Reflectance spectroscopic and geochemical characteristics of hydrocarbon microseepage-induced sediments from Assam–Arakan Fold Belt, India: Implications to hydrocarbon exploration

SANTOSH GARAIN¹, DEBASHIS MITRA² and PRANAB DAS³,*

ⁱOil and Natural Gas Corporation Limited, Dehradun, India.
²Indian Institute of Remote Sensing, 4, Kalidas Road, Dehradun, India.
³Department of Applied Geology, Indian Institute of Technology (Indian School of Mines), Dhanbad, India.
*Corresponding author. e-mail: pranab@iitism.ac.in

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Characterizations of hydrocarbon microseepage-induced surface sediments are essential to utilize remote sensing and geochemistry as effective petroleum exploration tools. However, only few researchers have attempted spectroscopic and geochemical characterizations of microseepage-affected sediments and that too are focussed on arid or semi-arid climatic regions. This article aims to delineate the spectral, mineralogical and geochemical characteristics of the microseepage-affected sediments in Assam–Arakan Fold Belt (AAF), NE India, dominated by intense precipitation. The analytical approach followed consists of diffuse reflectance spectroscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analyses. Reflectance spectroscopy reveals that microseepage-induced sediments are enriched in illitic clay and deficient in goethite than the unaffected regions. XRD studies support the presence of illitic clays in the sediments. Major element analyses indicate higher Al₂O₃ and K₂O and lower Na₂O and SiO₂ in the altered sediments. Trace element patterns point out enrichment of V, Cu, Zn, Ga, Zr, and Mo and depletion of Li, Cr, Co, Ni, Rb, Sr, Sc, and Y in the microseepage-affected sediments. Normalized rare earth element (REE) patterns are similar for both the altered and unaltered sediments, but the former are deficient in REE contents. Though based on limited sample analysis, the study indicates microseepage affected and unaffected sediments differ in spectral and geochemical characters. This may help in strengthening the microseepage model for hydrocarbons in high precipitation areas and thereby may help in reducing exploration risks in the basin.

Keywords. Hydrocarbon; microseepage; geochemical; alterations; sediments; reflectance spectroscopy; XRD; XRF; trace elements.

1. Introduction

Hydrocarbon reservoirs are not always perfectly sealed. Trace amounts of hydrocarbons move vertically or near vertically from subsurface reservoirs to the surface through the interconnected micro-pores or fractures slowly in the form of hydrocarbon microseepages which are invisible but pervasive in nature (Price 1986; Tedesco 1995; Schumacher 1999; Etiope 2015). Potential exploration tools could be developed on the basis of microseepage concept because microseepages are
the conclusive evidence of presence of reservoirs underneath, though the depth and commerciality of the reservoirs cannot be ascertained. Despite being invisible and slow process, long-term microseeping of hydrocarbons manifests the surface soil and sediment covers in several ways (Schumacher 1996). The migrating hydrocarbons are consumed by bacteria and other microbes present in the near-surface environment to produce carbon-dioxide, hydrogen sulphide and other organic acids, which changes the E_h–pH condition and create an acidic and reducing milieu (Schumacher 1996; Saunders et al. 1999; Warren 2012; Asadzadeh and de Souza Filho 2017). The new environment induces a series of mineralogical, geochemical, geobotanical and electrochemical manifestations in the surface soils and sediments (Schumacher 1996). Among the various diagenetic mineralogical and geochemical changes, the following are more commonly found in microseepage environments:

**Bleaching of ferric iron minerals:** The transformation of ferric to ferrous in response to the reducing environment is associated with changes in the colour of sediments (Donovan 1974; Segal et al. 1984, 1986; Schumacher 1996).

**Precipitation of clay minerals:** Among the clay minerals, kaolinite, montmorillonite, illite, vermiculite, and chlorite are more commonly found in microseepage environments (Asadzadeh and de Souza Filho 2020a).

**Formation of carbonate minerals:** Calcite and dolomite are, by far, the most common carbonate minerals found in microseepage environments. However, the formation of these minerals depends upon the availability of calcium and magnesium in the host rocks/sediments.

