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# Mineral, Elemental, and Hydrocarbon Potential Evaluation of a Carbonaceous Shale from a Lignite Opencast Mine in Amod Village, Bharuch, Gujarat, India

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**ABSTRACT**

A shale sample was evaluated for its elements, minerals and hydrocarbon potential. Elemental analysis by EDS (energy-dispersive x-ray spectroscopy), mineral analysis by XRD (x-ray diffraction), and hydrocarbon potential evaluation by Rock-eval pyrolysis was done. EDS showed Oxygen, Carbon, Silicon, Aluminum, Iron, and Titanium. XRD showed Kaolinite (Dickite), Thaumasite, Calcite, and Quartz as the minerals. Rock-eval showed TOC (total organic carbon) of 15% by weight. Evaluation suggests the shale to have a good hydrocarbon generation potential and Titanium.



## Introduction

The aim of this work was to characterize a carbonaceous (supposedly rich in carbon) shale sample and to evaluate its hydrocarbon potential. The shale sample was taken from the outcrop of Tadkeshwar formation found at a Lignite coal open cast mine in Bharuch, Gujarat. Since shales in the United States proved to have huge hydrocarbon production potential, a study on shales in organic rich Cambay Basin was done to evaluate their hydrocarbon potential.

Basic characterization included: 1) elemental analysis by EDS (energy-dispersive x-ray spectroscopy) and 2) mineral analysis by XRD (x-ray diffraction). The hydrocarbon potential evaluation was done by Rock-eval pyrolysis. The EDS measurements were done at IIT Roorke, XRD measurements at UPES, Dehradun, and Rock-eval measurements at ONGC Dehradun.

The EDS results showed Oxygen, Carbon, Silicon, Aluminum, Iron, and Titanium as the most abundant elements (note EDS cannot show Hydrogen). High amount of elemental Carbon indicated possibility of good amount of organic as well as mineral carbon. The high amount of Silicon indicated viable fracturing. The high amount of Titanium indicated possible Titanium extraction. The XRD results showed Kaolinite (Dickite), Thaumasite, Calcite, and Quartz as the major minerals. Around 100,000 mineral XRD peaks were compared against the sample peaks, by the auto feature of the XRD program while manual check was done to re-confirm. The XRD organics database is yet to be explored for identification of organic minerals. The TOC (total organic carbon) results indicated large amount of total organic carbon (15% by weight). The high TOC indicated potential for hydrocarbon oil generation and production with the help of in-situ pyrolysis since the shales seemed to be immature.

For the first time a comprehensive mineral, elemental and hydrocarbon potential evaluation is done for Tadkeshwar formation shales of the Cambay Basin. The evaluation suggests that the shale has a good potential for both hydrocarbon production and Titanium extraction.

## Background

Cambay Basin, located in the western part of Indian subcontinent (Fig. 1) is a proven sedimentary basin for production of hydrocarbons [3].

