First online volume
Jour. Indian Association of Sedimentologists, Vol. 35, No. 1 (2018), pp.89-98
ISSN 0970-3268

Characterization of carbonaceous matter from sandstone type uranium deposits of Umthongkut-Wahkut, West Khasi Hills District, Meghalaya.

Asoori Latha*, Jitu Gogoi, M.B.Verma** and L.K.Nanda***
Atomic Minerals Directorate for Exploration and Research
AMD Complex, Begumpet, Hyderabad-500016, India.
AMD, Northeastern Region, Nongmynsong, Shillong-79300, India.
Email: asoori.latha@yahoo.com

Abstract: The strong association between uranium and carbonaceous matter, more so in sandstone type uranium deposits world over is well known. In India, sandstone type uranium deposits are mainly located in Meghalaya. Wahkut and Umthongkut constitute two prominent areas in Meghalaya Plateau hosting sandstone type U-mineralization in Lower Mahadek Sandstone of Cretaceous age. In order to evaluate the contribution of carbonaceous matter in U-mineralization in these areas, core samples of Lower Mahadek Sandstone were studied in terms of Total Carbon (TC), Total Organic Carbon (TOC) to understand the relation between uranium mineralization and carbonaceous matter. The carbonaceous matter samples were also taken up for Carbon-Hydrogen-Nitrogen- Oxygen analysis (CHNO) and Functional Group specification by Fourier Transmitted Infrared Spectrometer to decipher the nature of carbonaceous matter that helped in fixation of uranium.

Keywords: Carbonaceous matter, U-mineralization, Lower Mahadek Sandstone, Umthongkut-Wahkut.

Introduction

Sandstone type uranium deposits form significant part of the world uranium resources. They constitute about 18% of world uranium resources and 41% of known deposits (Uranium 2014). Meghalaya is the third uranium rich state in the country after Jharkhand and Andhra Pradesh, accounting for 10% of India's uranium reserves (World Nuclear Association website), with deposits estimated to be around 25,000 tones. The Upper Cretaceous sediments especially the Mahadek Formation of southern Meghalaya plateau of fluvial origin, has been proved as potential host for sandstone type uranium deposit. The area forms a narrow belt extending in the west from Balpakram, Garo Hills to the Lumshong, Jaintia Hills in the east running for almost 180 km and covering about ~1800sq km (Nandy, 2001, GSI, 1974, Sen et.al., 2002). Wahkut and Umthongkut constitute proven areas of U-mineralization in this provenance (Fig.1). Carbonaceous matter is a prime constituent of these sandstones and plays an important role in U-mineralization in these areas Dhanaraju et.al (1989), Kaul Ravi et. al (1990), Sengupta et. al (1991) and Mahendra Kumar et.al (2008). The present studies were carried out to ascertain the nature and role of carbonaceous matter in concentrating uranium mineralization in this particular lithological unit, by estimating Total Carbon (TC) and Total Organic Carbon (TOC) content of the samples and estimation of Carbon-Hydrogen-Nitrogen-Oxygen content. Analysis has been also carried out for the first time for identification of prime Functional Groups by Fourier Transmitted Infrared Spectrometer.

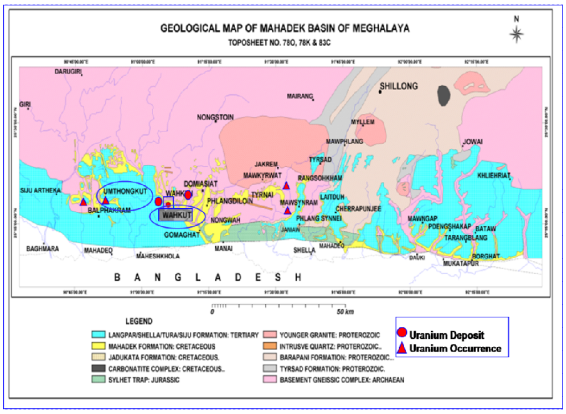


Figure.1 Geological Map of Mahadek Basin with locations of Umthongkut-Wahkut (http://www.amd.gov.in)

The basement rocks for these sediments are constituted by granite-gneisses of Archaean, Shillong Group rocks of Palaeo-Mesoproterozoic, intrusive granites of Neoproterozoic and Sylhet Trap of Jurassic. The lower members of this sedimentary sequence (Jadukata/ Mahadek of Upper Cretaceous period) comprise both fluvial (continental) as well as marginal marine sediments whereas the overlying upper members (Langpar and Shella) are mainly of marine origin (Table.1). The basement rocks are directly overlain by Lower Mahadek Formation at both Umthongkut and Wahkut areas.

