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Research paper

^{57}Fe Mössbauer spectroscopy study of organic rich sediments (source rocks) from test well CT-1, Chinnewala structure of Jaisalmer basin, India

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ABSTRACT

^{57}Fe Mössbauer spectroscopic study was carried out on the organic rich sedimentary samples collected at different depth intervals from newly drilled test well Chinnewala Tibba-1 (CT-1) located in Jaisalmer Petroliferous basin India. It is found that iron is mainly distributed in high spin Fe^{3+} and Fe^{2+} state in clay minerals. The plot of $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ indicates the presence of poor redox conditions in the samples. Results obtained are also compared with those already reported in the literature. This comparison shows that there may exist a correlation between prospecting of the basin, the redox environment in sediments and the nature of iron bearing minerals distributed in the sedimentary sequence.

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1. Introduction

^{57}Fe Mössbauer spectroscopy is particularly useful for characterization of iron bearing species because it probes the local environment of iron nuclei sensitivity. This method offers certain advantages over other conventional techniques such as chemical, optical, electron microscopic analysis etc. Indeed each technique has its own strength, but where Mössbauer spectroscopy can give results, it offers a quick reliable and simple method. Being non destructive technique in the sense that the sample either in powder form or thin slice is not altered during the experiment also in a single run, one can get information about all the iron phases present in the sample by proper deconvolution of the Mössbauer spectrum.

This technique is widely used for the study of geological samples including all types of sediments. As it is well known that oxidation state of iron metal in sediments is a measurement of oxidation-reduction condition of sedimentation. It is the only technique which provides crucial information about ferrous/ferric ratio in

sediments. To get better insight about the application of ^{57}Fe Mössbauer spectroscopy for geological samples, we refer to excellent review by [Tominaga and Minai \(1984\)](#). Mössbauer spectroscopy is also used widely to study organic rich sediments (source rocks) from different petroliferous basin. In fact source rocks are tiny generators of oil/gas or both. Source rock characterization is one of the important aspect for the exploration of oil/gas. To get more information about source rocks we refer to [Hobson and Tratsoo \(1981\)](#) and [Tissot and Welte \(1984\)](#).

The mineral matters present in source rocks also contain iron bearing minerals which can be characterized by Mössbauer spectroscopy.

In an early work [Mørup et al. \(1985\)](#) have studied the chemical state of iron in the organic rich sediments from Danish North Sea offshore and onshore wells. They have shown that in the offshore sediments, iron was mainly present in most of the samples in the form of Fe^{2+} in clay minerals and pyrites. In some samples siderites/ankerite was also present. This distribution of minerals suggests that North Sea offshore sediments were deposited in highly reducing environment. It is worthwhile to note that offshore region is major oil field of North Sea. In view of above study the detail study of chemical state of iron in subsurface sediments for four different petroliferous basin of India was carried out by our group

