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GEOCHEMICAL HETEROGENEITY OF CAMPANO- MAASTRICHTIAN OUTCROP SECTIONS AT BAWA HILLS, LOKOJA/ BASANGE FORMATION, ANAMBRA BASIN, MID – WESTERN NIGERIA.

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ABSTRACT

The geochemical heterogeneity of outcrop samples of different sections of bawa hills (Lokoja – basange formation) of the Anambra basin was investigated.Classical methods were employed to determine the percent total organic carbon (TOC) and the soluble organic matter (SOM) while instrumental method was employed to determine the percent nitrogen using the CarloErbaLeco NA-1500. The range of percent %TOC and SOM values obtained were (0.07-3.20) and (100-2,200ppm) respectively. The values of the %TOC and SOM for some of the units were above the 0.5% and 500ppm preliminary threshold values for petroleum generation. The Corg/N ratios range from 0.11 to 105 depicting the organic matter as a mixture of marine and terrestrial source input with a predominance of marine input , and indications of primary product alteration and selective degradation of the organic matter during diagenesis. None of the parameters showed any systematic variation but the %TOC and the SOM exhibited an irregular inverse variation. The entire sample suite exhibited heterogenous geochemical pattern.

INTRODUCTION

A sedimentary basin is a region on the earth, of long term subsidence creating accommodation space for infilling by sediments. It is from the lithification of these sediments that sedimentary rocks are formed. When these bed rocks or ancient superficial deposits are visibly exposed to the surface of the earth due to erosion or tectonic uplift, they become outcrops. Such exposure occurs frequently in areas where the erosion is rapid and exceeds the rate of weathering like the mountain ridges and tops; steep hillside, river banks and tectonically active areas (Hettinger, 1995).

Within the Niger-Delta region of Nigeria, there are a number of outcrop sections. For example, in Edo State we have the Bawa Hills at Igarra. Other outcrop sections in Edo State occur at Ogirameh, Ibillo, Ososo, Iguobazuwa. Within the Niger-Delta Province other outcrop locations include Mfamosing and Odukpani areas situated at the Calabar Flank, Southeastern Nigeria(Ibe et al; 2014)

The organic matters forming the sediments are from different biomass and contain different proportions of functional groups. Their potentials for generating gas, oil or none of these depend on a number of factors among which are the quantity of organic matter, organic matter type, environment of deposition, period of deposition (Ehinola et al; 2006). These factors can be assessed using different geochemical parameters. These parameters may be so heterogeneous that within a lithostratigraphic unit variation occurs. This investigation therefore, is an attempt to evaluate the geochemical heterogeneity of the outcrop sections of Bawa Hills of Lokoja- Bassange formation.

Geology of the study area

Bawa hills

GPS coordinates**:** N07^{O} 7' 12.4"
E006^{O} 13' 02.3"

Elevation: 209m above sea level

Fig 1: Exposure of the Bawa Hills Outcrop Section at Igarra

The exposed area of Bawa Hill exposure is along a section of road cut at the Auchi-Igarra road, before Ikpeshi town in Edo State, Nigeria. The extent of the exposureof Bawa Hill is about 163m in length, with a height of about 10m.The exposure stretchesfrom Auchito Agenebode in Edo State. It is part of the western Flank of the Anambra basin , formed in the Campanian – Maastrichtian times.This formation is somehow unnamed but it is thought to bewithin the Lokoja/ Bassangeformation, which was first mapped and named by the Geological Survey of Nigeria (Hockey et al; 1986). Nwajide(2013) opined that cartographically, the formation is represented east of the River Niger and south of the confluence but not across to the west of the River Niger – directly overlying the basement. He also classified the LokojaBassange Formation as the basal unit of the Coal Measures, stressing that it is ill defined both in stratigraphy and area. Due to its contact with the basement, he suggested that the LokojaBassange should be "subsumed" into Nkporo Group..

The sediments of this outcrop section consist of sandy horizons, siltstones, mudstones, and clay intercalations. There are also conglomerates. The sandstones are medium to coarse grained with sub-angular to angular grains. The grains are moderately to poorly sorted. The conglomerates occur close to the base as lag deposits. The siltstone

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and mudstones are thinly bedded. The sediment fine upwards with a lining up of the sequence with ferruginised sand cap at the top. Cementing materials tend to make them appear red(Rahaman, 1989).