Petrography

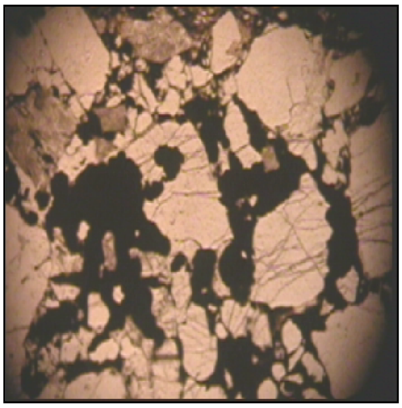
Lower Mahadek sandstone, based on its predominant clast composition and matrix content characterized as tuffaceous quartz wacke. These are matrix supported having poorly to moderately sorted, framework with angular to sub-angular clasts, fine to medium to coarse sand sized clasts with occasional gravel/ pebble sized clasts. Quartz forms the predominant clast component with subordinate feldspar. The clasts of quartz are mostly mono-crystalline with rare polycrystalline grains. The feldspar is represented by K-Feldspar (microcline, perthite) and minor plagioclase. It's content varies from rock

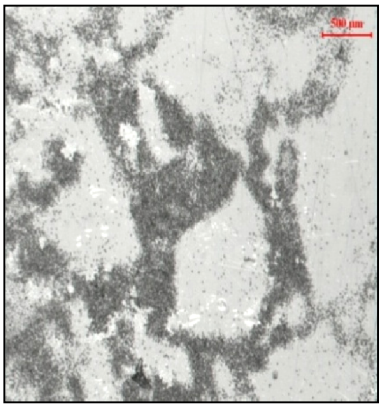
Geological Age	Group	Formation	Lithology
Miocene	Garo	Chengapara 700m	Sandstone, siltstone clay and marl
		Baghmara 530m	Feldspathic sandstone, conglomerate and clay shale, sandstone and marl
		Koipili-Rewak 500m	Shale, sandstone and marl
Eocene	Jaintia	Shella 600m	Alterntions of sandstone and limestone
Palaeocene		Langpar 50–100m	Calc shale, sandstone and impure limestone
Upper cretaceous	Khasi	Mahadek 215m	Upper: Coarse arkosic sandstone and shale (Purple colour typical) Lower: Grey, coarse to fine grained feldspathic sandstone, arkose.
		Jadukata 235m	Sandstone-conglomerate alternations
-------------------------------------Unconformity--------------------------------------			
Jurassic	Sylhet Trap		Basalt, Alkali basalt and acid tuff Alkaline rocks and carbonatite complexes
-------------------------------------Unconformity--------------------------------------			
Neoproterozoic	Mylliem		Coarse porphyritic granite, pegmatite, aplite and quartz vein. Epidiorite and dolerite
Mesoproterozoic	Shillong		Phyllite and quartzite sequence with basal conglomerate
-------------------------------------Unconformity--------------------------------------			
Archaean			Granite gneiss, migmatite, mica schist, sillimanite quartz schist, granulite

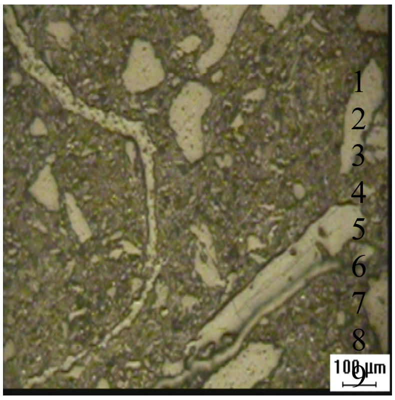
Table.1 Generalized Stratigraphic Succession of the Meghalaya Plateau (The succession is after Chottapadhyay and Hashimi (1984) and Ghosh et al.,(1991)

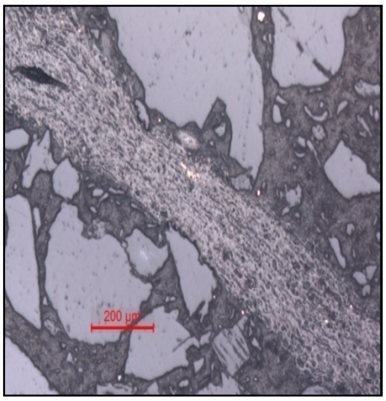
sample to rock sample and on the average constitutes ~ 20% of the total clast content (visual estimation). A few spangles of muscovite/ biotite are observed occurring in association with the matrix. The matrix consists of fine sized quartz, feldspar, chlorite, clay, tuffaceous matter and constitutes up to 25% of the rock by volume. It is frequently infiltrated by a hydrated iron oxide (limonite/ goethite). The tuffaceous matter is constituted by quartz of volcanic origin, defined by their shape, angularity and freshness; glass, devitrified shards and fine volcanic ash. The cement is mostly ferruginous with occasional carbonate cement. Zircon, monazite, xenotime, tourmaline, garnet and rutile are the heavy minerals present. Pyrite, ilmenite, magnetite, chalcopyrite, anatase, goethite, limonite, leucoxene and carbonaceous matter are the opaque phases noticed. Radioactivity is attributed to pitchblende replacing carbonaceous matter, coffinite, occurring in association with matrix frequently with pyrite, brannerite occurring as disseminated grains, adsorbed uranium occurring in association with carbonaceous matter/ matrix material/ leucoxenised ilmenite/ hydrated iron oxides.