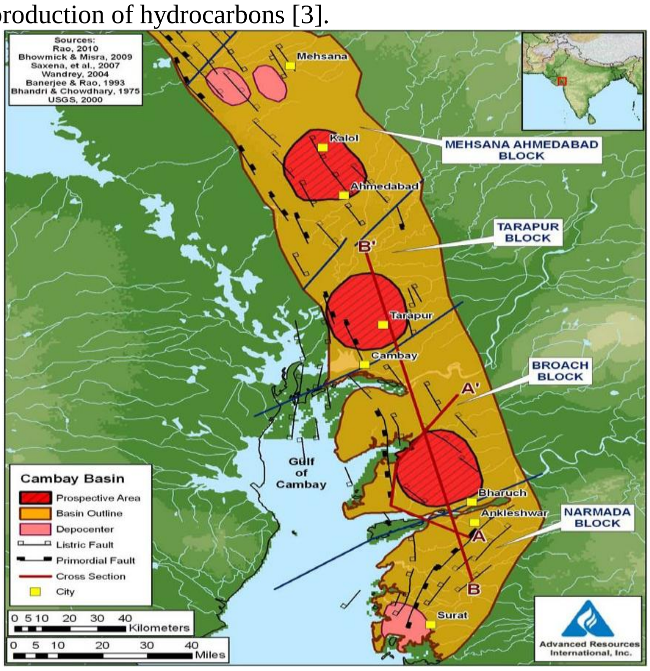


**Figure 1. Cambay basin with developmental blocks in the Sedimentary basins of Indian sub-continent.**

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It is also one of the four prospective basins for production of gas from shales [2]. Bounded by Saurashtra uplift in the west (in Gujarat) and Aravalli ranges in the east (in Rajasthan), it is an intracratonic N-S trending rift graben basin that is divided into five major blocks for development of fields for hydrocarbon production. The basin was mostly filled during the Cenozoic era (0-65 mya) with beginnings during the late Mesozoic era (~65-75 mya). Major tensional faults led to extensive outpour of underlying Deccan Basalts along with weathering of the Deccan basalt [9]. Marine transgression and regression phases [3] led to the varying basin formations made of carbonaceous shale, lignite, carbonates etc. Fig. 2 shows a schematic of the cross section of the graben Cambay basin while Table 1 lists details on the Cambay basin formations.

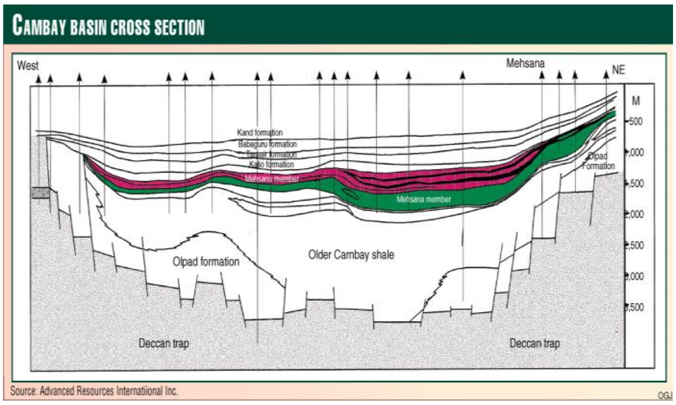


**Figure 2. Schematic of vertical cross-section of the Cambay basin showing various formations.**

The carbonaceous shale sample with hydrocarbon potential was specifically obtained from the Rajpardi lignite mines in Gujarat (Fig. 3). It was chiseled from the outcrop of the Tadkeshwar formation of Cambay basin found in these lignite mines near Bharuch in Jambusar-Broach block. Note this formation is also named as Tarkeshvar formation in the literature.

According to EIA [2], the Cambay shale formation (another bigger shale formation) of the Cambay basin (depth 6000-13,500 ft) has risked gas in place of 145.6 TCF with 29.5 TCF risked recoverable and 54.3 Billion bbl of risked oil in place with 2.71 Billion bbl's risked recoverable. However no estimate is provided for Tadkeshwar shale formations in this basin. We believe Tadkeshwar shale formation also holds significant gas and oil in place.


**Figure 3. Google Satellite Image [1] of the Amod Lignite Project from where the carbonaceous shale sample was chiseled out of the Tadkeshwar formation outcrop.**

Dayal's et al. [6] have also evaluated 5 shale samples from the same open cast mines of Rajpardi, Gujarat. They had also used Rock Eval pyrolysis and had found very high TOC (>10%) in the 5 shale samples. The formation from which the interbedded shale samples were taken were also mentioned as Tadkeshwar formation. Note Tadkeshwar shale formation is quite thick up to 346 meters (Table 1) with depths as high as 1200 meters (Table 1). They concluded these shales to have reached maturity with type II and III kerogen suitable for generation of gas. They recommended further studies on core samples that should be obtained from the sub-surface locations. This would help in delineating the vertical and lateral extent of these shales and their gas production potential. Our study verifies the fact that the Tadkeshwar shale has high TOC and compliments their TOC results. This study also recommends drilling horizontal wells and multi-staged fracturing for hydrocarbon production.

**Sample Analysis Techniques and Results**

Below are the details of the results of the EDS (for elements), XRD (for minerals) and rock eval pyrolysis (primarily for TOC) analysis for the shale sample.