The following sub-subfaciescan be recognized.

1. Conglomerate subfacies.
2. Arkosesubfacies.
3. Siliceous subfacies.
4. Cross-bedded subfacies.

Table 1: The lithostratigraphic units of theAnambra Basin

Age	Basin	Stratigraphic Units						
Thanetian	Niger Delta	Imo Formation						
Danian								
Maastrichtian	Anambra	Coal Measures	Nsukka Formation					
			Ajalli Formation					
			Mamu Formation					
Campanian		Nkporo Fm.	Nkporo Shale	Enugu Fm.	Owelli sandstone	Afikpo Sandstone	Otobi Sandstone	Liafia Sandstone
Santonian	Southern Benue Trough	Agwu Formation						

After Nwajide(2013)

MATERIALS AND METHODS

The 31 outcrop samples for this study were collected randomly from different layers of the Bawa Hills outcropping sections in Edo State, Nigeria using a digger. The samples were taken from 30cm depth after removing the surficial, weathered materials and other exogenic transformation materials to avoid contamination. They were put in glass bottles and properly labeled; dried at a temperature of about 35^{o}C before pulverizing. The portion for total organic carbon (TOC) and soluble organic matter (SOM) was sieved through a 0.4 micron sieve while that of total carbon and total nitrogen was left as the pulverized bulk samples. They were all kept in a desiccator prior to analyses.

Total Organic Carbon (TOC) Determination

The method of Walkley Black (1934) was employed in the determination of the total organic carbon. 1.0g of the sieved sample was placed in a 500ml conical flask and10cm^3 of 1N potassium heptaoxodichromate (VI) ($K_2Cr_2O_7$)added to the conical flask, followed by the addition of 20cm^3 concentrated tetraoxosulphate(VI) acid with a burette. The mixture was swirled for about a minute for proper mixing and allowed to stand for another 30 minutes. This is the digestion phase.

200cm^3 of distilled water was added to the reaction flask to dilute the digest (mixture), followed by the addition of 10cm^3 of concentrated phosphoric acid (H_3PO_4).

0.2g of sodium fluoride was added and 4 drops of diphenylamine indicator was also added to the content of the reaction flask. The mixture was titrated with 0.5N (0.25M) ferrous ammonium tetraoxosulphate (vi) solution with a colour change from dark brown through dark blue to bright green end point.

Dark brown □ dark blue □ bright green (end point).

The total organic carbon (TOC) was calculated using the formula:

$$TOC = 10\,(1 - T/S) \times F$$

Where T = sample titre value

S = standard or blank titre

F =

$$factor = \frac{1.0\times 12}{4000} \times 1.72 \times \frac{100}{w}$$

w = weight of sample

A standard or blank titration was carried out as outlined above but without a sample.

Determination of Total Carbon and Total Nitrogen

The elemental analyses for carbon and nitrogen from the bulk samples were accomplished using the Carlo ErbaLeco NA – 1500 Elemental Analyser.

Soluble Organic Matter (SOM)Determination

30g of the sieved outcrop sample was placed inside a thimble pre- extracted with hexane-acetone(1:1v/v) and extracted with same solvent mixture using a soxhlet extractor from 7- 10 hours. The extracts were cleaned by passing them through a column of anhydrous sodium tetraoxosulphate (VI).

