

Characterization of Source Rock Sediments from Test Well GGAG#699 Located in Gandhar Oil Field of Gujarat Petroliferous Basin, India, using ^{57}Fe Mössbauer Spectroscopy

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^{57}Fe Mössbauer spectroscopic studies on deep subsurface sediments collected from test well GGAG#699 located in Gandhar oil field of Cambay basin, Gujarat is reported. It is found that iron is mainly present in some clay (both in high spin Fe^{2+} and Fe^{3+} state) along with fluctuating amount of pyrite and siderite. The distribution trend of iron bearing minerals can provide useful information about redox environment and in estimating the quality of source rocks in sediments.

Keywords: Source rocks, ^{57}Fe Mössbauer spectroscopic study, Iron bearing minerals, Cambay basin.

1. INTRODUCTION

Sedimentary basins of India are broadly divided into four categories on the basis of hydrocarbon prospecting viz., (i) Category I (Petroliferous basin with commercial production), (ii) Category II (Petroliferous basin awaiting commercial production), (iii) Category III (Basin are geologically hydrocarbon producing) and (iv) Category IV (Basin poorly explored or have shown less productivity despite the geological predictions showing favorable conditions for hydrocarbon prospecting). Sediments which contain organic matter are regarded as the source rocks. This organic matter in sediments upon prolonged period attains a certain degree of diagenesis and transforms into oil or gas. The hydrocarbon prospecting in a basin mainly depends upon the amount and quality of source rock and the degree of diagenesis i.e. maturity of source rocks. A source rock is said to be mature when hydrocarbon generation takes place. The nature, quality and quantity of hydrocarbons in a basin very much depend upon the geo-chemical environment in which the source rocks were deposited. The information about the geo-chemical environment in which the source rocks were deposited is quite significant for the characterization of source rocks in a basin.

The formation of hydrocarbons is an organic process and the major factors which govern it are the biological activity in early stage then temperature and pressure [1]. It is obvious that during the physico-chemical transformation of organic matter in sediments, the inorganic matter present in sediments also undergoes variation in their composition. The sediments during their deposition undergoes varying geo-chemical environments resulting into variation in the organic matter as well as the inorganic matter present in it. The organic-inorganic interaction can take place during the different stages of sediments

deposition. Thus the mineralogical analysis of sediments containing source rocks is significant to understand the geo-chemical environment during the past history of sediments deposition. The inorganic matter also includes iron-bearing minerals which can be characterized by Mössbauer spectroscopy.

In an early work, Mørup and Lindgreen [2] and Mørup *et al.* [3] have reported a systematic study on chemical state of iron in Mesozoic & Cenozoic sediments from Danish North Sea oil wells. A significant correlation between ankerite and maturity of source rocks was indicated in the sediments of Danish North sea oil wells. In a similar kind of study, Nigam *et al.* [4], Sahi Ram *et al.* [5, 6] and Tripathi *et al.* [7] have reported Mössbauer studies on sediments of test wells drilled in Jaisalmer basin of Rajasthan, India. They have reported the chemical state of iron in source rock sediments and its correlation with hydrocarbon prospecting in Jaisalmer basin. Recently Bhatia *et al.* [8] and Meena *et al.* [9] have reported Mössbauer studies on marine sediments of Bikaner-Nagaur basin of Rajasthan, India. In present study, large number of sedimentary samples collected from different depth intervals of test well GGAG#699 drilled in Gandhar oil field located in Cambay basin of Gujarat petroliferous basin of India has been studied using Mössbauer spectroscopy. The present study is undertaken with an objective to understand the relative distribution of iron bearing minerals as a function of depth and to see if there exist some correlation in presence/absence of iron bearing minerals and the quality of source rocks in estimating the hydrocarbon prospecting in this basin.

2. BRIEF DESCRIPTION OF STRATIGRAPHY OF CAMBAY BASIN AND TEST WELL GGAG#699

The Cambay basin is a tertiary sedimentary basin located in the Gujarat state of western India and is a major commercial asset which is producing hydrocarbons in larger amount. The Cambay basin is a Category-I basin and covers an area of about 53,500 sq. km. It encompasses a narrow and elongated rift extending from Surat in the south to Sanchor in the north and lies in between the Latitudes 21° N and 25° N and Longitudes 71°15' E and 73°30' E. The Cambay basin has a geological history of deltaic sedimentation. On the basis of its basement depth, different faults and fault trend, this basin can be divided into four major blocks viz., (1) Narmada block – the area in the south of the Narmada river and a part of Aliabet island; (2) Jambusar-Broach block - the area between the Narmada river and the Mahisagar river; (3) Cambay-Tarapur block – the area between the Mahisagar river and the Sabarmati river and (4) Ahamedabad-Mehsana block – covers an area from the Sabarmati river up to a short distance north of Mehsana. The deccan trap of Late Cretaceous-Paleocene age forms the tectonic basement over which the sedimentation took place [10].