**Energy-dispersive X-ray spectroscopy for Elemental Analysis**

Energy-dispersive X-ray spectroscopy (abbreviated as EDS, EDX, or XEDS), or energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA),

**Table 1. Cambay basin formations from Agarwal 1986, Sahni 2006 and ONGC Bulletin 1998.**

| Formation | Thickness, m | Lithology | Age, mya | Epoch/Period |
|---|---|---|---|---|
| Narmada, Gujarat alluvium and Jambusar | 50-100 | Sandstone silt, Yellow and grey clays, gravels, colored sand and kankar | 2.58 | Recent-Pleistocene |
| Jhagadia | 200-300 | Sandstone, marls, gritstone, limestone, conglomerate, breccia, clay, silt | 1.8-15 | Pliocene to Middle Miocene |
| kand | 200-450 | Fossil, limestone, calcareous sandstone, gravelly clay. Marls, shale with sandstone bands and agate conglomerate | 5.3-2.3 | Miocene |
| Babaguru | 150-300 | Agate conglomerate, ferrugious sandstone, clays | 16-23 | Early Miocene |
| Tadkeshwar | 125-346 | Grey shale, Carbonaceous shale, Lignite, Lenses of Sandstone | 16-38 | Early Miocene to Late Eocene |
| Ankleshwar, Numulitic, Tarapur, Tharad, Bhavnagar, Kalol | 100-600 | Numulitic limestone, shales with sandstone lenses | 30-49 | Late Oligocene to middle Eocene |
| Cambay Shale | 1500 | Grey, dark grey thinly bedded shales | 41-58 | Middle Eocene to late Paleocene |
| Vagadkhol | 50-120 | Conglomerate, grit, friable sandstone, siltstone, variegated clays, bentonic shale | 49-66 | Early Eocene to Paleocene |
| Deccan Trap | | Basalt with basic intrusives, trachyte | 65-85 | Cretaceous |

The procedure was that a high-energy beam of X-rays was focused onto the shale sample, which excited electrons in the inner shells of the various elements of the shale sample, ejecting them while creating electron holes where the electrons were. Electrons from the outer, higher-energy shells filled the holes, while releasing the difference in energy between the higher-energy shells and the lower energy shells in the form of X-rays. The number and energy of these characteristic X-rays emitted from the shale sample were measured by the energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS technique indicated the elemental composition of the shale sample.

Table 2 shows the elements indicated by the EDS analysis obtained from four samples of the main shale sample. Note hydrogen, which is likely to be present, was not indicated since EDS spectroscopy can not indicate lighter elements up-to Sodium. The EDS results indicated around 9 – 38 % Carbon by weight. The other major element was Oxygen (12 – 45 %),

Surprisingly, Titanium was found to be significant in two sample runs with wt % around 70-80 %. This was quite an interesting finding as if this is the case then the shale can be used for extracting Titanium. Pundaree et. al [9] also showed about 10% $TiO_2$ in the same Tadkeshwar shale outcrop from Rajpardi Mines. Titanium extraction is usually done from Illmenite iron ore ($FeTiO_3$) to get a high grade Titanium. A process known as Kroll process is usually applied to extract Titanium. The same process could be applied to this carbonaceous shale of the Tadkeshwar formation to extract Titanium. Though we believe that the Titanium in the shale is not Illmenite since it did not show a measurable magnetic effect on the magnetic needles upon its proximity. It could be that Titanium is present as $TiO_2$ and not as $FeTiO_3$ (Illmenite ore, most abundant Titanium holding mineral). It could be the other predominant Titanium mineral, Rutile ($TiO_2$), as indicated by Pundaree [9] oxide analysis. Note our XRD mineral analysis showed $SiO_2$, which has similar spectrum as $TiO_2$.

Upon plotting only samples 2 and 4 results with minimal Titanium we see the elemental wt % as Oxygen (~ 45%), Carbon (~25%), Silicon (~15%), Aluminium (~10%) Iron (~2%), Titanium (1.5%), Calcium (<1%), and Magnesium (<1%) as shown in Fig 5.

**XRD Mineral Analysis**

X-ray diffraction is a common technique for studying crystal structures, atomic spacing and mineral identification. We utilized this technique to identify minerals in our shale sample.

The sample was powdered and XRD apparatus was utilized at our campus for mineral identification.

To describe, in this technique, incident X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiations, collimated to concentrate, and are directed toward the sample.

The interaction of the incident x-rays with the sample produces constructive interference (diffraction) when conditions satisfied Bragg's Law.

