Study of geo-chemical environment in organic rich sub-surface sediments of Jaisalmer petroliferous basin of Rajasthan, India, using Mössbauer spectroscopy

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Abstract. A ⁵⁷Fe Mössbauer Spectroscopic study was carried out on brown red coloured samples collected from different depth intervals of two wells (LNR-1 & DND-1) of Jaisalmer petroliferous basin, India. All these samples show a sextet corresponding to hematite along with two quadrupole doublets one correspond to iron in siderite and other correspond to Fe²⁺ in clay minerals. Relative presence of hematite is seem to be correlated with nature of gaseous hydrocarbon discovered in this basin. Our earlier studies also pointed out such correlation between redox environment and presence/absence of hydrocarbon in a basin. We suggest that such correlation is not surprising because rate of sedimentation determines both hydrocarbon prospecting and redox environment in the sediments.

1. Introduction
Sediments rich in organic matter are known as source rocks. These rocks are tiny generators of oil and gas in a basin. As the time passes the organic matter present in sediments is modified by bacteria and undergoes thermal alteration, commonly termed as maturation. The quality and maturity of the organic matter present in source rocks have a decisive effect on the hydrocarbon prospect and accumulation pattern in the basin. A systematic and excellent description on petroleum geology and its occurrence available in literature where the importance of study of inorganic phases for characterization of source rocks is highlighted [1].

Several workers have reported the Mössbauer spectroscopic studies on samples collected from wells drilled in different petroliferous basins. These studies show that, iron in sediments is mainly present only in four variety of minerals i.e in sulphur containing minerals, in carbonate minerals, in clay minerals (both Fe²⁺ and Fe³⁺ in octahedral site of clay minerals) and in oxides/oxyhydroxide but their relative amount varies from sample to sample and also from basin to basin.

As far as Jaisalmer Basin is concerned number of wells have been drilled in several parts of this basin 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 forms more than 80 percent of the gases discovered while in Dandewala structure (DND) it is less than 20 percent. In earlier studies our group have reported Mössbauer spectroscopic study on samples collected from several wells located in various structures of the Jaisalmer basin [4-10]. From Table 1, it can be seen that presence of hydrocarbons in North sea offshore wells and in Jaisalmer basin are markedly different. Main aim of earlier studies was to correlate this difference with relative distribution of iron bearing minerals in these two basins. It
was observed that pyrite was the dominating phase in Offshore wells while siderite was dominating phase in Jaisalmer basin samples. This difference clearly suggest that sediments in these two basins were deposited in different geochemical (redox) conditions. Number of wells in Jaisalmer basin were drilled from top to basement. In these wells brownish red coloured samples were encountered at larger depth (only in middle Jurassic and Lower Jurassic Sedimentary Sequence). Sample at such depth were not studied earlier. None of the samples from cretaceous rocks have shown this characteristic colour. In present investigation, we have carried the Mössbauer spectroscopic study on these brownish red coloured samples. Interestingly in Jaisalmer basin the Jurassic rocks also contain potential source rocks with adequate maturity. Here studies are confined to two typical wells LNR-1 and DND-1 as a representative wells.

Table 1. A Most general trend of authigenic iron-bearing minerals observed in different basins.

| Basin                  | Iron minerals which are dominantly present in majority of samples | Status of hydrocarbon discovery | Reference | Reducing environment on the basis of authigenic minerals present in basin |
|------------------------|---------------------------------------------------------------|-------------------------------|-----------|-------------------------------------------------------------------|
| Danish North Sea (Offshore) | Pyrite, Fe²⁺ in octahedral site in clay minerals             | Oil and gas are present       | 2, 3      | Good                                                               |
| Danish North Sea (Onshore) | Pyrite, appreciable presence of carbonate minerals             | Mainly dry                    | 2, 3      | Poor                                                              |
| Eastern Krishna-Godavary | Pyrite, iron in sulphate minerals                              | Oil and gas are present       | 9         | Good                                                               |
| Cambay                 | Pyrite, iron in sulphate minerals Iron in Carbonates, Fe³⁺ in octahedral site of clay minerals | Oil and gas are present (relatively it is gaseous field) | 10        | Good                                                               |
| Jaisalmer              | Iron in Carbonates, Fe³⁺ in octahedral site of clay minerals  | No oil but gaseous hydrocarbons mainly accompanied by large nitrogen and methane | 4-8       | Good                                                               |

2. Experimental
Mössbauer spectra were recorded at room temperature with a conventional constant acceleration Mössbauer spectrometer using a 10 mCi ⁵⁷Co source (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, method of sample preparation and fitting programme have been already reported earlier work [4-6].

3. Results and Discussions
In Figure 1, we display some representative Mössbauer spectra recorded at room temperature for samples collected from different depth intervals of wells LNR-1 and DND-1. Depth interval and name of the well from which the sample has been collected is marked in the figure itself. It can be seen from Fig 1 that all the samples show presence of intense sextet with HMF value (hyperfine magnetic splitting) 516 kOe, and IS value 0.34 mms⁻¹ and QS value -0.15 mms⁻¹ characteristic of hematite(α-Fe₂O₃). Apart from this sextet, two quadrupole doublets are also present. One corresponding to iron in siderite marked as BB and other corresponding to Fe²⁺ in octahedral site of clay minerals marked DD. In LNR-1 the thickness of sedimentary band containing hematite is...
600m (1900 m to 2500 m) while in well DND-1 only one sample collected from depth 4492 m has shown presence of hematite. The sample below this was devoid of hematite. In well DND-1 (Dandewala structure) the thickness of sedimentary sequence in which hematite is present is certainly very small in comparison of LNR-1 (Lunar structure). It is worth mentioning that hematite is formed in oxidising environment.
The most important finding is that in the structure (Lunar) where rigorous oxidizing conditions are present poor quality of hydrocarbon is found in comparison of where oxidizing condition are not so rigorous (Dandewala structure). Similar trend was also observed in other part of basin (Ghotaru Structure, Bhakri-Tibba Structure etc.). On the basis of present study and studies reported earlier (see Table 1) it can be suggested that redox condition may be one of the significant marker for hydrocarbon presence/absence provided other geochemical and geophysical parameters are same.

This correlation can be explained on the basis of following facts; as it is well known that hydrocarbon generation is highly correlated with rate of sedimentation because this affects the maturity of rocks and also controls early and late digenesis[1,11]. Simultaneously, the rate of sedimentation also controls the stability of authogenic minerals. If the rate of sedimentation is fast, it quickly cuts off sediment from environment and this favours formation of minerals like pyrite which are digenetically stable in reducing environment. Apart from this organic matter also escapes oxidation due to quick sedimentation. On the other hand if deposition rate is slow, sediments remain with contact of atmosphere relatively more time. This favour formation of minerals like carbonates, goethite, hematite etc. and the organic matter will also suffer oxidation. If we put these two facts together, the correlation between hydrocarbon prospecting and redox environment is not surprising. However more studies are needed to establish correlation conclusively. The ability of Mössbauer spectroscopy to provide information of geochemical environment in sediments can be utilised in future for discovery of oil and gas in a basin.

4. References
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