

## **Study of chemical state of iron in sedimentary samples obtained from Parh Formation in Tertiary sediments of Jaisalmer Basin, Rajasthan, India**

Sahi Ram

*Department of Physics, Jai Narain Vyas University, Jodhpur – 342001, India*

---

### **Abstract**

*The test well DND-1 is located in the Dandewala structure of Jaisalmer basin. Sedimentary samples collected from Parh formation of Tertiary sedimentary sequence were investigated using Mössbauer spectroscopy to understand the relative distribution of iron bearing minerals with depth. Samples showed predominant presence of iron in pyrite, while the relative amount of siderite is quite small. Iron is also found present in clay forming minerals,  $Fe^{2+}$  and  $Fe^{3+}$ , but in small amount. Iron is also found present in [Ca, Mg, Fe] carbonates. A significant variation in presence/absence of pyrite and siderite, presence of [Ca, Mg, Fe] carbonates is discussed in context to the environment of sedimentary deposition.*

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

---

### **I. Introduction**

The Jaisalmer basin is pericratonic basin forming the eastern flank of the Indus shelf over the Jaisalmer Mari platform. Among several test wells drilled in various structures of Jaisalmer basin, following sedimentary sequence were encountered; viz., Quaternary (Shumar), Paleocene (Bandah, Khuiala, Sanu), Tertiary (Parh, Upper Goru), Cretaceous (Lower Goru, Pariwar), Jurassic (Baisaki-Bedesir, Jaisalmer, Lathi) and Triassic (Shumarwali) sediments. In Jaisalmer basin, the Tertiary rocks are well exposed and identified as limestone, shale and sandstone [1, 2]. From among these sedimentary sequences, below the Paleogene, the Cretaceous and Jurassic sediments are believed to contain source rocks [3]. Source rocks are the fine grained organic rich sediments which have potential to generate hydrocarbons (mature) or had already generated hydrocarbons (post-mature).

In an early work, Nigam et. al. [4, 5], Ram et. al. [6, 7], Tripathi et. al. [8] has reported detailed Mössbauer spectroscopic investigations on source rock sediments collected from several wells (GT-1, GT-2, MT-1, KT-2, TOT-1, BT-1, BT-3, LNR-1, MNW-1 and DND-1) drilled in different structures of Jaisalmer basin. They have reported the chemical state of iron in source rock sediments and its correlation with hydrocarbon prospecting in Jaisalmer basin. Stratigraphically, this Parh Formation observed in well DND-1 was deposited in Late Cretaceous to early Tertiary sedimentary era and is resting over the Cretaceous sedimentary sequence which contains source rocks. The well DND-1 was drilled by Oil India Limited (OIL), India. Several wells drilled in Dandewala structure have shown good quality and appreciable amount of gaseous hydrocarbons. Stratigraphically, the well DND-1 penetrates through the following rock formations; viz, Parh (1300-1445 m) in Early Tertiary, Goru (1445-2017) in the Upper Cretaceous, Pariwar (2017-2509 m) in Lower Cretaceous, Baisaki-Bedesir (2509-3037 m) in Upper Jurassic, Jaisalmer (3037-4363 m) in Middle Jurassic and Lathi (4363-4498 m) in Lower Jurassic.