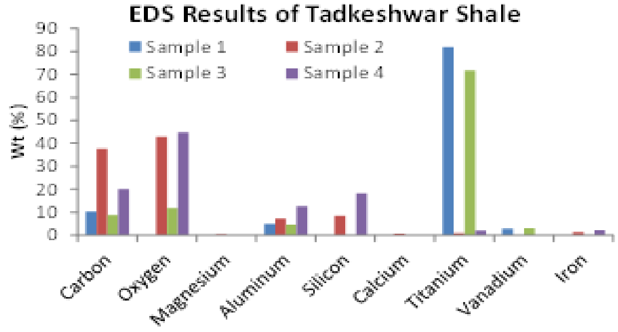


**Figure 4. Elemental weight (%) of all 4 samples analyzed by EDS technique.**

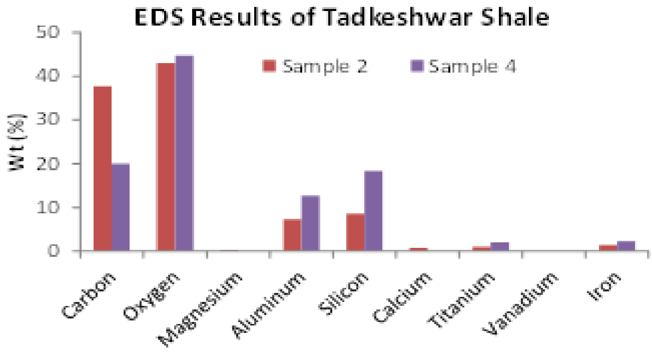


**Figure 5. Elemental weight (%) of 2 better representative samples analyzed by EDS technique.**

This law ($n\lambda=2d \sin \theta$), relates the wavelength, $\lambda$ of the x-ray, to the incident angle, $\theta$ with the normal to the crystal lattice plane and the lattice spacing, d in the crystalline sample). These diffracted X-rays are then detected, processed and counted. The sample is scanned through a range of incident angles. The diffraction peak angles (with large x-ray counts or intensity) are converted to d-spacings using Bragg's law. These d-spacings allowed identification of the mineral because each mineral has a set of unique d-spacings for its crystal lattices. Both manual and computer programs are used to identify the minerals from the reference minerals d-spacings database.

Fig. 6 shows the XRD diffraction peaks at various incident angles and the corresponding minerals identified. The d-spacings for the peaks of diffracted x-rays were calculated and compared with the d-spacings of the common minerals such as $SiO_2$ (Quartz), $CaCO_3$ (Calcite), and various clays such as Illite, Montomorillonite, Smectite, Chlorite, kaolinite that typically compose shales.

**Table 2. Shale sample elements from EDS analysis.**

| **Element** | | | **Weight (%)** | | | | **Atomic Weight (%)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Atomic No.** | **Atomic Wt.** | **Sample 1** | **Sample 2** | **Sample 3** | **Sample 4** | **Sample 1** | **Sample 2** | **Sample 3** | **Sample 4** |
| Carbon | 6 | 12.0107 | 10.32 | 37.67 | 8.82 | 19.99 | 30.61 | 48.44 | 22.93 | 29.39 |
| Oxygen | 8 | 15.9994 | | 42.93 | 11.88 | 44.7 | | 41.44 | 23.2 | 49.35 |
| Magnesium | 12 | 24.305 | | 0.34 | | | | 0.21 | | |
| Aluminum | 13 | 26.9815 | 4.89 | 7.31 | 4.53 | 12.63 | 6.45 | 4.19 | 5.24 | 8.26 |
| Silicon | 14 | 28.0855 | | 8.55 | | 18.31 | | 4.7 | | 11.51 |
| Calcium | 20 | 40.078 | | 0.75 | | | | 0.29 | | |
| Titanium | 22 | 47.567 | 81.83 | 1.03 | 71.71 | 2.07 | 60.87 | 0.33 | 46.75 | 0.76 |
| Vanadium | 23 | 50.9415 | 2.96 | | 3.06 | | 2.07 | | 1.88 | |
| Iron | 26 | 55.845 | | 1.42 | | 2.31 | | 0.39 | | 0.73 |
| Total | | | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

The matching of the peaks done by the program, indicated Dickite (Kaolinite, a silicate clay mineral, $Al_2Si_2O_5(OH)_4$), Thaumasite (a silicate mineral, $Ca_3Si(OH)_6(CO_3)(SO_4)\cdot 12H_2O$), Calcite ($CaCO_3$), and Quartz (framework of $SiO_4$ silicon–oxygen tetrahedral) as the predominant minerals in the shale sample. Around 100,000 minerals XRD peaks were checked by the XRD program. In the future, the XRD organics database is to be explored for any direct organic mineral identification.

