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Geochemical Techniques for the Analysis of Geochemical Data and its Application in the Nigerian Oil and Gas Industries

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Abstract

This paper dwells on the general applications of geochemical techniques in coastal and urban environments; it enumerated the application of geochemical techniques in geological media, such as: groundwater resources, natural and marine water resources, sediments, soils, particulates and rocks. The latter part dwells on the application of geochemical techniques in oil and gas; and Nigeria, a country in West Africa was used as case histories. This paper aims at revising the application of geochemistry on a global perspective; it further aims at comparing the approach of the geochemical techniques in Nigerian oil and gas industries with the current global trends and methodologies. It has further deduced the needs for effective integration of geochemical and geophysical techniques for a result-oriented scientific research in oil and gas.

Keywords: Geochemical surveys; Geological media; Geochemistry

Introduction

The name "Geochemistry" was first used by the Swiss Chemist Schonbein CF in 1838, as earth chemistry. Goldschmidt [1], re-defined geochemistry as the study of the distributions and amount of chemical elements in minerals, rocks, soils, water, and the atmosphere and also the study of the circulation of the elements in nature; on the basis of the properties of their atoms and ions.

Geochemistry has two branches: Inorganic Geochemistry which is the determination of quantity and distribution of individual elements and their inorganic compounds in various parts of the earth i.e., Atmosphere, Hydrosphere and Lithosphere and Organic Geochemistry; the determination of quantity and distribution of organic compounds in various parts of the earth i.e., Atmosphere, Hydrosphere and Lithosphere, [2]. The major concern of geochemistry is the general and overall evaluation of the abundances of the elements in the earth's crust and the major classes of rocks and minerals. The application of geochemistry to geological evaluation (history and re-construction), economic evaluation (mineral resources, oil and gas exploration) and environmental assessment (pollution studies) is a very powerful tool, when properly applied by those trained in the interpretation of analytical results. However, misinterpretation of data and/or lack of understanding of potential problems can lead to incorrect conclusions from raw or baseline chemical data. Geochemical surveys commonly have two objectives: (i) locating abnormal concentrations of ore-forming or pathfinder elements and (ii) characterizing the underlying host lithologies.

Geochemical prospecting

Geochemical prospecting is an important tool that is applied all over the world and has contributed significantly to the success of many important mineral exploration programs [3]. It is highly effective for locating ore bodies, that are often inaccessible, and it gives a strong signature to the orientation of target ore mineral. Geochemical methods of prospecting for oil and gas was developed by measuring the content of hydrocarbon gases in drill core and drilling mud to obtained information from key stratigraphic horizons. Therefore, it is always essential to carry out a geochemical prospecting prior to any feasible sampling exercise.

Geochemical anomalies

Mineral deposits have been described to represent anomalous concentrations of specific elements, usually within a relatively confined volume of the Earth's crust. Most mineral deposits were reported to consist of a central zone, or concentric bodies, in which the valuable elements or valuable minerals are concentrated, often in percentage quantities, to a degree sufficient to permit economic exploitation, [3]. The valuable elements surrounding ore-body are generally described to depreciate in concentration until they reach levels, measured in parts per million or per billion (ppb), which automatically is higher than the normal background level of the enclosing rocks. Primary halo is defined as the zone that surrounds ore.

Most of the ore minerals have been reported to undergo decomposition or disintegration; hence their chemical constituents become dispersed into weathering debris, soils, ground water, and plant tissue. The objectives of all geochemical prospectors entails the location, identification and exploitation of mineral deposits; either the form the geochemical anomalies [3], or mineral enrichment.

General Sampling Techniques

Sampling methods

Sampling methods will proceed after geochemical prospecting; these involve detailed evaluation and confirmation of prospects, contour maps can be drawn to show the distribution of elements. These may show the distribution of alluvial and eluvial deposits or the location of anomalies, indicating the presence of an ore body (where elements are most concentrated). Drilling or direct sampling or other mechanized

