



Using Iron and Sulphur Ratio Against Biomarkers to Delineate Oil Accumulation Depth in the Niger Delta

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ABSTRACT :

Iron/vanadium (Fe/V) and dibenzothiophene/phenanthrene (DBT/P) ratios are widely used, independently, as proxies for detrital input and reduced-sulphur availability during source-rock deposition. This study brings the two together, alongside a suite of biomarker maturity and source-input ratios, for six Niger Delta oils (Utorogu, Ohaji, Abo, Escravos, Bonga, and Agbada), to test whether their combined signature can help differentiate the relative burial or accumulation position of oils across the basin. Two facies groups emerge consistently across Fe/V, V/Ni, and DBT/P zonation: a low-Fe/V, high-V/Ni group (Utorogu, Ohaji) linked to restricted, reducing, terrestrially influenced settings, and a high-Fe/V, low-V/Ni group (Escravos, Bonga, Agbada) linked to more detrital-rich, sub-oxic marine to outer-delta settings, with Abo occupying an intermediate position. Biomarker maturity indices (S/(S+R) C₃₁ hopane), however, cluster tightly around 0.6–0.7 across all six wells, indicating a broadly uniform thermal history that does not track the Fe/V-DBT/P grouping. This suggests that, in the present dataset, iron and sulphur-proxy variability is controlled more by source facies and depositional redox than by differential burial depth. Because no elemental iron or sulphur measurements and no direct reservoir depth data were available for these samples, the iron and sulphur components of this study are represented by proxies (Fe/V and DBT/P) rather than bulk elemental values, and the conclusions regarding accumulation depth are offered as a testable framework rather than a calibrated depth model. A path toward a fully quantitative version of this approach combining a degree-of-pyritization-type iron–sulphur index with depth-tagged samples is outlined for future work.

Keywords: Iron/vanadium ratio; dibenzothiophene/phenanthrene; biomarker maturity; degree of pyritization; oil accumulation depth; Niger Delta

1. Introduction

Trace-metal and biomarker ratios are routinely used, each on their own terms, to reconstruct the source, redox conditions, and thermal maturity of petroleum systems. Vanadium and nickel concentrations track redox state and organic-matter type (Lewan, 1984), the dibenzothiophene/phenanthrene (DBT/P) ratio tracks the availability of reduced sulphur during deposition (Hughes, Holba, & Dzou, 1995), and hopane and sterane isomerization ratios track thermal maturity and, by extension, relative burial history (Peters, Walters, & Moldowan, 2005). What is less commonly attempted is bringing an iron-related trace-metal ratio, a sulphur-related aromatic ratio, and biomarker maturity together into a single framework aimed specifically at the question of accumulation or burial depth.

Iron is a natural candidate for this because its diagenetic fate is tightly linked to sulphur: under anoxic, sulphidic conditions, reactive iron is progressively converted to pyrite, and the degree to which this occurs — the degree of pyritization, or DOP — is a well-established indicator of bottom-water oxygenation and, indirectly, of the depositional setting in which a source rock accumulated (Raiswell & Berner, 1986; Raiswell, Buckley, Berner, & Anderson, 1988). If an iron–sulphur relationship of this kind is preserved, even indirectly, in the trace-metal and aromatic-sulphur signatures of the oils generated from a source rock, then combining it with independent, maturity-based evidence of burial history offers a plausible route toward differentiating oils by their relative accumulation depth within a basin.

This paper takes a first, deliberately cautious step in that direction using existing Niger Delta datasets. It does not have elemental iron or sulphur concentrations, nor does it have measured reservoir depths for the sample set; what it has is trace-metal ratios (V, Ni, Fe/V), the DBT/P sulphur-availability proxy, and a battery of biomarker source and maturity ratios for six wells. The objective is therefore narrower than the title might suggest at first glance: to test whether iron and sulphur proxies, read alongside biomarker maturity, produce a coherent and internally consistent picture that could support a genuine depth-calibration study once elemental and depth data become available, and to be explicit about where the present evidence stops

short of that goal.