Presence of quartz and calcite in the shale indicates fracking to be an option as these minerals fracture due to their brittle nature. Note fracking of the shale will lead to creation of larger surface area for higher oil and gas production.

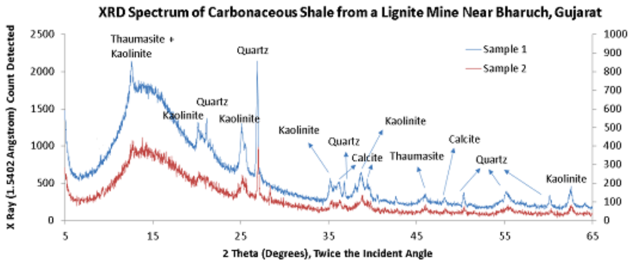


Figure 6: Minerals identified from XRD peak matching. Left axis for sample 1 and right axis for sample 2.

**Figure 6. Minerals in the shale sample identified by XRD analysis.**

**Rock-Eval Pyrolysis for Hydrocarbon Potential Evaluation**

Rock-eval pyrolysis was done to check the total organic carbon in the shale sample. Note pyrolysis is the decomposition of organic matter due to heating in the absence of oxygen. This process is routinely utilized to measure TOC and maturity of potential source rocks. The sample is heated in the absence of oxygen, then combusted and the amount of hydrocarbons and carbon dioxide released is measured. The most widely used pyrolysis technique is Rock-Eval.

The rock-eval pyrolysis was done at ONGC Dehradun. The sample was placed in a vessel and was progressively heated to 550°C under an inert atmosphere. Table 3 shows the rock eval pyrolysis results for the shale sample with some

The hydrocarbons present in the sample were volatized at a moderate temperature.

The amount of hydrocarbons released were measured and recorded with the peak value known as S1. Next kerogen present in the sample is pyrolyzed, generating more hydrocarbons, and hydrocarbon-like compounds with peak recorded as the S2 peak.

The $CO_2$ generated is also recorded with the peak value as S3 while the maximum residual carbon measured is recorded as S4.

We see reasonable amount of S1 and S2 values suggesting good hydrocarbon potential. The Petroleum Potential was calculated to be equal to 72.26 mg of HC / g of shale, 7.2% by wt). The S1 value of 1.81 mg of HC / g of rock indicates already existing free hydrocarbon oil present in the shale. If we use this value and calculate existing oil in place it comes around 29,000 bbl / acre / ft assuming bulk density of shale = 2.5 g/cc and 50 $^{o}$API oil.

The S2 value which is the pyrolyzable kerogen is equal to 70.45 mg of HC / g of rock which indicates good hydrocarbon generating potential. The temperature at which the maximum kerogen was pyrolyzed (peak S2 value) was 430 $^{o}$C (also known as $T_{max}$) indicates the shale to be immature to close to early mature source rock.

The total organic carbon was found to be around 15 % calculated by the S1, S2 and S3 values and also given by Rockeval. This value is significantly more than the minimum threshold (0.5-1%) value generally used for shale gas exploitation.

The hydrogen index (HI) of 467 indicated excellent hydrocarbon generating potential. The HI and $T_{max}$ suggested oil-generating potential while HI and OI (plotted on Van Krevlen diagram and shown in Figure 7) suggests the kerogen to be type II with likely algal bacterial marine origin.

The average depth of Tadkeshwar formation (around 1000-1200 m) falls in the depth range of Fayetteville shale gas reservoir (1500 – 6500 ft) that have been developed and have produced high amount of shale gas (2.5 MMscf/day per well).

Vitrinite reflectance, $R_o$ was calculated from $T_{max}$, [12], with relation as followed. $R_o = (0.0180\ T_{max} - 7.16)$. The $R_o$

