

Role of Organic Matter in Uranium Mineralisation in Vempalle Dolostone; Cuddapah Basin, India

Sukanta Goswami^{1*}, Sangeeta Bhagat¹, Syed Zakaulla¹, Suresh Kumar¹ and A.K. Rai²

Atomic Minerals Directorate for Exploration and Research, Department of Atomic Energy,

¹Bangalore – 560 072, ²Hyderabad- 500016, India

*E-mail: sukantagoswami.amd@gov.in

ABSTRACT

Dolostone of Vempalle Formation near Tummalapalle hosts large uranium deposit (>100,000 tonnes with an average grade of 0.045% U₃O₈). It is a unique type of uranium deposit because carbonate formations have been considered to be among the least uraniferous of all the rocks of the Earth's crust due to mobility of uranium in aqueous fluid in the presence of carbonate and bicarbonate ions. Vempalle dolostone hosts syn-sedimentary uranium mineralization in the form of discrete uranium phases (pitchblende and coffinite) associated with collophane, and adsorbed uranium in organic matter. The organic matter has played dual role of concentrating uranium from solution and also chemically reducing it to pitchblende and coffinite.

INTRODUCTION

Uranium resources of the world are estimated to be 5.5 million tonnes and the proven resources in India are of the order of 3% of the world resources (Chaki et al., 2010). The uranium mineralisation hosted by Vempalle dolostone accounts for 23% of the Indian resources (Chaki et al., 2010). Vempalle dolostone hosted uranium deposit is the largest uranium deposit in India (>100000 tonnes with an average grade of 0.045% U₃O₈) and it is a unique type of uranium deposit in the world. This higher concentration of uranium in dolostone is of syn-sedimentary type and its precipitation is attributed to organic activity (Rai et al., 2002; 2010). Carbonate rocks generally have been considered to be among the least uraniferous substances of the Earth's crust (Bell, 1963). It is well known that uranium is highly soluble in the presence of substantial concentrations of carbonate or bicarbonate ions. Among the impurities capable of holding small amounts of uranium are certain heavy-mineral resistates, marine apatite, fluorite, and some kinds of organic matter (Bell, 1963). Ore-forming processes in sedimentary environments frequently involve organic material of different origins and chemical composition. Organic matter has long been known to be associated with many types of mineral deposits, especially certain types of uranium deposits. Such an association of uranium and carbonaceous material can be attributed to metal organic compounds or to adsorption and precipitation mechanisms during the sedimentation (Spirakis, 1996). Organic matter is a very sensitive marker of the paleoenvironment and diagenetic history as well as alteration processes. Thus, it may provide useful information that is not easily studied through other rock components. The development of analytical tools in the field of organic geochemistry including 'Rock - eval pyrolysis' and Fourier transformed Infrared (FTIR) spectroscopy have contributed significantly to the understanding of metallogenetic processes and especially of uranium ore formation.

Dolostone hosted uranium mineralization occurs in the Vempalle Formation of Cuddapah basin intermittently over a strike length of 160 km from Reddypalle in NW to Maddimadugu in the SE. For the present study, drill core samples of uranium mineralized dolostone were collected from Rachakuntapalle to Motnupalapalle sector to

determine the nature and type of organic matter and its role in uranium mineralization.

GEOLOGICAL SETTING

The Cuddapah basin consists of sedimentary and associated volcanic rocks, having cumulative thickness of about 12 km, ranging in age from late Paleoproterozoic to Neoproterozoic (Bhaskar Rao et al., 1995; Ramam and Murty, 1997; Zachariah et al., 1999). Pioneering work was done in the basin in the eighteen seventies by V. Ball, T. Oldham, R. Bruce Foote and W. King. Systematic mapping by Geological Survey of India led to some significant changes in stratigraphy. A detail description of stratigraphy, structure, igneous activities, mineral potentiality and basin evolution is given by Nagaraja Rao et al. (1987).

The present study area along south western margin of cuddapah basin forms part of Papaghni Group with basal Gulcheru quartzite unconformably overlies the Archaean Dharwar batholithic granitoids (Fig. 1). The Vempalle Formation, overlying Gulcheru quartzite, consists of Massive dolostone, conglomerate, mineralised dolostone, purple shale and cherty dolostone from up dip towards down dip direction depicting the stratigraphic sequence (Fig. 2). These rocks are indicating shallow marine shelf to platformal environment in general and occasional sub-areal exposures and sea level fluctuation events. The general strike of Vempalle Formation in Tummalapalle – Rachakuntapalle – Kannampalle and surrounding areas is NNW-SSE; with dip ranging from 15° to 20° towards NNE (Fig. 3,4). Carbonate rock (Vempalle Formation) hosted strata-bound type uranium mineralization occurs along the bedding planes as two bands, hangingwall band and footwall band with a vertical separation of 1m to 3m. Both the bands show homogeneity along and across the strike in terms of thickness and metal content.

Stratabound Uranium Mineralization in Vempalle Formation

The stratabound uranium mineralisation hosted by Vempalle dolostone (Vasudeva Rao et al. 1989; Jeyagopal and Dhana Raju, 1998) along south-western margin of Cuddapah basin in Andhra Pradesh accounts 23% of the Indian resources (Chaki et al., 2010). Uranium mineralisation is hosted by impure phosphatic siliceous dolostone and extends from Reddypalle in the northwest to Maddimadugu in the southeast over a belt of around 160 km. intermittently with promising mineralisation at Tummalapalle, Rachakuntapalle area in the central part (Vasudeva Rao et al., 1989; Dhana Raju et al., 1993). Megascopically, the mineralized dolostone consists of alternating light to dark grey coloured thin layers consisting of fine to coarse grained dolomite, ultrafine collophane, and detritus component consisting of quartz, feldspar, tourmaline, zircon and monazite (Roy et al., 1990). Presence of primary sedimentary structures like mud cracks, ripple marks and abundant algal stromatolites associated with mineralized bed indicate a shallow marine environment of deposition (Roy and Dhana Raju, 1997). The study of the complete sequence of Vempalle

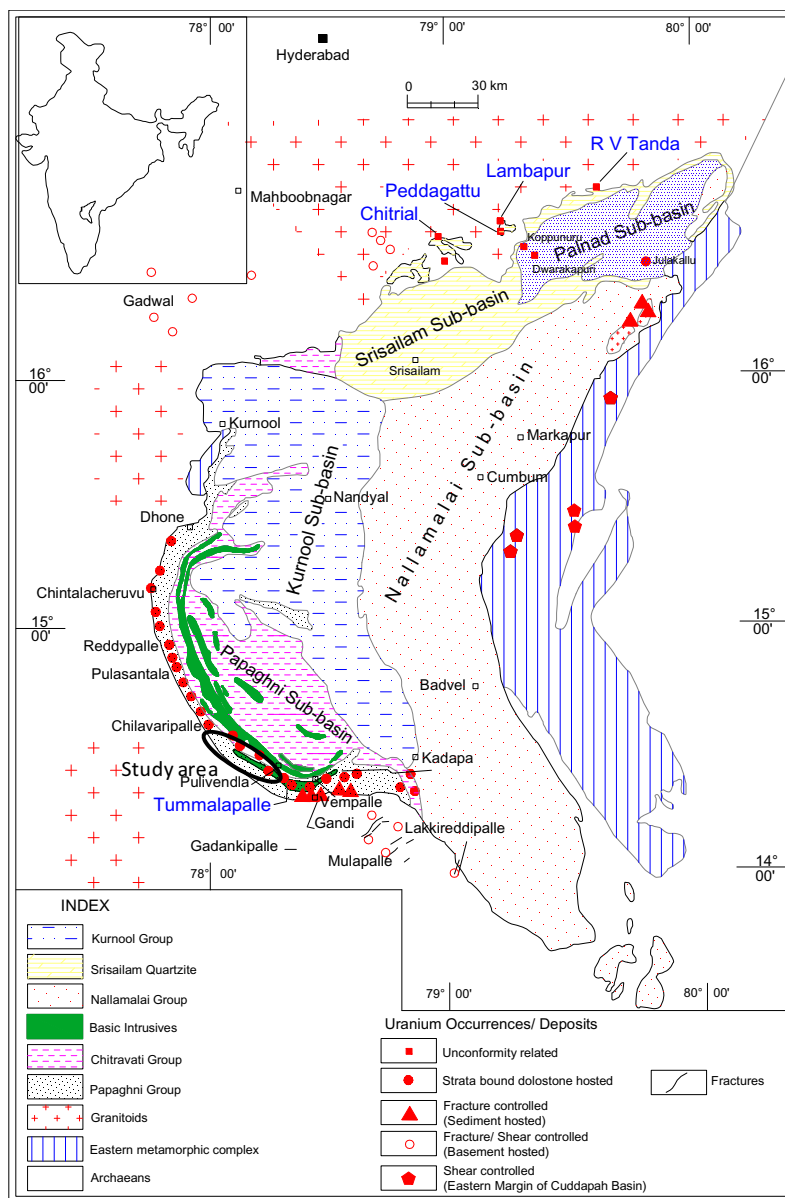


Fig 1. Geological map of Cuddapah basin showing the study area (Zakaulla et al., 2013).