2. Geological Setting

The Niger Delta Basin, located in southern Nigeria, developed during the separation of the African and South American plates in the Mesozoic and has since prograded seaward under a regime of rapid clastic sedimentation and syn-depositional deformation (Doust & Omatsola, 1990). Three diachronous lithostratigraphic units are recognised: the marine, prodelta Akata Formation shales, which form the principal source rock; the paralic, sand-shale alternations of the Agbada Formation, which host most of the reservoirs; and the continental Benin Formation. The basin is divided into a series of depobelts that migrated basinward through time, each with its own local subsidence and sediment-supply history — a structural framework that, in principle, should leave a trace-metal and biomarker signature reflecting each depobelt's particular mix of marine and terrestrial input, redox conditions, and burial history. The six wells examined here (Utorogu, Ohaji, Abo, Escravos, Bonga, and Agbada) sample different parts of this depobelt system.

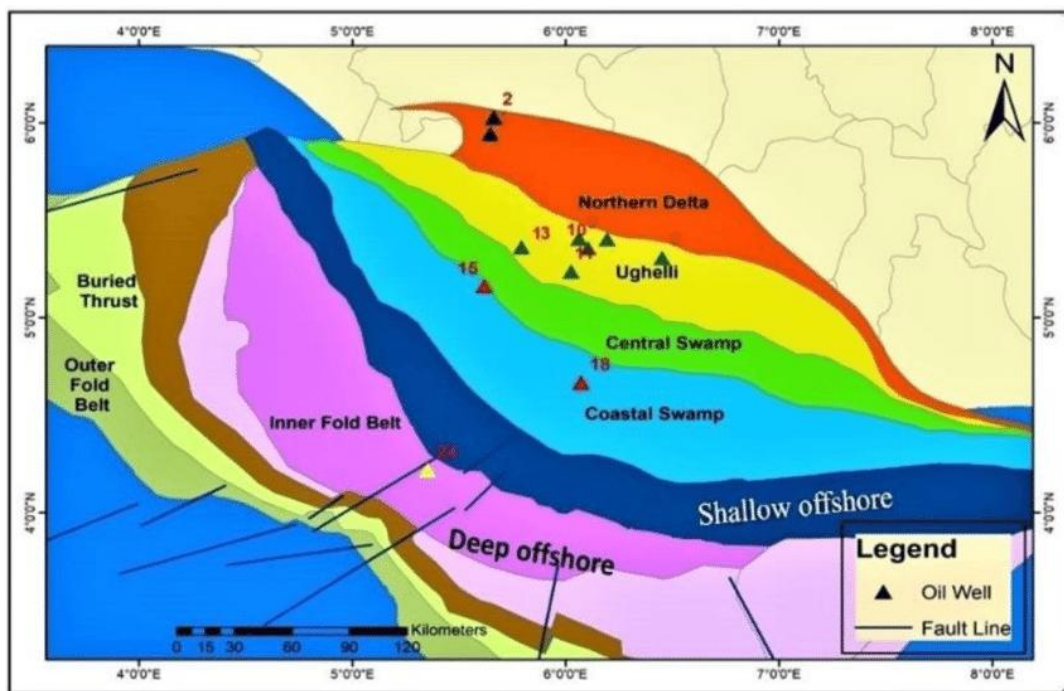


Figure 1: Map of Niger Delta Basin Showing different Depobelts (Doust, & Omatsola, 1990)

3. Theoretical Background

3.1 Iron and Vanadium as Detrital and Redox Proxies

Vanadium is preferentially incorporated into organic matter as vanadyl porphyrins under reducing, organic-rich conditions, while nickel is less redox-selective and more associated with detrital or terrestrial input (Lewan, 1984). The Fe/V ratio used in this study extends the same logic: because iron is supplied largely by detrital clay and iron-oxide/iron-sulfide phases rather than by direct incorporation into porphyrin structures, a high Fe/V ratio is generally read as evidence of stronger clastic dilution of the source interval, while a low Fe/V ratio points to a more organic-rich, less detrital-diluted, and potentially more reducing depositional setting.

3.2 DBT/P as a Sulphur-Availability Proxy

Hughes, Holba, and Dzou (1995) showed that the ratio of dibenzothiophene to phenanthrene, cross-plotted against pristane/phytane, separates source rocks into depositional and lithological fields on the basis of two largely independent controls: DBT/P reflects the availability of reduced sulphur species for incorporation into the forming kerogen (itself a function of sulphate supply and the degree of water-column or pore-water anoxia), while Pr/Ph reflects the oxicity of the depositional environment more generally. Because DBT/P is sensitive specifically to sulphur incorporation rather than to redox state alone, it is used here as the sulphur-related proxy in place of a bulk elemental sulphur measurement.