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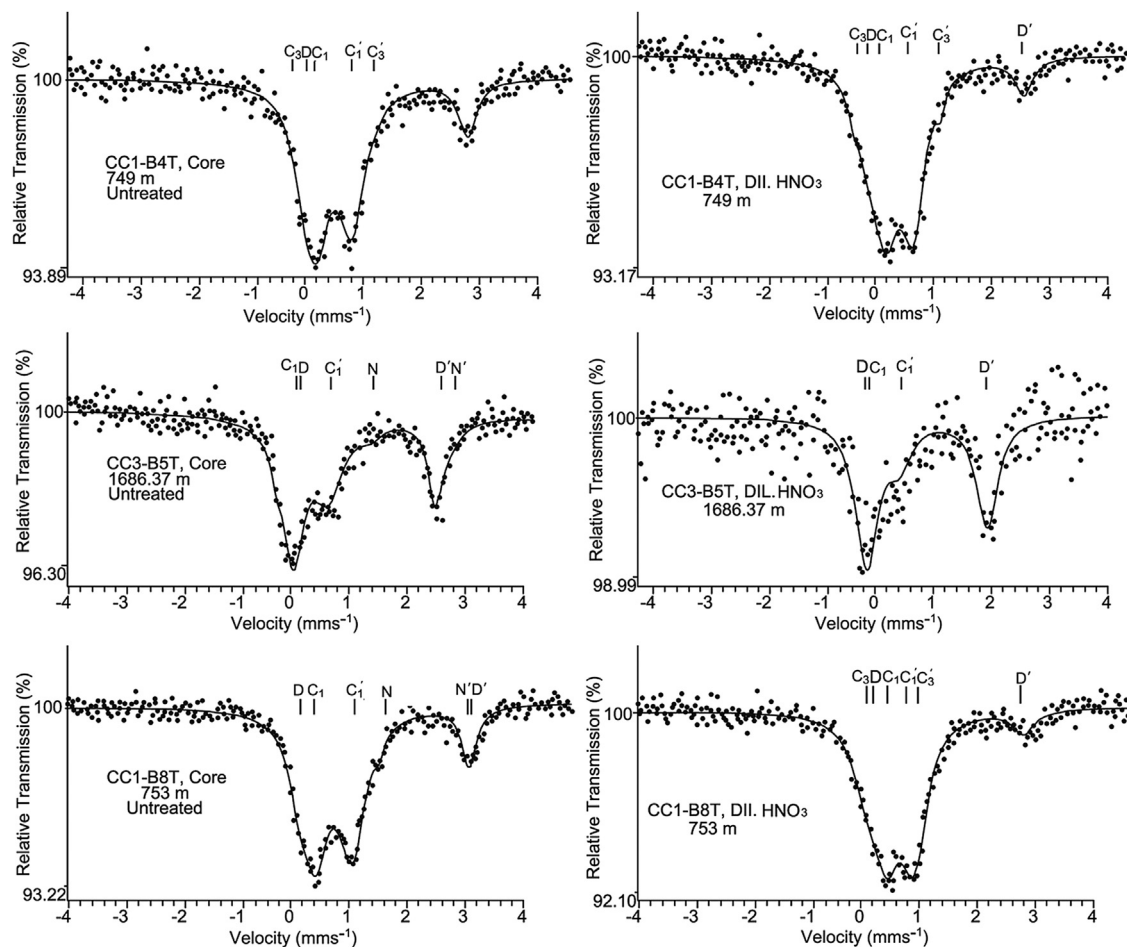


Figure 1. Mössbauer spectra of untreated and acid treated samples collected from well CT-1. Depths at which the samples were collected are given in figure itself.

(one of the authors RPT was associated with this work). These four basins are Eastern Krishna Godawari basin (EKG), Cambay basin, Bikaner-Nagaur basin and Jaisalmer basin. All these basins are located in different parts of our country, while EKG and Cambay basins are major fields of gaseous hydrocarbons, no oil/gas was discovered in Bikaner-Nagaur basin. In Jaisalmer basin no oil so far discovered but some structures have yielded hydrocarbons (mainly methane accompanied by significant amount of carbon dioxide and nitrogen). Our results of studies for these basins are already reported (Nigam et al., 1991; Ram et al., 1998; Tripathi et al., 2008; Kulshreshtra et al., 2004; Bhatia et al., 2012).

It is interesting to note that relative distributions of iron bearing minerals obtained for both EKG and Cambay sediments show almost similar trend, though both the basins are geographically far apart. Sediments of these basins exhibit presence of iron pyrite, Fe^{3+} and Fe^{2+} in sulphate minerals and Fe^{3+} in clay minerals. This distribution is markedly different from those observed in Danish North Sea offshore sediments. This indicates that sediments of EKG and Cambay basins were deposited in less reducing conditions as compared to North Sea offshore sediments. Further Bikaner-Nagaur basin where no conventional oil/gas is so far discovered shows presence of iron in $\alpha\text{-Fe}_2\text{O}_3$ that is in hematite and Fe^{3+} in clay minerals (Bhatia et al., 2012). This indicates that sediments of Bikaner-Nagaur basin show highly oxidizing condition of deposition. These studies point out that there may be some correlation between oxidation-reduction conditions of sedimentation and hydrocarbon prospecting of basin.