Map of Edo state showing study area

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RESULTS AND DISCUSSION

Table 2: Bulk geochemical values for the outcrop samples

SAMPLE	TOC (%)	SOM	C (%)	N (%)	C/N	Corg/N
BA 1	0.07	300	0.09	0.65	0.14	0.11
BA 2	0.25	200	0.25	0.70	0.36	0.35
BA 3	0.20	1300	0.90	0.45	2.00	0.44
BA 4	0.11	900	0.50	0.23	2.17	0.48
BA 5	0.14	1000	0.02	0.34	0.06	0.41
BA 6	0.15	300	0.30	0.05	6.00	3.00
BA 7	0.12	500	0.15	0.06	2.5	2.00
BA 8	0.33	200	0.45	0.35	1.29	0.94
BA 9	0.13	1400	0.22	0.10	2.2	1.30
BA 10	0.22	2200	0.25	0.06	4.17	3.67
BA 11	1.01	800	2.15	0.05	43.00	20.2
BA 12	0.27	500	1.10	0.55	2.00	0.49
BA 13	0.30	800	0.95	0.07	13.57	4.29
BA 14	0.86	1000	2.10	0.06	35.00	14.33
BA 15	0.71	1700	1.25	0.68	1.84	1.04
BA 16	0.50	350	1.00	0.08	12.5	6.25
BA 17	0.06	190	0.30	0.07	4.29	0.86
BA 18	1.05	450	0.15	0.01	15.00	105
BA 19	0.07	210	0.45	0.05	9.00	1.40
BA 20	0.95	300	0.22	0.26	0.85	3.65
BA 21	2.05	250	1.85	0.50	3.7	4.10
BA 22	1.11	500	1.85	0.45	4.11	2.47
sBA 23	1.92	120	2.10	0.65	3.23	2.95
BA 24	3.20	190	2.55	0.55	4.63	5.82
BA 25	1.25	350	1.11	0.08	13.88	15.63
BA 26	1.30	230	1.45	1.10	1.32	1.18
BA 27	1.15	200	1.35	0.95	1.42	1.21
BA 28	0.25	100	1.00	0.45	2.22	0.56
BA 29	0.31	185	0.90	0.65	1.38	0.48
BA 30	0.95	210	1.10	0.75	1.47	1.27
BA 31	1.25	150	1.20	0.09	13.33	13.89

TOC/ SOM

The % total organic carbon ranged from 0.07 to 3.20 while the soluble organic matter ranged from 100 to 2,200ppm (Table 1). About 60% of the TOC values were below the preliminarily agreed threshold of 0.5 for hydrocarbon generation and the values were quite variable without any systematic pattern of variation from the base to the top of the hill. However, the %TOC values were predominantly lean at the base than at the top of the hill (Fig.3). This suggests that erosive forces were much more intense at the base than the top of the hill resulting in the weathering of the basal organic materials.

A similar pattern of variation was observed for the soluble organic matter (SOM), with less than 40% of the samples having the minimum 500ppm preliminarily required for a siginificant generation of petroleum. The TOC and the SOM organic matter were very heterogeneous as reflected in their correlation coefficient (-0.29) and shown in figure 3. Figure 4 shows this inverse relationship, where the soluble organic matter is more pronounced at the base and thins upwards to the top of the hill. This suggests a complex hydrodynamics of the system and its effects on grain size distribution vis-à-vis the total organic carbon distribution (Oyo-Ita et al., 2010). Other factors related to the paleo-depositional environment, the kinetics of the organic matter transport and the speciation of the organic matter may have contributed to the observed heterogeneity.