Formation in the explored areas shows that the carbonate facies commences with massive dolostone, followed by thin intermittent conglomerate/grit band, mineralised phosphatic dolostone, purple shale and cherty dolostone. Presence of secretory structures, oolites and stromatolites favour deposition of biogenic material during sedimentation in an inter-tidal mud-flat environment (Rai et al., 2002). Fertile basement granite bordering the Cuddapah basin is believed to be the source for uranium. Other ore forming factors are influx of oxygen during Mid-Proterozoic leading to chemical liberation and concentration by biochemical reduction under euxinic conditions.

The study area along Motnupalapalle – Rachakuntapalle tract (Fig 3) is chosen due to the availability of fresh drill core samples.

ANALYTICAL TECHNIQUES

Rock - Eval pyrolysis, a method for rapid evaluation and characterisation of organic matter in sediments by programmed temperature heating, was carried out in the Organic Geochemistry laboratory, Department of Earth Sciences, IIT Bombay (Rock-Eval-6; Vinci technologies, France, SA-27B, with IFP 55000 is the standard used in this analysis.). Ten core samples from TPL-II-83 bore hole (Table 1) were analysed for TOC content, maturity and type of kerogen,

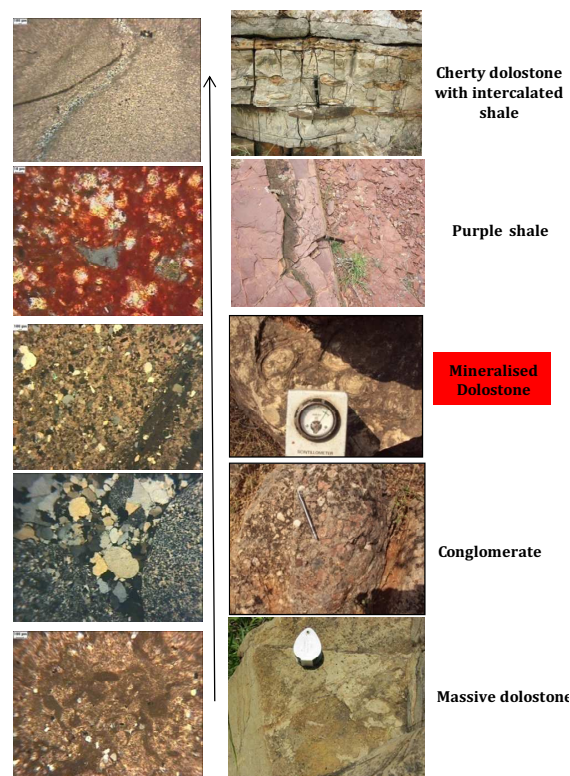


Fig 2. Stratigraphic column of Vempalle Formation showing different lithounits in microscopic and mesoscopic scale.

hydrogen index (HI) & oxygen index (OI) etc throughout the Vempalle Formation.

FTIR spectroscopic analysis was carried out on 30 core samples collected from five blocks (Rachakuntapalle to Motnupalapalle) (Fig 3), at SAIF, IIT Bombay (Bruker, Germany, 3000 hyperion microscope with vertex 80 FTIR system). From each bore hole 2 samples were selected from the mineralised upper and lower bands and one from the barren zone in between (Table 2). Samples were prepared by pressed pellet technique using KBr as binding material (French et al. 1954). The spectrums produced from analysis shows how the percentage transmittance varies with the frequency of the infra-red radiation (Fig. 6). Peaks at around 3510 cm^{-1} , $2900\text{--}2990\text{ cm}^{-1}$, $2300\text{--}2410\text{ cm}^{-1}$, $1456\text{--}1667\text{ cm}^{-1}$, 1110 cm^{-1} of medium to weak intensity corresponds to KBr and absorbed water molecules. At around 1490 cm^{-1} , 1430 cm^{-1} , 885 cm^{-1} and 800 cm^{-1} wave numbers are due to presence of MgO in the dolostone (Huang and Kerr, 1960). CaO exhibit peaks at around 3510 cm^{-1} , 1493 cm^{-1} , 1429 cm^{-1} and Na_2CO_3 at 2530 cm^{-1} , 1795 cm^{-1} , 1450 cm^{-1} , 881 cm^{-1} and 700 cm^{-1} .

Petrographic study including identification of radioactive phases by alpha sensitive cellulose nitrate film was carried out in petrology laboratory, AMD, Bangalore.

Rock - Eval Ppyrolysis

Table 1 summarizes the parameters and data obtained from the analysis of the ten core samples. Parameter S_1 is a measure of the amount of hydrocarbon liberated at 300°C . Peak S_2 is the amount of hydrocarbon released during temperature programmed pyrolysis ($300\text{--}600^\circ\text{C}$). TOC is determined by oxidizing the pyrolysis residue in a second oven (600°C in air). The analysis indicates that the sediments as a whole have TOC content ranging from 0.26 to 0.02%. S_2 ranges from 0.01 to 0.05 mg hydrocarbon (H.C.)/g sample. This range indicates a very low source rock potential for oil. S_1 values in general

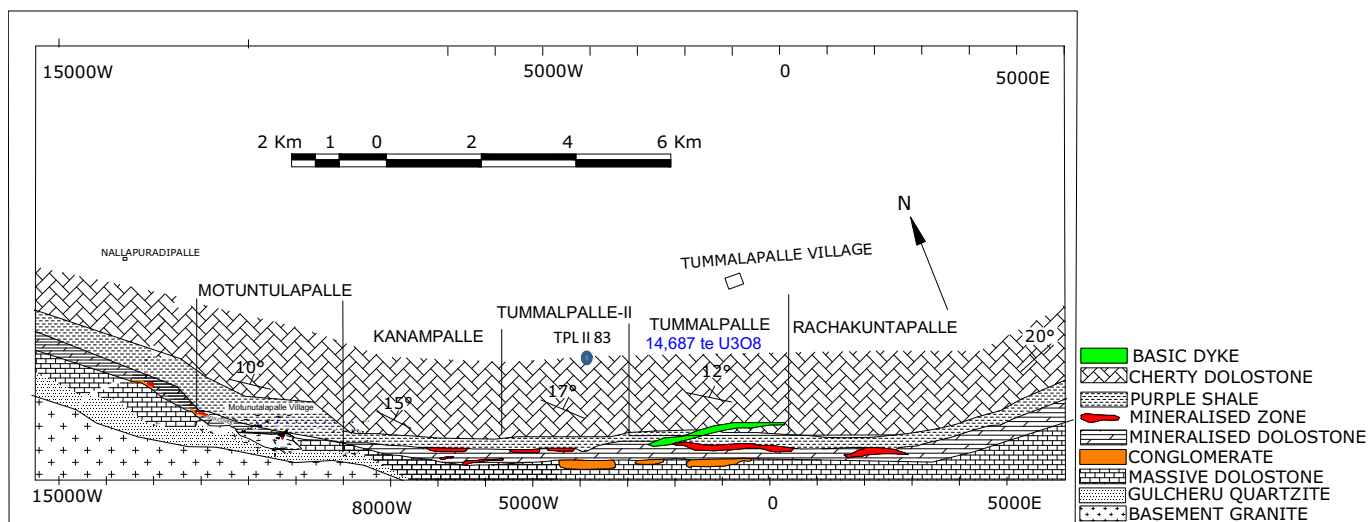


Fig 3. Geological map showing five blocks in the study area along Motnutalpalale – Rachakuntalpalale.