If there is any correlation between redox environment and hydrocarbon prospecting of the basin then sediments of Jaisalmer basin would exhibit poor reducing environment. This is in context that in Jaisalmer basin no oil is so far discovered and quality of gaseous hydrocarbon is poor. Though earlier studies reported by our group show appreciable presence of siderites in sediments collected from Jaisalmer basin, indicating poor reducing environment in this basin. But the better index to determine oxidation and reducing condition of sediments is to determine the relative distribution of iron in Fe^{2+} and Fe^{3+} in clay minerals. Therefore in present investigation we have extended our study on the subsurface sedimentary samples collected from recently drilled well CT-1 located in Chinnewala Tibba at different depth interval and at different stratigraphic level of Jaisalmer basin. Sample used for present investigation belongs to Paleocene and Cretaceous. The organic matters present in these samples are basically of humic type with type-III Kerogen.

The aim of our study is to get better understanding of oxidation and reducing conditions of Jaisalmer sediments.

2. Experimental details

The 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 the absorber was always kept constant. Mössbauer spectra were recorded at room temperature (300 K) with a conventional constant acceleration, the

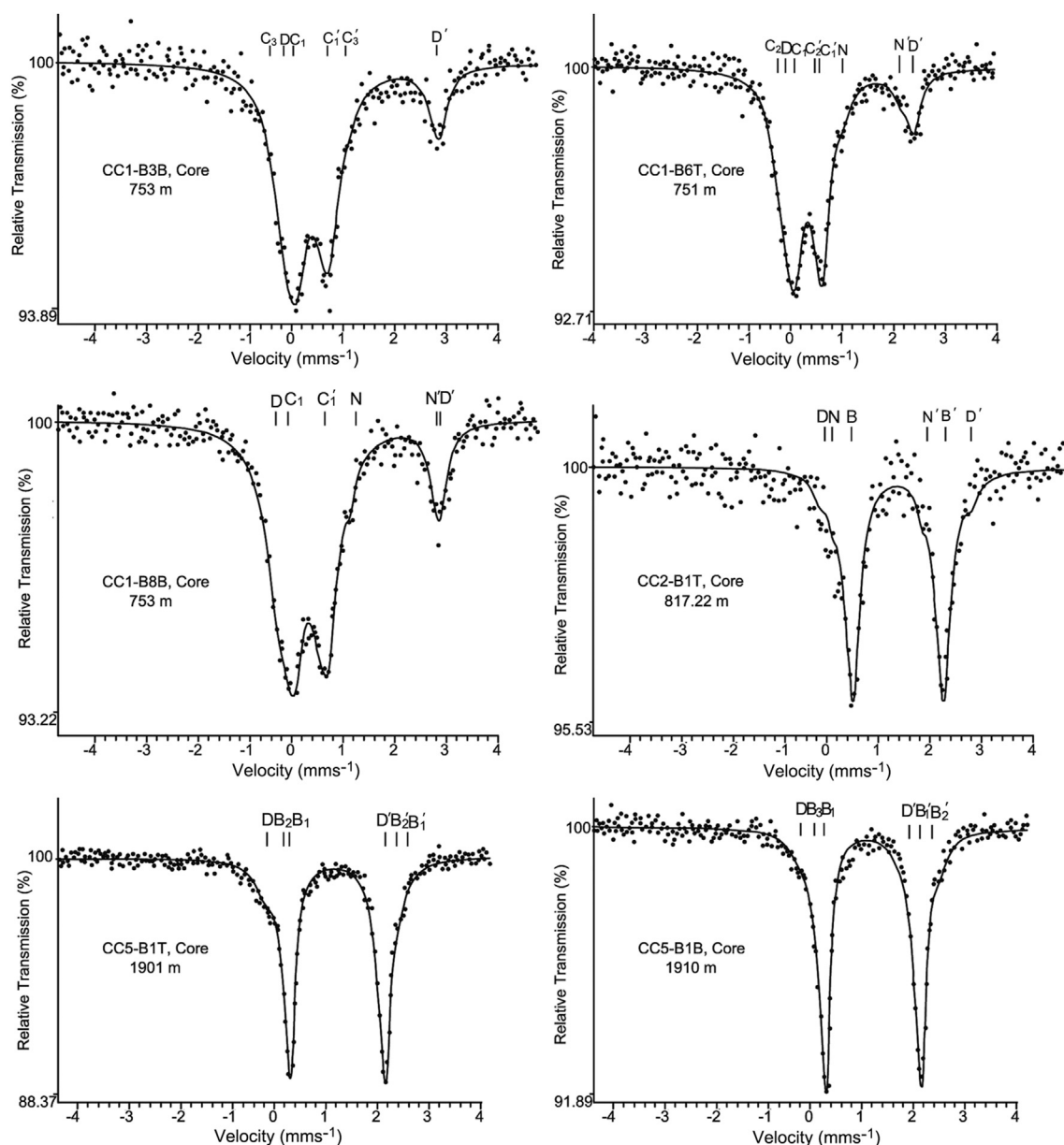


Figure 2. Room temperature Mössbauer spectra of core samples collected from well CT-1. Depths at which the samples were collected are given in figure itself.

