

# <sup>57</sup>Fe Mössbauer Spectroscopic Study of Sedimentary Samples from Goru Formation in Well MNW-1 of Jaisalmer Basin, Rajasthan, India

Samay Singh Meena, Sahi Ram\*, Beena Bhatia, and R.P. Tripathi  
Department of Physics, Jai Narain Vyas University,  
Jodhpur-342005, India

\*Corresponding author: sr.panwar@yahoo.co.in

*The test well MNW-1 is located in the Manewala structure of Jaisalmer basin. The Cretaceous sediments are believed to contain source rocks in this basin, the samples collected from Goru formation of upper Cretaceous sedimentary sequence were investigated using Mössbauer spectroscopy to understand the relative distribution of iron bearing minerals with depth.*

*Iron was found present mainly in siderite, Fe<sup>2+</sup> in clay minerals and Fe<sup>3+</sup> in clay minerals. Large abundance of Fe<sup>3+</sup> in clay minerals in comparison Fe<sup>2+</sup> in clay minerals results into lower ferrous to ferric ratio in this Formation. This is an indication of poor reducing environment which is not favorable for transformation of organic matter into hydrocarbons.*

**Keywords:** Source rocks, Mössbauer spectroscopy, Iron bearing minerals.

## 1. INTRODUCTION

The Jaisalmer basin represents mainly the westerly dipping eastern flank of the Indus shelf and occupies an area of about  $3 \times 10^4$  sq. km [1]. The palynological and geochemical studies have predicted good availability of hydrocarbons in this basin. The Cretaceous and Jurassic sediments are believed to contain source rocks in this basin [1]. The organic rich sediments are the source rocks in a basin. A source is said to be mature when hydrocarbons generation take place and post mature when hydrocarbons are burnt out. The hydrocarbons prospecting in a basin require the proper evaluation of a source rocks to estimate the amount, type and maturity of organic matter. The biological activity in early stage, and temperature and pressure after words decides the evolution of organic matter. The inorganic solid phase associated with the source rock sediment also undergoes same activities resulting into occurrence of organic-inorganic interaction at different stages of sediments evolution. Thus mineralogical analysis of sediments is also considered important to understand the evolution of a source rock. The mineral matter also includes in iron bearing minerals. For the characterization of iron-bearing minerals and to study their relative distribution, Mössbauer spectroscopy has been regarded as the most suitable technique because of its extreme sensitivity to the chemical environment of the iron nuclei. An extensive study of organic rich sediments was reported by Mørup *et al.* [2,3] on Danish North sea sediments. In similar kind of study, we have undertaken a detailed Mössbauer spectroscopy on the chemical state of iron in deep surface sediments of Jaisalmer petroliferous basin of Rajasthan India.