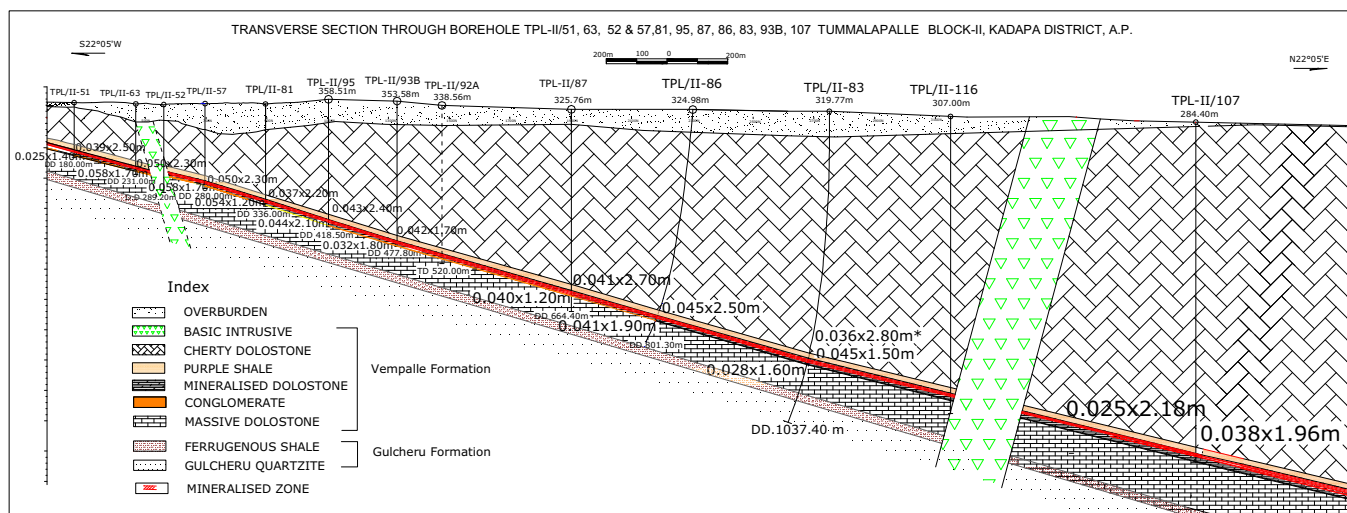


Fig 4. Transverse section showing uranium mineralization in Vempalle Formation.

are 0.01 to 0.02 mg H.C./g. S_3 ranges from 0.02 to 0.1 mg CO_2/g sample. HI values are from 12 to 50 mg H.C/g TOC and this represents no oil and gas potential. From the measured values, some other parameters may be calculated. HI is the normalized S_2 value (S_2/TOC), expressed as mg HC/g of TOC, which allows the types of organic matter to be estimated and the S_2 vs TOC plot gives linearity indicating less matrix effect. OI varies from 12 to 150 with an average of about 90. According to the HI vs.OI diagram (Fig. 5A), organic matter in the samples can be classified as type IV kerogen. The HI vs T_{max} (Fig. 5B), OI vs T_{max} (Fig. 5C), and S_1 vs TOC (Fig. 5D) plots have also been studied. The T_{max} values ranges from 315° to 483°C. S_2 values ranges from 0.01 to 0.05 which represents very low hydrocarbon contents. Therefore the corresponding T_{max} values are not reliable indicator of thermal maturity. The very low H.C. content represents overmature kerogen of type IV category, possibly derived from algae.

Fourier Transform Infrared Spectroscopy

The spectra of 30 samples of dolostone show strong absorption bands between 3050 and 2850 cm^{-1} , 2650 and 2500 cm^{-1} , 1800 and 1820 cm^{-1} , 1400 and 1500 cm^{-1} , 865 and 885 cm^{-1} , 715 and 730 cm^{-1} . The FTIR bands detected at 3013 to 3016 cm^{-1} and 2625 to 2630 cm^{-1} are combination frequencies (Nguyen et al., 1991), and the band at 710 to 730 cm^{-1} corresponds to the in-plane bending (ν_4) mode of

CO_3^{2-} in the dolomite structure (Farmer, 1974). Bands at 2625 to 2630 cm^{-1} and 710 to 730 cm^{-1} are attributed to dolomite in the samples. The absorption bands at the 2600 to 2550 cm^{-1} region indicate S-H bonding. In the spectra of these carbonate samples the out of plane bending (ν_2), asymmetric stretching (ν_3), and the in-plane bending (ν_4) modes of the carbonate ions are found to be active. Asymmetric stretching (ν_3) is prominent in 3 samples (F1, F2 and F4), whereas other samples show dominant bending motion during interaction with electromagnetic radiation. Besides the first order internal modes, the $\nu_1 + \nu_4$, $2\nu_2 + \nu_4$ and $2\nu_3$ combination modes are observed (Table 2).

All the samples have more or less strong bands related to the presence of bound water (3300 to 3500 cm^{-1}). The bands at 1035 to 1045 cm^{-1} , 775 to 800 cm^{-1} , 520 to 530 cm^{-1} , and 455 to 465 cm^{-1} indicate the presence of silicate phases (Si-O vibrations).

Other than the above mentioned spectra of inorganic phases no spectra corresponding to organic phases are present. It may be noted that Rock-eval pyrolysis has shown negligible organic carbon content in the samples.

PETROGRAPHY

The uranium mineralised siliceous phosphatic dolostone is fine grained, banded and consists of dolomite, siliciclastic minerals and pelloids. Some of the dolostones have bands of dolomite, chert,

Table 1. Rock-eval pyrolysis sample list from TPL-II-83 bore hole for routine analysis of organic matter throughout the Vempalle Formation.

Sample no	Rock type	Grade (%U ₃ O ₈)	Depth (m)	Quantity	S1	S2	S3	HI	OI	PI	T _{max}	TOC
IFP 55000	Standard	—	—	60mg	0.72	10.24	1.09	357	38	0.07	421	2.87
SG/AMD/1	Cherty Dolostone	—	122.40	60.1mg	0.01	0.03	0.06	43	86	0.24	483	0.07
SG/AMD/2	Cherty Dolostone	—	690.00	61.6mg	0.01	0.01	0.04	17	67	0.46	339	0.06
SG/AMD/3	Impure Dolostone	<0.01	822.45	60.8mg	0.01	0.01	0.02	50	100	0.4	330	0.02
SG/AMD/4	Mineralised Dolostone	0.013	825.51	60.8mg	0.01	0.02	0.06	22	67	0.31	322	0.09
SG/AMD/5	Mineralised Dolostone	0.08	827.30	61.5mg	0.02	0.03	0.04	50	67	0.39	359	0.06
SG/AMD/6	Mineralised Dolostone	0.06	828.20	60.7mg	0.01	0.02	0.06	50	150	0.34	341	0.04
SG/AMD/7	Impure Dolostone	<0.01	834.60	60.4mg	0.01	0.01	0.02	50	100	0.32	315	0.02
SG/AMD/8	Grey shale	—	840.20	60mg	0.01	0.03	0.04	33	44	0.28	348	0.09
SG/AMD/9	Conglomerate	—	841.65	60.5mg	0.01	0.05	0.1	50	100	0.15	428	0.1
SG/AMD/10	Massive Dolostone	—	859.50	60.4mg	0.02	0.03	0.03	12	12	0.38	422	0.26

Table 2. FTIR Sample list of dolostone from different drilling blocks and Vibrational frequency assignments