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methods; AUV, ROV, dredging or gravity coring may commence. These exercise is majorly carried out to obtain representative samples either for metallic mineral deposits (such as Au, Ag, Pt, Fe, Mn, Cr, V, MO, W, Ni, CO, Ti, Cu, Pb, Zn, Sn, Sb, Bi, Li, Mg, Be, Al, U, Th, Ta, Cd, Hg, REE) non-metallic mineral deposits (coal, lignite, oil and gas, sulphur, and others). The ore bodies may be formed in a porous limestone bed, capped by impermeable shale; escaping some mineralizing fluid upwards along a pre-existing faults [3]. In Figure 1, as a result of hydrothermal mineralization. Non-metallic mineral deposits; Petroleum and natural gas, oil shale, gas hydrate coal and lignite, gemstones, diamond, industrial minerals; abrasive minerals; feldspar, dolomite, clays and host of others [4-6] can also be a targeted mineral resources for geochemical exploration. Having the idea of the orientation of the mineralization after geochemical prospecting, then test drilling for the mineral deposit can commence. The large area expanse of land will be reduced, more concentration will be directed to the mineralized area as seen in the difference in the map shown in Figures 2 and 3 [7,8].

Trace metal and its oceanic geochemistry

The major ions in the ocean have been attributed to form complexes or chelates with trace metals such as hydroxides, chlorites and carbonates which upon its speciation are dependent in the nature of redox reaction in the environments [9]. Cu, MO, Rh, V and Cd act as a historical record in oceanic sediments. Therefore electrochemical techniques have been highlighted as the liable to expose bioactive trace metals (e.g., Cu, Fe, Co. and Cd) that are organically bonded in surface sea water, thereby causing a low level concentration of bio-available inorganic elements that can be deleterious to aquatic biota. Some other elements such as iron (Fe) have also been reported to act as a limiting nutrient in oceanic environment [10].

The residence time of different trace metals in the ocean differ, this is based on the fact that some are scavenged (i.e., Al); thereby exhibiting strong bond with particulates; some are highly metalliferous (i.e., related with hydrothermal vents and or effluents). Iron (Fe) have been formed together with manganese (Mn) and altogether co-precipitates with sulfides [10], forming economic abyssal sediments deposits.

Geochemistry and hydrocarbon

The geochemical techniques that is being applied to hydrocarbon exploration differs in many aspects to the a little bit raw approach in the search for metallic mineral deposits; hydrocarbon geochemistry chiefly involves the detection and study of organic substances found during drilling, mineral deposit geochemistry chiefly involves detection and study of inorganic substances at the surface as rightly explained in the introductory part. Geochemical applications may be applied at several stages during exploration of sedimentary basins for hydrocarbons. During the initial stages of exploration, when only a few wells have been drilled, geochemistry can provide valuable information on the petroleum-generating potential of a basin and permit recognition of major source rocks. This is followed by extraction, chemical analysis, and microscopic study of kerogen from rocks sampled by drilling. Kerogen is a complex polymer, formed from organic matter originally incorporated in sedimentary rocks, and is an intermediate stage in the formation of oil and gas (Table 1).

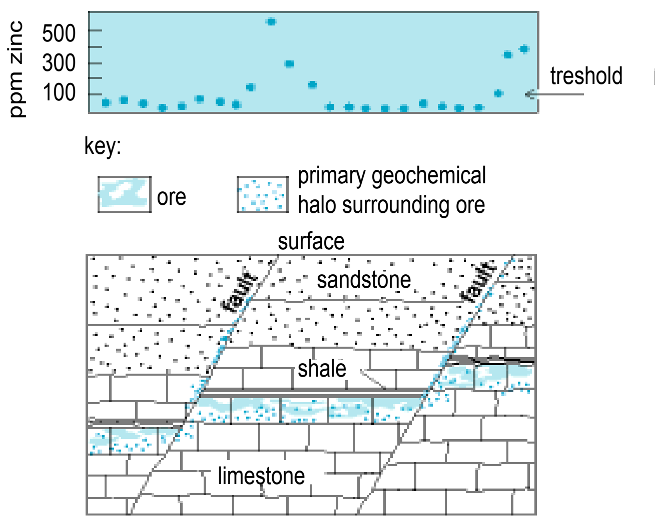

Figure 1: A typical geochemical design on geochemical anomaly map after [3].

Once accumulations of hydrocarbons have been discovered, their classification into geochemical families becomes highly essential. This may permit recognition of similar sources, hydrologic histories, timing of generation, pathways of migration, and loci of accumulation. Predictions of hydrocarbon potential in previously unexplored areas can often then be made; geochemical techniques reliably solve these challenges.

The final stages of detailed exploration may involve complex multivariate computer aided modeling of all available geological, geochemical, geophysical, and hydrological data; the objectives would be to determine the ultimate hydrocarbon potential of a given basin. I will dwell more on all these in the later stages of this paper and use Nigerian oil and gas as case histories.