solution was filtered, waste and residue was dried. Spectrometer using a 10-mCi source ^{57}Co in an Rh matrix. 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 (1975). This programme assumes the spectrum to be the sum of Lorentzians. In most of the cases, width and intensity of the two halves of a quadruple doublet were constrained to be equal. The relative intensities of various mineral components or sites were calculated by adding the areas of the two halves of the corresponding doublet and are expressed as a fraction of the total area of resonant absorption. Solid lines in the spectra reported here represent computer-fitted curves, and dots represent the experimental points. For the fit to be statistically acceptable, it is required that value of parameter chi square should lie between $\nu + 2.2 - 3.3 \sqrt{\nu}$ and $\nu + 2.2 + 3.3 \sqrt{\nu}$, where ν is the number of degrees of freedom. In the present study, the chi square values are generally obtained in this range. However, a little deviation in the chi square has been accepted on the few occasions when the iterations do not

yield to further improvements in chi square. Such a situation arises when weak lines are present.

We have treated samples with dilute HNO_3 , for 24 h and the solution was filtered, washed and finally residue was dried. The Mössbauer spectrum of this residue was recorded at room temperature. The acid treatment was used to distinguish if doublet is corresponding to pyrite/ Fe^{3+} in silicate minerals. The method used is same as reported by Verma and Tripathi (2000).

3. Assignment of quadruple doublets

Mössbauer spectra of samples were resolved into different quadruple doublets. The positions of these doublets are marked in figure itself as C_1C_1' , C_2C_2' , C_3C_3' , DD' , BB' depending on their appearance in the Mössbauer spectrum. The relative intensities of these doublets vary from sample to sample. It is not necessary that all these doublets are present simultaneously in the samples. However, most of the samples exhibit an intense quadruple