Bore hole No.	Sample No.	Rock type	Depth (m)	Grade (core assay) (%U ₃ O ₈)	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	ν_4 (cm ⁻¹)	$\nu_1 + \nu_4$	$2 \nu_2 + \nu_4$
MTL-73	F1	Dolostone	226.25	0.088	-	878.71	1441.23	727.06	1819.91	2531.25
MTL-73	F2	Dolostone	228.65	<0.01	-	879.07	1438.08	726.46	1818.90	2531.38
MTL-73	F3	Dolostone	231.00	0.086	-	878.99	-	726.14	1816.45	2531.11
MTL-71	F4	Dolostone	232.70	0.025	-	879.73	1452.23	726.63	1817.04	2531.29
MTL-71	F5	Dolostone	233.70	<0.01	-	879.18	-	725.71	1817.92	2531.14
MTL-71	F6	Dolostone	235.65	0.092	-	878.84	-	725.77	1816.46	2531.73
TPL-II-27	F7	Dolostone	276.35	0.085	-	878.64	-	725.81	1818.01	2531.50
TPL-II-27	F8	Dolostone	279.25	<0.01	-	879.90	-	726.58	1816.33	2531.01
TPL-II-27	F9	Dolostone	281.45	0.051	-	880.28	-	725.56	1816.85	2530.76
TPL-II-68	F10	Dolostone	102.40	0.055	-	879.32	-	726.42	1817.20	2531.25
TPL-II-68	F11	Dolostone	106.65	<0.01	-	880.11	-	725.80	1816.80	2530.00
TPL-II-68	F12	Dolostone	108.35	0.047	-	879.93	-	725.60	1816.17	2531.45
TPL-7	F13	Dolostone	270.45	0.081	-	879.99	-	725.72	1816.41	2530.99
TPL-7	F14	Dolostone	272.70	<0.01	-	880.36	-	725.09	1817.25	2530.99
TPL-7	F15	Dolostone	277.05	0.073	-	880.39	-	726.91	1815.60	2531.27
TPL-44	F16	Dolostone	320.70	0.082	-	878.81	-	726.04	1818.42	2530.77
TPL-44	F17	Dolostone	324.00	<0.01	-	881.00	-	728.88	1815.39	2530.99
TPL-44	F18	Dolostone	326.30	0.140	-	880.07	-	726.52	1816.12	2530.33
RKL-29	F19	Dolostone	314.10	0.055	-	880.06	-	725.49	1816.03	2530.54
RKL-29	F20	Dolostone	317.75	<0.01	-	880.83	-	726.38	1816.77	2530.38
RKL-29	F21	Dolostone	319.50	0.079	-	877.91	-	726.80	1815.28	2530.05
RKL-60	F22	Dolostone	387.50	0.069	-	875.01	-	726.28	1817.01	2530.35
RKL-60	F23	Dolostone	389.85	<0.01	-	876.83	-	732.20	1792.22	2530.87
RKL-60	F24	Dolostone	393.42	0.176	-	879.10	-	725.69	1816.46	2532.05
KNL-51	F25	Dolostone	187.90	0.044	-	879.61	-	727.36	1815.56	2531.83
KNL-51	F26	Dolostone	188.85	<0.01	-	879.19	-	728.43	1818.92	2531.56
KNL-51	F27	Dolostone	191.55	0.095	-	878.63	-	725.19	1816.35	2531.64
KNL-33	F28	Dolostone	266.45	0.052	-	879.42	-	725.68	1816.34	2531.57
KNL-33	F29	Dolostone	268.10	<0.01	-	880.81	-	725.04	1816.77	2531.24
KNL-33	F30	Dolostone	271.08	0.100	-	869.58	-	727.02	1815.49	2530.23

collophane and siliciclastic minerals. Chert rich band also consists of euhedral grains of dolomite. The samples contain detrital sand grains, oolites, peloids and chemically-precipitated minerals either as pore-filling cement, or as products of recrystallization. Three radioactive phases are noted in the samples: discrete uranium phase in the form of very fine grained pitchblende, adsorbed uranium on organic matter and refractory phase in the form of monazite, zircon and metamict minerals.

Terrigenous Admixture

Quartz is the dominant siliciclastic mineral with minor amount of microcline and plagioclase feldspar. Siliciclastic minerals along with peloids rich in opaques are set in fine grained groundmass of dolomite. Presence of heavy minerals like zircon and tourmaline indicate a granitic source. Quartz grains are both monocrystalline as well as polycrystalline pointing to mixed provenance. Presence of rounded zircon indicates significant transportation from the provenance. The

dominant opaque minerals are pyrite with subordinate amount of sphalerite, chalcopyrite and covellite.

Cement

Dolomite is both micritic as well as sparry in nature. Average sparry dolomite size is 0.03 to 0.04mm and micritic dolomite has an average size of 4 to 8µm. Dolomite overgrowth suggests more than one stage of dolomitisation. Apart from cherty groundmass along with dolomite, authigenic silica is also present in the form of overgrowth on siliciclastic minerals. In addition to dolomite as major mineral, calcite and siderite are also present in the dolostone. They are mainly sparry in nature.

Studies of Features Related to Organic Activity

Stromatolitic layering, peloids, framboidal pyrite and carbonaceous matter are present in the dolomitic groundmass (Fig 7A and 7B). Framboidal pyrite is present as aggregate with peloids (Fig 8). These framboidal pyrite are related to primitive micro-

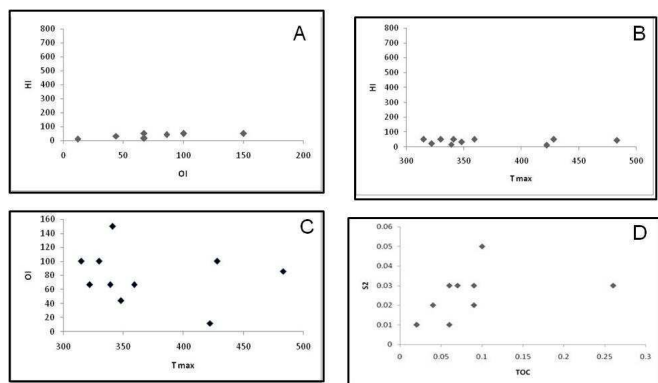


Fig 5. (A.) HI vs OI plots for sample data; **(B.)** HI vs T max plots for sample data; **(C.)** OI vs T max plots for sample data; **(D.)** S1 vs TOC plot.

organisms (Roy et al., 2012). Opaques with anhedral grains are present in the dolomitic groundmass. These are identified as organic matter with stringers of pyrite (Fig 9A). Fine grained pitchblende replaces pyrite at places (Fig 9B). Stromatolitic impure dolostone gives medium to high density alpha tracks (Fig 10) corresponding to black, phosphatic, collophane rich bands (Fig 11).

Petrographic Differences between Mineralised and Non-Mineralised Dolostones

Petrographic study reveals the following differences between mineralised and non-mineralised dolostones in the Vempalle Formation.

1. Detrital siliciclastic minerals content in mineralised dolostone shows a specific range (10 - 20%), whereas non mineralised dolostone shows random siliciclastic mineral distribution (5 - 50%).
2. Collophane is more distinct in radioactive dolostones as compared to non radioactive dolostones.

3. Frequency of pelloids is more in radioactive dolostones in comparison to non radioactive dolostones.
4. Microbial activity (indicated by framboidal pyrite, stromatolites) is relatively more conspicuous in radioactive dolostones.

DISCUSSION AND CONCLUSION

Based on field observation it can be found that the geological setup is favourable for uranium mineralisation in the study area. Fertile basement granitic provenance with average U_3O_8 content of up to 100 ppm is present in the hinterland. Low porosity and permeability of chemically precipitated carbonate rocks do not permit circulation of mineralizing solutions. However, the Vempalle dolostone consists of significant detritus impurities enhancing the porosity and permeability of the rock. The organic matter contained in dolostone must have given the required reducing environment for uranium mineralization and the overlying impervious shale has contributed to its preservation. Presence of framboidal pyrite visible under microscope suggests microbial activities. Precambrian marine biosphere was flooded with microbial communities (Hagadorn and Bottjer, 1997; Schopf, 1999) and their influence on carbonate sedimentary basin-fill has been commonly recorded in the form of stromatolites and associated carbonate structures. The algal debris might have decomposed to produce H_2S . The H_2S and the remaining organic matter could have created the necessary reducing environment for the formation of pyrite and precipitation of uranium in these sediments (Rai et al., 2010; Dhana Raju et al., 1993; Roy and Dhanaraju, 1997). Although organic matters are stronger reductants than H_2S , experiments have shown that the hydrogen sulphide is more aggressive reductant (less kinetically inhibited) and in some deposits H_2S , derived from reduction of sulphate by organic matter may have reduced uranium (Landais, 1995). Once U-deposits were formed organic matter maintains the reducing environment which protects the deposit from oxidation and destruction. The stable form of U in natural waters including seawater is $[UO_2(CO_3)_3]^{4-}$. The main removal process of U is diffusion of $[UO_2(CO_3)_3]^{4-}$ from the water column to the sediments, reduction and