Sampling preparations and geochemical analysis

The aim of sample preparation is to produce a sample that is representative, suitable and homogeneous sample feasible for laboratory analytical processes. Sample preparation is essential for elemental liberation or targeted compounds; it aids in decomposition techniques, and reduces particle size effects in geochemical techniques such as X-ray fluorescence (XRF). The end result of geochemical samples is a typical fine, dry material or powder.

Laboratory analysis for inorganic geochemical samples: Regional, large-scale geochemical projects demand special requirements for chemical analysis:

(a) The analytical accuracy must also be good, with good oriented result

(b) Data and other records related to the analysis and testing must be fully documented and retrievable.

(c) The analytical methods used must be highly sensitive to allow detection of wide range of targeted determinants' in all of the sample media at background levels;

The importance of points (a) and (b) in particular is that some geochemical data are planned to be used for the basis of environmental purposes, such as in the assessment of background concentrations of elements in different materials; It was reported to be highly important for setting up or updating national maximum contaminant levels. The Global geochemical Baseline project is highly regarded for this, it caught across the globe, and it is currently being carried out in Nigeria. Accuracy of the Nigerian baseline geochemical data set is therefore taken very serious; since it may be used to 'normalize' other geochemical data at national and international scales worldwide. The methods used for this project are also likely to become standard

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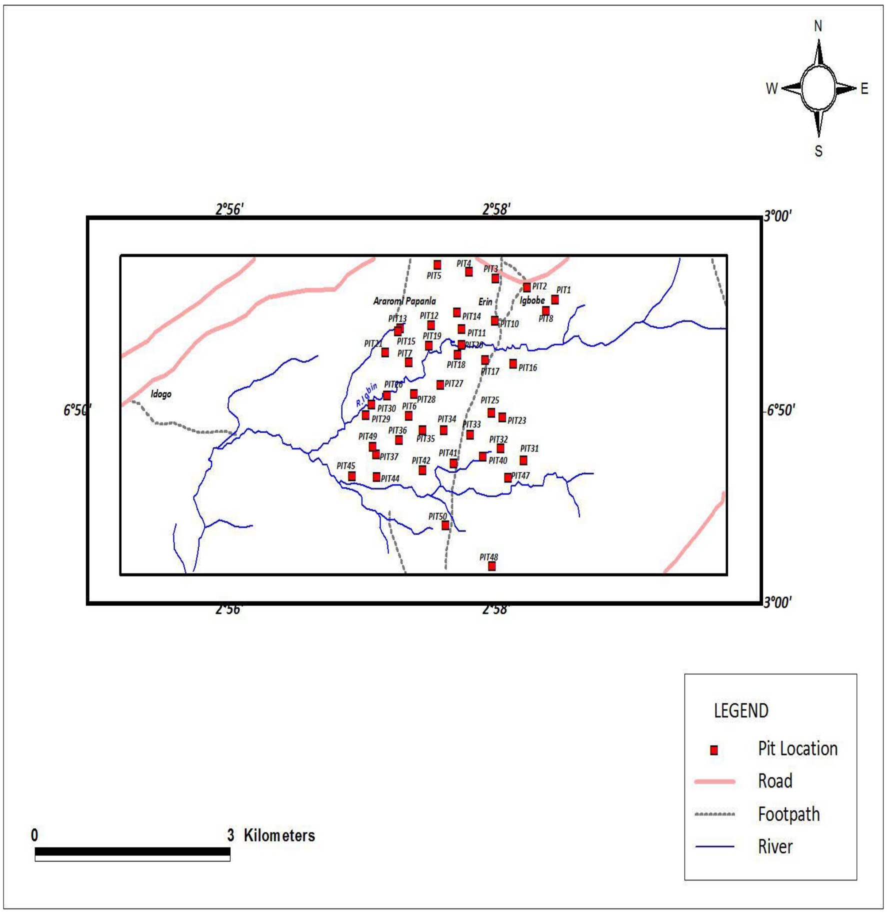

Figure 2: Map of pitting and trenching exercise to demarcate mineralized carbonate rocks concentration [5]; a typical example of geochemical prospecting technique.

