Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 6 (1): 11-14, 2006
ISSN 1812-5654

Preliminary Assessment of Rare Earth Element Contents of Niger Delta Oils

[1]A. Akinlua, [2]T.R. Ajayi and [3]B.B. Adeleke
[1]Department of Chemistry,
[2]Department of Geology, Obafemi Awolowo University, Ile-Ife, Nigeria
[3]Department of Chemistry, University of Ibadan, Ibadan, Nigeria

Abstact: A preliminary study of the rare earth element contents of some Niger Delta oils was carried out to evaluate their influence on petroleum system of the Niger Delta Basin. The oil samples were obtained from an onshore field in the Niger Delta and analyzed using Inductively Coupled Plasma Mass Spectrometric (ICP-MS) analytical technique. Four Light Rare Earth Elements (LREE), La, Ce, Nd and Pr were detected. Their concentrations varied from 0.009 to 0.49 ppb, 0.058 to 1.58 ppb, 0.01 to 0.47 ppb and 0 to 0.18 pbb, respectively. All the LREE showed significant and positive correlation with each other and also have significant correlation with aromaticity index (Toluene/nC_7). The study showed that REE are not good for classification of oils but provide another tool in oil-oil correlation.

Key words: Rare earth elements, Niger Delta, oil-oil correlation, cluster analysis

INTRODUCTION

Trace elements distribution especially transition metals in oils had been used for oil source rock correlation, classification, maturity of oils and depositional environment of organic matter[1-3] among others. It is now well known that the concentration, distribution and nature of metals in crude oils can give information on the origin and migration of petroleum[4,5].

The origin of transition metals particularly in form of organometallic species in petroleum source rocks may include incorporation from biomass and formation during sedimentation. They may also be incorporated during diagenesis of organic molecules as well as from abiogenic sources during migration of oil.

A lot of data had been published on transition metals of Nigerian crude oils; however, no study has been reported on rare earth elements distribution in crude oils. Largely, rare earth element geochemistry has been more or less restricted to the study of provenance of sediments and petrogenesis of hard rocks. Therefore, the origin of rare earth elements in crude is not known. This preliminary study presents rare earth element data for some Niger Delta oils and attempts to evaluate the influence of rare earth element contents of crude of oils on petroleum systems of the Niger Delta.

MATERIALS AND METHODS

The Niger Delta is located on the continental margin of southern Nigeria and covers an area over 70,000 km^2. The Tertiary wedge of sediments in the Niger Delta consists of three lithostratigraphic units, which show an overall upward transition from pro-delta shales (Akata formation) through sand shale paralic sequence (Agbada formation) to sands and gravels (Benin Formation[6,7]. The habitats of oils in the Niger delta are mainly the Eocene to Pliocene sandstone reservoirs in the Agbada Formation[7].

Twelve crude oil samples obtained from an onshore field in the Niger Delta were selected for the rare earth elements study. These samples had been previously analyzed for various organic geochemical parameters[8] and thus afforded a basis for comparison with the rare earth element data. The crude oil samples were digested with concentrated sulphuric acid and 50% hydrogen peroxide. Blank was prepared under the same conditions. Replicate samples of the oils were analyzed for rare earth element contents using VG Plasma Quad-3 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

RESULTS AND DISCUSSION

Out of about twenty rare earth elements determined only four; La, Ce, Nd and Pr were identified (i.e., those with values above the detection limits of the instrument). The four elements identified are light rare earth elements. This indicates that the oils are depleted in Medium Rare Earth Elements (MREE) and Heavy Rare Earth Elements (HREE). Lanthanum concentrations range from 0.01-0.49 ppb (Table 1), cerium levels range from 0.01-1.58 ppb, neodymium concentrations range from 0.01-0.47 ppb

Corresponding Author: Dr. Akin Akinlua, Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

Table 1: Rare earth element data of crude oils (values in ppb)