**Trace element anomalies:** Duchscherer (1984) reported anomalous concentrations of trace metals like V, Cr, Ni, Co, Cu, Mn, U, Zn, Pb, Mo over oil fields, forming geochemical halos.

Remote sensing and geochemistry are two cost-effective unconventional tools in microseepage mapping. However, studies on the use of these tools are only scanty and are limited to arid or semi-arid climatic regions of certain geographical areas such as the United States and China (Asadzadeh and de Souza Filho 2017) and are, therefore, underutilized. The effective application of remote sensing and geochemistry in microseepage exploration requires a thorough understanding of the spectral, mineralogical and geochemical characteristics of the microseepage-affected sediments. However, the spectral and geochemical characterizations of microseepage induced sediments have been attempted by few researchers only and detailed characterizations of microseepage-affected sediments are therefore lacking. Asadzadeh and de Souza Filho (2020a, b) described geochemical and spectral characteristics of microseepage-induced sediments in Upper Red Formation, Qom region, Iran.

The present study is intended to fill up the literature gap and attempts to describe the spectral, mineralogical and geochemical characteristics of the microseepage induced sediments around Cachar area of Assam–Arakan Fold Belt (AAFB), NE India and is distinct in two following ways:

- It takes an integrated approach consisting of diffuse reflectance spectroscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) to characterize the hydrocarbon-affected sediments.
- It is carried out in a basin located in humid temperate climate characterised by heavy precipitation.

## 2. Study area

### 2.1 Geological setting

The study area is located in the Assam–Arakan Fold Belt (AAFB) in northeast of India, covering Cachar district of Assam. Geographically, the study area is bounded by the latitude 24°31’N/24°57’N and longitude 92°37’E/93°07’E with an area of about 2400 km² (figure 1a). A false colour composite (FCC) image formed by the bands 5-4-3 of the Landsat 8 image in the RGB space depicting the distribution of land use and vegetation is presented in figure 1(b). The climate of the area is tropical humid with the dominance of rainfall and short dry winter season. The average annual rainfall is very high (about 3100 mm/year). The mean temperature during winter ranges between 12–20°C and 16–30°C for the rest of the year. A major part of the study area is covered by dense tropical evergreen forests. Physiographically, the study region is characterized by plain lands formed by the alluviums of river Barak and its tributaries, with occasional small hillocks surrounded by hilly terrains to the north, east, and south.

Assam–Arakan Fold Belt (AAFB) is located at the front of the Indo-Burma Ranges. The basin is
bounded to the north by E–W trending Dauki Fault, to the east by N–S trending Kaladan Fault and towards west by the undeformed foreland of Bengal Basin. The basin is thought to be evolved as a result of eastward subduction of Indian Plate under the Burmese Plate (Angelier and Baruah 2009). Being located in the collisional zone, the basin has been subjected to intense tectonic disturbances and is dominated by a number of structural elements like folds, faults, and thrusts.

Figure 1. (a) Location map of the study area. (b) False colour composite (FCC) map of the study area formed by Landsat 8 bands 5-4-3 in RGB space.
study area, long narrow north–south trending anticlines with their intervening broad synclines are conspicuous (Ganguly 1983, 1993). The anticlines are dissected by several cross faults limiting the folded structures (Khar and Ganju 1984). The surface geological map of the study area is presented in figure 2.

The basin is comprised of thick clastic sediments deposited under marine to continental environments ranging in age from Paleocene to Recent. The generalized stratigraphic succession of the basin is shown in table 1. The sedimentary sequence appears to thicken towards the south and east (Chakravorty et al. 2011). Several exploratory wells for hydrocarbons have been drilled in the basin, but the complete stratigraphic succession has not been penetrated. Jenam Formation of Barail group is the oldest stratigraphic unit encountered in exploratory wells (Chatterjee et al. 2006). Surma and Tipam Group of sediments belonging to the Mio-Pliocene age are extensively exposed to the anticlinal structures in the basin (Ganguly 1993). A large part of the basin is covered under the alluvium.