Media for	Processes	What Deposits do Geochemists Search
(1) Rocks	Magmatic concentration Metamorphism Hydrothermal processes	(**a**) Early magmatic –Disseminated crystallization, segregation and injection (**b**) Late magmatic residual liquid segregation, residual liquid injection, immiscible liquid Segregation and injection, pyro-metasomatic mineral deposits. Metamorphosed, metamorphic deposit, contact Metasomatic deposits. Cavity fillings and replacement processes
(2) Sediment Stream sediments Ocean sediments	Sedimentation Evaporation Accumulation Deposition	Sedimentary deposits, evaporates (salts), placer deposits (Au, Ag, Pt etc) Fe-Mn deposits, polymetallic nodules, manganese nodules, hydrothermal vents, gas hydrates, oil and gas accumulations, geochemical/isotopic signatures of pelagic, Terrigenous, biogenic and Sedimentations and many others.
(3) Water Ground water Ocean water Pore water	Erosion Transportation regression Transgression Glacier/ice Turbidity current.	Event plume, carbonate mineralization, hydrothermal signature, oil and gas seeps, coastal, marine and groundwater pollution studies, Portable groundwater geochemical studies and Climate studies, turbidities and others.
(4) Air Elements (Hg) air	Particulates	Trace metal concentrates Biogeochemical particulates, CO_2,CH_4 emission and others Aerosol, condensates, particulate matter,H_2S,hydrocarbon gases, organic particulates, PCBS, POPS, volatile borne particulates matter and others
(5) Plant	Biogeochemistry	trace elements, dispersion halos, evidence for soil Mineralization.
(6) Soil Glacial till	Allochthones (transported) Autochthonous (*in-situ*)	Heavy mineral, clay mineral, heavy metals, XRD, minor and trace Elements, isotopic signatures, supergene sulfide enrichments etc. Hydrocarbons, geochemical anomaly, Pentane condensates, light Hydrocarbon and others [6-8,32]

Table 1: The general geochemical techniques.

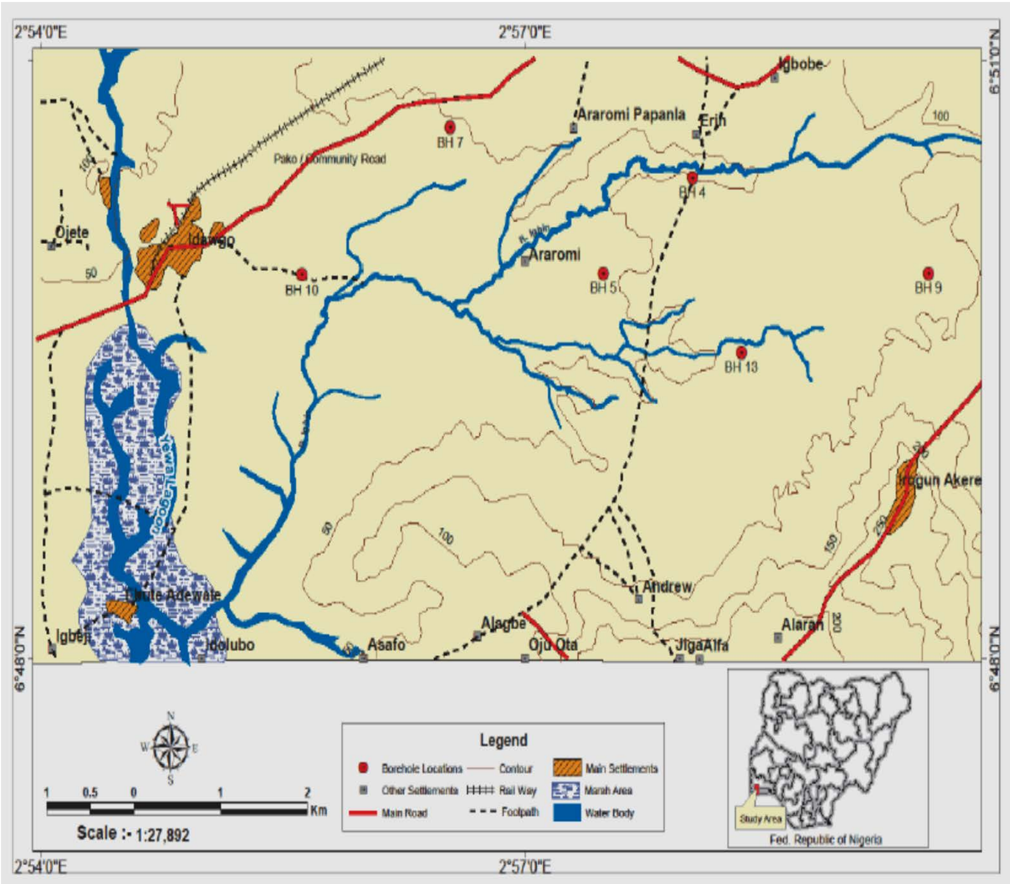

Figure 3: Map of core drilling points (for carbonate mineralization samples) after the geochemical prospecting exercise had given a focus and idea on mineralized area [4,5].

operating procedures (SOPs) for the global project, and hence should be reproducible in various laboratories throughout the world (http://ngsa-nig.org/content/geochemical-mapping).