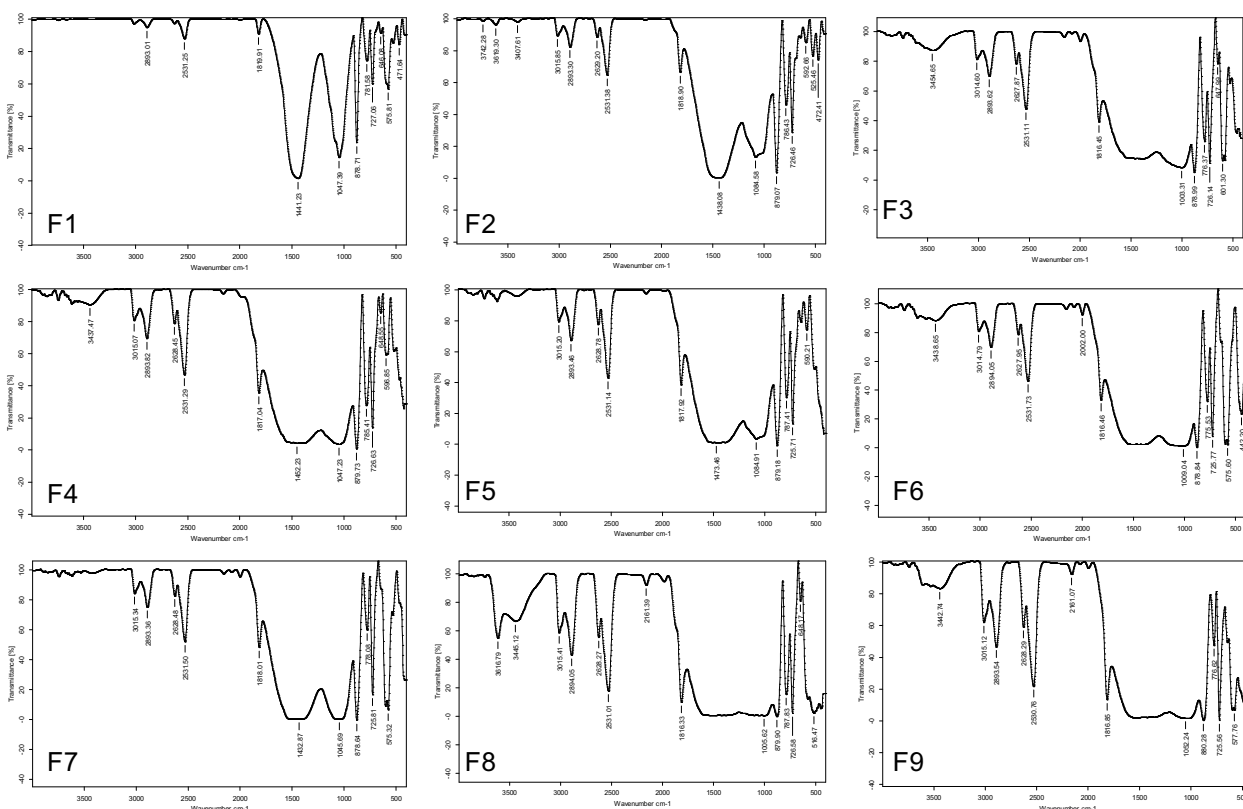


Fig 6. Representative FTIR spectra of Vempalle dolostone.

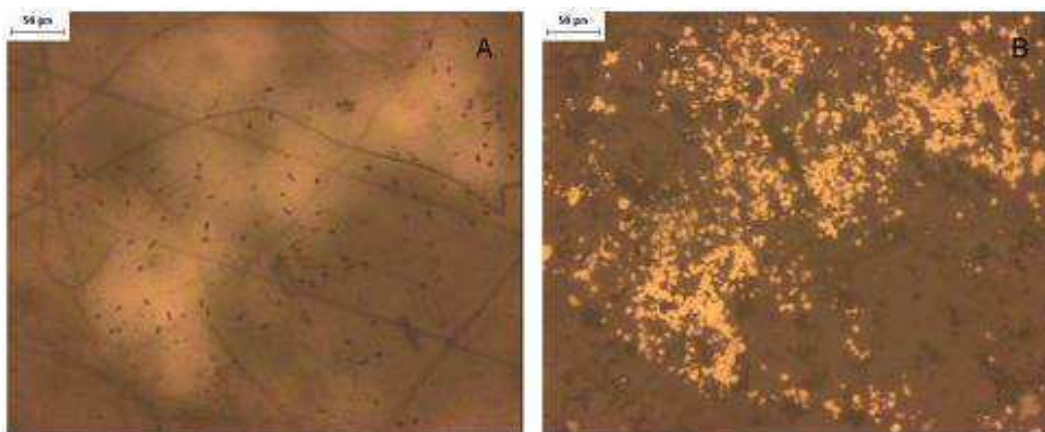


Fig 7. A. Sparse tracks on organic matter with framboidal pyrite. **B.** Framboidal pyrite with organic matter (10X, RL, 1N).



Fig 8. A. Framboidal pyrite as aggregates in association with peloids and carbonaceous matter (20x, TL, 1N). **B.** Sparse tracks due to adsorbed uranium on carbonaceous matter (20x, TL, 1N). **C.** Peloid with pyrite and carbonaceous matter (20x, RL, 1N).

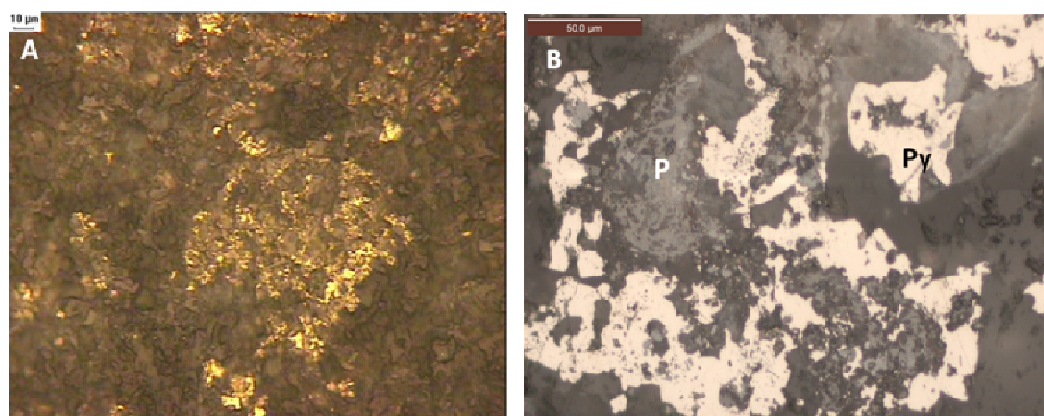


Fig 9. A. Pyrite with organic matter 20X, RL, 1N **B.** Pitchblende (P) of dark grey colour replacing pyrite (Py) in impure dolostone 50X, RL, 1N.

subsequent adsorption or precipitation, possibly as uraninite (Crusius et al., 1996). The whole column of Vempalle Formation in Papaghni sub-basin is dolomitised (Roy and Dhanaraju, 1997). Due to intense evaporation there was increasing concentration of Mg in the water, leading to intermittently intense dolomitization of the whole column of sediments in the basin by supersaturated brine. Evaporation leads to formation of gypsum at places (Fig. 12). The presence of mud cracks indicate occasional sub areal exposure while syneresis cracks indicate shrinkage and swelling in soft substrate as a result of salinity change (Chakrabarti et al. 2012).

Collophane is the main carrier of uranium in dolostone of Vempalle Formation (Rai et al., 2011). Collophane is cryptocrystalline apatite, a common product of organic matter diagenesis, and is known to incorporate substantial amounts of U^{+4} during precipitation. U^{+4} can substitute for Ca^{+2} in the crypto crystalline apatite structure because of their close ionic sizes (0.97 and $0.99 \text{ \AA}$, respectively) whereas U^{+6} can be fixed only in adsorbed state outside the structure (most probably

as uranyl carbonate complex by surface tension). U^{+6} can occur as oxyanion with the chemical formula UO_4^{+2} with a dumbbell shaped structure. Hence the ionic radii along two directions is represented as ($3.1 \times 1.4 \text{ \AA}$). Algae may have extracted phosphorous as one of the nutrient available in the water. The algal blooms in the site of sedimentation may have generated vast amounts of marine organic matter. Phosphate rich laminations in uraniferous dolostone may be organic residues after algal mats. In general, uranium content increases with phosphate content, but the ratio is not constant, thereby suggesting that some uranium probably is attached to clay and organic material. The role of blue-green algae must be one of the most significant (Roy et al., 1990). Although rarely calcified themselves, the blue-green algae play an important role in the formation of carbonate sediments. They are mostly responsible for the formation of a dark micritic layer on the periphery of numerous carbonate fragments. This micritization results from the repeated marginal perforation of these grains by endolithic bluegreen algae and the subsequent filling of this fine network of



Fig 10. Stromatolite within impure dolostone and corresponding CN film showing dense alpha tracks.