2.2 Petroleum system

Petroleum exploration in AAFB dates back to the beginning of the twentieth century. Presently, it is classified as Category-I (proven commercially productive) basin in the hydrocarbon map of India (Biswas 2012). Presence of several commercial oil and gas fields authenticates the existence of adequate petroleum system in the basin. Multiple petroleum systems have been envisaged for the AAFB, out of which the Jenam–Bhuban–Bokabil is the most significant. A brief account of the petroleum system of the basin established from various exploration activities is described as follows:

![Figure 2. Surface geological map of the study area (adapted from Mazumder et al. 2016; Kamaraju 2010).](image-url)
2.2.1 Source

Sain et al. (1995) showed that Renji, Bhuban, Baokabili, and Tipam could not be considered as potential source rocks for petroleum due to their low TOC contents (average TOC < 0.5%). Outcrop sample analysis from Jenam Formation by Natarajan et al. (2003) indicates that it could be the effective source rock with TOC: 0.81–4.85%, S2: 1.09–1.84 mgHC/g rock, T_max: 445–4480°C and VRo: 0.767–0.847%. Petroleum system modelling by Chandrasekaran (2009) pointed out that Plio-Pleistocene sediments cannot be effective source rocks for the hydrocarbons in the basin.

2.2.2 Reservoir

There is no dearth of reservoir facies in Assam–Arakan Fold Belt. Sand intervals of Bhuban and Bokabil Formations are considered as good reservoirs (Biswa 2012). However, the reservoirs in the basin are thin and not laterally extensive.

2.2.3 Cap rocks

The impervious shales or claystones in Bhuban and Bokabil Formations constitute effective cap rocks for the petroleum reservoirs.

2.2.4 Traps

Pervasive anticlinal structures formed in response to the collision between India and Burma plates make appropriate traps for hydrocarbon accumulation in the basin. The time of formation of the structures also matches the timing of generation

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Table 1. Generalized stratigraphic succession of AAFB basin (after Chandrasekaran et al. 2006 and GSI 2009).

<table>
<thead>
<tr>
<th>Age</th>
<th>Group</th>
<th>Formation</th>
<th>Lithology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recent</td>
<td>Alluvium</td>
<td>Sand, silt, clay, pebble or boulder deposit</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dihing</td>
<td>Pebble beds, clay, sandstone and conglomerate</td>
<td></td>
</tr>
<tr>
<td>Pleistocene</td>
<td>Dupitila</td>
<td>Conglomerate, sandstone, mottled clay, coal beds and pebbles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gobindpur</td>
<td>Mottled clays with subordinate sandstone.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tipam Sandstone</td>
<td>Coarse to gritty ferruginous sandstone with minor clay/ shale</td>
<td></td>
</tr>
<tr>
<td>Pliocene</td>
<td>Tipam</td>
<td>Dominantly shale/claystone with minor siltstone and sandstone.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tipam Group</td>
<td>Predominantly arenaceous unit with minor shale.</td>
<td></td>
</tr>
<tr>
<td>Miocene</td>
<td>Surma</td>
<td>Dominantly argillaceous unit with occasional sandstone beds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Upper Bhuban</td>
<td>Dominantly sandstone with minor siltstone and shale.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Middle Bhuban</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lower Bhuban</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oligocene</td>
<td>Renji</td>
<td>Thick bedded sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jenam</td>
<td>Shale or carbonaceous shale with subordinate sandstone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Laisong</td>
<td>Sandstone with minor shale</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Un-differentiated</td>
<td>Dark grey shale with thin sandstone</td>
<td></td>
</tr>
<tr>
<td>Cretaceous to Eocene</td>
<td>Disang Group</td>
<td>Basement not exposed</td>
<td></td>
</tr>
</tbody>
</table>

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and expulsion of hydrocarbons from the source rocks.

3. Materials and analytical methods

3.1 Fieldwork and sampling

Sampling was carried out from both microseepage-affected and -unaffected sites. Microseepage-bearing areas were detected by the spectral enhancements of Landsat-7 enhanced thematic mapper plus (ETM+) images and their subsequent validation by surface soil gas geochemical studies in our previous studies (Garain et al. 2019). Due to heavy rainfall almost throughout the year, fieldwork was conducted during the short dry winter season. Samples were collected from shallow depths (1–2 m) by manual digging. Due care was taken to avoid contamination and root zones of plants. A total of 57 soil/sediment samples (21 from microseepage-bearing areas and 36 from non-microseepage areas) were collected. The samples were packed and kept in air-tight polythene bags to avoid any degradation until their preparation for laboratory analyses. The soil/sediment samples were mostly sandy to clayey in nature with yellowish tints (figure 3).