A number of different analytical techniques for the analysis for inorganic geochemical materials are used within the laboratory, including X-ray Fluorescence (XRF) Spectrometry; Laser Ablation (LA-ICP-MS), and solution Inductively Coupled Plasma Mass Spectrometry (ICP-MS), carbon, hydrogen, moisture analysis and several others. The modern and effective model and their applications are briefly discussed. The Wavelength Dispersive XRF is used for analyzing fusion and pressed powder samples for elements with an atomic number greater than 9. The equipment can measure concentrations as low as 1 ppm and as high as 100%. It is used for the determination of organic and inorganic carbon, as well as bound water, in rock and soil samples. This instrument can measure the quantity of carbon and hydrogen present in the sample, and the temperature at which they are liberated.

The ICP-MS is traditionally used with solutions, made by acid digestion of the fused discs previously analyzed by the XRF. The ICP-MS is equipped with an automated sample loader and online data processing software; it has been reported to have the capacity analyze approximately more than 40 trace elements with detection limits down to parts per billion levels.

Portable Mineral Analyzer is a field-portable, shortwave infrared spectrometer which provides rapid data on rocks and minerals; it was reported to be accompanied with software that contains a library of mineral spectra allowing easy interpretation of unknown spectra.

The electron probe micro-analyzer (EPMA) can be used for the analysis of elements in very small areas such as individual mineral grains. It is equipped with wavelength dispersive X-ray spectrometers and an energy dispersive spectrometer (WDS-EDS). It is equipped with Cathode luminescence and backscattered electron images that can be applied in scanning mode, an instrument primarily used for major element micro analysis. Scanning Electron Microscope (SEM) has been reported to be useful in sample imaging via scanning with high energy beam of electrons; it is was termed a useful tool for photonics research based on its Nano-scale surface feature and topographic view in a 3D shapes and shadows; while Transmission Electron Microscope (TEM) was reported to be highly effective based on its energetic electrons, that reveal detailed crystallographic, compositional and morphological sample characteristics at 1 nm magnification.

Geochemical data processing

A substantial part of the exploration expenses in the oil industry is carried out via drilling activities. Effective computer modeling of the feasibility of finding oil had been reported as one of the most promising approaches to reduce the risk of drilling dry wells. Oil and gas is generated from kerogen particles embedded in petroleum source rocks. Kerogen is a composite of biological sedimentary material of marine and terrigenous origin; its composition determines the relative amounts and nature of oil and gas that can be generated upon maturation of the source [2]. Hence utmost care and attention is highly needed in this aspect. There are several approaches at this, one of which is the use of multivariate statistical analysis.

Multivariate statistical analysis

Multivariate methods offer significant improvements for integrated geochemical characterization of kerogen, and lead to more precise computer modeling of petroleum provinces. Series of geochemical software package had been used by researchers all over the world [11]. In the Nigerian oil and gas, researchers such as [12-15] and others had applied multivariate geochemical statistical approach at predicting the; petroleum source rock, maturity, geological environments and kerogen classifications.

Relevance of geochemical techniques in oil and gas industry

Petroleum Geochemistry is a special branch of geochemistry that deals with the composition and distribution of petroleum and related substances in sedimentary basins [2]. The primary aim of petroleum geochemist is to understand the origin, migration, accumulation and post-accumulation alteration of petroleum in sedimentary basins. The question remains what are the major roles of Petroleum geochemists in the increasingly digital technological dominated oil and gas industries?

Geochemical surveys constitute an integral part of performance of geological prospecting works. In particular, the surveys enable the determination of oil source rocks and the quantitative assessment of their ability to generate various hydrocarbon fluids.

Obtained information from geochemical survey serves as basis for building a 3D model of a sedimentary basin and its thermal evolution at the well drilling and completion stage. Other applications are:-

(i) The determination of types of basin modeling at different stages of geological prospecting

(ii) A reliable method used in the exact determination, place, volume and time of shale oil generation.