The hydrocarbon accumulation in Cambay basin ranges from Paleocene to Miocene age and the source rock intervals ranges from early Paleocene to Oligocene in age. The early to middle Cambay shales are the main source rocks in this basin [11]. The Gandhar oil field is one of the main onshore Cenozoic hydrocarbons bearing asset located in Northern-Western part of Cambay basin. The test well GGAG#699 is located in Gandhar oil field. Starting from the top, the well penetrates through the following rock formations viz., (1) Dadhar Formation in the Oligocene age; (2) Ankleshwar Formation in Middle to upper Eocene age. The Ankleshwar Formation is further subdivided in to four

sub lithological sequences namely Telwa, Ardol, Kanwa and Hazad; and (3) Cambay Formation in the Paleocene age. The stratigraphic details of well GGAG#699 are given in Table 1.

Table 1: Stratigraphic details of well GGAG#699.

Depth interval (meters)	Formation		Age
2030 – 2190	Dadhar Formation		Oligocene
2245 – 2630	Ankleshwar Formation	Telwa	Eocene
		Ardol	
		Kanwa	
		Hazad	
2725 – 2903	Cambay Formation		Paleocene

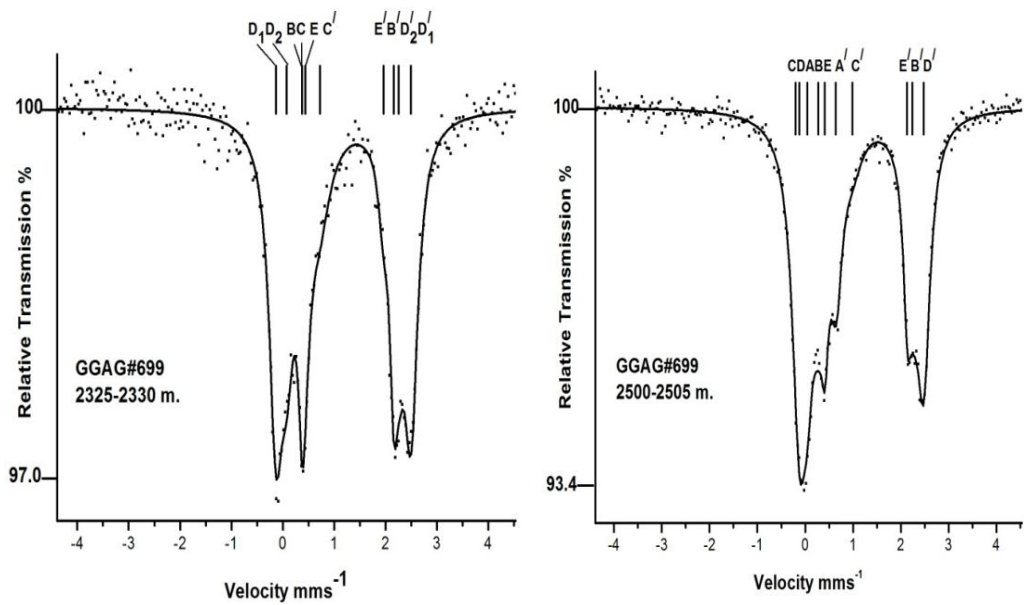
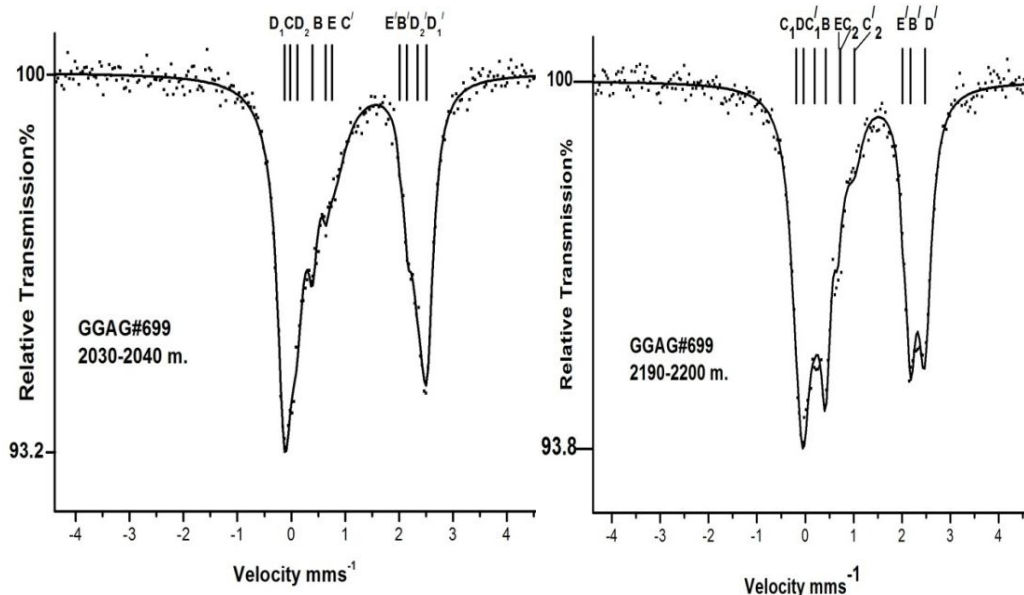
The Cambay Formation is further divided into older Cambay shale (OCS) and younger Cambay shale (YCS). The older Cambay shales are attributed to early marine sedimentation in this basin while the older Cambay shales are deposited in shallower sedimentation [12].