Carbonaceous matter occurs as irregular streaks (Fig.2), seams and as globules, mostly occupying pore spaces (Fig.3 & 4). It is both radioactive and non-radioactive. Optically these two types show differences in color and reflectance. The non-radioactive carbonaceous matter is grey in color, comparatively lower reflectance, isotropic and takes a smooth polish (Fig.5). The radioactive species is generally brownish grey, comparatively higher reflectivity, shows faint reflection pleochroism and bi-reflectance and have









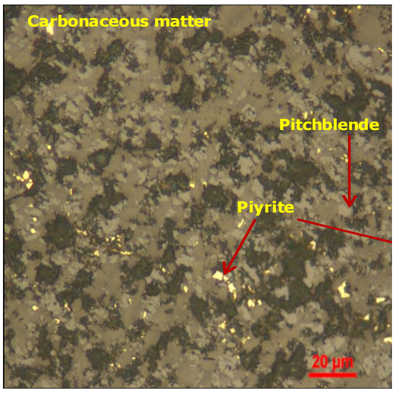


Figure.2 Carbonaceous matter occurring as irregular streaks in Lower Mahadek sandstone.
Figure.3 Radioactive carbonaceous matter along pore spaces of Lower Mahadek sandstone. Transmitted Light, 1 Nicol.
Figure.4 Alpha tracks on CN film corresponds to radioactive carbonaceous matter in Fig.3. Transmitted Light, 1 Nicol.
Figure.5: Non-radioactive carbonaceous matter. Reflected Light 1 Nicol.
Figure.6:Radioactive carbonaceous matter. Reflected Light 1 Nicol.
Figure.7: Pitchblende and pyrite replacing carbonaceous matter. Reflected Light 1 Nicol

Samples & Methodology

Lower Mahadek Sandstone contain variable amount of carbonaceous matter in dispersed state and is intimately associated with uranium bearing minerals. With an intention to ascertain the role of carbonaceous matter in fixing uranium, borehole core samples from different boreholes containing variable content of uranium, including non-mineralized zones were analyzed for Total Carbon (TC) and Total Organic Carbon (TOC). The carbonaceous matter samples were analysed for Carbon-Hydrogen-Nitrogen-Oxygen and Functional Groups by Fourier Transmitted Infrared Spectrometer.

A total of 25 core samples from Wahkut and Umthongkut area were analyzed by Elementar Liqui TOC-B instrument, Chemical Laboratory, AMD Hyderabad for Total Carbon (TC) and Total Organic Carbon (TOC). Sample was heated at 850^0C in a closed furnace in presence of Synthetic Air (Zero Air). Evolved CO2 was estimated by NDIR detector. TOC was estimated after acidolysis of the sample. The precession at 1% TC/TOC is ~10%. Radiometric analysis of borehole core sample for the estimation of uranium, U3O8, is done by beta gamma method, in Physics Lab of AMD, NER, Shillong. In this method, simultaneous beta and gamma radiations are measured. The PC based five channel counting system, consists of NaI (Tl) crystal (solid or well type) for gamma measurement with four single channel analysers and pancake type beta tubes for total beta counting. Based on the U_3O_8 content, the samples were classified into three groups; Group- I containing <100 ppm U_3O_8, Group- II containing 100 to 1000 ppm U_3O_8 and Group- III containing >1000 ppm U_3O_8, so as to understand the correlation between uranium mineralization and carbonaceous matter. Details of total carbon, total organic carbon and uranium content of are given in Table.2.