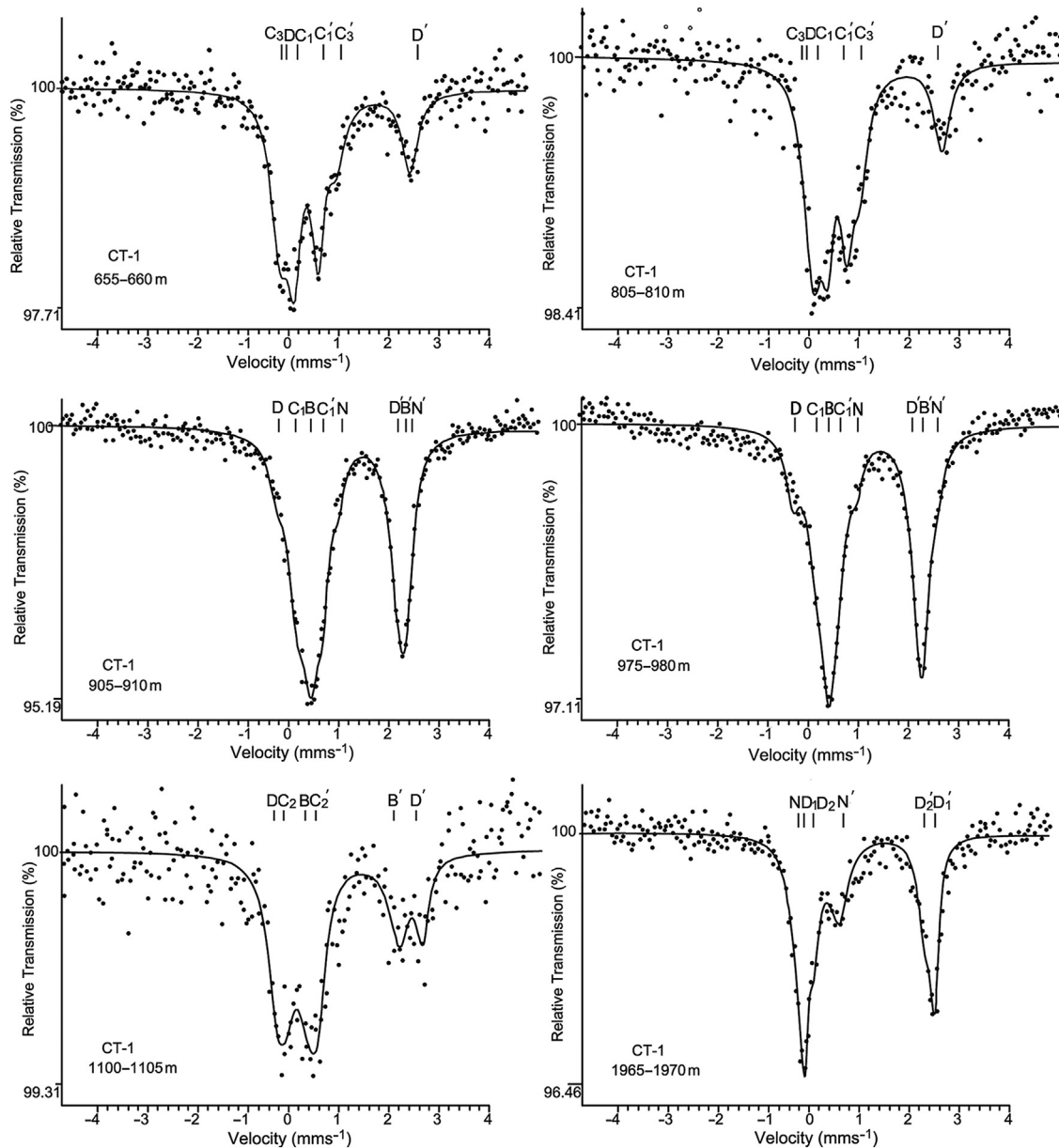


Figure 3. Room temperature Mössbauer spectra of cutting samples collected from well CT-1. Depths at which the samples were collected are given in figure itself.

doublets (center doublet marked as C_1C_1' in figures). Range of isomer shift (IS) value for this doublet is $0.26\text{--}0.36\text{ mm s}^{-1}$ and range of quadruple splitting (QS) value is $0.56\text{--}0.64\text{ mm s}^{-1}$.

These parameters are typical of Fe^{3+} in octahedral site of the clay minerals. However, the parameters for low spin Fe(II) in pyrites are also identical as observed for quadruple doublet C_1C_1' . To settle this issue if the doublet C_1C_1' is due to high spin Fe^{3+} or low spin Fe(II) sedimentary samples were treated with dilute HNO_3 . We know that dil HNO_3 leaches out selectively pyrite for the sample leaving clay mineral unaffected (Verma and Tripathi, 2000). If the pyrite is present in the sample the relative intensity of doublet C_1C_1' should drastically reduce in the Mössbauer spectrum of the samples treated with dilute HNO_3 . In Fig. 1 we provide Mössbauer spectrum of both treated and untreated samples. It can be seen from Fig. 1 that intensity of central doublet C_1C_1' only marginally changed indicating absence of pyrite in the sample. So we can safely assign doublet C_1C_1' to the high spin Fe^{3+} present in silicate