3. 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 (300K) 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 [13]. This programme assume 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.

4. RESULT AND DISCUSSION

The Mössbauer spectra of all the sedimentary samples were resolved into quadrupole doublets corresponding to iron in different mineral species. The doublets are marked as AA', BB', CC', DD' and EE'. Some typical Mössbauer spectra are displayed in Figure 1. The depth from which the sample is collected is displayed in the figure itself.



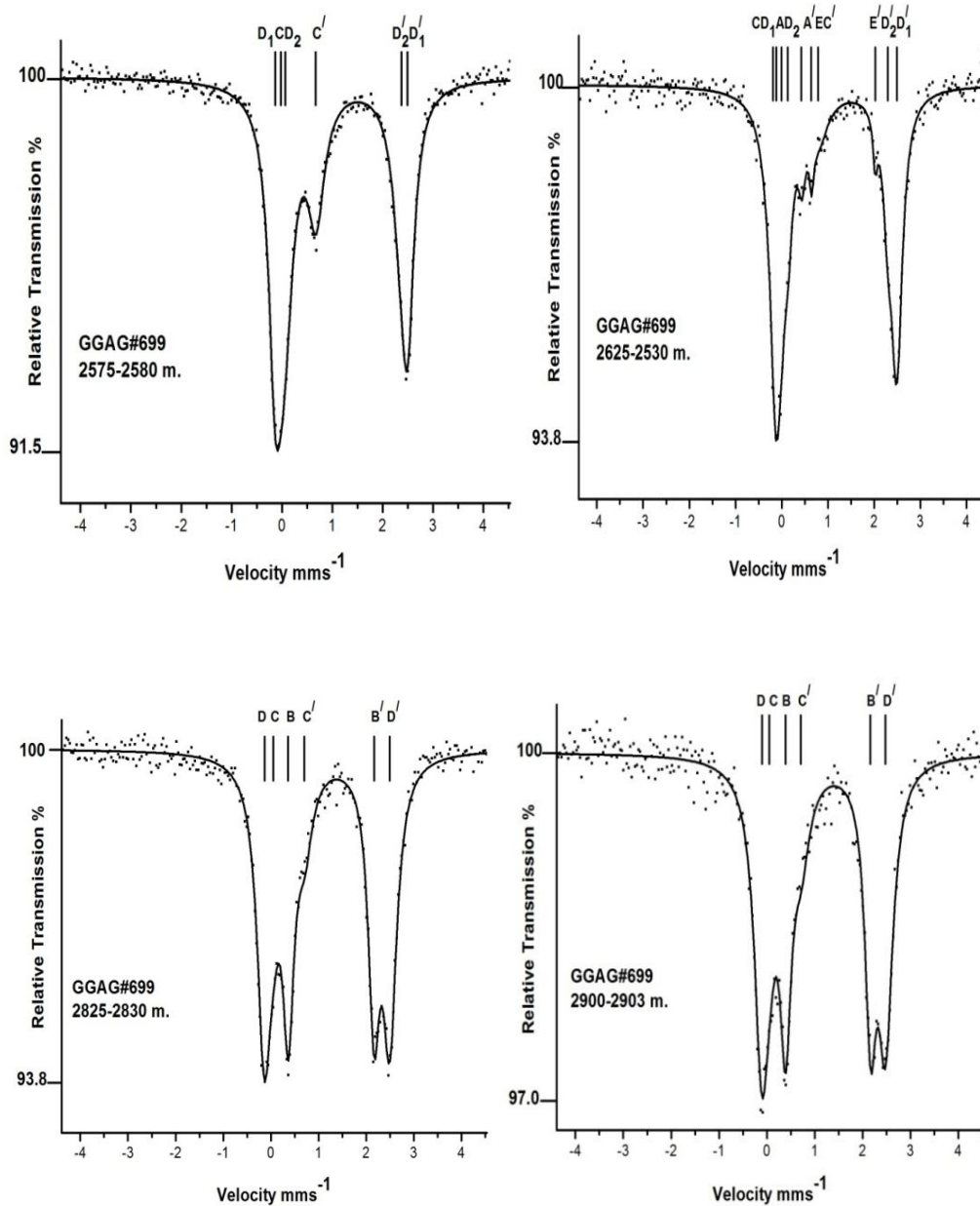


Fig. 1: Room temperature Mössbauer spectra of some sedimentary samples of well GGAG#699.

The ranges of Mössbauer parameters i.e. isomer shift (IS), quadrupole splitting (QS) values obtained for different mineral components marked as AA', BB', CC', DD' and EE' are given in Table 2.

Table 2: Ranges of Mössbauer parameters for minerals present in sedimentary samples of well GGAG#699 of Cambay basin, India.

Component	Temperature (K)	QS (mms ⁻¹)	IS (mms ⁻¹)	Assignment
AA'	300	0.52-0.67 [#]	0.26-0.36 ^{##}	Pyrite/little Fe ³⁺ (iron in 2:1 layer silicate)
BB'	300	1.65-1.92	1.21-1.28	Siderite
CC'	300	0.20-1.40 [*]	0.15-0.70 ^{**}	Fe ³⁺ in layer silicates (clay) In <i>cis</i> or <i>trans</i> or both
DD'	300	2.00-2.90	1.00-1.18	Fe ²⁺ in layer silicates (clay) In <i>cis</i> or <i>trans</i> or both
EE'	300	1.50-1.55	1.23-1.26	(Ca, Fe, Mg) carbonate

In most of the sedimentary samples it was centered around 0.60 mms⁻¹

In most of the sedimentary samples it was centered around 0.30 mms⁻¹

* In most of the sedimentary samples it was centered around 0.70 mms⁻¹