3.2 Reflectance spectroscopy

Reflectance spectroscopy in the wavelength region of ultra-violet-visible-near infrared and short-wave infrared (UV-VNIR-SWIR) in the interval 250–2500 nm is a non-destructive and effective technique to identify and quantify constituent minerals in rocks and soils (Clark and Roush 1984). Viscarra Rossel et al. (2009) measured colour and mineral composition of Australian soils by in-situ measurement of VNIR spectroscopy. Camargo et al. (2015) utilized reflectance spectroscopy to measure the contents of clay, iron oxide and phosphate in soils from Brazil. Prado et al. (2016) used reflectance spectroradiometry to characterize and evaluate mineral distribution in the iron deposit of Brazil. Bishop (2019) provided detailed spectral characteristics in the VNIR wavelength for a variety of minerals to enable their detection in earth and planetary bodies. Justin George et al. (2020) used VNIR spectroscopy to determine soil organic carbon employing artificial neural network.

Nineteen samples from microseepage-affected areas and seven samples from microseepage unaffected areas were analyzed for reflectance spectroscopy. The field-collected samples were air-dried, pulverized to fine level in an agate mortar and pestle, and then sieved appropriately to
separate any organic matter. The samples were analyzed in a spectrophotometer of Agilent Cary 5000 having a Tungsten-halogen and deuterium light source. The diffuse reflectance values were measured at 1 nm interval of wavelength. The minerals were identified by their characteristic absorption features. The quantitative amounts of the constituent minerals were attempted by the analysis of the continuum-removed (CR) reflectance spectra of the samples. The spectra of the standard minerals for identification were taken from the USGS spectral library.

3.3 X-ray diffraction (XRD) study

XRD analysis was carried out to identify the constituent minerals in a qualitative manner. Nineteen samples from microseepage-affected areas and eight samples from microseepage-unaffected areas were analyzed by XRD. The specimens were mounted in random orientation to identify all the constituent minerals and their crystal planes. The samples were analyzed in an XPERT-PRO X-ray diffractometer system using a Cu Kα X-ray (\(\lambda = 0.15406 \text{ nm}\)) over the 2θ range from 4.5 to 101 degrees in the steps of 0.0170 (2θ) degrees in continuous scanning mode at room temperature. The XRD spectra were processed and analyzed in X’Pert High Score Plus software. The identification of minerals was carried out manually by matching with the published ICDD cards. Considering the challenges involved in the quantitative analysis of XRD data, only qualitative analysis was attempted.

3.4 X-ray fluorescence (XRF) study

XRF analysis was carried out to quantify the major element oxide concentrations in the samples. The abundance of 11 major oxides – SiO\(_2\), Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\)(Total), MgO, CaO, MnO, TiO\(_2\), Na\(_2\)O, K\(_2\)O, P\(_2\)O\(_5\) and LOI (loss on ignition) were determined. Thirteen soil samples from microseepage areas and ten samples outside the microseepage areas were analyzed for major element oxides by XRF. The powered samples were mixed with the binding agents (cellulose) and then palletized with a hydraulic press in stainless steel set by applying the optimum amount of pressure. Due care was taken in the sample preparation process to avoid any sample-to-sample cross-contamination. The pallets were physically checked thoroughly for any cracks or voids before inserting them into the XRF spectrometer.

The following geochemical indices were determined to get a better understanding of the degree of alterations and weathering of the sediments:

1. Chemical index of alteration (CIA): It is the most commonly used index to quantify the degree of chemical weathering of sediments and is expressed as (Nesbitt and Young 1982):

   \[
   \text{CIA} = \left( \frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}} \right) \times 100.
   \]

   High CIA values indicate washing out of the more mobile elements like Ca, Na, and K with respect to relatively immobile Al and thus represent high chemical weathering. The greatest CIA values (close to 100) correspond to kaolinite weathering; values between 75 and 90 represent illite, and for feldspars, it is 50 (Nesbitt and Young 1982; Fedo et al. 1995; Nadłonek and Bojakowska 2018).