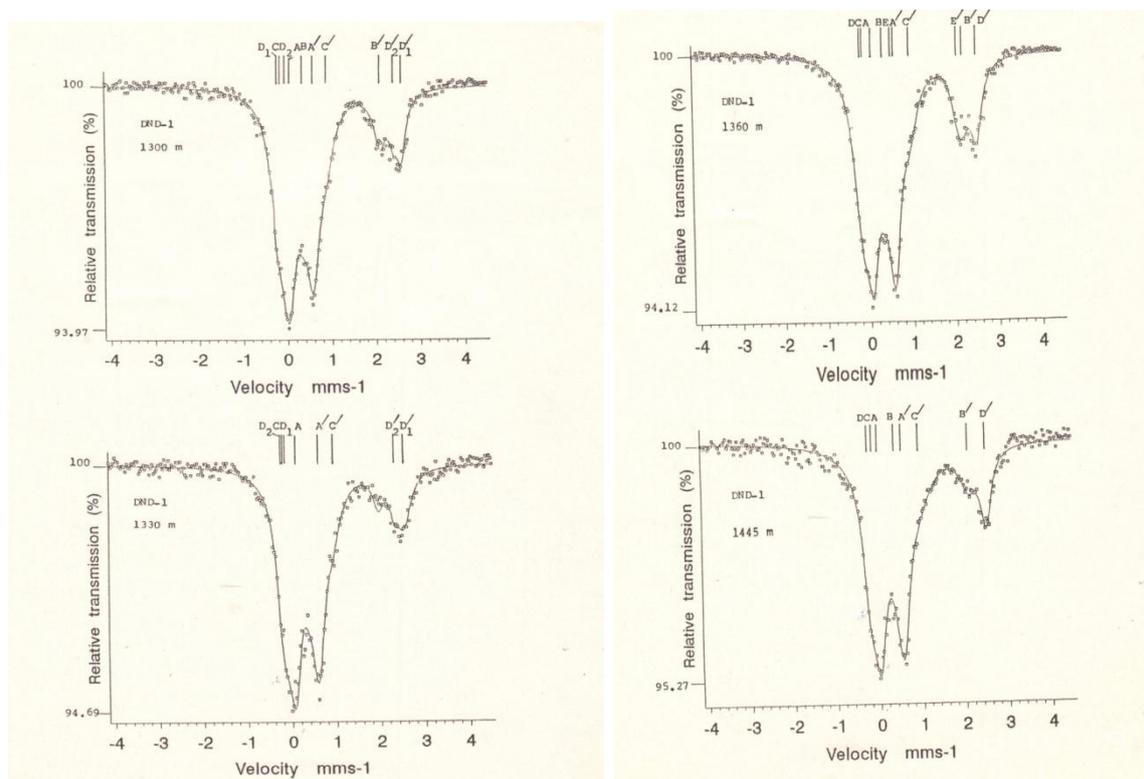
In present paper,  $^{57}Fe$  Mössbauer spectroscopic study on some sedimentary samples collected from Parh Formation in Tertiary sediments of well DND-1 have been reported with an objective to understand the relative distribution of iron-bearing minerals.

### **II. Experimental**

To prepare the absorber, the sediment samples were first ground to fine powder and then 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. The Mössbauer spectra of these powdered samples were recorded at 300 K using a conventional constant acceleration Mossbauer spectrometer. using a  $^{57}Co$  source of 10 mCi initial strength. The Isomer shift has been reported with respect to centroid of a 25  $\mu m$  thick  $\alpha$ -iron foil spectrum. All spectra were computer fitted using a least squares routine programme [9] by assuming each spectrum to be a sum of Lorentzian functions. Details of experimental setup and fitting programme have been already reported [4]. During the curve fitting, the width and the intensity of the two halves of a quadrupole doublet were constrained to be equal. The quality of fit was judged from the value of chi-square which was close to 1.0 per degree of freedom in most of the cases. However, a deviation in the value of chi-square has been accepted in some occasion when iterations did not improve the value of chi-square.

### III. Result And Discussion

Typical Mössbauer spectra of sedimentary samples recorded at room temperature are shown in Figure 1. The depth interval from which the samples were collected, are given in corresponding Figure itself. The Mössbauer spectra of all samples were resolved into several quadrupole doublets corresponding to iron in different mineral species. In Figure, these doublets are marked as AA', BB', CC', DD', D<sub>1</sub>D<sub>1</sub>', D<sub>2</sub>D<sub>2</sub>' and EE'. The relative intensity of doublets was found to vary from sample to sample. On the basis of studies reported earlier by Nigam et al. [4, 5], Ram et. al. [6, 7], Mørup and Lindgreen [10], Mørup et. al. [11], Karl and Zuckerman [12], on the spectra, the quadrupole doublets marked AA' corresponds to iron in pyrite (FeS<sub>2</sub>), BB' corresponds to siderite (Fe,Mg)CO<sub>3</sub>, CC' corresponds to clay in high spin Fe<sup>3+</sup> state, DD' corresponds to clay in high spin Fe<sup>2+</sup> state, D<sub>1</sub>D<sub>1</sub>' corresponds to clay in Fe<sup>2+</sup> (*cis* site), D<sub>2</sub>D<sub>2</sub>' corresponds to clay in Fe<sup>2+</sup> (*trans* site) and EE' corresponds to (Ca,Mg,Fe) carbonates.