** In most of the sedimentary samples it was centered around 0.40 mms⁻¹

On the basis of studies reported earlier [4,5,6], on the spectra, the quadrupole doublet marked AA', BB', CC', DD' and EE' corresponds to iron in pyrite (FeS₂), siderite (FeCO₃), clay in high spin Fe³⁺ state, clay in high spin Fe²⁺ state and ankerite. The assignment of doublet BB' and DD' is unambiguous and is already discussed in earlier communication [4,5] while the assignment of doublet AA' and CC' need little discussion. In most of the samples, the IS value for doublet AA' is centered around 0.60 mms⁻¹ which is the value characteristic for both iron in pyrite and for iron in high spin Fe³⁺ clay minerals. Therefore, the assignment for the doublet AA' is not always unambiguous. But, on the basis of studies of preheated samples [14], the doublet AA' is attributed to the iron in pyrite. It is worth mentioning that the doublet AA' may contain an unresolved Fe³⁺ contribution therefore this doublet AA' has been regarded as the uppermost limit of pyrite in corresponding sample. The doublet marked CC' has exhibited QS and IS value characteristic of iron high spin Fe³⁺ state. In most of the samples, the QS and IS values for this doublet were centered around 1.10 mms⁻¹ and 0.40 mms⁻¹ respectively. In some samples this doublet has shown values of QS < 0.50 mms⁻¹ and value of IS < 0.30 mms⁻¹. This larger variation in QS and IS value for ferric is due to the Fe³⁺ in clay lattice which is not only substitute as an impurity but is also formed due to the conversion of Fe²⁺ in to

Fe^{3+} through hydroxylation and de hydroxylation processes. These factors cause large fluctuations both in chemical environment and symmetry around Fe^{3+} in clay structures. Therefore in present study, doublet CC' has been regarded as the lower most limit of Fe^{3+} in corresponding sample.