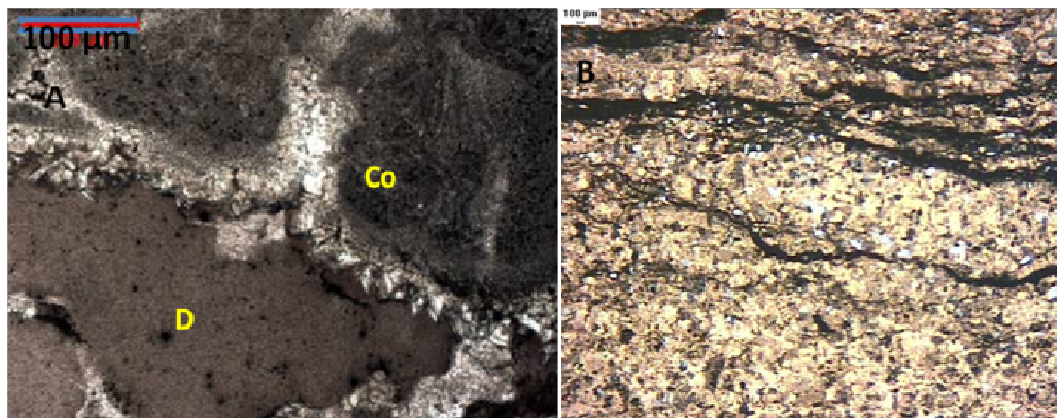


Fig 11. **A.** Shrinkage cracks & cavities in collophane(Co); At the margins of dolomite and collophane, the second generation of euhedral dolomite is developed, 5X, TL, XN; **B.** Dark coloured collophane rich phosphatic band in impure dolostone 2x, TL, XN

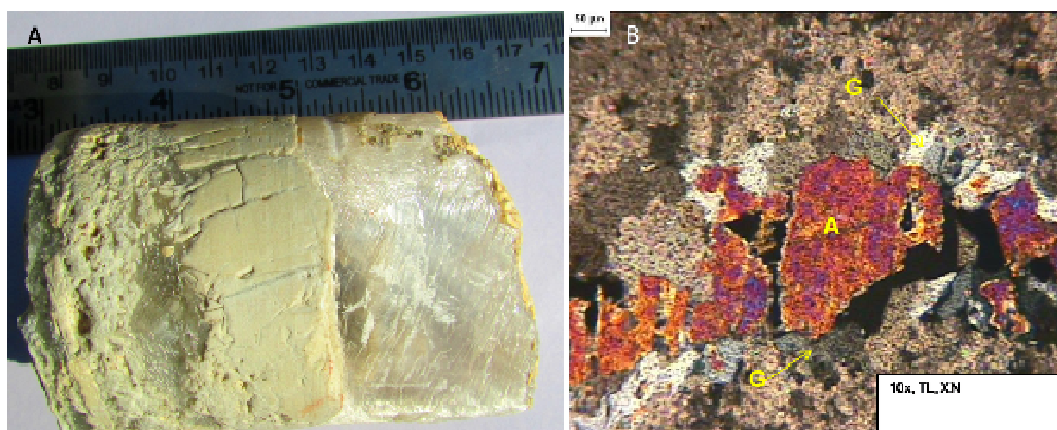


Fig 12. **A.** Gypsum in litho core; **B.** Anhydrite (A) with gypsum (G) in impure dolostone under microscope 2x, TL, XN

cavities by calcareous ooze locally enriched in organic matter (Chamley, 1990). Therefore, with repetition of this alteration phenomenon the complete micritization from margin up to interior may result in formation of peloids without recognizable structures. Micritization of sand - size ooids is related to peloid genesis. Some blue-green algae inhabit the surface of the particle and aid in the binding and/or precipitation of additional calcium carbonate laminae as the ooid grows. Hence, collophane and organic matter are present in association with pyrite and peloids. Petrographic study also suggests that mineralised dolostone contains more peloids, detritus, framboidal pyrite and thus associated microbial activities. Cyanophyceae/ blue-green algae also participate in the formation of algal mats and stromatolites. The stromatolites indicate intertidal to supratidal sea shores where detrital

or, precipitated materials were bound together by the action of blue-green algae. The morphological differences (Fig 13) between various algal structures result from differences in the environmental conditions such as depth, wave energy, sequence and amplitude of tides, supply of detritus, etc. Since, the Paleo to Mesoproterozoic Cuddapah sediments consist of stromatolites derived from algal activities, the kerogen also should have been derived from algae.

According to Rock-eval pyrolysis data highly oxidised type IV kerogen indicates their role as reductant. Now, it is known from sediment characteristics and associated primary sedimentary structures that the depositional environment was shallow marine to fluvial. Therefore the expected kerogen should be of Type I or Type II category. But, the data suggests Type IV, which might have been derived from

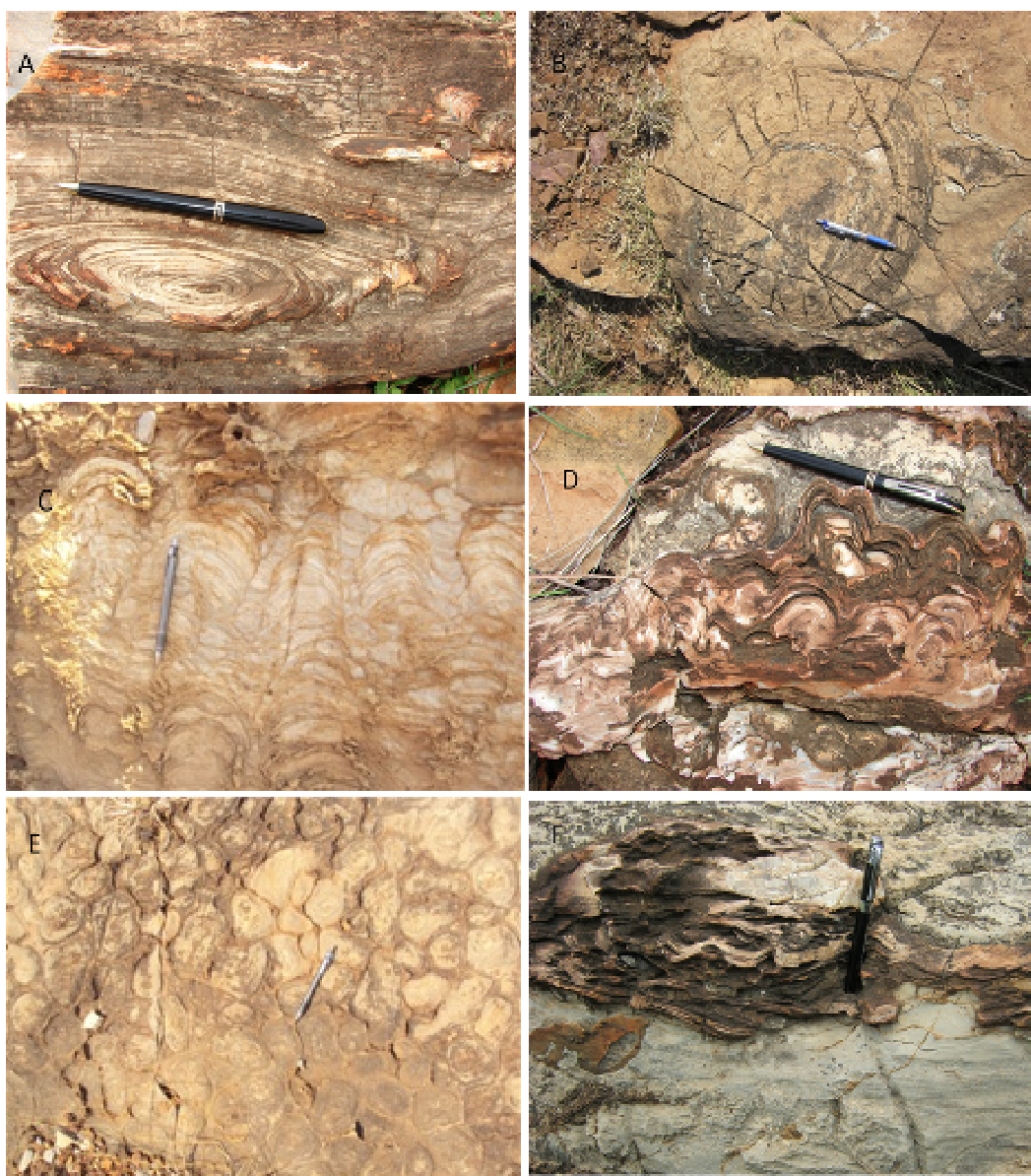


Fig 13. Stromatolites of different morphologies from different areas **(A)** Rachakuntapalle **(B)** Korivipalle **(C)** M. C. Palle **(D)** Rachakuntapalle **(E)** M. C. Palle and **(F)** Motnutalapalle area.