**Table 3. Results and analysis from Rock-Eval pyrolysis for hydrocarbon potential.**

| | | **Rock Eval Results** | **Calculated from equations** | | **Equations** |
|---|---|---|---|---|---|
| Gaseous to condensate range hydrocarbons thermally liberated | So | | | mg HC/g rock | |
| Free hydrocarbons (comparable to extractable hydrocarbons) | S1 | 1.81 | | mg HC/g rock | |
| Hydrocarbons released during the pyrolysis of kerogen | S2 | 70.45 | | mg HC/g rock | |
| Temp at which the maximum rate of yield of S2 hydrocarbons is obtained | Tmax | 430 | | deg C | |
| Organic carbon dioxide released | S3 | 6.17 | | mg HC/g rock | |
| Residual carbon | S4 | 87.3 | | mg HC/g rock | |
| Pyrolyzable Carbon | PC | 6.37 | 5.93 | wt % | 0.082*(So+S1+S2) |
| Residual Carbon | RC | 8.73 | 8.73 | wt % | S4/10 |
| The total organic carbon in weight percent | TOC | 15.1 | 14.7 | wt % | 0.082*(So+S1+S2)+S4/10 |
| Hydrogen Index | HI | 467 | 481 | | S2/TOC*100 |
| Oxygen Index | OI | 41 | 42 | | S3/TOC*100 |
| Gas Production Index | GPI | | 0 | | So/(So+S1+S2) |
| Oil Production Index | OPI | | 0.03 | | S1/(So+S1+S2) |
| Total Production Index | TPI | | 0.03 | | (So+S1)/(So+S1+S2) |
| Production Index | PI | 0.03 | 0.03 | | S1/(S1+S2) |
| Quality Index | QI | | 11.42 | | S2/S3 |
| Petroleum Potential | PP | | 72.26 | mg HC/g rock | S1+S2 |
| Migration Index | MI | | 0.12 | | S1/TOC |

value upon calculation is 0.58, which again suggests the shale to be oil prone shale.

Other studies such as microfossil study was also done at the Wadia Institute, Dehradun. However apparently no microfossils in the shale sample were identified. Thin sections also could not be obtained successfully due to soft nature of the carbonaceous shale sample.

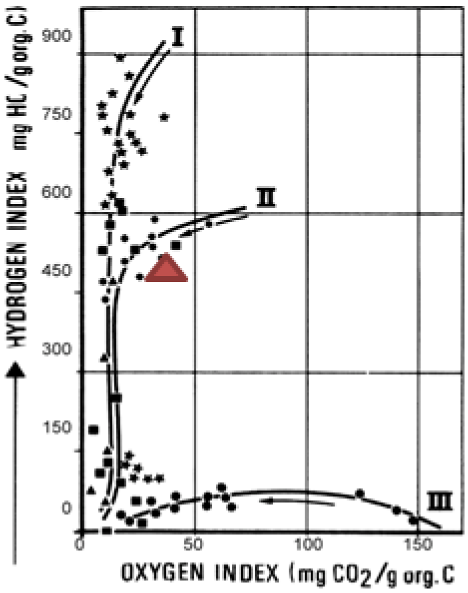


**Figure 7. HI and OI of the shale sample on the modified Van Krevlen diagram.**

**Conclusions**

1. EDS indicated Oxygen, Carbon, Silicon, Aluminum, Iron, and Titanium as the most abundant elements in the carbonaceous shale of Tadkeshwar formation (note EDS cannot show Hydrogen).
2. XRD analysis indicated Dickite (Kaolinite, a silicate clay mineral, $Al_2Si_2O_5(OH)_4$), Thaumasite (a silicate mineral, $Ca_3Si(OH)_6(CO_3)(SO_4)\cdot 12H_2O$), Calcite ($CaCO_3$), and Quartz (framework of $SiO_4$ silicon–oxygen tetrahedral) as the predominant minerals in the Tadkeshwar formation shales.
3. Significant amount of carbon (organic and mineral) as high as 15 % by wt. is found in the shale sample as indicated by the TOC analysis from Rock-eval and elemental analysis from EDS.
4. Some amount of silica and carbonate is found which suggests viable fracturing, needed for brittle hydraulic fracturing.
5. Total organic carbon was found to be 15% by wt. with pyrolyzable organic carbon around 7 % from rock eval pyrolysis. This suggests the shale to have an extremely good hydrocarbon generating potential. The shale however seems to be immature to close to maturity as indicated by $T_{max}$ of 430 deg F. In-situ pyrolysis along with horizontal wells and hydraulic fracturing should definitely result in shale oil and gas production from these shales of Tadkeshwar formation.
6. More exploratory wells should be drilled along with Geo-chemical logging to be done in wells already drilled through Tadkeshwar formation carbonaceous shales to investigate further on the subsurface TOC and maturity of these Tadkeshwar formation shales.

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