The relative amount of iron (%) in different minerals as a function of depth in well GGAG#699 is displayed in Table 3. The iron is found present mainly in pyrite, siderite, Fe^{2+} in clay, Fe^{3+} in clay and ankerite. The amount of various iron-bearing minerals is found to be fluctuating from sample to sample and also with depth.

Table 3: Relative amount of iron (%) in sedimentary samples of well GGAG#699.

Depths (m.)	Pyrite (RA)	Ankerite (RA)	Siderite (RA)	Fe^{2+} (RA)	Fe^{3+} (RA)	Formation
2030-40	0	1.31	10.14	58.28	30.25	Dadhar
2190-00	0	2.96	29.02	39.94	28.05	
2245-50	0	0	22.07	51.35	26.55	Telwa
2300-05	39.47	12.32	0	33.91	14.28	Ardol
2325-30	0	6.18	12.76	63.36	17.68	
2400-05	0	9.57	25.69	39.18	25.59	
2450-55	19.36	1.61	0	58.66	20.34	
2500-05	21.72	9.32	21.49	39.24	8.22	Kanwa
2525-30	0	0	51.77	26.54	21.68	
2545-50	18.50	1.89	20.37	45.44	32.29	Hazad
2566-68	18.32	2.81	15.12	51.82	11.90	
2575-80	0	0	0	68.73	31.25	
2600-05	16.74	5.00	0	64.28	13.95	
2625-30	7.90	3.92	0	72.70	15.45	Cambay Formation
2725-30	0	9.47	25.23	42.26	22.99	
2750-55	0	9.14	0	60.23	30.61	
2770-72	0	11.55	0	51.25	37.19	
2775-80	0	0	9.26	64.96	25.75	
2800-05	0	3.18	0	64.11	32.69	
2825-30	0	0	36.29	49.87	13.82	
2850-55	0	0	12.22	73.84	13.92	
2895-00	0	0	19.04	66.07	14.88	
2900-03	0	0	33.76	50.34	15.88	

The Dadhar formation (2030-2190 m) which comprises of a thin sedimentary sequence is encountered in Oligocene age. Two samples investigated in this formation contain dominantly iron in some clay (both in high spin Fe^{2+} and Fe^{3+} state) along with siderite. Mineral ankerite is also found present but in almost negligible amount. The larger presence of iron in clay minerals is attributed to the terrestrial source of iron.

The Ankleshwar Formation (2245-2630 m) is observed in Eocene age and is further subdivided into four lithological zones namely Telwa, Ardol, Kanwa and Hazad. Only one sample was available from depth 2245-50 m from Telwa zone has shown dominantly iron in some clay (both in high spin Fe^{2+} and Fe^{3+} state) along with siderite. The observations are identical with Dadhar formation. In Ardol zone ranging from depth 2300-2505 m five samples have been studied. Dominant present mineral is iron in clay along with pyrite, siderite and ankerite. Interestingly in some samples pyrite is present while siderite is absent and vice-versa. In one sample from lower depth both pyrite and siderite are present almost in equal amount and jointly contributes to about 41% of iron content in sample. This trend of pyrite/siderite distribution is also identical in Kanwa zone. Among the two sample studied from Kanwa zone, one contain only iron in clay and siderite while another contain iron in clay along with pyrite and siderite both in equal amount jointly contributing to about 39% of iron content in sample. Similarly in Hazad zone, one sample at depth 2566-68 m showed presence of both pyrite and siderite along with iron in clay while other samples are devoid of siderite but pyrite is present in meager amount along with larger amount of iron in clay. In one sample at depth 2575-80 m only mineral present is iron in clay.

The well terminates in the Cambay Formation (2725-2903 m) which is encountered in Paleocene age lying above the Deccan trap. Large number of samples has been studied from this formation shown adequate presence of iron in clay (both in high spin Fe^{2+} and Fe^{3+} state) along with siderite. Samples from depth 2725-30 m, 2750-55 m and 2770-72 m has shown presence of mineral ankerite but in small amount contributing about 10% of total iron content in samples is quite negligible. None of the sample in Cambay Formation has shown presence of mineral pyrite.