3.3 Biomarker Maturity as a Burial-History Proxy

Hopane and sterane isomerization ratios evolve systematically and largely irreversibly with increasing thermal stress, which in a single burial history is itself a function of depth and residence time. The S/(S+R) ratio at C₃₁ rises from a biological value near zero to an equilibrium value of approximately 0.57–0.62 as maturity increases (Peters, Walters, & Moldowan, 2005), after which further burial cannot be resolved by this ratio alone — it saturates. Moretane/hopane ratios behave in a complementary way, decreasing with maturity as the thermodynamically less stable moretane ($\beta\beta$) configuration converts to the hopane ($\alpha\beta$) configuration. Used together, these ratios provide an indirect, and in the present study the only available, proxy for the relative thermal/burial history of the sampled oils.

3.4 The Missing Link: An Elemental Iron–Sulphur Diagenetic Index

A fully quantitative iron–sulphur burial-depth index would most naturally be built around a degree-of-pyritization-type parameter — the proportion of reactive iron converted to pyrite (Raiswell & Berner, 1986) — calibrated against depth-tagged samples, with DOP values below about 0.46 associated with oxic bottom waters, 0.46–0.75 with dysoxic or restricted conditions, and above 0.75 with euxinic conditions (Raiswell, Buckley, Berner, & Anderson, 1988). This requires direct measurement of pyritic and acid-soluble iron and total sulphur on rock or oil samples, none of which is available in the present dataset. Section 6 returns to this point as the central limitation of the present analysis and the specific data gap that would need to be closed to test the depth-delineation hypothesis directly.

4. Materials and Methods

This study is a secondary, integrative analysis of existing trace-metal and biomarker datasets for six Niger Delta oils (Utorogu, Ohaji, Abo, Escravos, Bonga, and Agbada), compiled from prior GC-MS and ICP-based geochemical work on these wells. Table 1 lists the parameters used and their source. No new laboratory analyses were carried out for this paper.

Important scope note. Two substitutions were necessary and are treated as a core finding of the study rather than an incidental limitation:

- (i) “Iron” is represented here by the Fe/V ratio derived from whole-oil trace-metal analysis, not by an elemental iron concentration or a rock-based degree-of-pyritization measurement.
- (ii) “Sulphur” is represented by the DBT/P ratio, an aromatic-hydrocarbon biomarker proxy for reduced-sulphur incorporation (Hughes et al., 1995), not by a bulk elemental sulphur (wt%) measurement.
- (iii) No reservoir or accumulation depth values were available for any of the six wells. Relative burial/thermal history is inferred instead from the C₃₁ hopane S/(S+R) isomerization ratio and, qualitatively, from the moretane/hopane and extended-hopane (C_{31–35}/C_{30–35}) ratios.

Table 1: Parameters Used, What They Represent, and What They Substitute For

Parameter	Represents	Direct measurement it substitutes for
Fe/V ratio	Detrital/clastic input, indirectly redox	Elemental Fe (wt% or ppm); degree of pyritization
DBT/P ratio	Reduced-sulphur availability at deposition	Elemental S (wt%)
V/Ni ratio	Redox state of depositional environment	— (used as originally defined)
S/(S+R) C ₃₁ hopane	Thermal maturity (isomerization)	Vitrinite reflectance / measured depth
Moretane/C ₃₀ hopane	Thermal maturity (isomerization)	Vitrinite reflectance / measured depth
C ₂₇ /C ₂₉ , C ₂₈ /C ₂₉ sterane	Organic-matter source (marine vs. terrestrial)	— (used as originally defined)
Oleanane/C ₃₀ hopane	Angiosperm/terrestrial input	— (used as originally defined)

5. Results

Table 2 reports the trace-metal and biomarker ratios for the six wells with a complete parameter suite. Fe/V ranges from 2.14 (Utorogu) to 5.08 (Agbada), a more than two-fold spread; V/Ni ranges from 0.77 (Abo) to 1.36 (Ohaji).