Sl. No	Sample No	% U_3O_8	% TC	% TOC
Samples with U_3O_8 content <100ppm				
1	WKT/C-43/BOX-1/11	0.003	0.61	0.3
2	WKT/C-43/BOX-1/12	0.003	0.49	0.29
3	WKT/C-43/BOX-3/123	0.006	0.57	0.34
4	WKT/C-43/BOX-3/124	0.005	0.62	0.35
5	WKT/C-43/BOX-4/144	0.002	0.52	0.31
6	WKT/C-43/BOX-4/147	0.002	0.67	0.39
7	WKT/C-43/BOX-5/203	0.002	0.73	0.48
8	UKT/C-57/B-1/20	0.002	0.79	0.49
9	UKT/C-57/B-1/42	0.001	0.74	0.44
10	UKT/C-57/B-1/43	0.001	0.6	0.33
	Av.	0.0027	0.634	0.372
Samples with U_3O_8 content 100 -1000ppm				
1	WKT/C-43/BOX-2/73	0.025	2.08	1.83
2	WKT/C-43/BOX-3/108	0.068	0.65	0.4
3	WKT/C-43/BOX-3/122	0.024	1.83	1.58
4	WKT/C-43/BOX-4/171	0.034	0.63	0.36
5	UKT/C-57/B-1/53	0.025	0.56	0.33
6	UKT/C-57/B-1/54	0.036	0.58	0.35
7	UKT/C-57/B-1/55	0.025	0.63	0.36
8	UKT/C-57/B-1/68	0.015	0.57	0.36

9	UKT/C-57/B-1/69	0.016	0.63	0.38
10	UKT/C-57/B-1/70	0.011	0.69	0.45
	Av.	0.0279	0.885	0.64
Samples with U_3O_8 content >1000ppm				
1	WKT/C-43/BOX-3/110	0.166	0.8	0.53
2	WKT/C-43/BOX-3/118	0.273	1.83	1.61
3	UKT/C-57/B-1/48	0.122	0.92	0.71
4	UKT/C-57/B-1/49	0.32	0.64	0.42
5	UKT/C-57/B-1/50	0.219	0.72	0.46
	Av.	0.22	0.982	0.746

Table.2 Uranium vs Carbon content

Twelve carbonaceous matter samples of radioactive (n=6) and non-radioactive (n=6) sandstone were analysed for Carbon-Hydrogen-Nitrogen and Oxygen (CHNO) at CSIR lab, Jorhat, Assam. The results are given in Table.3

Sl. No.	Sample No	C	H	H/C	N	O	Remarks
1	UKT/C-13/23	56.05	3.86	0.069	0.79	39.3	Samples collected from Radioactive horizon
2	UKT/C-30/16	43.01	2.75	0.064	0.6	53.64	
3	UKT/C-43/6	7.59	1.48	0.19	0.26	90.67	
4	WKT/C-45/95	80.68	4.41	0.06	1.03	13.88	
5	WKT/C-18A/135.20	68.79	4.4	0.064	0.87	24.09	
6	WKT/C-44/176.45	35.77	2.29	0.064	0.54	56.89	
	Average	48.65	3.20	0.085	0.68	46.41	
7	UKT/C-7/11	46.59	3.05	0.065	0.63	49.73	Samples collected from Non-Radioactive horizon
8	UKT/C-1/39	79.94	4.55	0.057	0.95	13.36	
9	UKT/C-15/11	28.86	1.54	0.053	0.42	69.18	
10	WKT/C-38A/B-2/51	61.23	3.82	0.062	0.85	33.18	
11	WKT/C-45/167.80	66.62	3.78	0.057	1.3	28.3	
12	WKT/C-42/228.85	80.63	4.7	0.058	3.8	10.87	
	Average	60.64	3.57	0.058	1.32	34.10	