minerals. Doublets C_2C_2' , and C_3C_3' also show Mössbauer parameters characteristic of high spin Fe^{3+} in silicate mineral. For doublet DD' the IS value ranges between 1.10 and 1.20 mm s^{-1} and QS value ranges between 2.6 and 2.8 mm s^{-1} . Mössbauer parameters for this doublet DD' are characteristic of Fe^{2+} iron in silicate/clay minerals. IS value for doublet BB' ranges between 1.23 and 1.28 mm s^{-1} and QS value ranges between 1.60 and 1.80 mm s^{-1} .

These parameters are typical in iron in siderites. Therefore doublets DD' and BB' are attributed to iron in Fe^{2+} state in clay mineral and siderite respectively. Apart for this in some samples one more additional doublet with weak intensity marked as NN' in figures was also resolved. However, intensity of this doublet is so small that we have not attempted to identify the mineral phase associated with this doublet because it will not be going to alter our conclusion. We are interested only in the relative distribution of iron in Fe^{3+} and Fe^{2+} states, since iron occupies only in the octahedral sites of silicate/clay minerals irrespective of the nature of the

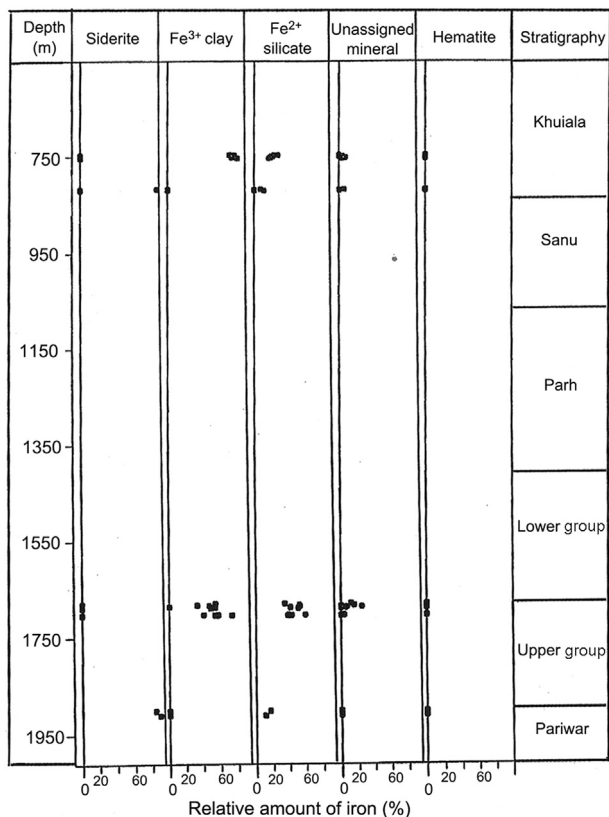


Figure 4. Relative amount of iron in different minerals of core samples as a function of depth from well CT-1.

clay mineral. Therefore we have not attempted to identify individual mineral components in which these ions are present. When two quadruple doublets correspond to cis- and trans-site, they are marked as D_1D_1' and D_2D_2' in figures instead of DD' as in most of the samples it is not possible to resolved them separately.

4. Results and discussion

Some representative Mössbauer spectrum of core and cutting samples are shown in Figs. 2 and 3 respectively. The relative distribution of iron in various mineral/sites as a function of depth is provided in Figs. 4 and 5 for core and cutting samples respectively. We have also plotted in Fig. 6 the ratio $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ as a function of depth. To obtain this ratio we have added the relative intensity of all three Fe^{3+} doublets C_1C_1' , C_2C_2' and C_3C_3' to get total Fe^{3+} . For Fe^{2+} if needed we have added the intensity of doublets D_1D_1' and D_2D_2' , otherwise the intensity of doublet DD' corresponding to iron in Fe^{2+} state in the sample is added. In present work we have taken same value of recoil free fraction i.e. f-fraction for different iron phases. This approximation is used frequently for Mössbauer spectroscopic studies of sedimentary samples.