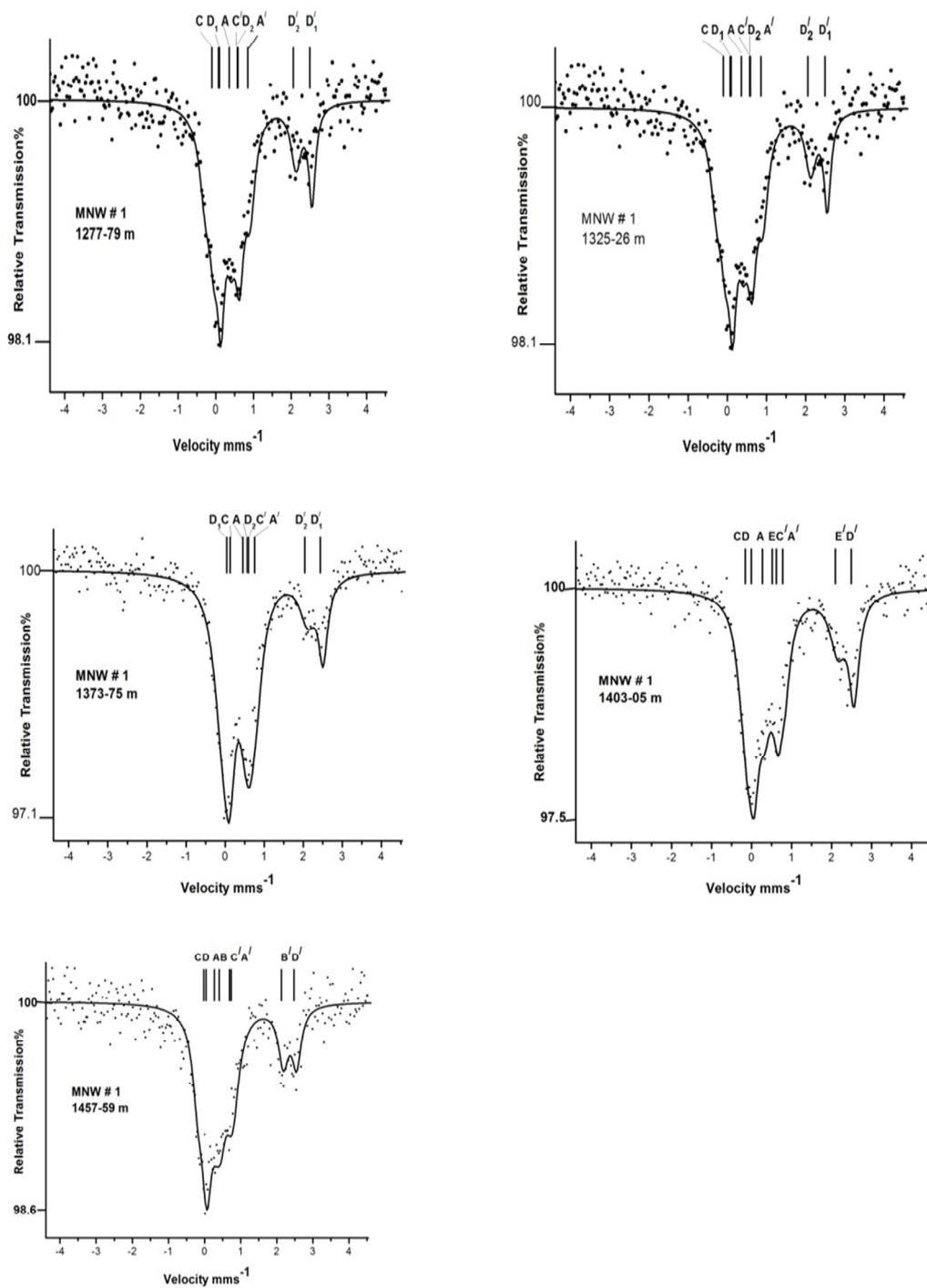
In present work, we report here the relative distribution of various iron-bearing minerals with depth in Goru Formation of upper Cretaceous sedimentary sequence of well MNW-1 with an objective to see if there exist some correlation between the presence/absence of iron-bearing minerals and the quality of source rocks.

## 2. EXPERIMENTAL

Mössbauer absorbers were prepared by sandwiching finely ground sediment samples between two paper discs in a sample holder (25 mm in diameter). The thickness of absorbers was always kept constant. Mössbauer spectra were recorded at room temperature (300<sup>0</sup>K) with a conventional constant acceleration spectrometer using a 10 m Ci source in a Pd-matrix. Detailed of the experimental set-up are similar as reported earlier by Nigam *et al.* [4]. The isomer shift (IS) has been reported with respect to the centroid of a 25 µm thick α-iron foil spectrum. Each spectrum was fitted using a computer program written by Meerwall [5]. This program assumes the spectrum to be sum of Lorentzians. In most of cases, width and intensity of two halves of a quadrupole doublet were constrained to be equal. Solid lines in the spectra reported here represent computer fitted curves and dots represent the experimental points. For the fit to be statistically acceptance, it is required that the value of parameter  $\chi^2$  (chi-square) should lie between  $\nu + 2.2 - 3.3\sqrt{\nu}$  and  $\nu + 2.2 + 3.3\sqrt{\nu}$ . In the present study, the  $\chi^2$  values are generally obtained in this range. However, a little deviation in the  $\chi^2$  has been accepted on few occasions when the iterations do not yield to further improvements in  $\chi^2$ . Such situation arises when weak lines are present.

## 3. RESULT AND DISCUSSION

The well MNW-1 is located in the Manewala structure of the Jaisalmer basin. Sedimentary samples collected from different depths in Guru Formation of upper cretaceous sequence have been investigated using <sup>57</sup>Fe Mössbauer spectroscopy. The typical Mössbauer spectra recorded at room temperature are displayed in Figure 1. The depth from where the sample is collected is indicated in the figure itself. The Mössbauer spectra of all the samples were resolved into quadrupole doublets corresponding to iron in different mineral species. In present study none of the samples has shown the presence of sextet corresponding to oxide minerals.