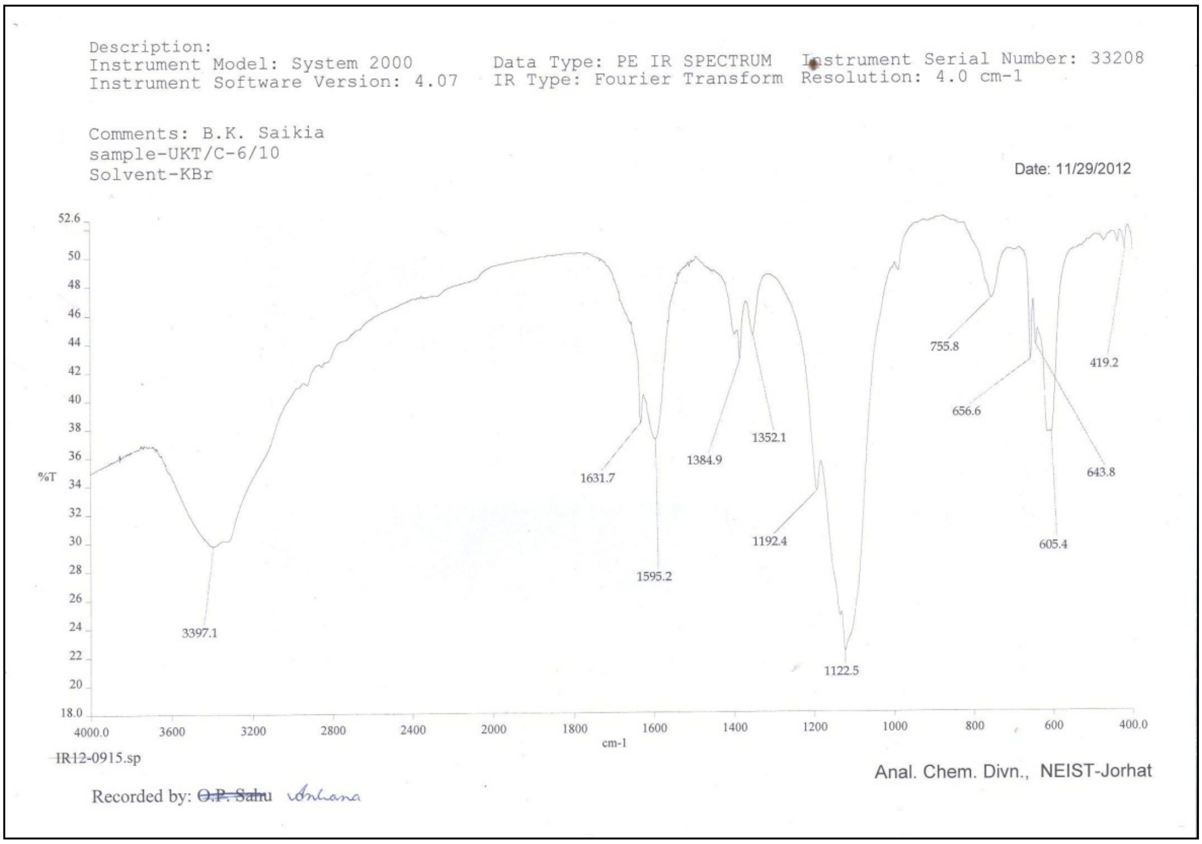
Table.3 CHNO Analysis of carbonaceous matter

Similarly 12carbonaceous matter samples of Umthongkut (n=6) and Wahkut (n=6) were analysed for identification of Functional Groups by Fourier Transform Infrared Spectrometer (FTIR) at CSIR, laboratory, Jorhat, Assam. The study was carried out to decipher the presence of specific Functional Groups that play a key role in uranium fixation. The sample was ground to −200# BS before using it for FT-IR. The FT-IR spectrum was recorded in FT-IR Spectrophotometer Model 2000 (Perkin Elmer) with KBr pellet. The detector used was deuteratedtriglycinesulphate (DTGS). The total number of scans was 50 with the spectral resolution of 4 cm−1 during the recording of the spectra (Fig.8). The results indicate presence of similar functional groups in all the samples. The Functional Groups in carbonaceous matter are given in Table.4.

Sl.No	Sample No	Radiometric assay % U3O8
1	UKT/C-13/23	0.095
2	UKT/C-30/16	0.080
3	UKT/C-43/6	0.020
4	WKT/C-45/95	0.020
5	WKT/C-18A/135.20	0.045
6	WKT/C-44/176.45	0.085
7	UKT/C-7/11	<0.01
8	UKT/C-1/39	<0.01
9	UKT/C-15/11	<0.01
10	WKT/C-38A/B-2/51	<0.01
11	WKT/C-45/167.80	<0.01
12	WKT/C-42/228.85	<0.01

Absorption (cm^{-1})	Functional groups
3614.9	Phenols (O-H)
3421.5	Amines (N-H bond) & Phenols (O-H)
2959.7	Alkanes (CH_3, CH_2,CH)
2908.0	
2333.3	Alkynes (CΞC)
1632.1	Aromatic C=C, vinylic C=C
1458.0 1384.4	CH_2, and partly O-H, C=C group, Sulfoxide (S=O)
1118.4	C=S thiocarbonyl
1030.8	The peak between 1100 cm^{-1} to 400 cm^{-1} can be assigned to presence of clay minerals, quartz etc.
884.5	
855.9	
801.4	
752.6	
534.7	

Table.4 Functional Groups in carbonaceous matter



Description:
Instrument Model: System 2000
Instrument Software Version: 4.07
Data Type: PE IR SPECTRUM
IR Type: Fourier Transform
Instrument Serial Number: 33208
Resolution: 4.0 cm-1