2. The silicification index (SI) (after Pirajno 2009) is a measure of silica content and is defined as:

   \[
   \text{SI} = \left( \frac{\text{SiO}_2}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \right) \times 100.
   \]

3. Alteration index (AI) is a measure of the degree of the alteration as suggested by Ishikawa et al. (1976) and is determined by

   \[
   \text{AI} = \left( \frac{\text{K}_2\text{O} + \text{MgO}}{\text{K}_2\text{O} + \text{MgO} + \text{Na}_2\text{O} + \text{CaO}} \right) \times 100.
   \]

4. A new geochemical index to quantify the hydrocarbon microseepage-related alterations termed as Microseepage-Induced Alteration Index (MIAI) has been introduced by Asadzadeh and de Souza Filho (2020a). The MIAI is defined as under:

   \[
   \text{MIAI} = \left( \frac{\text{CaO} + \text{K}_2\text{O}}{\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO}} \right) \times 100.
   \]

MIAI calculates the abundance of characteristics gained elements with respect to the sum of characteristics lost and gained elements in a microseepage environment (Asadzadeh and de
Souza Filho 2020a). A higher MIAI value is indicative of microseepage influence.

3.5 Inductively coupled plasma emission-mass spectrometry (ICP-MS) study

The trace elemental analyses of the sediment samples were carried out by ICP-MS method in an Agilent ICP-MS 7900 instrument with standards WGB-1 (Canada), AGV-2 (USGS), SBC-1 (England) and BCR-2 (USGS). Eight soil samples from microseepage-unaffected and four samples from microseepage-affected areas were analyzed for trace elements by ICP-MS. The specimens were prepared by dissolving finely pulverized sediments in a mixture of HNO₃ and HF in a closed vessel. The concentrations of Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Se, Rb, Sr, Pb, Bi, Cd, Cs, Zr, Nb, Mo, Ge, Ta, Sc, Y, and the REEs were determined by the ICP-MS analyses.

4. Results

4.1 Reflectance spectroscopic study

Three groups of minerals comprising ferric irons, clays and carbonates, frequently reported to be found in the hydrocarbon microseepage environments, were attempted to identify by reflectance spectroscopy. The most common ferric iron minerals in sediments are hematite and goethite. Hematite shows three distinct absorption bands at 520, 650, and 880 nm (Clark 1999; Viscarra Rossel and Behrens 2010), while goethite exhibits weaker absorptions at 420, 480, 600, and 1700 nm and a strong absorption near 920 nm (Zheng et al. 2016). Clay minerals exhibit diagnostic absorption features near 1400 nm (caused by OH overtones), 1900 nm (overtones caused by water molecules), 2200 nm (due to Al-OH combination tones) and some weaker absorptions in the 2300–2500 nm range due to the presence of Fe- or Mg–OH (Clark 1999; Fang et al. 2018; Zhao et al. 2018). Carbonate minerals show characteristic spectral absorptions near 2350 and 2500 nm (Hunt and Salisbury 1971).

The spectra of the sediments from both the hydrocarbon microseepage affected as well as unaffected areas show diagnostic absorptions near 480, 920, 1400, 1900, 2200, 2340, and 2440 nm (figure 4). The absorptions near 480 and 920 nm are characteristics of ferric iron minerals (goethite). It is observed that the sample spectra show a similar absorption feature of fine-grained goethite coating (ID: MPCMA2-B of USGS Spectral Library) in the wavelength range 800–1000 nm (figure 4). The shallow and asymmetric shape of the absorption feature centred at 900 nm indicates that the goethites are fine-grained and non-crystalline in nature and mostly occur as grain coatings (Fang et al. 2018).