Samples	Ce	La	Nd	Pr	∑LREE
T_1	0.54	0.22	0.17	ND	0.93
T_2	0.01	0.01	0.03	ND	0.05
T_3	0.18	0.11	0.1	ND	0.39
T_4	0.05	0.01	0.04	ND	0.1
T_5	0.15	0.05	0.05	ND	0.25
T_6	0.51	0.18	0.13	0.1	0.92
T_7	1.58	0.49	0.47	0.18	2.72
T_8	0.41	0.14	0.15	ND	0.7
T_9	0.07	0.01	0.04	ND	0.12
T_{10}	0.08	0.05	0.01	ND	0.14
T_{11}	0.19	0.1	0.04	ND	0.33
T_{12}	0.44	0.1	0.18	0.11	0.83
Range	0.01-1.58	0.01-0.49	0.01-0.47	0-0.18	
Mean	0.35±0.43	0.12±0.13	0.12±0.13	0.03±0.06	
Av. Shale *	83	41	38	10.1	172.1

Av. Shale*; Average shale values from Piper (1974) INAA results in ppm
ND; Not Detected

while praseodymium concentrations vary from ND 0.18 ppb. The values are low compared to values of average shale of Piper[9] (Table 1). Also they show large variation. The ∑LREE varied from 0.05-2.72 ppb. The highest value of 2.72 recorded for T 7 is accounted for the high Ce content of 1.58. Generally Ce accounts for between 25 and 63% of the ∑LREE. The relatively high Ce values are due to the fact that in ocean, Ce is oxidized to the 4^+ oxidation state, forms insoluble compounds and is preferentially precipitated.

All the rare earth elements show significant positive correlations with one another (Table 2). This is as expected because they have striking similar nature of occurrence with exhibition of 3^+ oxidation state. The four rare earth elements identified in this study usually occur together. One of the major sources of these elements is monazite sand, which is a mixture of trivalent lanthanide orthophosphate with 30% thorium phosphate, La, Ce, Nd and Pr make up over 60% of monazite sand[10].

Each of the rare earth elements correlates strongly with total rare earth elements (∑LREE). La/Ce and Nd/Ce ratios have strong correlations (r = 0.897). This seems to suggest that cross plot of these ratios will be useful in discrimination of oils. Each of the rare earth elements and ∑LREE correlate strongly with Toluene/nC_7 (aromaticity index) (Table 2). The rare earth elements do not have significant correlation with the organic parameters except Toluene /nC_7 (aromaticity index).

Petroleum Systems: Inference from Rare Earth Elements Contents: Genetic classification and oil quality evaluation of these oils could not be obtained on the basis of Rare Earth Element (REE) contents. As indicated earlier rare earth elements do not have significant correlation with the organic geochemical parameters that are source and environment of deposition indicators (Table 2).

The grouping of these oils on the basis of dendrogram cluster analysis using rare earth elements as variables (Fig. 1) does not compare well with the grouping obtained from the cross plot of Pr/nC_{17} vs Ph/nC_{18} (Fig. 2). Cross plot of Pr/nC_{17} vs Ph/nC_{18} discriminated the oils into two groups, one group consists of T_1, T_3, T_6, T_8, T_9, T_{10} and T_{12}, which are normal oils while the second group consists of T_2, T_4, T_5, T_7 and T_{11}, which are slightly degraded oils. Cluster analysis of the oils using rare earth elements as variables (Fig. 1) discriminated the oils into three groups. One group consists of T_2, T_3, T_4, T_5, T_9, T_{10} and T_{11}, which are combinations of normal and degraded oils, the second group consists of T_1, T_6, T_8 and T_{12}, which are normal oils and the third group consists of T_7 only-degraded oil. Although, a level of separation of normal and degraded oils was obtained but not effective.

A significant positive correlation of REE and Toluene/nC_7 (aromaticity index) suggest that REE may be useful in the evaluation of evaporative fractionation of oil by gas washing since aromaticity index has been a good tool in the evaluation of evaporative fractionation of oil but further study and analysis of more oil samples need to be done to ascertain this.