**Fig. 1:** Room temperature Mössbauer spectra of sediment samples from well MNW-1 collected at different depths.

The Mössbauer parameter QS (quadrupole splitting), IS (isomer shift), LW (line width) and RA (relative area) obtained in present study are reported in Table 1.

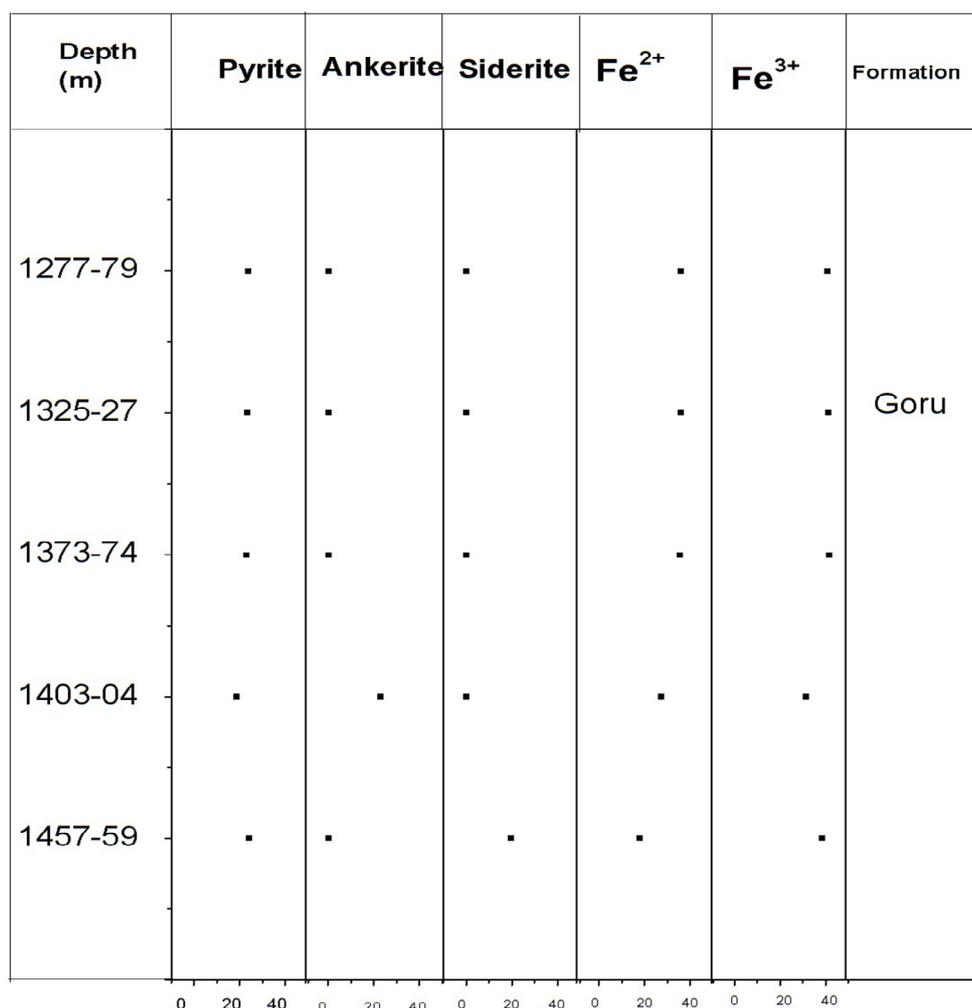
**Table 1:** Mössbauer parameters observed in sediments of well MNW-1.