Table 2: Trace-Metal and Biomarker Source Ratios for Six Niger Delta Oils

Well	V/Ni	Fe/V	C27/C29	C28/C29	Pr/Ph	OL/C30 hopane	C31–35/C30–35
Utorogu	1.29	2.14	0.82	0.57	1.85	0.42	0.68
Ohaji	1.36	2.17	0.88	0.71	2.12	0.39	0.72
Abo	0.77	3.21	0.59	0.45	2.63	0.67	0.53
Escravos	0.79	4.26	0.47	0.32	2.97	0.74	0.41
Bonga	0.86	4.68	0.54	0.40	1.96	0.59	0.48
Agbada	0.89	5.08	0.66	0.55	2.45	0.62	0.56

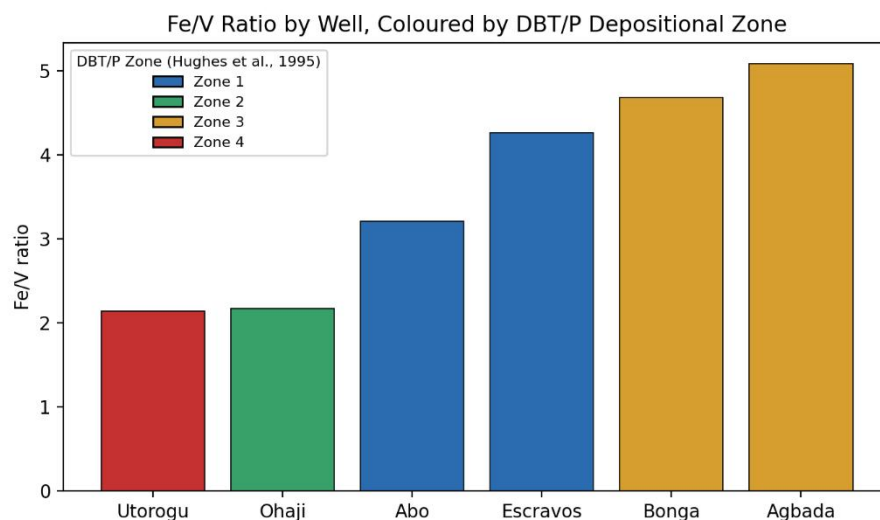
Table 3 adds the available maturity indices for the same six wells. Two values for Utorogu — moretane/C₃₀ hopane (1.7) and C₂₉/C₃₀ hopane (5.0) — are roughly an order of magnitude outside the range of all other wells (0.1–0.2 and 0.5–0.8, respectively) and are flagged rather than interpreted; they read as probable transcription or decimal-placement errors in the source compilation and should be verified against the raw chromatographic peak data before use. The oleanane/C₃₀ hopane values reported in the source maturity table also disagree with those in Table 2 for Abo, Ohaji, and Utorogu specifically (Escravos, Bonga, and Agbada agree reasonably well between the two source tables); Table 2 values are used throughout this paper as the better cross-checked figures, and the discrepancy is noted here rather than silently resolved.

Table 3: Biomarker Maturity Indices for Six Niger Delta Oils

Well	S/(S+R) C31 hopane	Moretane/C30 hopane	C29/C30 hopane
Abo	0.6	0.1	0.8
Agbada	0.6	0.2	0.7
Bonga	0.7	0.2	0.6
Escravos	0.6	0.2	0.7
Ohaji	0.6	0.1	0.5
Utorogu	0.6	1.7†	5.0†

† Flagged as likely data-entry outliers; excluded from interpretation (see text).

The DBT/P vs. Pr/Ph cross-plot places the wells into four depositional zones after Hughes et al. (1995): Escravos and Abo fall in Zone 1 (marine and lacustrine, sulphate-rich, DBT/P generally above 0.8); Ohaji falls in Zone 2 (lacustrine, sulphate-poor, DBT/P below 0.5); Bonga and Agbada fall in Zone 3 (marine shale and other lacustrine settings, DBT/P below 0.5 but Pr/Ph above 2.0); and Utorogu sits at the Zone 3/Zone 4 boundary, with DBT/P close to zero, consistent with an essentially sulphate-free, terrestrial depositional setting.