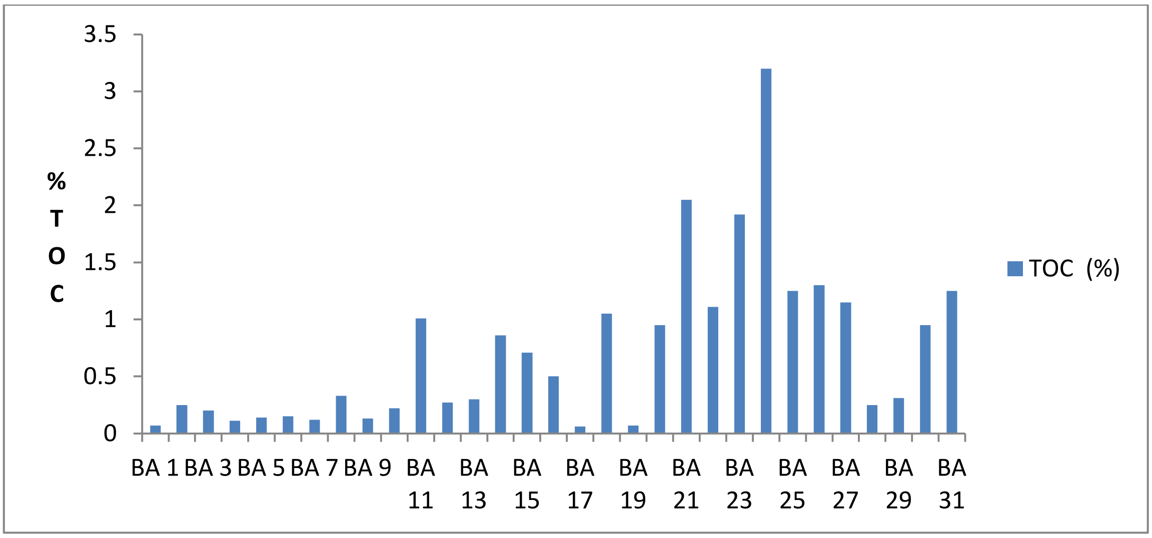

Fig. 3: Bar Chart of % TOC

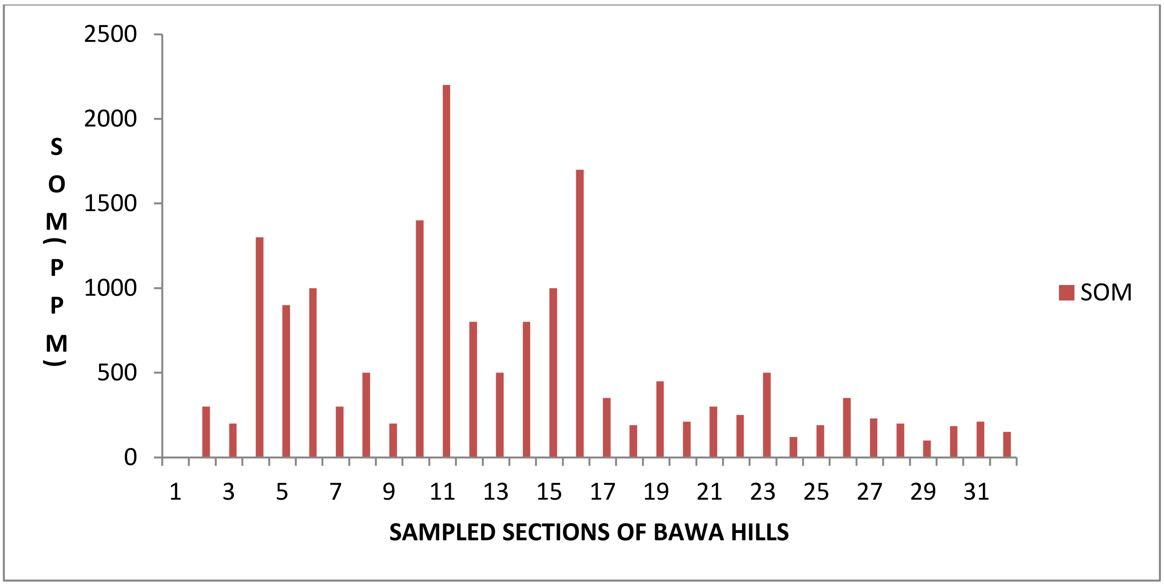

Fig. 4: Bar Chart of SOM

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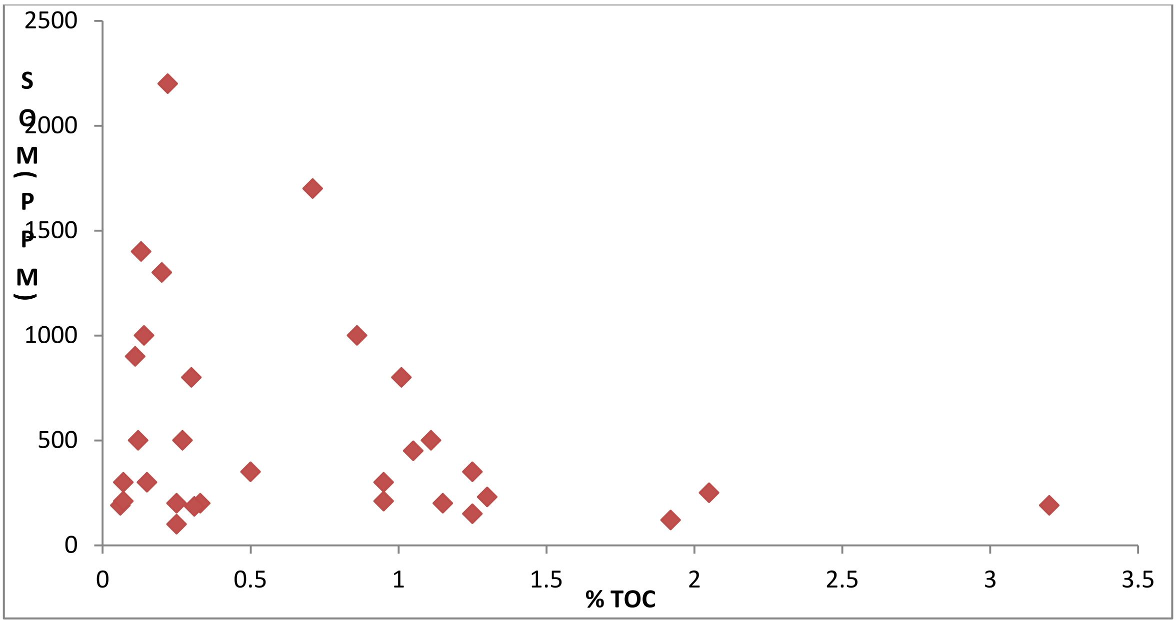

Fig.5: SOM versus TOC

CARBON – NITROGEN(C/N) RATIO

The ratio of total organic carbon to total nitrogen, C/N has been commonly used in the reconstruction of organic matter sources (Algal and land plant origins) to sediments (Meyers, 1977 ;Huc, 1988 and Sillman et al., 1996). There is generally an extensive biological reworking in soils and during transportation from the terrestrial catchment. Thus, the organic material supplied to the sedimentary basin is heavily altered and is impoverished in hydrogen and nitrogen. The nitrogen rich proteinaceous with cellulose free materials from algae have C/N ratios between 4 and 10 while carbon – rich cellulosic materials of terrestrial higher plants have C/N ratios greater than 20 (Meyers, 1994). However, alteration of primary product and mineral associations