Comments: B.K. Saikia
sample-UKT/C-6/10
Solvent-KBr

Date: 11/29/2012

IR12-0915.sp

Recorded by: ~~O.P. Sahu~~

Anal. Chem. Divn., NEIST-Jorhat

Figure.8 Representative spectra for FTIR

0
1

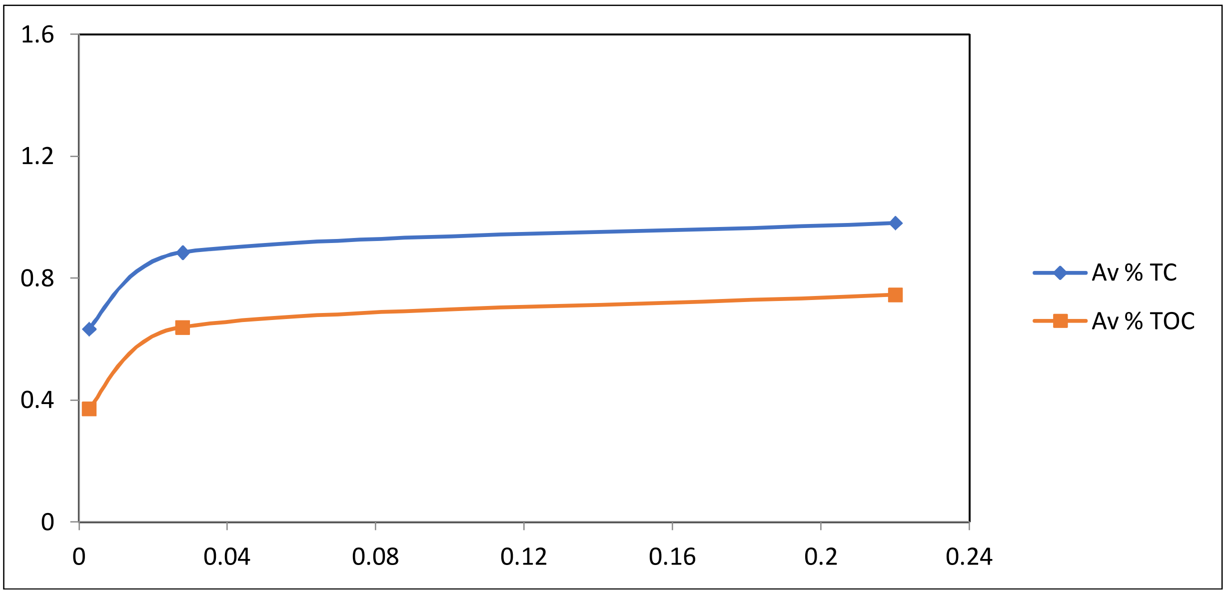
Discussion

The results obtained from Total Carbon (TC) and Total Organic Carbon (TOC) analysis show a positive correlation with uranium content,Table.5, Fig.9. The results clearly indicate that uranium content is more in the samples having more total carbon as well as total organic carbon. The Hydrogen/ Carbon (H/C) ratio for radioactive samples is more, average 0.085, (n=6), as compared to the non radioactive samples, average 0.058, (n=6), indicating more humic nature for the radioactive samples, which is in corroboration with Nash, 1981, who stated that the uranium has the strongest affinity for humic materials. Besides, the Oxygen/ Carbon ratio is also higher in radioactive samples (2.66) as compared to the non radioactive samples (0.78).

Group	Av % U_3O_8	Av % TC	Av % TOC
Group I (<100 ppm)	0.0027 ↓	0.634 ↓	0.372 ↓
Group II(100-1000 ppm)	0.0279	0.885	0.64
Group III(>1000 ppm)	0.22	0.982	0.746

Table.5 Comparisons between TC, TOC and U_3O_8 results

1



2

Figure.9 Correlation of Total Carbon (TC) and Total Organic Carbon (TOC) with uranium content

Van Krevelen diagram, a plot of atomic oxygen/carbon (H/C) versus atomic hydrogen/carbon (O/C) derived from elemental analysis of specific type of organic matter can be used to indicate both biological source (type) and thermal maturity. So, accordingly the average value of H/C vs O/C of carbonaceous matter of radioactive samples (Umthongkut & Wahkut) were plotted in Van Krevelen Diagram (1961, 1984) and Jones and Edison (1978) showing the evolution of the four Kerogen Types with maturation, through the stage of diagenesis, catagenesis and meta genesis. The analysed carbonaceous matter falls in the category of Type-III- Kerogen, Fig.9. Type III Kerogen has low H/C (<1.0) and high O/C (up to ~0.3) (Peters and Moldowan, 1993). Such low hydrogen organic matter is polyaromatic and derived mostly from higher plants. Type III kerosene is the chemical equivalent of vitrinite, telinite, collinite, huminite, and so-called humic or woody kerogen (Miles, 1994).