Depths(m)	Peaks	IS (mms <sup>-1</sup> )	QS(mms <sup>-1</sup> )	LW	Assignment	RA	$\chi^2$
1278	CC'	0.2345	0.6790	0.254	Fe <sup>3+</sup>	40.84	1.12
	AA'	0.6090	0.5040	0.318	Pyrite	23.54	
	D <sub>1</sub> D <sub>1</sub> '	1.2897	2.3905	0.216	Fe <sup>2+</sup> low spin	18.40	
	D <sub>2</sub> D <sub>2</sub> '	1.1620	2.6530	0.328	Fe <sup>2+</sup> high spin	17.16	
1326	CC'	0.2345	0.6290	0.254	Fe <sup>3+</sup>	40.96	1.11
	AA'	0.6090	0.5040	0.318	pyrite	23.34	
	D <sub>1</sub> D <sub>1</sub> '	1.2897	2.3905	0.216	Fe <sup>2+</sup> low spin	18.26	
	D <sub>2</sub> D <sub>2</sub> '	1.1620	2.6530	0.328	Fe <sup>2+</sup> high spin	17.40	
1374	CC'	0.3605	0.4690	0.321	Fe <sup>3+</sup>	41.50	1.10
	AA'	0.6020	0.3080	0.410	pyrite	22.84	
	D <sub>1</sub> D <sub>1</sub> '	1.2390	2.3940	0.289	Fe <sup>2+</sup> low spin	18.88	
	D <sub>2</sub> D <sub>2</sub> '	1.3020	1.4840	0.480	Fe <sup>2+</sup> high spin	16.62	
	CC'	0.2362	0.7665	0.243	Fe <sup>3+</sup>	31.36	

1404	<b>AA'</b>	0.5285	0.4970	0.325	<b>Pyrite</b>	18.52	1.00
	<b>DD'</b>	1.2460	2.4920	0.306	<b>Fe<sup>2+</sup></b>	27.16	
	<b>EE'</b>	1.3020	1.575	0.476	<b>ankerite</b>	22.90	
1458	<b>CC'</b>	0.3325	0.7140	0.473	<b>Fe<sup>3+</sup></b>	38.32	1.25
	<b>AA'</b>	14580.5092	0.4515	0.410	<b>Pyrite</b>	24.14	
	<b>DD'</b>	1.2582	2.4395	0.308	<b>Fe<sup>2+</sup></b>	17.86	
	<b>BB'</b>	1.2652	1.7080	0.343	<b>siderite</b>	19.64	

The assignment of doublets has been made in reference to the earlier reported studied by our group [6-10]. In Figure these doublets are marked as AA', CC', and DD' corresponding to iron in pyrite, Fe<sup>3+</sup> in clay and Fe<sup>2+</sup> in clay respectively. In most of the samples, the IS value for the doublet AA' is centered around 0.30 mms<sup>-1</sup> and QS value is centered around 0.60 mms<sup>-1</sup>, which is the value characteristic for both iron in pyrite as well as for high spin Fe<sup>3+</sup> in clay minerals. Due to this overlap of Mössbauer parameters for both these components, on the basis of studies of preheated samples [3], the doublet AA' is attributed mainly to the iron in pyrite. However, in doublet AA' has contribution of Fe<sup>3+</sup> in clay minerals can not be ruled out. Therefore in present study, doublet AA' has been regarded as the upper most limit of pyrite in corresponding samples.

The distribution of relative amount of iron in various minerals with depth is displayed in Figure 2.

