^{57}Fe Mössbauer Spectroscopic Study of Cretaceous Sediments of Jaisalmer Petroliferous Basin of Rajasthan, India

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^{57}Fe Mössbauer spectroscopy study was carried out on sedimentary samples collected from different depth interval in Cretaceous sedimentary sequence. These samples were collected from different test wells drilled in Jaisalmer petroliferous basin and also for each well the samples were collected from different depths. The chemical state of iron in Cretaceous sediments has been studied. Iron is found present in pyrite, carbonates and clays. A possible correlation in relative abundance of iron-bearing minerals and the environment of deposition is discussed.

Keywords: Mossbauer spectroscopy, Cretaceous sediments, pyrite, carbonates.

1. INTRODUCTION

Large number of wells has been drilled in several parts of Jaisalmer basin (India), by drilling agencies like ONGCL (Oil and Natural Gas Corporation India Limited) and OIL, India (Oil India Limited), but economically viable oil has not been explored so far. However many structures have yielded hydrocarbons; mainly methane accompanied with appreciable amount of nitrogen and carbon dioxide for example in Lunar structure (LNR) nitrogen is more than 80 percent while in Dandewala structure (DND) it is less than 40 percent [1].

Stratigraphically, starting from the top, the wells penetrates through the rock formations; Shumar (sub-recent), Bandah, Khuiala and Sanu (Middle-Eocene to Paleocene), Goru (Albian-Cenomanean-Upper Cretaceous), Pariwar (Lower Cretaceous), Baisaki-Bedesir (Upper Jurassic), Jaisalmer (Middle Jurassic) and Lathi (Lower Jurassic). The present study has been restricted to source rock sedimentary samples from Cretaceous sedimentary sequence because the Cretaceous and Jurassic sediment (below Cretaceous) are believed to contain the source rock rocks in Jaisalmer basin [1]. The aim of present study is to study the sedimentary samples collected from different depths from three wells located in Jaisalmer petroliferous basin in (India) using Mössbauer spectroscopy to understand the relative distribution of iron-bearing minerals in Cretaceous sedimentary sequence and to see if there is any correlation exist between the presence/absence of iron-bearing minerals and the availability of hydrocarbons in a basin. In present study three wells namely DND-1 located in Dandewala structure, MNW-1 located in Manewala structure and LNR-1 located in Lunar structure of Jaisalmer basin have undertaken for investigation.

The systematic description of petroleum geology and its occurrence is available in literature [2,3]. The studies show that temperature of sediments increase with burial depth i.e. temperature attained by sediments at larger depth will be more than that at shallower depth. It is also clearly mentioned by Tissot and Welte [2] that the sedimentary sequence that have attained high maturity or rather over maturity generate large N_2 & methane. Similar situation is observed in Jaisalmer basin, where nature of hydrocarbons points that sediments must have attained high degree of maturity.

2. EXPERIMENTAL

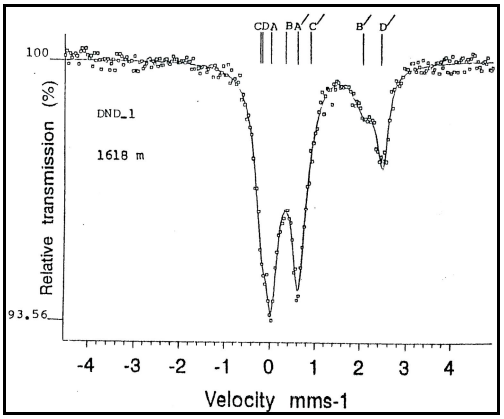
The Mössbauer absorber were prepared by sandwiching finely ground sediment samples between two paper disc in sample holder (25 mm diameter). All Mössbauer spectra were recorded at room temperature with a conventional constant acceleration Mössbauer spectrometer using a ^{57}Co source of 10 mCi initial strength. The Isomer shift has been reported with respect to centroid of a 25 μm thick α-iron foil spectrum. Details of experimental setup and fitting programme have been already reported [4-10].

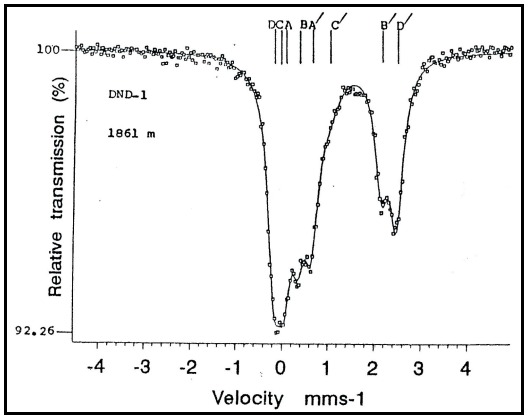
Table 1: Range of Mössbauer parameters for minerals present in sedimentary samples from Jaisalmer basin.