within the water column and the selective degradation of organic matter components during early diagenesis have the potential to modify C/N ratios of organic matter in sediments (Ekpo et al; 2012).

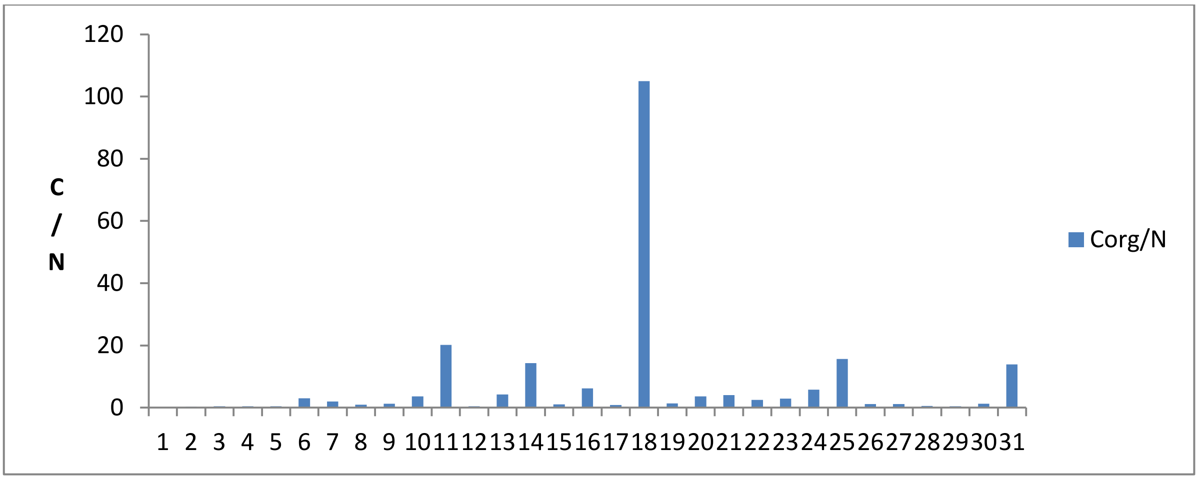

Fig. 6: Bar chart of Corg/ N ratio

The weight percent ratio of the TOC and total nitrogen content (Corg/N)(Table1) expresses the amount of protein in organic matter. It is evident from figure 6 that the section is a mixture of marine and terrestrial organic matter but predominantly marine. However, the occurrence of ratios below 4 might be as a result of alteration of primary product and mineral associations within the water column as noted by Ekpo et al., 2012 and the selective degradation of organic matter components during early diagenesis which has the potential to modify C/N ratios of organic matter in sediments.
However, we have employed C/N ratio incharacterizing our Cretaceous samples with the assumption that the source signals are preserved (Nzoussi-Mbassani et al., 2003).