(iii) It is essentially applied in the oil source rock determination and gives a quantitative assessment of their ability to generate various hydrocarbon fluids.

(iv) Geochemical applications is used in the analysis of; borehole-core, sludge liquids and gaseous information to identify inter-reservoir overflows and oil-gas developmental stages.

(v) Geochemical principles are applied to determine the; genetic origin, hydro dynamically isolated zones, production reserves, thermal maturity, reservoir fluid types (isotope geochemistry) and marine versus terrigenous input in oil and gas industry.

(vi) Geochemical techniques are being used to estimate the risk associated with non-hydrocarbon production gases (CO_2, N_2 and H_2S).

(vii) Isotope geochemical techniques (e.g., ^{13}C, can be determined with GC-IRMS equipment) are used in oil correlation (oil-oil source).

(viii) Lastly; geochemical methods and principles are used in; elemental analysis (GCMS-biomarker); Total organic content (TOC), Sulphur content and others.

Case Studies on the Application of Geochemical Techniques in Nigeria Oil and Gas

Nigeria (Figure 4) is the most populous African nation (with a teeming population of over 170 million people; http://worldpopulationreview.com/countries/nigeria-population); located on the west coast of Africa, Latitudes 4° north of the Equator and Latitudes 3° and 14° on the east of the Greenwich Meridian. It shares boundaries with the Republics of Benin and Niger in the west, Cameroon in the east, Niger and Chad in the north and the Gulf of Guinea in the South. The country has an approximate surface area of about 924,000 square kilometers comprising thirty six (36) provincial states with the Federal Capital Territorial (FCT) at Abuja. It consists of 374 ethnic groups with Hausa, Igbo Yoruba constituting the major languages. To oil explorers, Nigeria has good prospects.

Petroleum exploration began in Nigeria as far back as 1908. The first commercial discovery was made in 1956 at Oloibiri in the on-shore of Niger delta; ever since then production and continuous research commenced. Early geologist and geochemist, such as [16-19] carried out intensive research on: source rock evaluation, depositional environments, kerogen type and litho-geological characterization on the Nigerian basement complex and sedimentary basin.

Based on their joint research they concluded that "half of Nigeria's landmass is composed of three main basement complexes located in the west, the north-west and the south-east. Between these basement rocks, sedimentary basins are strung out, along a north-east/south-west axis from Lake Chad to the Niger Delta, i.e., along the length of the "Lower Niger-Benue river systems".

On this basis, they divided Nigeria into seven major sedimentary basins viz: (from the oldest), (i) the Calabar Flank, (ii) the Benue Trough, (iii) the Chad Basin, (iv) SE lullemmenden (Sokoto) Basin, (v) the Dahomey Basin, and the (vi) Niger Delta Basin. They earmarked Middle Mesozoic to Recent age sedimentary successions to these basins. With the advent of improved technology and multi-disciplinary approach, more researchers such as [20-23] re-defined the earlier classifications of the Nigerian sedimentary basin into: coastal formations (i) Calabar Flank, (ii) Niger Delta, (iii) Dahomey Basin and (iv) interior basins (Benue Trough, Chad Basin, Nupe Basin, SE lullemmeden Basin).

They further subdivided the sedimentary succession based on lithology into three namely:

(i) Basal continental sandstones, siltstones and mudstones.

(ii) Middle marine shales and limestones interbedded with sandstones and siltstones.

(iii) Upper sandstone sequence that is continental or paralic.

Getting up to 60 years of intensive explorations (1956-2016). Niger Delta is still considered as the major oil prospective basin compared to other sedimentary basins in Nigeria. Several other researchers have continued the research trends from the likes of [21,23] and the earlier listed researchers in the Nigerian sedimentary basin. I hereby highlight some of the geochemical techniques that had been applied in the Nigerian sedimentary basin by their continuity.

In [24] worked on suite of fresh uncharacterized crude oil samples from two different oil fields in the southwestern part of the Niger delta to determine its ;source, depositional conditions and maturity levels. He used saturated biomarker as the geochemical techniques to evaluate the; depositional environments, organic matter source and biodegradation extent. He utilized GC flame ionization detector (FID) and Gas chromatograph-mass spectrometry (GC-MS) analytical instrument to determine elemental ratio: Pr/Ph and isoneprenoide/n-alkenes. With these geochemical principles he was able to trace the formation of the oil to a mixed source (marine and terrestrial kerogen origin). He also identified oxic palaeo-environment with no maturity trends as the depositional conditions of the oil.