A pictorial representation of the abundance of the REE contents of these oils (Fig. 3) makes a unique geochemical signature. All the oils form similar REE patterns irrespective of post generative alterations that might have taken place. They only differed from each

Table 2: Pearson correlation matrix of rare earth elements and hydrocarbon ratios of some Niger Delta oils

	La	Ce	Nd	Pr	TREE	Nd/Ce	La/Ce	Pr/Ph	Pr/nC_7	CP_I	Tol/nC_7
La	1										
Ce	0.979	1									
Nd	0.951	0.983	1								
Pr	0.763	0.846	0.839	1							
TREE	0.838	0.839	0.759	0.822	1						
Nd/Ce	-0.3	-0.28	-0.23	-0.2	-0.25	1					
La/Ce	-0.24	-0.27	-0.24	-0.2	-0.22	0.897	1				
Pr/Ph	0.22	0.153	0.164	-0.09	-0.02	-0.13	0.1	1			
Pr/nC_7	0.196	0.224	0.189	0.107	0.186	0.362	0.247	0.081	1		
CP_I	0.31	0.304	0.367	-0.02	0.098	-0.03	-0.15	0.217	0.246	1	
Tol/nC_7	0.746	0.737	0.679	0.567	0.613	-0.17	-0.11	-0.13	0.457	0.21	1

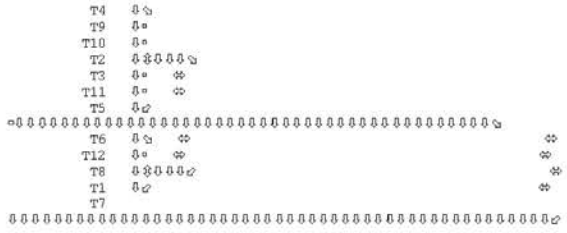

Fig. 1: Dendrogram cluster analysis of some Niger Delta oils using rare earth elements as variables

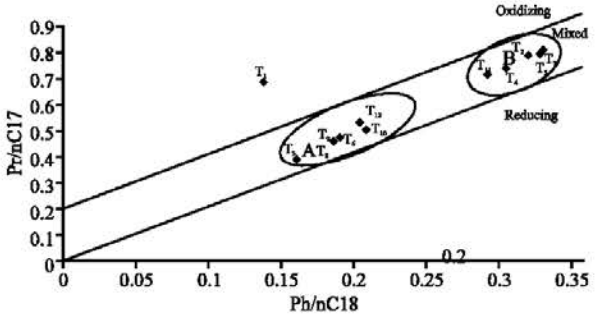

Fig. 2: Cross plot of Pr/nC_{17} versus Ph/nC_{18} of some Niger Delta oils

other in terms of abundance of each REE .The similarity in the REE distribution patterns reveals that the oils have common origin, which supports the results based on organic geochemical data[8]. REE contents of the crude oils will therefore be a useful tool to distinguish oils from different sources, which will make an effective tool in oil-oil correlation.

Sources of rare earth elements in crude oils: The sources of many transition elements in crude oils are already well established and documented in the literature[1-3] among others. But the source (s) of rare earth elements in crude oils are not known yet.

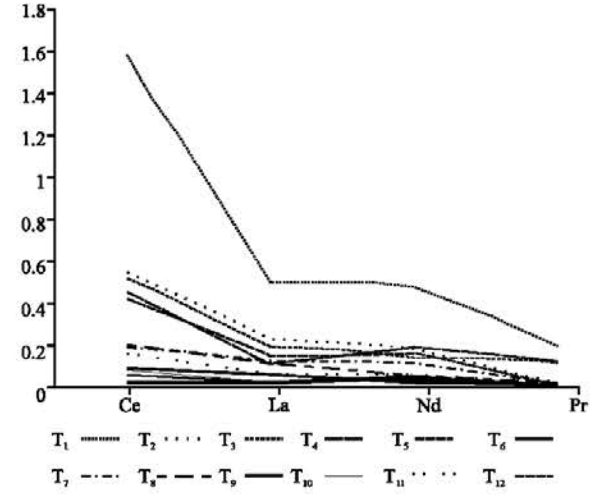

Fig. 3: Pictorial representation of abundance of rare earth elements in some Niger Delta oils

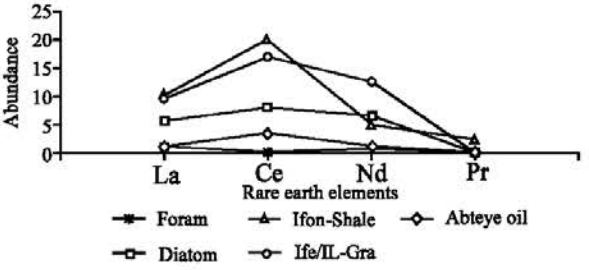

Fig. 4: Comparison of REE patterns of the oils and other sources

Monazite sand, one of the major sources of light rare earth elements could not be the possible source of the rare earth elements identified in this study because no significant amount of thorium, which constitutes about 30% of monazite sand, was identified and as such, monazite sand is ruled out.