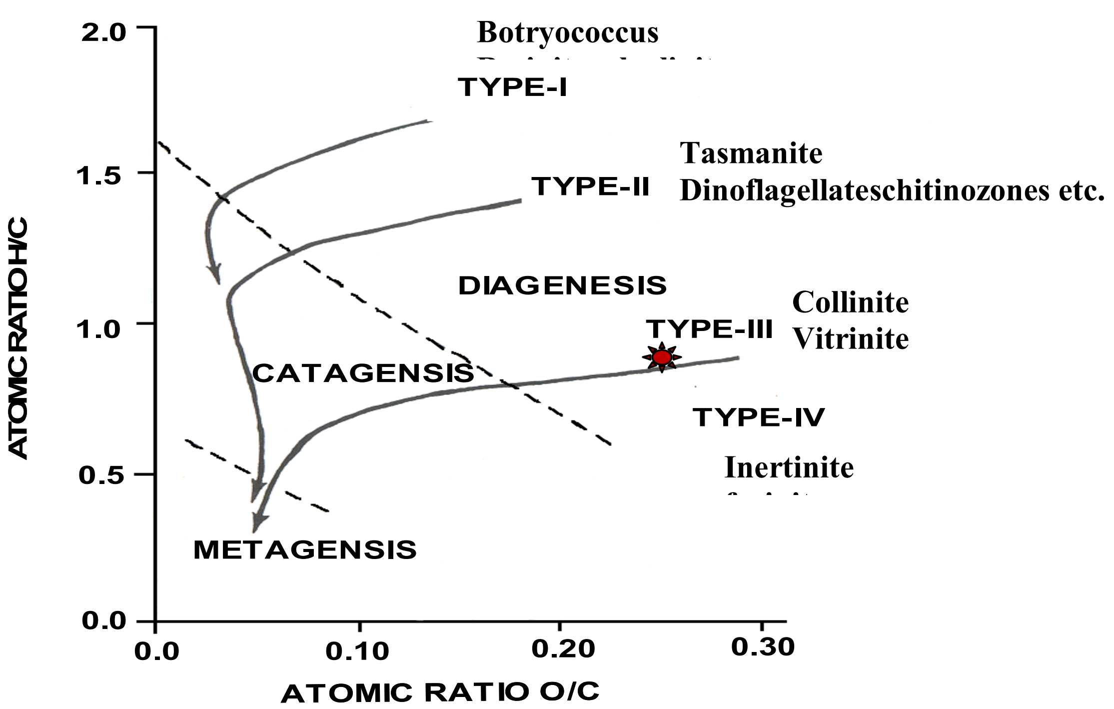


Figure.10 Van Krevelen Diagram (1961, 1984) and Jones and Edison (1978) showing the Kerogen Type of carbonaceous matter of radioactive samples (Umthongkut & Wahkut)

✹- Average H/C vs O/C of carbonaceous matter of radioactive samples (Umthongkut&Wahkut).

The natural organic materials to which uranium is attracted all contain oxygen bearing function group (Moieties, Nash1981). Organic substance found in decomposing plant decries have many oxygen bearing functional group– principally carboxyl (-COOH), carbonyl (-COO) and hydroxyl or phenolic group (-OH). In the process of complexing uranium, the oxygen sites in these groups can be looked upon as performing a function similar to the oxygen in inorganic ligands such as carbonate, phosphate and hydroxyl. The FTIR study found presence of Functional groups like -OH, -COOH and aromatic C=C groups that play a vital role in fixation of uranium. The mechanism by which uranium forms complex with soluble organic matter ligands are chelation, ion exchange and chemi-sorption, etc., which describe fixing of uranium by both dissolve and solid species.

The association of uranium and organic matter has been primarily attributed to two processes, (i) syngenetic or epigenetic reduction/ fixation of uranium by the organic matter, and (ii) mobile hydrocarbon replacing as well as solubilizing primary uranium minerals (Ekain and Gize, 1992). The nature of association organic matter in Umthongkut and Wahkut areas suggests the first process. Immediate burial of sediments without much sorting, alteration and preservation of organic structures in the carbonaceous matter provided anaerobic sapropelic conditions of degradation, except for some parts where humic conditions might have prevailed due to restricted oxygen supply. Uranium carried by circulating ground waters, partly deposited as pitchblende under anaerobic conditions, due to reduction by bacterogenic H_2S, and part in the form of organo-uranyl complexes by complexion with organic matter. Reduction of organo-uranyl complex into pitchblende has taken place during diagenetic and radiolysis induced maturation of the organic matter. During the organic acid stage of maturation of organic matter, changes as solubilization of silica, and formation of organo-silica complexes, secondary organic matter and uranium–clay association and precipitation of coffinite as well as partial conversion of early formed uraninite to coffinite took place (Krishna Raoet. al 1995).