**Figure 1:** Room temperature Mössbauer spectra of sedimentary samples collected from Parh Formation in well DND-1.

The relative amount of iron in various minerals as a function of depth in Parh Formation of well DND-1 is given in Table 1.

**Table 1:** Relative amount of iron-bearing minerals found present in sediment samples of Parh Formation in well DND-1

Depth (meter)	Relative amount (in arbitrary unit)						
	AA' (pyrite)	BB' (siderite)	CC' (Fe <sup>3+</sup> in clay)	DD' (Fe <sup>2+</sup> in clay)	D <sub>1</sub> D <sub>1</sub> ' (Fe <sup>2+</sup> ( <i>cis</i> site) in clay)	D <sub>2</sub> D <sub>2</sub> ' (Fe <sup>2+</sup> ( <i>trans</i> site) in clay)	EE' (ankerite/ferroan dolomite)
1300	44.72	14.25	20.25	-	14.65	6.10	-
1330	50.57	-	16.29	-	17.26	6.36	-
1360	39.02	11.68	22.33	19.80	-	-	7.17
1445	40.80	13.95	26.06	19.19	-	-	-

From Table 1, it is seen that in all samples, pyrite is present in appreciable amount. The relative amount of pyrite decreases at lower depth. Siderite was found to be present in all samples except at depth 1330 m. However, in all samples, the relative amount of siderite is seen to be quite less in comparison to the relative amount of pyrite. In sample at depth 1300 m, the dominant presence of pyrite and simultaneous absence of siderite indicate that pyrite-siderite compete each other. According to Berner [13], the Eh-pH relations among pyrite, siderite indicate that pyrite is the only stable Fe<sup>2+</sup> mineral at the higher sulphur level of modern sea water and siderite is stable Fe<sup>2+</sup> mineral at

low sulphur level. Siderite in ancient rocks suggests low sulphur level water such as fresh water lakes and swamps. Burner [13] also proposed another model for siderite deposition according to which, the siderite in sediments can be deposited in two different diagenetic environments. First, in the phase of decomposition of organic matter (if present), the sediments get deprived of oxygen but sulphate reduction does not take place. In this condition siderite is deposited as post-oxic siderite. Secondly, if large amount of organic matter is present to dissolve all available sulphate, then during methane fermentation, siderite will be more stable. The siderite so formed is called the methanic siderite. In both conditions, the favourable environment for deposition of siderite will be less reducing. The pyrite formation is also controlled by the availability of reactive-Fe (in form of suspended particulate matter) which limits the FeS formation [14]. Pyrite precipitates in reducing diagenetic environment and is stable in absence of air, in the presence of dissolved sulphide, it is an indicator of anaerobic, sulphidic diagenesis. So the competing presence of siderite in samples can be attributed to fluctuating redox environment of deposition.

In one sample at depth 1360 m, ankerite like component eg. Iron in ferroan-dolomite is also found present but in very meager amount. The ankerite like carbonate mineral ferroan-dolomite deposits due to the late diagenesis of siderite and other carbonate minerals [15]. Most probably it is at the expense of mineral siderite, because at the depth where this component is present, the relative amount of siderite was found to be decreased.

In all sediment samples, Fe<sup>2+</sup> and Fe<sup>3+</sup> clay forming minerals are found present. Fe<sup>2+</sup> in clay is also found present in high spin *cis* and *trans* sites. The relative amount of both Fe<sup>2+</sup> and Fe<sup>3+</sup> clay forming minerals is approximately equal but in less amount. The relative amount of Fe<sup>3+</sup> clay increases with depth while relative amount of Fe<sup>2+</sup> in clay decreases with depth. The relatively small amount of Fe<sup>2+</sup> in clay indicates that in Parh Formation. In all samples, the total clay (Fe<sup>2+</sup> + Fe<sup>3+</sup>) is present in marked abundance, indicates terrestrial source of iron and stability of iron bearing minerals is attributed to stable rate of sedimentation [16].

#### IV. Conclusion

In sedimentary samples of Parh Formation in DND-1 well, iron was found present mainly in pyrite, siderite, Fe<sup>3+</sup> in clay, Fe<sup>2+</sup> in clay, ankerite. The dominant presence of pyrite and competing presence of siderite indicate fluctuating redox environment in sediments. The relatively small amount of Fe<sup>2+</sup> in clay and marked presence of total clay indicates the source of iron is mainly terrestrially derived and attributes to stable rate of sedimentation.