**Figure 2: Fe/V Ratio by Well, Coloured by DBT/P Depositional Zone**

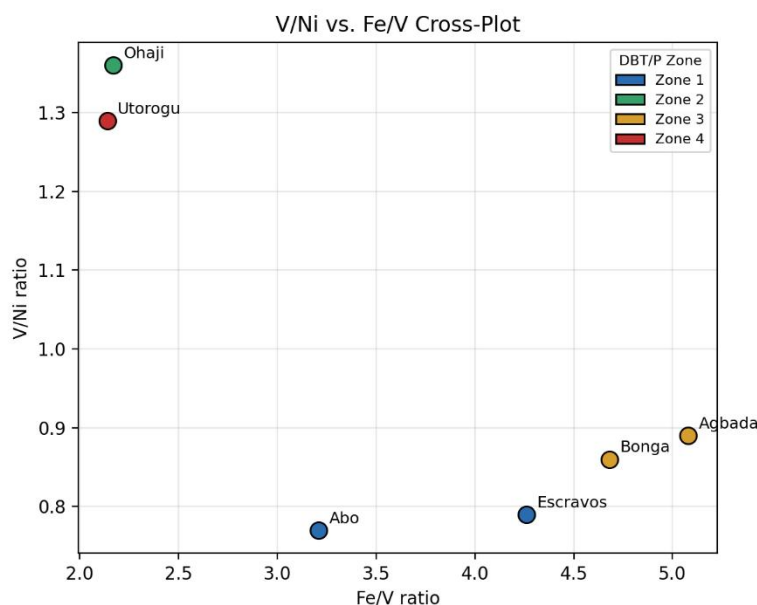


Figure 3: V/Ni vs. Fe/V Cross-Plot, Coloured by DBT/P Zone

Figure 2 and Figure 3 show that Fe/V and V/Ni co-vary with the DBT/P zonation in a broadly consistent way: the two Zone-3 wells (Bonga, Agbada) and the Zone-1 well Escravos have the highest Fe/V values (4.26–5.08) and the lowest V/Ni values (0.79–0.89), while Utorogu (Zone 3/4 boundary) and Ohaji (Zone 2) have the lowest Fe/V values (2.14–2.17) and the highest V/Ni values (1.29–1.36). Abo (Zone 1) is intermediate on Fe/V (3.21) but patterns with the low-V/Ni group (0.77) on redox grounds, indicating that Fe/V (detrital input) and V/Ni (redox) are related but not fully coincident axes of variation in this dataset.

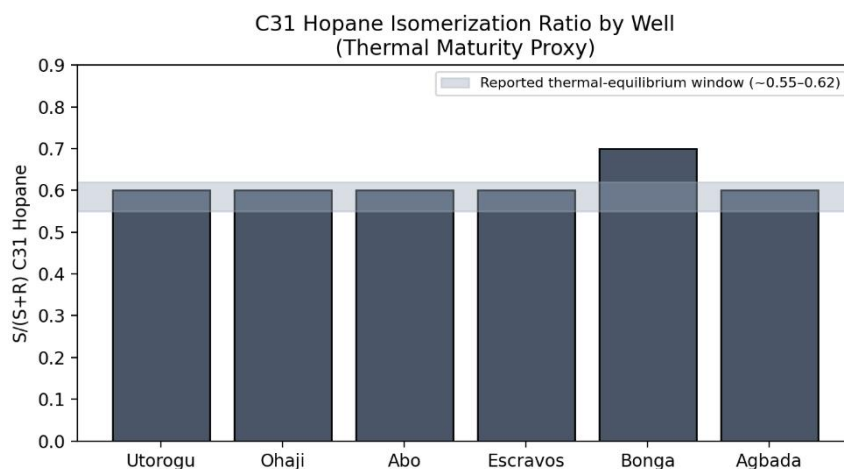


Figure 4: C31 Hopane Isomerization Ratio by Well

Figure 4 shows the central result of this study: despite the clear Fe/V–V/Ni–DBT/P differentiation between wells, the S/(S+R) C₃₁ hopane ratio is essentially uniform across all six wells (0.6, with Bonga at 0.7), sitting at or just above the commonly reported thermal-equilibrium window of approximately 0.55–0.62 (Peters, Walters, & Moldowan, 2005). All six oils therefore appear to have reached a comparable, mature stage of thermal evolution, regardless of their Fe/V or DBT/P grouping.