Component	QS (mms-1)	IS (mms-1)	Assignment
$AA^{/}$	0.52 – 0.67	0.26 – 0.36	Pyrite/little Fe^{3+} (clay)
$BB^{/}$	1.65 – 1.92	1.21 – 1.28	Siderite
$CC^{/}$	0.20 – 1.40	0.15 – 0.70	Fe^{3+} (clay) in *cis* or *trans* or both
$DD^{/}$	2.00 – 2.90	1.00 – 1.18	Fe^{2+} (clay) in *cis* or *trans* or both
$EE^{/}$	1.50 – 1.55	1.23 – 1.26	(Ca,Mg,Fe)carbonate

3. RESULT AND DISCUSSION

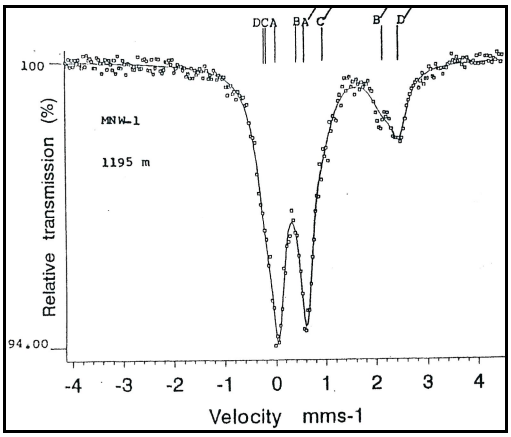
In Figure 1, 2 and 3 we display some representative Mössbauer spectra recorded at room temperature for samples collected from different depth intervals of wells DND-1, MNW-1 and LNR-1 respectively.. Depth interval from which the sample is collected has been marked in the figure itself. Majority of the spectra exhibit five doublets marked as $AA^{/}$, $BB^{/}$, $CC^{/}$, $DD^{/}$ and $EE^{/}$. The relative intensity of doublets varies from sample to sample. For doublet $AA^{/}$, the Isomer shift (IS) value is centered around 0.30 mms^{-1} and Quadrupole splitting (QS) value is around 0.60 mms^{-1}. Such IS and QS value are exhibited by both pyrite and Fe^{3+} in some clay minerals [11,12]. To settle the issue we took the help of acid treatment. It is well known that dilute HNO_3 leaches out pyrite from the samples and have no effect on the clay minerals. The Mössbauer spectra obtained after acid has no effect on this doublet $AA^{/}$, indicating that this doublet was not due to pyrite. Hence undoubtedly this doublet $AA^{/}$ is attributed to Fe^{3+} in some clay mineral [4-10]. For doublet $DD^{/}$ the IS and QS values are centered around 1.10 mms^{-1} and 2.60 mms^{-1} respectively corresponding to iron in Fe^{2+} state in clay minerals. Doublet $BB^{/}$ with IS and QS values centered around 1.24 mms^{-1} and 1.80 mms^{-1} respectively is attributed to iron in siderite. The doublet $EE^{/}$ with IS and QS values centered around 1.25 mms^{-1} and 1.65 mms^{-1} is attributed to iron in carbonate minerals other than siderite [8].