The important findings of this study can be summarized as follows:

- (1) From Figs. 4 and 5 it can be seen that iron in samples of well CT-1 irrespective of core and cutting samples is mainly present in the form of Fe^{3+} in clay mineral, Fe^{2+} in clay minerals and siderite (siderite is present only in limited number of samples). It is observed that core and cutting samples show similar behaviour.
- (2) The most important observation is that in most of the samples pyrite is either absent or meagerly present. The absence of

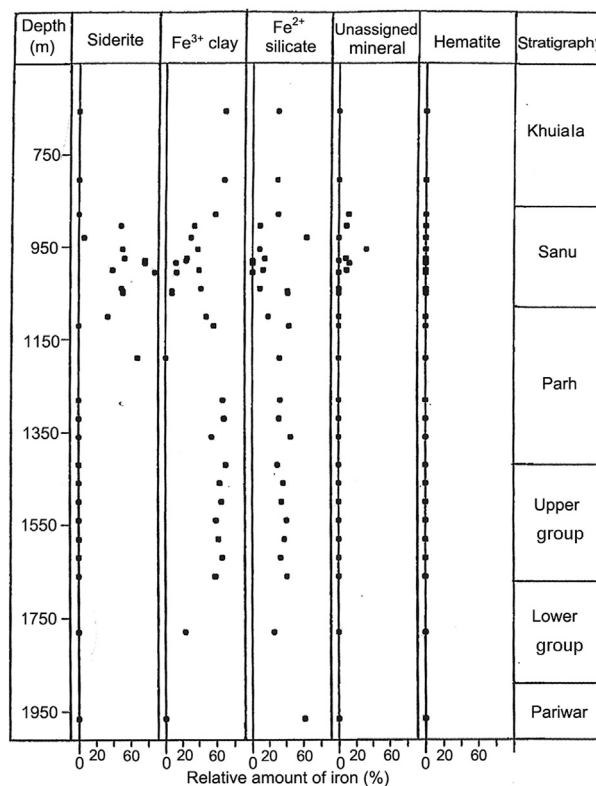


Figure 5. Relative amount of iron in different minerals of cutting core samples as a function of depth from well CT-1.

pyrite itself shows that the sedimentary sequence of Jaisalmer basin was deposited in poor reducing conditions. In Fig. 6 the ratio $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ as a function of depth conclusively shows that sedimentation of Jaisalmer basin took place relatively in oxidizing condition.

There may exist a correlation between relative distribution of iron in source rocks (it provides information about oxidation-reduction condition) and prospects of basin. Oil rich basin Danish North Sea offshore shows highly reduce condition, while reducing condition decreases markedly where only gaseous hydrocarbons are present (EKG and Cambay). Reducing condition further decreases (oxidizing condition increases) in Jaisalmer basin which show poor presence of hydrocarbon and in Bikaner-Nagaur basin

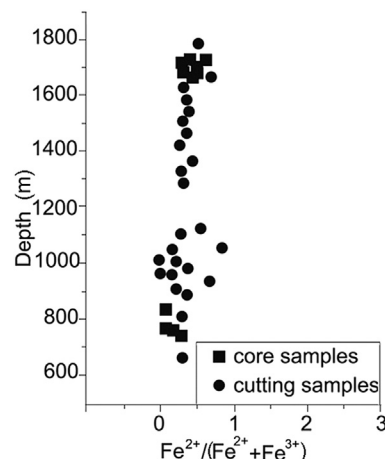


Figure 6. Ratio of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ as a function of depth.