The characteristics absorption features at 1400, 1900, and 2200 nm wavelength indicate the presence of clay minerals. The presence of kaolinite is ruled out by the absence of its characteristic spectral doublets near 2160 and 2210 nm (Fang et al. 2018) in the samples. Also, the absorption features characteristics of montmorillonite, vermiculite, and chlorite do not match with any of the spectra of the samples implying their absence in the samples. The characteristic prominent absorptions at 1400, 1900, 2205 nm, and the two weaker absorptions near 2340 nm and 2440 nm indicate that the clay mineral is illite. The reflectance spectrum of illite with sample ID: IL 101 of USGS Spectral Library perfectly matches with the clay absorption features of the samples (figure 4). Also, the spectra of the sediments do not show any characteristic absorption feature of carbonate minerals.

The abundance of the constituent minerals was attempted by analyzing the continuum removed (CR) spectral curves of the samples. The band depth (BD) at the diagnostic absorption wavelength of a mineral was calculated by subtracting the continuum removed reflectance value from 1 (Viscarra Rossel et al. 2009) and was used as a measure of the mineral abundance. Characteristics absorption for goethite and illite were taken at 941 and 2205 nm, respectively (figure 5). As seen in figure 5, the continuum removed spectrum of fine-grained goethite standard (MPCMA2-B) of the USGS spectral library also exhibits absorption at the 2205 nm band wavelength. Thus, it is evident that the presence of goethite also influences the band depth at 2205 nm for illite. Assuming a linear mixing model in the whole rock, the actual band depth of illite at 2205 nm was calculated by subtracting the band depth contribution of goethite from the gross band depth at 2205 nm. The CR band depth calculation shows that the average band depth of goethite at 941 nm is lower (0.0227) in the hydrocarbon microseepage bearing sediments than that of the non-microseepage sediments (0.0280). It is also observed that the average CR band depth of illite at 2205 nm is higher (0.03128).
for sediments from microseepage bearing areas compared to the microseepage-affected sediments (0.0265). Very shallow CR band depth at 2350 nm indicates low concentration of carbonates in the sediments.

4.2 X-ray diffraction (XRD) study

The X-ray diffractograms of the sediment samples from both the hydrocarbon-affected and -unaffected areas show prominent peaks for quartz,
illite, muscovite, and feldspar. Illite is identified from the diagnostic peaks near 10, 4.48, and 3.33 Å d-spacings (figure 6). However, the characteristic peak of goethite at 4.18 Å d-spacing is not present in the XRD curves of the sediments. Also, the XRD spectra do not show any characteristics peaks of carbonate minerals.

4.3 X-ray fluorescence (XRF) study

Geochemical analyses showing concentrations of major element oxides in the sediments are shown in table 2. The table reveals that the microseepage-affected sediments have higher mean concentrations of Al$_2$O$_3$ and K$_2$O and lower SiO$_2$ and Na$_2$O contents. Concentrations of Fe$_2$O$_3$ (Total), MgO,
CaO, MnO, TiO\(_2\) and P\(_2\)O\(_5\) are nearly the same for both the microseepage affected and unaffected sediments.

The average CIA value for the microseepage-affected sediments (85.89) is nearly the same as that of the hydrocarbon-unaffected sediments (85.80). It is observed that the average SI value is lower (72.76) for the microseepage-affected sediments in comparison to the unaffected samples (74.51). The calculation reveals that the average AI for the microseepage-induced sediments is higher (83.14) than that of the unaffected sediments (81.29). The MIAI calculation shows that the mean MIAI value is higher (54.95) for microseepage-affected sediments with respect to the microseepage-unaffected sediments (52.54).

4.4 Trace elements study

The result of the trace elements (excluding REEs) is shown in table 3. The distribution of the trace element concentrations reflects that the hydrocarbon-bearing sediments are enriched in average V, Cu, Zn, Ga, Zr, and Mo, and are depleted in Li, Cr, Co, Ni, Rb, Sr, Sc, and Y.

The REE values of the sediments were normalized with respect to Post-Archaean Average Australian Sedimentary rock (PAAS) (McLennan 1989) values. The average normalized values of the REEs are shown in table 4. The table indicates that the average REE content is higher in the hydrocarbon unaffected sediments. The PAAS normalized REE patterns for the samples are shown in figure 7. The patterns are similar for both hydrocarbon-affected and -unaffected sediments. Concentrations of REEs were plotted in relation to major elements to get an idea of petrogenetic inputs of the sediments and are shown in figure 8. As evident from figure 8, REEs show a poor negative correlation with SiO\(_2\) and positive correlations with Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), TiO\(_2\) and K\(_2\)O.