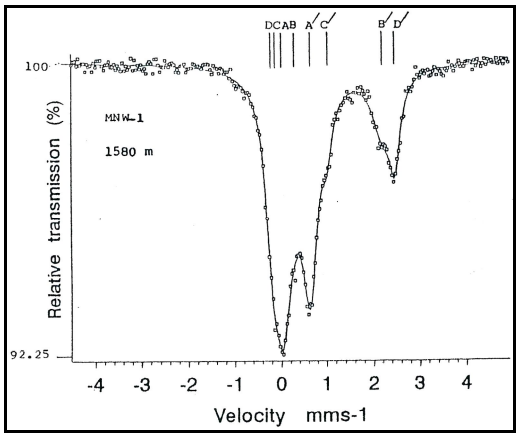




1(a): depths 1618 m **1(b):** depths 1861 m

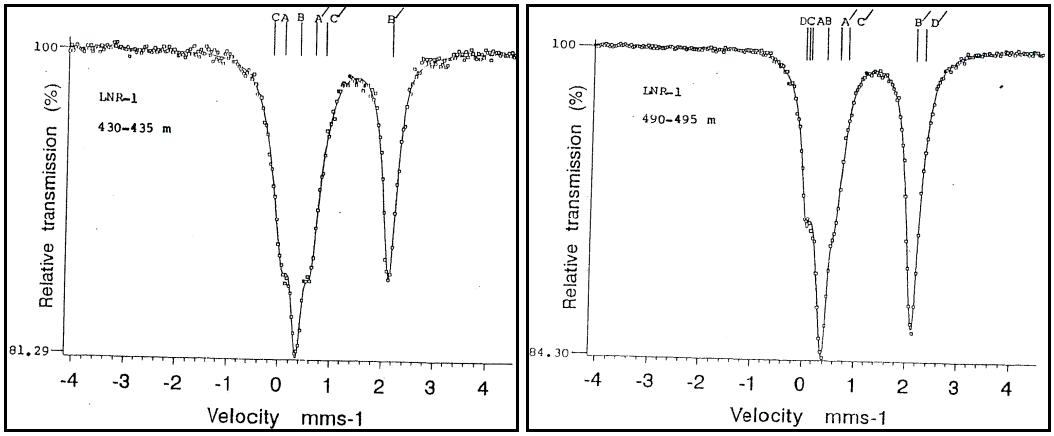
Figure 1: Room temperature Mössbauer spectra of samples collected from different depths 1618 m and 1861 m in well DND-1.





2(a): depths 1195 m **2(b):** depths 1580 m

Figure 2: Room temperature Mössbauer spectra of samples collected from different depths 1195 m and 1580 m in well MNW-1.



3(a): depths 430-435 m **3(b):** depths 490-495 m

Figure 3: Room temperature Mössbauer spectra of samples collected from different depths 430-435 m and 490-495 m in well MNW-1

In Figure 4, 5, and 6 we display the relative distribution of various iron-bearing minerals as a function of depth in wells DND-1, MNW-1 and LNR-1. In well DND-1, the Cretaceous sedimentary sequence comprises of three Formations, namely Parh (1300-1445 m) and Goru (1445-2017 m) in the Upper Cretaceous and Pariwar (2017-2509 m) in the Lower Cretaceous. Samples studied from Parh Formation show predominant presence of pyrite, while the relative amount of siderite is quite small. In clay minerals Fe^{3+} and Fe^{2+} are also present but in small amount. The Quadrupole splitting value of component $EE^{/}$ in the samples from Parh Formation obtained at depths 1330m and 1360m are slightly below the values normally found for siderite and it is possible that some component with ankerite-like parameter is also present, e.g., iron in ferroan-dolomite. In Goru Formation, the relative amount of siderite and Fe^{2+} in clay increases at lower depths, but srill pyrite is the dominating mineral. The relative amount of Fe^{3+} in clay is quite small. In the Pariwar Formation, the amount of Fe^{2+} in clay decreased with an increase in Fe^{3+} in clay. Also at the lower depths of this formation, the amount of pyrite decreased and that of siderite increased.

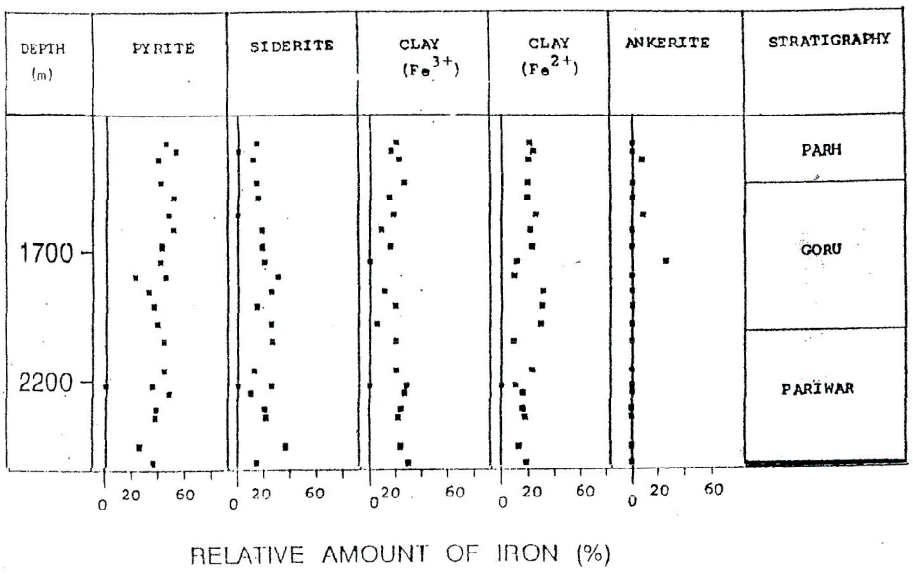


Figure 4: Relative amount of iron in different minerals as a function of depth in well DND-1.