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Figure 4: Map of Nigeria showing its border country.

Sonibare et al. [24] used Gas chromatography-mass spectrometry(GC-MS) and isotope mass spectrometry abundance(isotope geochemistry) to characterize the abundance of Pentacyclic triterpenes of hopane, oleanane skeletons and C27-C29 sterane on 10 crude oil samples from on-shore and offshore Niger delta. He also deduced a mixed source (marine and terrestrial kerogen source) to the observed samples. He further used oil computed maturity parameters and aromatic sulfur compounds (thophenes) for the aromatic geochemical biomarker. He was able to confirm an increasing thermal maturity with increasing reservoir depth. He was also able to identify the different time of formation of the oils and associated gas.

From Ref. [25] carried out whole oil gas chromatography organic geochemical techniques on suite of oil samples from the on shore-swamp field in the Northwestern Niger delta. He aimed at correlating and evaluating the post generative alterations of the hydrocarbons systems by using light hydrocarbon based organic geochemical parameters. He further correlated the light hydrocarbon parameters to the higher molecular weight hydrocarbon parameters. He observed strong discriminations in the 2 correlations, which he termed a reflection of post generative alteration-biodegradation processes. He singled out light hydrocarbon distributions as having a dominant influence on the evaporative fractionation of the oils.

From Ref. [26] used stable carbon isotope organic geochemical analyses, with the use of organic geochemical biomarker and n-alkane compounds on 58 crude samples from shallow and deep water wells of Niger Delta. They aim to predict the depositional environments and organic matter characteristics of the potential source rock of the study area; using a source organ facies prediction approach from oil geochemistry. They observed relatively abundant C27 steranes; C30 24-n propyl cholesstane; low oleanane index, relatively low Pr/Ph ratio and positive to nearly flat C12-C30 n alkane compounds. The specific stable isotope profile they generated suggested that the expelled oil source facies contain significant marine derived organic matter; that have been deposited under sub-oxic and stratified column conditions. This report is in contrast with the earlier terrigenous organic matter dominated source ascribed to the shallow water part of the Niger delta [27,28].

He further suggested a terrigenous and mixed marine terrigenous source to the shallow water area of Niger delta. He also indicated that the terrigenous part has been expelled from its source; which contained overwhelmingly plant source organic matter. He deduced oxic source depositional conditions and a combination of a mixed marine-terrigenous family biomarker properties to the study area.

Akinlua and Ajayi, carried out organic geochemical studies (normal alkanes, aliphatic, isoprenoids hydrocarbons, aromatic hydrocarbons and biomarkers) using Gas chromatography (GC) and mass spectrometry (GC-MS) on six oil fields from the central Niger delta. They aim to assess the origin, well maturity and the depositional environments of the organic matter from which they were derived. They also aim to evaluate the similarities and or differences among the central part of Niger delta oil facies in comparison with those from other parts of the delta. They applied n-Alkane and aliphatic isoprenoid ratio, Pr/nc17 and they obtained range values of 0.56-0.86; the Pb/nc18 ratio also ranged between 0.22-0.31. These values indicated that the oil were derived from organic matter of both terrestrial and marine origin. The Pristane/Phytane ratio (2.67-3.50) and the Olenane index (0.07-1.39) suggest oxidizing environments deposition of the organic matter; and marine-terrestrial organic matter biomarker indication. The saturated and biomarker geochemical data indicated thermally matured source oil. They concluded their findings that the Central Niger delta oil has the same organic geochemical characteristics with other parts of Niger delta oil; but with a different aromatic hydrocarbon distribution.

Obaje et al. also carried out organic geochemical studies on 4 wells (kemar-1, Murshe-1, Tuma-1 and Ziye-1) in the Nigerian sector of the Chad basin which is one of the largest intra-cratonic basin in the Central west Africa [29]. They analyzed Total organic carbon (TOC), Tmax and organic geochemical biomarker chromatogram. They observed that the source rock are entirely gas prone, although; Biomarker chromatograms and extract vs. TOC plot indicate the presence of oil in the Ziye well at depth 1210 m, but not at economically viable quantity. This is one of the numerous geochemical researches that further confirm the monopoly of Niger delta as the major productive basin in Nigeria.