oxidation of Type I or Type II kerogens. The plots of Rock eval data (Hydrogen index Vs Oxygen index) usually show low petroleum potential for various coals and kerogens from uranium deposits (Landais, 1995). However, oxidation is probably the most common alteration process occurring in uranium deposits (Granger and Warren, 1979). It can be related to weathering, leaching by meteoric water, bacterial alteration and reduction of oxidised species, metal fixation or even radiolysis (Landais, 1995). Oxidation of organic matter may also indicate the involvement of the organic material in maintaining a reducing environment as well as participating in the formation and preservation of the mineralization. The S2 vs. TOC plot (Fig 5D) indicates the petroleum potential and the type of kerogen present. Rocks with S2 greater than 5 and 10 mg HC/g rock are considered to have a good and a very good oil source rock potential respectively. The boundary to separate type I from type II kerogens in the S2 vs. TOC diagram is along 700 mg HC/ g TOC (i.e., organic material with 70 wt. % hydrocarbons). However, the present data shows type IV kerogen suggesting oxidised organic matter belonging to the inertinite maceral group which has essentially no hydrocarbon potential. Rock-Eval data indicate that the petroleum potential of the bitumens (HI) decreases with the increasing T_{max} . Such an evolution may be interpreted as a

“thermal maturation” effect (Fig 5B). Organic material in uranium deposits shows that T_{max} generally ranges between 420° and 450°C for type III kerogen and coals, thus indicating a maturation stage corresponding to the end of the diagenetic stage and the beginning of the catagenetic stage (Landais, 1995). However the data shows wide range of thermal maturity. Rock-Eval T_{max} vs. oxygen index diagram (Fig 5C) may show different types of alteration processes like (1) thermal maturation; (2) oxidation; (3) mineralization + radiolysis. Alteration phenomena have frequently been recognized in uranium deposits. They can be related to different interactions between organic matter and meteoric water or bacteria as well as radiolytic processes. Most of the organic matter closely associated with uranium mineralization displays geochemical characteristics which are very different from those expected from their origin and thermal history. Oxidation, biodegradation, radiolysis, and thermal degradation have been recognized as the main alteration processes of organic matter occurring in uranium deposits (Landais et al., 1987). However, oxidation is probably the most common alteration process in this uranium deposit. It can be related to weathering, leaching by meteoric oxygen rich water, bacterial alteration, reduction of oxidised species, metal fixation or even radiolysis. In the chemical reaction organic

matter oxidised and simultaneously reduced the uranium for precipitation and because of oxidation organic matter were removed from the system by leaching and therefore rock eval data shows low TOC content.

FTIR spectra do not show bonding between uranium and organic component, therefore the alpha tracks on organic matter are attributed to adsorbed uranium. Adsorbed uranium is present with limonite and organic matter. Once buried, reducing chemical microenvironments exist around buried decomposing organic material. Anaerobic bacteria reduce S from organic matter and dissolved inorganic sulfate to H₂S. Interstitial iron is locally mobilized toward these reducing “pockets” where the reducing environment causes transformation of ferric to ferrous iron. The Fe⁺² combines with S⁻² in H₂S to form monosulfide FeS, which further combines with elemental S to form pyrite (FeS₂) (Speyer and Brett, 1988; Donner and Lynn, 1989). The effect of organic matter on the uranium chemistry and on oxidation-reduction reactions of a solution has been established by experimental studies (Hostetler and Garrels, 1962; Langmuir, 1978) related to the formation of sedimentary uranium deposits. Thus sulfate reducing bacteria can oxidise the organic matter to form H₂S which then reduces U⁺⁶ to U⁺⁴ leading to its precipitation.

Following chemical reactions are very significant to visualize the precipitation and concentration mechanism of uranium in stratabound deposits (De Voto, 1978).

Reduced Organic Matter + SO₄⁻² → Oxydised Organic Matter + H₂S

H₂S + Metal → Metal sulfide

S + 2 H⁺ + 2e⁻ = H₂S

6H₂S + 2Fe₂O₃·H₂O → FeS + Fe₃O₄ + 5S⁰ + 8H₂O

FeS + H₂S = FeS₂ + 2H⁺ + 2e⁻

UO₂⁺² + 4H⁺ + 2e⁻ = U⁺⁴ + 2H₂O

Pyrite, chalcopyrite and molybdenite are also found in mineralised dolostone. These appear to have been concentrated in dolostone under oxygen deficient environment. The two mineralised bands correspond to two stages of terrestrial supply from uplifted basement provenance. Enrichment of phosphate can lead to eutrophication of fresh and inshore marine waters, leading to algae bloom because of excess nutrients. Over time, geological processes can supply phosphorus in to ocean sediments. The algae during that time absorbed phosphates binding the phosphate into organic compounds. After death, those algae decayed and in that way phosphates were returned to the sediments after forming compound with calcium in the form of collophane. Nash et al., 1981 suggested that concentration of uranium by adsorption onto organic matter or a mineral surface preceded reduction and accelerated the process of reduction of uranium. In addition it has also provided the reducing environment necessary for uranium precipitation. Siliciclastic impurities in dolostone have also reduced the Eh-pH conditions favourable for uranium precipitation. Undoubtedly the organic matter has been oxidized, but under natural ground water chemistry and flow conditions the time for oxidation is long enough so that the deposits of paleo-Proterozoic age have been preserved.

Based on the present studies, it can be concluded that:

1. Very low TOC, H.I. values and higher O.I. values represent overmature kerogen of type IV category.
2. Organic matter plays a dual role of concentrating uranium from solution and also of chemically reducing it to insoluble pitchblende and coffinite.
3. FTIR spectra do not show bonding between uranium and organic component, therefore uranium is present as adsorbed phase with organic matter.

Acknowledgements: We express our sincere gratitude to Dr. R. Mohanty, Additional Director (R&D), AMD for encouragement and infrastructure support to publish the part of the assigned work. We also extend our sincere thanks to S/Shri Suryendu Dutta, Department of Earth Sciences, IIT Bombay for helping in Rock eval pyrolysis data generation. The faculty members of department of SAIF, IIT Bombay are also acknowledged for giving the opportunity and providing the research facilities in the department.