#### Acknowledgements

The author is thankful to Oil India Limited (OIL), India for supplying the samples. Author is also thankful to UGC-DST for providing experimental facilities in the department of Physics, Jai Narain Vyas University, Jodhpur to carry out this study.

#### References

- [1]. Singh, N. P., "Mesozoic lithostratigraphy of the Jaisalmer basin, Rajasthan" J. Palaeontol Soc. India, Vol. 51(2), pp. 1-25 (2006)
- [2]. Patra, A., Singh, B. P. and Srivastava, V. K., "Provenance of the Late Paleocene sandstone of the Jaisalmer basin, Western India", J. Geol. Soc. India, Vol. 83, pp. 657-664 (2014)
- [3]. Datta, A. K., "Geological evolution and hydrocarbon prospects of Rajasthan basin", Petroleum Asia (India), vol. 1, p.93-100 (1983)
- [4]. Nigam, A.N., Tripathi, R.P., Singh, H.S., Gambhir, R.S. and Lukose, N.G., "Mössbauer studies on Ghotaru Well No.1 of Jaisalmer Basin", Fuel, vol. 68, p. 209 (1989)
- [5]. Nigam, A.N., Tripathi, R.P., Singh, H.S., Gambhir, R.S., "Source Rock evaluation of some wells in Jaisalmer Basin (India) using Mössbauer spectroscopy" Fuel, vol. 70, p. 262-266 (1989)
- [6]. Ram, S., Patel, K. R., Sharma, S. K. and Tripathi, R. P., "Distribution of Fe<sup>2+</sup> in clay minerals in sub-surface sediments of the Jaisalmer basin (India) using Mössbauer spectroscopy", Fuel, Vol. 76, No.14/15 p.1369 (1997)
- [7]. Ram, S., Patel, K. R., Sharma, S. K. and Tripathi, R. P., "Distribution of iron in siderite in sub-surface sediments of Jaisalmer Basin (India) using Mössbauer spectroscopy", Fuel, vol. 77, No 13, pp. 1507-1512 (1998)
- [8]. Tripathi, R. P., Sharma, S. K., Patel, K. R., Shrivastava, K. L. and Ram, S., "A Mössbauer approach to hydrocarbon prospecting in Jaisalmer basin of Rajasthan, India", Ind. J. Petrol. Geol., vol. 7, No. 1, pp. 47-58 (July 1998).
- [9]. Meerwall, E.V., "A least-square spectral curve fitting routine for strongly overlapping Lorentzians or Gaussians" Computer physics communications, vol. 9, p.117-128 (1975)
- [10]. Mørup, S. and Lindgreen H.B., "Applications of Mössbauer Spectroscopy in Oil Prospecting", Application of Mössbauer effect, ICAME, Jaipur, India, 1981; Indian National Science Academy, New Delhi, p. 290-292 (1982)
- [11]. Mørup, S., Franck, J., Wouterghem, J., Poulsen, R. and Larsen, L., "Mössbauer spectroscopy study of the chemical state of iron in Danish Mesozoic sediments", Fuel, vol. 64, p. 539 (1985)
- [12]. Karl, R. E. and Zuckerman, J. J., "Mössbauer spectroscopy and its chemical applications" (Eds. Steven J. G. and Shenoy G. K.), American Chem. Soc., p. 221 (1981).
- [13]. Berner, R. A., "A new geochemical classification of sedimentary environments" in Journal of Sedimentary Petrology, vol. 51 (3), p. 359 (1981)
- [14]. Neumann T., Rausch N., Leipe T., Dellling O., Berner, Z and Bottcher E. M., "Intense pyrite formation under low-sulphate conditions in the Achterwasser Lagoon, SW Baltic sea" Geochimica et Cosmochimica Acta, Vol. 69, No. 14, pp. 3619-3630 (2005)
- [15]. Boles, J. R., in "Clay and resource geologist" (short course handbook) ed. Longstaffe F. J.), Min. Assoc. Canada, vol. 7, p. 148 (1981).
- [16]. Bhatia, B., Tripathi, A., Sharma, R., and Tripathi, R. P., "Mössbauer spectroscopy study of sediments collected from test wells drilled in the Bikaner-Nagaur Basin", Fuel, Vol. 98, pp.140-148 (2012)