Table 1
Comparison of reducing condition in sediments and presence of hydrocarbons in the basins.

| Basin | Chemical state of iron in sediments containing source rocks | Reducing condition of sedimentation using iron mineralogy as finger print | Availability of presence of hydrocarbons |
|---------------------------|---|---|---|
| Danish North Sea offshore | Fe ²⁺ in clay minerals and pyrites | Highly reduced | Potential oil field |
| Danish North Sea onshore | Appreciable presence of Fe ³⁺ in clay minerals | Poor reducing condition | No oil discovered |
| EKG | Pyrite Fe ²⁺ in clay minerals, Fe ²⁺ in sulphate minerals | Moderate reducing condition | Potential gas field |
| Cambay | Pyrite Fe ²⁺ in clay minerals, Fe ²⁺ in sulphate minerals | Moderate reducing condition | Potential gas field |
| Jaisalmer | Siderite Fe ³⁺ in clay minerals and absence of pyrite | Poor reducing condition | Presence of gaseous hydrocarbons mixed with appreciable amount of carbon dioxide and nitrogen |

sediments show high degree of oxidizing condition where no oil and gas was present. This sequence strengthens our argument that redox conditions present in organic rich sediments are correlated with the prospecting of the basin (c.f. Table 1).

The exact reason for this correlation is not known because it can be cumulative effect of many parameters. One of the reasons may be the migration of hydrocarbon of source rocks, for example in recent study Zheng et al. (2010) have also reported Mössbauer spectroscopic investigation on samples collected from the Dushanzi Mud-volcano system. It should be noted that Mud-volcano is a typical petroleum leaching system, which results in leaching effect of surrounding rocks. They observed variations in iron species, in bleached and unbleached rocks, the bleached rocks are dominated by reducing iron species such as paramagnetic ferrous iron (para-Fe²⁺), ferrous iron in siderite (sid-Fe²⁺), and in pyrite (pyre-Fe²⁺) where as the original reddish rock is enriched with ferric iron including iron in hematite and paramagnetic ferric iron (para-Fe³⁺). A reduction of ferric iron species and hydrolysis of iron along with oxidation of hydrocarbons should be one of the main processes along leaching by hydrocarbon to rocks.

Other possibility for this correlation is the rate of sedimentation. It is known that the hydrocarbon generation is also influenced by the rate of sedimentation. This controls the maturity of source rocks and also early and late diagenesis of organic matter (Hobson and Tratsoo, 1981; Tissot and Welte, 1984). It also controls the stability of minerals including iron bearing mineral, e.g. if the rate of sedimentation is fast it quickly cuts off sediment from environment and this may favour formation of minerals like pyrite which are digenetically stable in reducing environment. Simultaneously organic matter also escapes oxidation and becomes more favourable for the generation of oil. But if sedimentation rate is slow sediments will remain in contact with atmosphere for more time. This may result in oxidation of organic matter making it unfavorable for the generation of oil and favours minerals like siderite, iron oxide etc. depending upon the degree of redox condition.

This correlation can also be viewed that the physicochemical transformation of organic matter during the geological history of sedimentary basin cannot be regarded as an isolated process. It is controlled by the same major factors that determine the variation of the composition of the inorganic solid phase of sediments; that is to say, biological activities in the early stage, and temperature and pressure afterwards decide the evolution of both the organic matter and the inorganic solids.

This work becomes important when discovery of oil and gas is not in coincident with the estimation predicted on the basis of conventional geophysical and geochemical parameters. In that circumstances ⁵⁷Fe Mössbauer study becomes an important tool to study reducing condition under which source rocks were deposited using iron mineralogy as finger print. The crucial information obtained by ⁵⁷Fe Mössbauer spectroscopic study may be correlated with the oil prospecting of the basin.

5. Conclusion

The results obtained in the present study are compared with those already present in the literature and suggest that there exist an empirical correlation between reducing condition in the sediments of basin and presence of hydrocarbons. Since the Mössbauer spectroscopy is the only technique which provides information about the redox condition (oxidation state of iron metal). This technique also provides nature of iron bearing minerals in the sediments. More Mössbauer spectroscopic study is needed for other petroliferous basins also to get crucial information to strengthen this correlation.

Acknowledgement

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