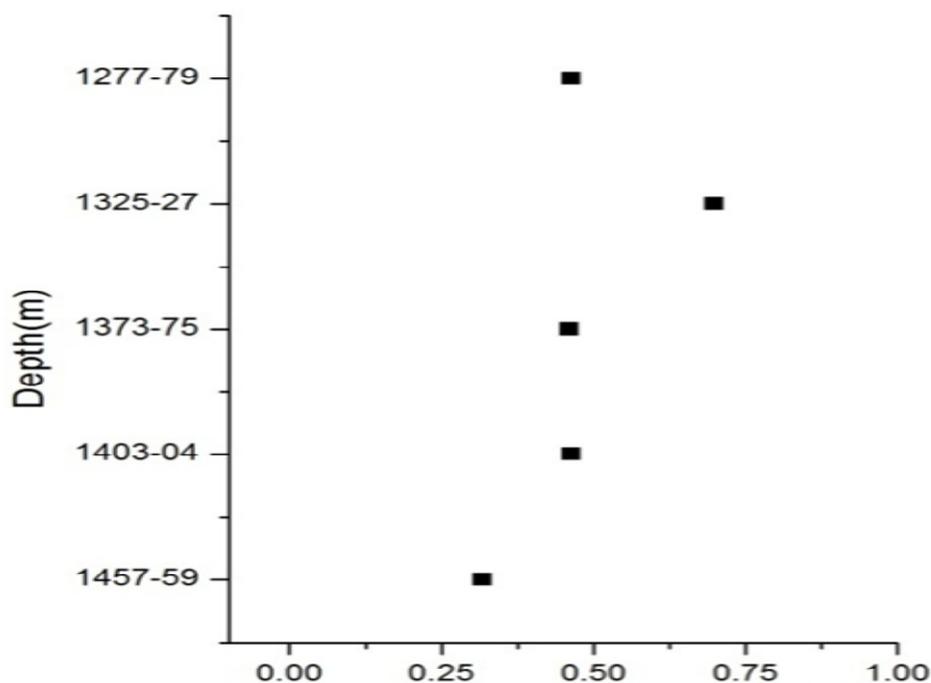


**Fig. 2:** Relative amounts of iron in different minerals as function of depth in the samples collected from well MNW-1 located in Jaisalmer basin.

In almost all the samples, iron is found present mainly in pyrite, siderite, Fe<sup>2+</sup> in clay, Fe<sup>3+</sup> in clay and ankerite, but their relative amount was found to be fluctuating from sample to sample. The relative distribution of Fe<sup>2+</sup> in clay and Fe<sup>3+</sup> in clay is quite significant. It can be seen from Figure 2 that almost all the samples contain appreciable and equal amount of both Fe<sup>2+</sup> and Fe<sup>3+</sup> component. The relative amount of iron in clay (Fe<sup>2+</sup> + Fe<sup>3+</sup>) is remarkably larger in comparison to other iron-bearing minerals in particular sample. This observation can be explained on the basis of the fact that sedimentation process is influenced very much by the size of particles. The smaller size particle travel larger distance in water before they are finally removed from the floating material. Because clay flakes have smaller size, it is expected that more clay flakes will be deposited in deep water than in shallow water. Therefore, this presence of iron in clay (Fe<sup>2+</sup> + Fe<sup>3+</sup>) in

larger amount is quite significant and can be attributed to shallow marine condition of sediments deposition. The source rocks which are deposited under this condition are transformed into type III 'kerogen' which can generate only gaseous hydrocarbons methane accomplished by larger amount of nitrogen [11].

The other significant iron bearing minerals present in these samples are pyrite and siderite. From Figure 2, it can be seen that mineral siderite is present in only one sample at lower depth 1457-59 m while mineral pyrite is present in all samples, however the relative amount fluctuates from sample to sample. This significant presence of pyrite in all samples and absence of siderite in most of the samples can be explained on the basis of Eh-pH relations among pyrite, siderite and hematite [12] according to which pyrite is the only stable  $Fe^{2+}$  mineral at sulphur level of modern sea water. Earlier Lukose *et al.* [13] carried out source rock palynological studies on samples of well No. 1 of Ghotaru structure of Jaisalmer basin and found the presence of fine grained organic matter and attributed it to be sapropelic. The larger presence of iron in clay minerals in present study is in consistent to the sapropelic nature of organic matter in sediments of Goru formation. Furthermore, if we compare the ratio of  $(Fe^{2+})/(Fe^{2+}+Fe^{3+})$  displayed in Figure 3, the average value of this ratio also points towards the fluctuating environment from reducing to oxidizing as we move from top to bottom.



**Fig. 3:** Distribution of  $(Fe^{2+})/(Fe^{2+}+Fe^{3+})$  ratio with depth in the samples collected Goru formation in well MNW-1 located in Jaisalmer basin.

At lower depth 1403-04 m mineral ankerite is also found present. According to Boles [14] the presence of ankerite is attributed to higher temperature gradient  $\approx 120^{\circ}C$  favourable for transformation of organic matter into hydrocarbons. Recently, Bhatia *et al.* [15] and

Meena *et al.* [16] has also observed that in Bikaner-Nagaur basin, mineral ankerite was dominantly present in those Formations which contained source rocks and where oil prone hydrocarbons were discovered. In view of this, it is indicative that the lower depth sequence of Goru Formation might have gone through high temperature gradient.

From present study, it seems that in Goru Formation of well MNW-1 has encountered highly fluctuating environment i.e. from reducing to oxidizing condition which is not favorable for the transformation of organic matter into hydrocarbons. Source rocks deposited in this type of redox conditions are not considered as good quality source rocks in context to hydrocarbon prospecting. This small piece of information obtained from Mössbauer spectroscopy when coupled with other established geological and geochemical techniques can provide useful results in hydrocarbon prospecting in a basin.