References

- Bell, K.G. (1963) Uranium in carbonate rocks. USGS Prof Paper 474-A.
- Bhaskar Rao, Y.J., Pantulu, G.V.C., Damodar Reddy, V. and Gopalan, K. (1995) Time of early sedimentation and volcanism in the Proterozoic Cuddapah basin, south India: evidence from Rb-Sr age of Pulivendla mafic sill. *Mem. Geol. Soc. India*, no.33, pp.329-338.
- Chaki, A., Purohit, R.K. and Mamallan, R. (2010) Low grade uranium deposits of India – a bane or boon. *Energy Procedia*, **00**, 000-000. Asian Nuclear Prospects 2010.
- Chakrabarti, G., Debasish Shome and Subhasish Kumar (2012) Sedimentology of the Vempalle Formation of Proterozoic Cuddapah Basin on Dharwar Craton, India: Implications for the Palaeoenvironmental dynamics and Precambrian biosphere evolution. *Recent Res. Environ. Biomedicine*, v.76, pp.19-24.
- Chamley, H. (1990) *Sedimentology*. Springer-Verlag, Science. 244p.
- Crusius J., Calvert S., Pedersen T. and Sage D. (1996) Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth Planet. Sci. Lett.*, v.145, pp.65-78.
- De Voto R.H. (1978) Uranium geology and exploration. Lecture notes and references. Colorado school of mines, Golden, Colorado 80401p.
- Dhana Raju R, Roy Minati, Roy Madhuparna, Vasudeva S.G., (1993) Uranium mineralization in the southwestern part of the Cuddapah basin: A petromineralogical and geochemical study. *Jour. Geol. Soc. India*, v.42, pp.135-149.
- Doner, H.E. and Lynn, W.C. (1989) Carbonate, halide, sulfate, and sulfide minerals. *In: Dixon, J.B. and Weed, S.B.(Ed.)*, Minerals in Soil Environments, Soil Science Society of America, ____p.
- Dwivedy, K.K. (1995) Economic Aspect of Cuddapah Basin with Special Reference to Uranium - An Overview. *Geol. Soc. India, Annual Convention*, Tirupathi, pp.116-138.
- Farmer, V.C. (1974) Infrared spectra of minerals. *In: V.C. Farmer (Ed.)*, Mineralogical Society Monograph no. 4. Mineral. Soc., London, 399p.
- French, R.O., Wadsworth, M.E., Cook, M.A. and Cutler, I.B., (1954) The quantitative application of infrared spectroscopy to studies in surface chemistry. *Jour. Phys. Chem.*, v.58, pp.805-811
- Granger, H.C. and Warren, C.G. (1979) The importance of dissolved free-oxygen during formation of sandstone-type uranium deposits. *U.S. Geol. Surv. Open File Rept.*, 79-1603, 22p.
- Hagadorn, J.W. and Bottjer, D.J. (1997) Wrinkle structures: Microbially mediated sedimentary structures common in subtidal siliciclastic settings at the Proterozoic-Phanerozoic transition. *Geology* v.25, pp.1047-1050.
- Hostetler, P.B. and Garrels, R.M. (1962) Transportation and precipitation of uranium and vanadium at low temperatures, with special reference to sandstone type uranium deposits. *Econ. Geol.*, v.57, pp.137-167.
- Huang, C. K. and Kerr, P. F. (1960) Infrared study of the carbonate minerals. *American Mineralogist*, v.45, pp.11-324.
- Jeyagopal, A. V. and Dhana Raju, R. (1998) Recognition criteria and sedimentology of dolostone-hosted stratabound uranium mineralisation in Vempalle Formation, Cuddapah basin, Andhra Pradesh, India. *In: R.N. Tiwari (Ed.) Proceedings of the National Symposium on “Recent Researches in Sedimentary Basins”*, Indian Petroleum Publishers, Dehra Dun, pp.172-179.
- Landais, P. (1995) Organic geochemistry of sedimentary uranium ore deposits. *Ore Geol. Rev.*, v.11, pp.33-51.
- Langmuir, D. (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore-deposits. *Geochim. Cosmochim. Acta*, v.42, pp.547-569.
- Nagaraja Rao, B.K., Rajurkar, S.T., Ramalingaswami, G. and Ravindra Babu, B. (1987) Stratigraphy, structure and evolution of Cuddapah basin. *In: B.P. Radhakrishna (Ed.)*, Purana Basins of peninsular India. *Mem. Geol.*

- Soc. India, no.6, pp.33-86.
- Nash, J.T., Granger, H.C. and Adams, S.S. (1981) Geology and concepts of genesis of important types of uranium deposits. *Econ. Geol.* 75th anniversary volume, pp.63-116.
- Nguyen, T.T., Janik, L.J. and Raupach, M. (1991) Diffuse reflectance Infrared Fourier Transform (DRIFT) Spectroscopy in soil studies. *Australian Jour. Soil Res.*, v.29, pp.49-67.
- Rai, A.K., Zakaulla, S., Jeygopal, A.V., Vasudeva Rao, M., Naghbhushna, J.C. and Vardaraju, H.N. (2002) Uranium Mineralisation in Southwestern part of Cuddapah Basin, Andhra Pradesh. *Expl. Res. Atomic Minerals*, v.14, pp.79-94.
- Rai, A.K., Zakaulla, S. and Chaki, A. (2010) Proterozoic stratabound carbonate rock (dolostone) hosted uranium deposits in Vempalle formation in Cuddapah basin, India, IAEA, International Symposium on uranium raw material for Nuclear Fuel Cycle, June 22-26, 2009, Vienna, Austria.
- Rai, A.K., Zakaulla S., Vidyasagar, D., Murgan, M.G., Birua, M. K. and Sivasubramanian, R. (2011) Geochemistry of the uraniferous dolostones from areas around Kanampalle in south western margin of Cuddapah Basin. *Indian Minerals*, v.45, pp.24-35.
- Roy, Minati, Dhanaraju, R., Vasudeva Rao, M. and Vasudeva S.G. (1990) Stromatolitic uraniferous dolostone of the Vempalle Formation, Cuddapah Supergroup, Andhra Pradesh, India: nature and bearing of stromatolites on uranium mineralization. *Expl. Res. Atomic Minerals*, v.3, pp.103-113.
- Roy, Minati and Dhanaraju, R. (1997) Petrography and depositional environment of the U-mineralized phosphatic siliceous dolostone of Vempalle Formation, Cuddapah basin, India. *Jour. Geol. Soc. India*, v.50, pp.577-585.
- Roy, Minati and Dhanaraju, R. (2012) Comparative study of uranium mineralised and nonmineralised dolostone of Vempalle Formation, Cuddapah Supergroup, Andhra Pradesh and its implication on role of algae and phosphate in uranium mineralisation. *Expl. Res. Atomic Minerals*, v.22, pp.173-187.
- Ramam, P.K. and Murty, V.N. (1997) Geology of Andhra Pradesh. *Geol. Soc. India*, Bangalore, 245p.
- Schopf, J.W. (1999) *Cradle of Life: The Discovery of Earth's Earliest Fossils*. Princeton University Press, Princeton, New Jersey, 367p.
- Speyer, S.E. and Brett, C.E. (1988) Taphofacies models for epeiric sea environments: Middle Paleozoic examples. *Palaeogeog. Palaeoclimat. Palaeoeco.*, v.63, pp.225-262.
- Spirakis, C.S. (1996) The roles of organic matter in the formation of uranium deposits in sedimentary rocks. *Ore Geol. Rev.*, v.11, pp.53-69.
- Sundaram, S.M., Sinha, P.A., Ravindrababu, B. and Muthu, V. T., (1989) Uranium mineralisation in Vempalle Dolomite and Pulivendla conglomerate/Quartzite of cuddapah basin, Andhra Pradesh. *Indian Minerals*, v.43, pp.98-103.
- Vasudeva Rao, M., Nagabhushna, J.C. and Jeyagopal, A.V. (1989) Uranium mineralization in the Middle Proterozoic Carbonate rock of the Cuddapah Supergroup, Southern Peninsular India. *Expl. Res. Atomic Minerals*, v.2, pp.29-38.
- Zachariah, J.K., Bhaskar Rao, Y.J., Srinivasan, R. and Gopalan, K., 1999: Pb, Sr, Nd isotope systematic of Uranium mineralized stromatolitic dolomites from the Proterozoic Cuddapah Supergroup, South India : Constraints on age and provenance. *Chem. Geol.*, v.162, pp.49-64.
- Zakaulla, S., Suresh Kumar and Vidyasagar, D., et al. (2013) Achievement Report for 2012-13, Southern Cuddapah Basin Investigations, AMD, Department of Atomic Energy, India.

(Received: 7 September 2015; Revised form accepted: 6 May 2016)

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/313108765>

Role of organic matter in Uranium mineralisation in Vempalle Dolostone; Cuddapah Basin, India

Article in *Journal of the Geological Society of India* · February 2017

DOI: 10.1007/s12594-017-0578-y

CITATIONS

5

READS

493

5 authors, including:



Sukanta Goswami

Atomic Minerals Directorate for Exploration and Research

30 PUBLICATIONS 61 CITATIONS

[SEE PROFILE](#)



Sangeeta Bhagat

Atomic Minerals Directorate for Exploration and Research

11 PUBLICATIONS 21 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Quality of Life in Glaucoma [View project](#)



Current Practices in Ophthalmology: Glaucoma [View project](#)