Thus, the results indicate that presence of carbonaceous matter in these sandstones has played a significant role in the formation of U-minerals. The dehydrogenation process of organic matter helped in reducing UO2^{2+} complexes to U^{4+}there by precipitating the U-bearing minerals such as pitchblende and coffinite. Besides, the carbonaceous matter functioned as a physical barrier and as a chemical reducing agent, that helped in preserving the reducing conditions even in the presence of oxidizing fluids, over this long period, thereby sustaining these deposits.

Conclusions

Lower Mahadek Sandstone contain significant quantity of carbonaceous matter in dispersed state.

Within the Lower Mahadek Sandstone, uranium content is more in samples having more Total Carbon as well as Total Organic Carbon.

Carbonaceous matter of the radioactive samples is of more humic in nature with high H/C ratio.

When U^{+6} in ground water comes in contact with carbonaceous matter in sediments, it is reduced to U^{+4} and gets precipitated to form uranium mineral.

Presence of functional groups like Aromatic C=C and Phenols (O-H) which acts as U-fixing agents were inferred from FTIR data of carbonaceous matter of mineralized sandstones.

Thus the content and nature of carbonaceous matter has influenced in fixing uranium in these deposits and further preserving them.

Acknowledgements

The authors are grateful to Director, AMD for his kind permission to publish this paper. JORHAT, Assam is thankfully acknowledged for analysis of carbonaceous matter samples.

References

Atomic Minerals Directorate for Exploration and Research website http://www.amd.gov.in/app16/content.aspx?link=35

Chattopadhyay N and Hashmi S (1984). The Sung Valley alkaline carbonatite Complex, East Khasi and Jaintia Hills districts, Meghalaya; Records Geological Survey of India113, 24-33.

Dhana Raju R, Paneer Selvam A and Virnave SN (1989). Characterization of Upper Cretaceous Lower Mahadek Sandstone and its uranium mineralisation in the DomiasiatGomaghatPdengshakap area Meghalaya India Explo. Res. At. Miner. 2, 1-27.

Ekain and Gize(1992). Reflected-light microscopy of uraniferous bitumen; Mineralogical Magazine 56, 85-99.

Ghosh S, Chakravorty S, Bhalla JK, Paul DK, Sarkar A, Bishui PK and Gupta SN (1991). Geochronology and geochemistry of granite plutons from East K. Hills, Meghalaya; J. Geol. Soc. India 37, 331–342.

Geological Survey of India(1974). Geology and Mineral Resources of India; Geol. Surv. India, Misc. Publ. Calcutta 30, 77.

Jones RW and Edison TA (1978). Microscopic observations of kerogen related to geochemical parameters with emphasis on thermal maturation, in D. F. Oltz, ed., Low temperature metamorphism of kerogen and clay minerals; SEPM Pacific Section, Los Angeles, October, 1-12.

Kaul Ravi and Varma HM (1990). Geological evolution and genesis of the sandstone-type uranium deposit at Domiasiat, West Khasi Hills district, Meghalaya, India; Explor. Res. At. Miner. 3, 1-16.

Krishna Rao N, Sunil Kumar T S and Narasimhan D (1995). Uraniferous Organic Matter in the

Sandstone-Type Uranium Ore from Domiasiat, Meghalaya, India. J. Geol. Soc. India 45407-425.

Mahendra Kumar K, Bhattacharjee P and Ranganath N (2008).Uranium mineralization in the Lower Mahadek Sandstones of Laitduh Area, East Khasi Hills District, Meghalaya; Explor. Res. At. Miner. 18, 101-108.

Miles A J (1994).Glossary of Terms Applicable to the Petroleum System. In: The Petroleum System-from source to trap; Edited by Magoon L B and Dow W G. AAPG Memoir 60, 644.

Nandy DR (2001).Geodynamics of Northeastern India and adjoining Region; ACB Publications, 209.

Peters KE and Moldowan JM (1993). The biomarker guide: Interpreting molecular fossil in petroleum and ancient sediments; Prentice Hall, London 363.

Sengupta B, Bahuguna R, Kumar Sunil Singh R and Kaul R (1991).Uranium exploration in the Cretaceous Mahadek sediments of the Meghalaya Plateau; Curr. Sci. 61, 46-47.

Sen DB, Sachan AS, Padhi AK and Mathur SK (2002).Uranium exploration in the Cretaceous Mahadek sediments of the Meghalaya Plateau; Explor. Res. At. Mine.14, 29-58.

Uranium 2014; Resources, Production and Demand- A Joint Report by the OECD Nuclear Energy Agency and the International Atomic Energy Agency.

World Nuclear Association websitehttp://www.world-nuclear.org/information-library/nuclear-fuel-cycle/uranium-resources/geology-of-uranium-deposits.aspx

Van Krevelen D W (1961).Coal; New York, Elsevier, 514.

Van Krevelen D W (1984).Organic geochemistry-old and new;Organic Geochemistry 6, 1-10.