5. Discussions

In arid to semi-arid climates, meteoric or ground-water water does not play a vital role in the mobilization of elements or minerals and therefore, alteration products remain in-situ. But in humid regions, materials are moved in and out of the microseepage system by water and consequently, the effects of alterations are significantly different. Chemical weathering of non-calcareous rocks in humid temperate climates promotes formation of goethite and decomposition of feldspar to form illite (Hillel 2004). This phenomenon accounts for the presence of goethite and illite in the sediments of the study area. Presence of goethite imparts yellowish colour to the sediments. Reducing condition of the hydrocarbon microseepage environment induces formation of clay minerals by the decomposition of feldspar or mica and transformation of ferric iron minerals into ferrous iron phases. As a consequence, microseepages in a warm, humid climate will add some extra clay minerals and tend to diminish the ferric iron contents of the sediments. The observed deficiency of goethite and enrichment of clay minerals in the microseepage-bearing sediments, as reflected by
spectroscopic study, thereby authenticate the influence of microseepages. The dearth of carbonates in the microseepage-affected sediments may be attributed to (a) the composition of the parent rocks, which consist of shales and sandstones with little CaO contents and/or (b) dissolution of carbonates in the abundant surface water in the acidic microseepage environment and their subsequent mobilization from the system. The deficit of CaO in the parent rocks is evident from geochemical studies by Borah et al. (2020) and Lalmuankimi (2014) from nearby areas, where the authors reported CaO contents varying from 0.48 to 2.88%, with an average of 0.97% for sandstones and 0.46–1.07% with an average of 0.69% for shales, respectively.

Presence of illite in the XRD spectra of the sediments is consistent with the spectroscopic observations. However, goethite identifiable in spectroscopy lacked characteristic peaks in XRD due to their occurrence as fine coatings which are opaque to XRD (Swayze et al. 2000). Absence of conspicuous characteristic peaks of carbonate minerals in the XRD spectra is indicative of carbonate deficiency in the sediments.

Geochemical analyses for major element oxides reveal several important facts about microseepage-induced sediments. Enrichment of K2O and depletion of Na2O in the microseepage-affected sediments can be interpreted by the formation of illite at the expense of sodium by the decomposition of Na-rich feldspars. The carbon-di-oxide produced by the bacterial actions in the microseepage environment, when reacted with the groundwater, produces carbonic acid (Saunders et al. 1999), which causes partial dissolution of

Table 4. PAAS normalized REE concentrations of the microseepage-affected and hydrocarbon-unaffected sediments.

<table>
<thead>
<tr>
<th>REE (PAAS normalized values)</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC affected Average</td>
<td>0.546</td>
<td>0.637</td>
<td>0.615</td>
<td>0.600</td>
<td>0.777</td>
<td>0.898</td>
<td>0.902</td>
<td>0.801</td>
<td>0.743</td>
<td>0.684</td>
<td>0.732</td>
<td>0.704</td>
<td>0.675</td>
<td>0.634</td>
</tr>
<tr>
<td>Median</td>
<td>0.497</td>
<td>0.573</td>
<td>0.614</td>
<td>0.593</td>
<td>0.755</td>
<td>0.846</td>
<td>0.846</td>
<td>0.747</td>
<td>0.718</td>
<td>0.621</td>
<td>0.702</td>
<td>0.676</td>
<td>0.690</td>
<td>0.613</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.280</td>
<td>0.235</td>
<td>0.278</td>
<td>0.273</td>
<td>0.334</td>
<td>0.321</td>
<td>0.356</td>
<td>0.298</td>
<td>0.231</td>
<td>0.213</td>
<td>0.190</td>
<td>0.163</td>
<td>0.145</td>
<td>0.134</td>
</tr>
<tr>
<td>HC unaffected Average</td>
<td>0.723</td>
<td>0.737</td>
<td>0.746</td>
<td>0.727</td>
<td>0.906</td>
<td>1.039</td>
<td>1.051</td>
<td>0.872</td>
<td>0.777</td>
<td>0.737</td>
<td>0.754</td>
<td>0.728</td>
<td>0.687</td>
<td>0.649</td>
</tr>
<tr>
<td>Median</td>
<td>0.671</td>
<td>0.728</td>
<td>0.716</td>
<td>0.696</td>
<td>0.894</td>
<td>0.994</td>
<td>1.038</td>
<td>0.877</td>
<td>0.780</td>
<td>0.716</td>
<td>0.778</td>
<td>0.724</td>
<td>0.714</td>
<td>0.670</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.201</td>
<td>0.240</td>
<td>0.204</td>
<td>0.192</td>
<td>0.254</td>
<td>0.303</td>
<td>0.307</td>
<td>0.252</td>
<td>0.214</td>
<td>0.193</td>
<td>0.197</td>
<td>0.196</td>
<td>0.169</td>
<td>0.157</td>
</tr>
</tbody>
</table>