It is interesting to note that the relative presence of siderite and ankerite compete each other. Mineral ankerite showed its presence in several samples of late Paleocene age while siderite is almost absent. In samples from lower depths ankerite is absent in all samples while siderite is present in marginal amount. It is worthwhile to understand this iron mineralogy i.e. absence of pyrite and competitive presence/absence of siderite and ankerite. The following facts need consideration

- (i) Siderite in ancient rock suggests low sulphur water. Terrestrial sedimentary environment is most favorable for siderite precipitation as a consequence of microbiologically mediated iron reduction with consistence increased alkalinity in sediments.
- (ii) Environments are characterized by the presence or absence of oxygen and dissolved sulphides. The precipitation of siderite can take place where decomposition of organic matter has led to the depletion of oxygen in sediments but has not proceeded to the point of sulphate reduction.

- (iii) If the organic matter is present in larger amount and leads to available sulphate consumption without using up the organic matter, methane fermentation begins and siderite is formed as a consequence of little available sulphate.
- (iv) The presence of mineral ankerite can be attributed to the late diagenesis of carbonate minerals [2] which takes place at 100°C or above this temperature.
- (v) The sedimentary pyrite formation during the early diagenesis can be considered as a controlling process for the oxygen level of atmosphere and the sulphate concentration in sea water over deep burial.
- (vi) The organic matter in sediments is also a major controlling factor on pyrite formation in normal terrigenous marine sediments where dissolved sulphur and iron minerals are abundant.
- (vii) The Eh-pH relations among pyrite and siderite are also a controlling factor in formation of pyrite or siderite [15].

All samples studied in present investigation have shown presence of iron in clay minerals in adequate amount. Other iron bearing minerals like pyrite, siderite and ankerite are either absent or are found present in lesser amount. The absence of pyrite in Dadhar and Cambay Formation indicates poor reducing environment of deposition while in Ankleshwar Formation pyrite is present in several samples however its amount fluctuates from sample to sample indicating fluctuating redox conditions. Interestingly in some samples either pyrite or siderite is present and in some samples both pyrite and siderite are present jointly contribution to only about 40% of total iron in samples. The larger presence of iron in clay is due to the terrestrial source of iron [8] and simultaneous presence of pyrite and siderite only in tiny amount can be attributed to presence of larger amount of organic matter in sediments. If the organic matter is present in larger amount and leads to available sulphate consumption without using up the organic matter, methane fermentation begins and siderite is formed as a consequence of little available sulphate. Also in normal terrigenous marine sediments where dissolved sulphur and iron minerals are abundant the pyrite is formed.

This competing presence of siderite with pyrite and siderite with ankerite, indicates that the Ankleshwar Formation is deposited in fluctuating redox environment. The Late Eocene sediments are deposited in lesser reducing environment in comparison to early Eocene sediments i.e. Hazad sequence. Thus, the organic matter presence in Hazad sequence indicates better maturity in comparison to the organic matter in Telwa, Ardol and Kanwa zones. The source rocks deposited in Hazad zone can be considered to be adequately mature to generate oil/gas.

From top to bottom, the dominant present mineral is iron in some clay (both in high spin Fe²⁺ and Fe³⁺ state). From Table 3 it can be seen that all samples show dominant presence of clay in Fe²⁺ in comparison to clay in Fe³⁺ state however their individual amount fluctuates from sample to sample. This larger presence of iron in clay is attributed to terrestrial source of iron which is not favorable for generation of hydrocarbons. Furthermore, the larger presence of Fe²⁺ in clay and simultaneous absence of pyrite is also contradictory. It is possible that irrespective of environment of deposition the rate of sedimentation has influenced this larger abundance of iron in clay. As clay flakes have smaller size it is expected that they may travel longer distance in

water before being removed from the floating material. It is possible that clay flakes due to their smaller size gets deposited in deep water rather than in shallow water. This relatively larger presence of Fe^{2+} in clay flakes can also be correlated with the size of organic matter in sediments. If fine grained organic matter is deposited then this deposition is also controlled by the same kinematical factors which controls the deposition of clay flakes i.e. more presence of reactive organic matter will correspond to better reducing condition in the sediments and hence larger the Fe^{2+} in clay flakes. The rate of deposition is also a controlling factor for presence of iron in clay. The larger Fe^{3+} in clay is attributed to slower rate of deposition which does not allow complete anoxic conditions [8,15]. Hence the larger presence of Fe^{2+} in clay can be attributed to faster rate of deposition. It is well known that rate of deposition also controls the maturation in organic matter and the faster rate of deposition is not favorable for good maturity of organic matter. The presence of larger clay in Fe^{2+} state in this well can be regarded as a consequence of faster rate of deposition which is not suitable of the organic matter present in sediments to attain adequate maturity. The information obtained in present study can be useful if coupled with other available geological and geochemical parameters for hydrocarbon prospecting in this oil field.

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