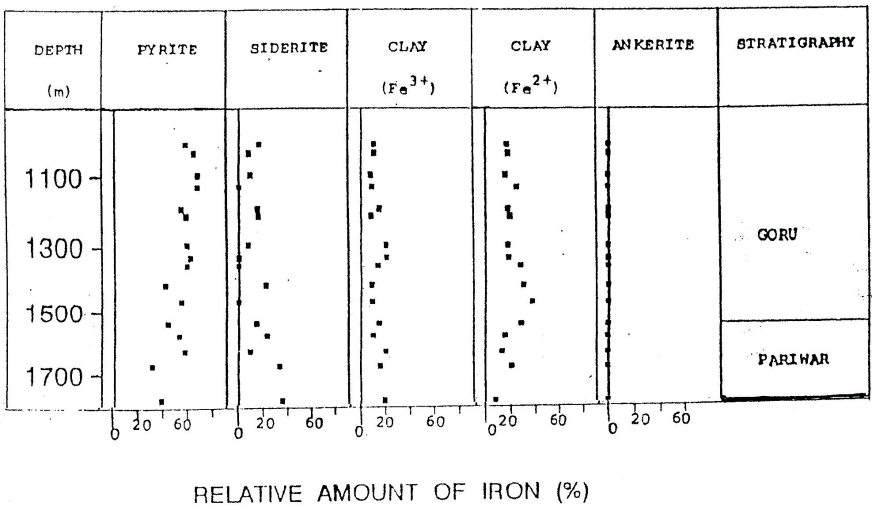


Figure 5: Relative amount of iron in different minerals as a function of depth in well MNW-1.

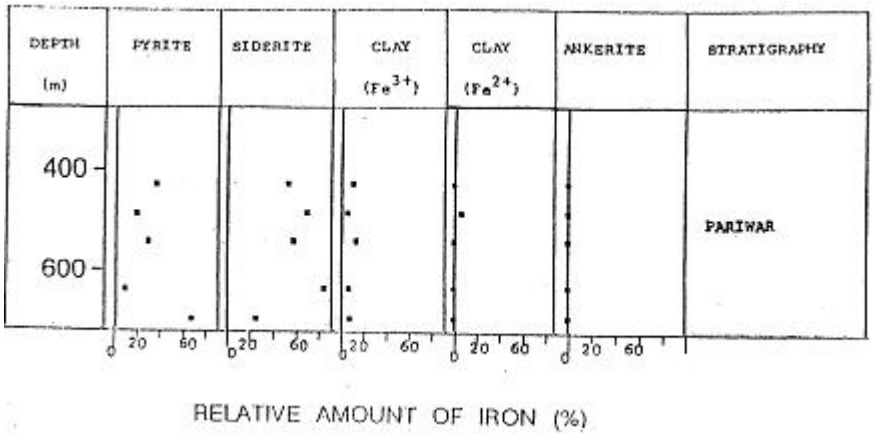


Figure 6: Relative amount of iron in different minerals as a function of depth in well LNR-1.

In well MNW-1, the Cretaceous Sedimentary sequence comprises of Goru Formation (1005-1540 m) and Pariwar Formation (1540-1779 m). Samples from Goru Formation show that predominant iron-bearing mineral is pyrite with little amount of siderite and Fe^{3+} in clay. At lower depth of Goru Formation the Fe^{2+} in clay is also found present in appreciable amount. In Pariwar Formation, a variation in relative amount of iron-bearing minerals was observed. The relative amount of pyrite and Fe^{2+} in clay decreased with a marked increase in the amount of siderite and Fe^{3+} in clay minerals.

In well LNR-1, the Cretaceous Sedimentary sequence comprises of Pariwar Formation (281- 710 m) in the Lower Cretaceous sequence. Samples from Pariwar formation have shown relatively large amount of siderite, except in sample obtained at depth 710m where relative amount of pyrite is in excess. .

In all the investigated wells, there is a significant variation in the presence/absence of pyrite and siderite. It is observed that where the amount of pyrite is large, the amount of siderite is small and vice-versa. It seems that pyrite and siderite compete with each other. Since pyrite precipitates in more reducing environment while the siderite is observed in less reducing environment. At lower depths, the increase in relative amount of Fe^{2+} in clay also points towards higher crystalline behavior [13,14] in which Fe^{3+} transforms in to Fe^{2+}. The presence/absence of particular iron-bearing minerals can indicate the environment of deposition whether it is reducing (more favourable for transformation of organic matter in oil/gas) or oxidizing (less favourable for transformation of organic matter into oil/gas.

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