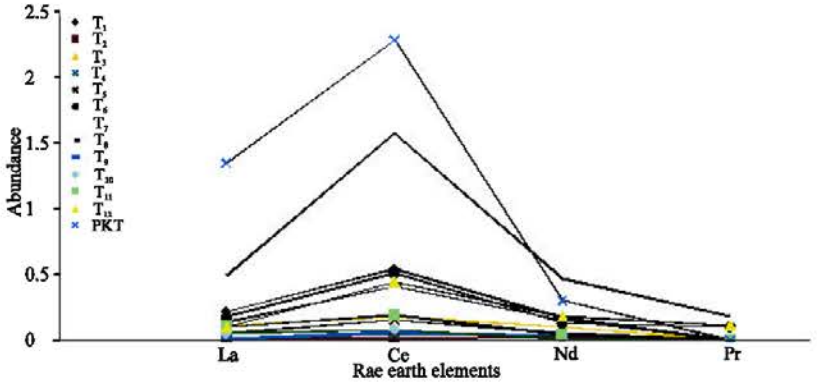

Fig. 5: Comparison of rare earth element patterns of the oils and plankton

The distribution patterns of LREE of these oils when compared with those of sediments derived from igneous rocks show different trends (Fig. 4). Also, the REE patterns of forams and diatoms are at variance with the REE patterns of these oils.

A comparison of the REE patterns of the oils and bulk plankton (Fig. 5) shows strong similarity. This suggests that the REE contents of these oils could have biological source input but study continues on this subject in order to know the actual source of rare earth elements in oils.

CONCLUSIONS

The rare earth element data of some Niger Delta oils revealed that the REE concentrations are low and show large variations. The groupings based on rare earth elements did not agree with organic geochemical data based classification. Therefore Rare earth elements may not be useful to classify oils. The REE distribution patterns showed that the oils have common origin, which agreed with the organic geochemical data. The REE contents may be a useful for evaluation of evaporative fractionation of oils by gas washing.

ACKNOWLEDGMENT

The authors are grateful to Chevron Texaco Nigeria Limited for providing the samples and the permission to publish the results.

REFERENCES

1. Barwise, A.J.G., 1990. Role of nickel and vanadium in petroleum classification. Energy and Fuels, 4: 647 - 652.
2. Nwachukwu, J.I., A.F. Oluwole, O.I. Asubiojo, R.H. Filby, C.A. Grimm and S. Fitzgerald, 1995. A Geochemical Evaluation of Niger Delta Crude Oils. In: Oti, M.N. and G. Postma (Eds.). Geology of Deltas. A.A. Balkema/ Rotterdam/brookfield, pp: 287-300.
3. Udo, O.T., S. Ekwere and S. Abrakasa, 1992. Some trace metals in selected Niger Delta crude oils: Applications in oil-oil correlation studies. J. Min. Geol., 28: 289-291.
4. Elirich, J., A.V. Hirner and H. Stark, 1985. Distribution of trace elements in crude oils from southern Germany. Chem. Geol., 48: 313-323.
5. Hirner, A.V., 1987. Metals in Crude Oils, Asphaltenes, Bitumen and Kerogen of Molasse Basin, southern Germany. In: ACS Sysposium Series 344, Filby and Branthaver Eds., pp: 146-153.
6. Short, K.C. and A.J. Stauble, 1967. Outline of geology of Niger Delta. AAPG Bull., 51: 761-779.
7. Evamy, B.P., J. Haremboure, P. Kamerling, W.A. Knoop, F.A Molly and P.H. Rowlands, 1978. Hydrocarbon habitat of tertiary Niger Delta. AAPG Bull., 62: 1-39.
8. Akinlua, A., 2004. Petroleum geochemistry of oils and sediments of Abiteye field in the Niger Delta, Ph.D. Thesis, University of Ibadan, Nigeria.
9. Piper, D.Z., 1974. Rare earth elements in the sedimentary cycle. A summary. Chem. Geol, 14: 285-304.
10. Lee, J.D., 1994. Concise Inorganic Chemistry. Chapman and Hall, London, pp: 1032.