### ACKNOWLEDGEMENTS

The authors are thankful to Oil and Natural Gas Commission Ltd., India for supplying the samples. Also thanks to UGC-DST for providing experimental facilities in the department for carrying out this study.

### REFERENCES

- [1] A.K. Datta; "Geological evolution and hydrocarbon prospects of Rajasthan basin", *Petrol Asia J.*, Vol. 6, pp. 93-100, 1983.
- [2] S. Mørup, and H. Lindgreen; "Applications of Mössbauer Spectroscopy in Oil Prospecting", *Application of Mössbauer effect*, ICAME, Jaipur, India, 1981; *Indian National Science Academy*, New Delhi, pp. 290-292, 1982.
- [3] S. Mørup, J. Franck, J.V. Wouterghem, H.R. Poulsen and L. Larsen; "Mössbauer spectroscopy study of the chemical state of iron in Danish Mesozoic sediments", *Fuel*, Vol. 64(4), pp. 528-539, 1985.
- [4] A.N. Nigam, R.P. Tripathi, H.S. Singh, R.S. Gambhir and N.G. Lukose; "Mössbauer studies on Ghotaru Well No.1 of Jaisalmer Basin", *Fuel*, Vol. 68(2), pp. 209-212, 1989.
- [5] E.V. Meerwall; "A least-square spectral curve fitting routine for strongly overlapping Lorentzians or Gaussians", *Computer physics communications*, Vol. 9, pp.117-128, 1975.
- [6] A.N. Nigam, R.P. Tripathi, R.S. Singh, R.S. Gambhir and N.G. Lukose; "Source rock evaluation of some wells in Jaisalmer Basin (India) using Mössbauer spectroscopy", *Fuel*, Vol. 70(2), pp. 262-266, 1991.
- [7] S. Ram, K.R. Patel, S.K. Sharma and R.P. Tripathi; "Ditribution of iron in siderite in sub-surface sediments of Jaisalmer Basin (India) using Mössbauer spectroscopy", *Fuel*, Vol. 77(13), pp.1507-1512, 1998.

- [8] S. Ram, K.R. Patel, S.K. Sharma and R.P. Tripathi; "Distribution of Fe<sup>2+</sup> in clay minerals in sub-surface sediments of the Jaisalmer basin(India) using Mössbauer spectroscopy", Fuel, Vol. 76(14-15), pp.1369, 1997.
- [9] R.P. Tripathi, S.K. Sharma, K.R. Patel, K.L. Shrivastava and Sahi Ram; "A Mössbauer approach to hydrocarbon prospecting in Jaisalmer basin of Rajasthan, India", Ind. J. Petrol. Geol., Vol. 7(1), pp. 47-58, July 1998.
- [10] K.R. Patel, S. Ram, A. Tripathi, R. Sharm and R.P. Tripathi; "Study of geo-chemical environment in organic rich sub-surface sediments of Jaisalmer petroliferous basin of Rajasthan, India, using Mössbauer spectroscopy", ICAME, 2009. doi: 2010, 1088/1742-6596/217/1/012061
- [11] B. Tissot and D. Welte; "Petroleum Formation and Occurrence. A new approach to oil and gas exploration", Springer-Verlag, 11n Ed., Berlin, West German, pp. 699, 1984.
- [12] R.A. Berner; "A new geochemical classification of sedimentary environments", Journal of Sedimentary Petrology, Vol. 51(2), pp.359-365, 1981.
- [13] N.G. Lukose, B.S. John and Iftikharuddin; "Report on source rock Palynology Ghotaru well No. 1, Jaisalmer basin Rajasthan (India)", ONGC (india) report, 1986.
- [14] J.R. Boles; "Active ankerite cementation in the subsurface Eocene of southwest Texas", Contrib. Mineral. Petrol., Vol. 68(1), pp.13-32, 1978.
- [15] B. Bhatia, A. Tripathi, R. Sharma and R.P. Tripathi; "Mössbauer spectroscopy study of sediments collected from test wells drilled in the Bikaner-Nagaur Basin", Fuel, Vol. 98, pp.140-148, 2012.
- [16] S.S. Meena, S. Ram, B. Bhatia and R.P. Tripathi; " Mossbauer Studies on the Test Well P#1 Located in Phulasar Structure of Bikaner-Nagaur Basin of Rajasthan, India", International Journal of Engineering, Management & Sciences (IJEMS), Vol. 3(9), pp. 5-11, 2016.