From [30] carried out Total organic carbon (TOC), soluble organic matter (SOM) and Hydrogen Index (HI) on the Anambra basin; with the aim to determine the hydrocarbon potential of the basin. They observed moderate to fair hydrocarbon source, T max range of 425-434°C, Bitumen to TOC ratio of 1638-7211 mgcx/g TOC, and their observed spore/pollen colour index suggest low thermal maturation levels for the active source rock. This further confirms the productive monopoly of Niger delta. However, inorganic geochemistry can also give a clue to the hydrocarbon source rock. These methods had been used and proven to be effective in the Niger Delta [31], carried out detailed geochemical study of oil samples from onshore field in the Niger Delta for their characterization and correlation; coupled with the use of Gas Chromatographic (GC), Gas Chromatographic-Mass Spectrometric (GC-MS) for elemental analysis: CPI, Pr/Ph, Pr/*n*C17, and Ph/*n*C18. He used Inductively Coupled Plasma-Mass Spectrometric (Inorganic) analytical techniques to determine the results of Nickel (Ni) vs. Vanadium (V), Co/Ni vs. Ni cross plots and cluster analysis. The elemental analytical evaluation suggests that both oil types have identical source rocks and also indicated that the oils are thermally mature. The Biomarker data also discriminated the oils into two groups on the basis of biodegradation and revealed that the oils are mature and generated at almost the same thermal maturity level. The similarity in the results of both organic and inorganic geochemistry of these oils [31], shows that an integrated organic and inorganic geochemical data are reliable tool for the evaluation, characterization and correlation of crude oils in the Nigerian sedimentary basin.

From Ref. [29] carried out organic, and inorganic geochemical analyses, on the shale outcrop of the cretaceous Fika formation in the upper Benue trough. They aim to document shale gas potential and prospectivity of the cretaceous Benue trough, which had been earlier described as gas-prone [28]. They carried out Total organic content (TOC), source rock evaluation, rock eval pyrolysis using GC chromatography, petrographic and mineralogical evaluation using scanning electron microscope (Inorganic geochemical methods), on the samples. They observed a high TOC values greater than the minimum threshold values of 0.5%wt; the result of their S2 vs TOC plot, falls within the Type 11 oil prone and Type 111 gas prone type kerogen [32-36].

The Tmax value, from the Rock eval pyrolysis, range between 422°C to 436°C; suggesting immature to early source rock formation for the study samples. The results of the inorganic geochemical techniques applied (petrographic and mineralogical analyses) indicate high silica content (>30%). The relatively low swelling clay in the samples; suggest a highly frackable shale lithology. The integrated petrographic techniques (inorganic) and TOC, Tmax and S2 (organic) suggest a potential for a viable shale gas deposit. They further stressed that other factor such as: stress regimes, timing, burial depth and proximity of water fill aquifer are important additional parameters that can aid in the quantification of shale gas in the study area. This further confirmed that geochemical techniques preceded geophysical methods in oil and gas; and the integration of both methods gives a solid foundation to exploration oriented result [37-41].

Conclusions

Thermal and basin modeling geochemical techniques has not been effectively explored. More research needed to be carried out on the use of geochemical principles in the estimation of the risk associated with non-hydrocarbon production gases (CO_2, N_2, and H_2S). The GC-MS, GC-IRMS and GC-MSD and some other effective analytical instrument are not too common; except very few places. The most common GC equipment is GC-FID and TCD; this has prompted some geochemists to send their samples to developed countries for geochemical analyses.

The inorganic geochemical techniques which has been used successfully by most geochemist in combination with organic geochemical techniques also suffer the same fate; ICPMS, EPMA, SEM and some high resolution equipment are scarce; Atomic Absorption spectrophotometer (AAS) and X-ray fluorescence spectrometer (XRF)/XRD are the more conversant inorganic geochemical instrument.

From most of the available past and present research, more effort on geochemical techniques had hitherto been directed to; sludge liquids and gaseous information from already drilled borehole core, geochemical research on secondary well (already drilled oil-well), source rock evaluations, pyrolysis, crude-oil biodegradation and biomarker geochemical techniques; there is a need to do more.

Recommendations

Geochemical techniques is an important tool in oil and gas exploration, quality research on geochemical exploration methodologies; thermal and basin modelling, geochemical-geophysical data integration and investment in quality organic and inorganic geochemical exploration methodologies and analytical instruments is hereby recommended for effective and smooth operations in the Nigerian oil and gas industries.

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