6. Discussion

The pattern in Sections 5 supports a specific, falsifiable interpretation: the iron and sulphur proxies used here differentiate the six oils primarily along a source-facies and depositional-redox axis — a detrital-rich, sub-oxic, low-sulphate group (Escravos, Bonga, Agbada) versus a low-detrital, more reducing, restricted or terrestrial group (Utorogu, Ohaji), with Abo intermediate — rather than along a burial-depth axis. If Fe/V and DBT/P were primarily tracking burial depth in this dataset, some corresponding spread in the maturity indices would be expected; instead, the maturity data are essentially flat at the equilibrium value. The most defensible reading of the combined evidence is therefore that iron and sulphur proxies, on their own,

are recording where an oil's source organic matter was deposited within the basin's facies mosaic, not how deep the resulting oil now sits or how deeply its source was ultimately buried.

This does not mean the original hypothesis — that a joint iron–sulphur–biomarker signature could help delineate accumulation depth — is wrong, only that it cannot be tested with the data compiled here. Two additions would be needed. First, an elemental or mineralogical iron–sulphur measurement (ideally a degree-of-pyritization index; Raiswell & Berner, 1986; Raiswell, Buckley, Berner, & Anderson, 1988) computed on source-rock or produced-water/rock samples tied to each well, since Fe/V and DBT/P are oil-phase proxies one step removed from the sedimentary iron–sulphur system itself. Second, and more directly, actual reservoir or accumulation depths for each sampled well, against which the maturity indices, Fe/V, and DBT/P could be regressed. Because the S/(S+R) hopane ratio saturates at maturity levels apparently already reached by all six oils, a vitrinite-reflectance or other non-saturating maturity parameter would likely be needed alongside depth data to resolve any residual depth-related signal once the source-facies effect documented here is accounted for.

6.1 A Proposed Iron–Sulphur–Maturity Framework for Future Calibration

Building on the structure established here, a future, data-complete version of this study could construct a composite index of the form $ISMI = f(DOP, DBT/P, M)$, where DOP is the elemental degree-of-pyritization value for the source rock, DBT/P is retained as the oil-phase sulphur-availability proxy, and M is a non-saturating maturity parameter (e.g., vitrinite reflectance or a biomarker ratio calibrated against it). Regressing ISMI against measured accumulation depth across a well set with full elemental, biomarker, and depth control would directly test whether iron and sulphur diagenetic indicators retain a depth-related signal once source-facies variation, of the kind identified in Section 6, is statistically separated out. No such regression is attempted here, since the elemental and depth inputs it requires are not yet available.

7. Limitations

This study is best read as a proxy-based, hypothesis-generating analysis rather than a validated depth model, for the following specific reasons:

- i. No elemental iron or sulphur concentrations were available; Fe/V and DBT/P are used as indirect, oil-phase proxies, not as direct measurements of the sedimentary iron–sulphur system.
- ii. No reservoir or accumulation depth data were available for any well; “depth” in this paper is inferred only indirectly, via a maturity index that appears to have saturated across the whole sample set.
- iii. The dataset with a full parameter suite covers only six wells, which limits the statistical power of any grouping identified.
- iv. Two data points (Utorogu moretane/C30 hopane and C29/C30 hopane) are flagged as likely errors and were excluded from interpretation; they should be re-verified against the original chromatographic data.
- v. The oleanane/C30 hopane values for Abo, Ohaji, and Utorogu differ between two source compilations of the same wells; this study used the better cross-checked values (Table 2) and flags rather than resolves the discrepancy.

8. Conclusion

Combining an iron proxy (Fe/V), a sulphur proxy (DBT/P), and biomarker maturity indices for six Niger Delta oils shows a clear, internally consistent facies grouping on the iron–sulphur–redox axis, but a flat, near-equilibrium signal on the maturity axis. Read together, this indicates that iron and sulphur proxies in this dataset are recording depositional facies and redox conditions rather than burial or accumulation depth, and that testing the depth-delineation hypothesis in the paper's title will require elemental iron–sulphur measurements (ideally a degree-of-pyritization index), a non-saturating maturity parameter, and real depth-tagged samples — none of which were available for the present analysis.

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