This ratio, like other parameters studied was highly variable without any systematic pattern of variation. This could also be as a result of the same geochemical phenomenon earlier stated.

The study of the Bawa Hills Outcrop sections of the Campano – Maastrichtian age revealed a complex hydrodynamics during the early stage of diagenesis which may have given rise to the high variability of the parameters studied without trend.

REFERENCES

Ehinola, O.A., Sonibare, O.O. Falana, A. M. and Jarvie, D. (2006). Organic geochemistry and biomarker evaluation of shales units of the Maastrichtian Patti Formation, Bida basin. National Association of Petroleum Explorationists Bulletin, 19(1): 80-84.

Ekpo, B.O., U.J. Ibok, N. Essien and H. Wehner (2012). Geochemistry and organic petrography of Cretaceous sediments of the Calabar Flank, Southeastern Nigeria. Marine and Petroleum Geology ,35: 252 - 268

Ibe, K.A. and. Osabor, V.N. (2014). Use of TOC, SOM and porphyrins as indices for reconstructing sedimentation pattern as exemplified by Campano – Maastrichtianshales of Nkporo Formation, Calabar Flank, South Eastern Nigeria. Journal Chemical society of Nigeria, 39(1):14 – 20.

Hettinger, R.D. (1995). Sedimentological descriptions and depositional interpretations, in sequence stratigraphic context, of two 300 meter cores from the Upper Cretaceous Straight Cliffs Formation, Kaiparowits Plateau, Kane County, Utah. US Geological Survey Bull. No. 2115 –A, pp.32

Hockey, R.D., Sacchi, R., De Graaf, W.P. F.H. and Muotoh, E.O.G. (1986). The geology of Lokoja-Auchi Area. Geol. Survey of Nigeria Bull. No. 39, pp.71.

Huc, A.Y. (1988). Sedimentology of organic matter. Humic substances and their role in the environment. F.H. Frimmel and R.F. Christman (eds). DahlemKonferenzen, Wiley, Chichester, pp. 45.

Meyers, P.A., (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. Chem. Geol., 114:289-302.

Meyers, P.A., (1997). Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org. Geochem., 27: 213-250

Nwajide, C.S. (2013). Geology of Nigeria’s sedimentary basins. CSS bookshops Limited, 1st edition, Lagos pp. 227-278

Scientia Africana, Vol. 14 (No.2), December 2015. Pp 65-73
 ISSN 1118 – 1931

Nzoussi-Mbassani, P., Disnar, J.R., Laggoun-Défarge, F., (2003). Organic matter characteristics of Cenomanian Turonian source rocks: implications for petroleum and gas exploration onshore Senegal. Marine Pet. Geol. 20:411-427.

Oyo-Ita, O.E., Ekpo, B.O., Oros, D.R., Simoneit, B.R.T., (2010a). Distributions and sources of aliphatic hydrocarbons and ketones in surface sediments from the

Cross River estuary, S.E. Niger Delta, Nigeria. J. Appl. Sci. Environ. Sanit., 5: 24–34.

Rahaman, M.A. (1989): Review of the Basement Geology of Southwestern Nigeria. In Geology of Nigeria, edited by C. A Kogbe 2nd edition. Rockview (Nig) Ltd. Jos, Nigeria, pp. 39 – 63.

Silliman, J.E., Meyers, P.A., Bourbonniere, R.A., (1996). Record of postglacial organic matter delivery and burial in sediments of Lake Ontario. Org. Geochem., 24: 463.

Wehner, H., Teschner, M., (1981). Correlation of crude oil and source rocks in the German Molasse Basin. J. Chromatogr., 204: 481-490.