basin (Fig. 12). This observation points to variable deposition and preservation conditions of organic matter at these sites, whereby large accommodation space located in the northern and southern parts was more favorable for organic matter preservation, as opposed to the western and eastern part that correspond to the basement high terraces of the basin margin, where organic matter was easily destroyed by oxidation and diluted by clastic input.

5.5.2. Palaeogeographical controls of source rock source rock potential during the Toarcian (Nondwa Formation)

Continued rifting during the Toarcian coincided with transgression, resulting in an opening between the Mandawa Basin and Malagasy Trough that allowed marine in-/transgression, which led to deposition of regional source and cap rocks such as the Nondwa Shale (Gama and Schwark, 2022) (Fig. 13). Existing paleo-highs in the western and eastern parts, rise in sea level and differential subsidence affected the paleogeographic evolution of the area. Sedimentation was mainly marine with partial terrigenous influx along the East-West margins. The paleogeographic map of the Toarcian period shows variations in TOC and programmed pyrolysis data for sediments of the Nondwa Formation penetrated by 5 wells, with higher average TOC, S2 and HI values than

in sediments from the Mbuo Formation, which is attributed to the Toarcian transgression and rifting that enhanced organic matter preservation conditions (Fig. 12). Palaeogeographical maps show that the average TOC values in Nondwa sediment are all ≥1 wt%, with the highest values found in the Mandawa-7 and Mihambia-1 wells. The source rock potential (S2, HI) varies spatially, with the highest values observed in the southeastern and northwestern parts, suggesting that these areas were more favorable for the deposition and preservation of organic matter. Low source rock potential, observed in the Mihambia-1, Mbuo-1, East Lika-1 wells on the palaeogeographical maps (Fig. 13), would indicate degraded organic matter and significant terrestrial influx from the emerging lands in the western and eastern parts. These sediments were probably deposited in shallow, well-mixed and oxygenated waters with low to moderate productivity. The high source rock potential observed in the sediment of the Mandawa-7 well indicates that the southwestern area had persistently high productivity in the surface water accompanied by a dysoxic to anoxic water column, which promoted the preservation of organic matter.

The observed distribution in TOC and source rock potential of the sediment in Mandawa Basin displayed on the paleogeographical maps may be related to changes in depositional conditions in an evolving rift basin, driven by changes in relative subsidence, eustatic sea level and sediment influx. Organic matter was poorly preserved when high sediment flux exceeds subsidence rate, generally in the eastern and western but also southern part. Whenever high subsidence rates coupled to eustatic rise in sea level and lower sediment supply occurred, this enhanced productivity and preservation of organic matter in deep lake to restricted marginal marine conditions as shown in the Mandawa-7 well.

6. Conclusions

In this study, organic matter types and qualities in sediments of Lower Jurassic successions (Mbuo, Nondwa and Mihambia Formations) in the Mandawa Basin, SE Tanzania, have been characterized by programmed pyrolysis and isotope analysis. Programmed pyrolysis data show that organic matter is composed mainly of type III (gas prone) to IV (inert) kerogens with lesser contribution by mixed type II-III kerogen (oil-gas prone). Sediments have been deeply buried (>2000m) and undergone a wide range of thermal diagenesis, from early to overmature stages. Isotopic composition ($\delta^{13}C_{org}$) data of organic matter are consistent with pyrolytic kerogen typing, indicating preferentially terrestrial organic matter sources that changed to marine organic matter upon marine incursions, accompanied by a shift from heavier (–19 to –22‰ V-PDB) to lighter (–24 to –27‰ V-PDB) isotopic composition.

The data indicate that source intervals found within the sediments of Lower Jurassic successions from the Mbuo-1, East Lika-1 and Mita Gamma-1 wells have poor to fair source rock potential. There are only few intervals in the Upper Mbuo, Nondwa, and Mihambia Formations in the Mita Gamma-1 and East Lika-1 wells, as well as in the Lower Mbuo Formation in the Mbuo-1 well that have been locally enriched due to periodic marine ingression that persisted since the Pliensbachian period. This finding has implications on source rock screening in the Mandawa Basin, as most of the previous studies were based on a few samples per formation that only provided discrete points in the heterogenous and thick Pindiro Group. More detailed sampling and data quality assurance in this study allowed identification of source rock intervals and their stratigraphic variability. Synthesis of data generated in this study with literature data was used to reconstruct organic facies in a paleogeographical context revealing that the southeastern and northwestern parts of the study area appeared to have the highest source potential. This is attributed to enhanced organic matter surface productivity and preservation in the dysoxic to anoxic water column. In contrast, the eastern and western parts generally show low source potential, indicating degraded organic matter and significant terrestrial influx from emerging lands that were deposited in shallow, well-mixed and oxygenated water with low to moderate organic matter productivity.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in the submitted manuscript.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.marpetgeo.2023.106505.

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