Figure 7. PAAS normalized REE distribution patterns of the microseepage-affected and -unaffected sediments.
feldspars, causing removal of sodium (DiPietro 2013). During the transformation of feldspar into clay minerals, Si\(^{4+}\) is released and forms silicic acid (H\(_4\)SiO\(_4\)), which tends to leach from the soil in humid regions (Foth 1990). This accounts for silica (SiO\(_2\)) deficiency in the microseepage-affected sediments. Higher potassium content in microseepage-affected sediments is due to substitution of water by potassium in illite structure (Asadzadeh and de Souza Filho 2020b). Abundance of illite- an Al-rich phyllosilicate explains the higher content of Al\(_2\)O\(_3\) in the microseepage-induced sediments. Calcium in sandstones and shales is typically present in carbonate cements and, to a lesser extent, in calcic feldspars. Very low contents of CaO in the sediments indicate they are deficient in carbonate minerals and are consistent with spectroscopic and XRD observations. Fe\(_2\)O\(_3\) in the analyses represents total ferrous and ferric iron oxide contents and therefore, reduction in ferric iron content cannot be ascertained from the major element oxide analyses. The chemical index of alteration (CIA) values of the sediments indicate an illitic stage of weathering, supporting both spectroscopic and XRD results. Low silicification index (SI) for the microseepage-induced sediments demonstrate some silica dissolution in response to the microseepage process. Alteration index (AI) is a measure of the degree of sodic feldspar decomposition and therefore, higher AI value for the microseepage-induced sediments indicate their increased feldspathic alterations. Elevated MIAI for microseepage-affected sediments reveals influence of microseepage on the sediments.

Trace elements are attached or incorporated to their preferred minerals and consequently, their concentrations in soils depend upon the abundance of the particular minerals. The low E\(_{\text{pH}}\) condition of the microseepage environment also affects the solubilities of trace elements. Enrichment of vanadium (V), copper (Cu) and zinc (Zn) in the microseepage-bearing sediments of the study area may be due to the abundance of clay minerals to which they are finely incorporated (Kabata-Pendias 2011). Vanadium (V) as heavy metal occurs in crude oils in appreciable amount causing its higher concentration in microseepage areas (Al-Shahrstani and Al-Atyia 1972). Higher content of Cu and Zn in the microseepage-affected sediments supports the geochemical observations by Petrovic et al. (2012). Strontium (Sr) is preferentially accumulated in feldspar (Petrovic et al. 2012), and therefore, its lower content in the hydrocarbon-affected sediments indicates the deficiency of
feldspars. Lithium (Li) is a mobile element and is released during weathering in the presence of acid media, accounting for its lower content in the microseepage-bearing sediments. Chromium (Cr) is soluble in reducing conditions and possibly leaves the microseepage areas by water, causing its low concentration in the microseepage sediments. Nickel (Ni) is usually incorporated in iron oxides making its high concentration in the microseepage unaffected soils.

Studies on REE distribution patterns of microseepage-induced rocks or sediments are only a few in literature. Asadzadeh and de Souza Filho (2020a) studied REE patterns of the Upper Red Formation, Qom region, Iran and observed inconsistent patterns between microseepage affected and unaffected rocks, which they attributed to the presence of two different sediment provenances. REEs are good indicators of the provenance as they are chiefly transported as particulate matter (Rollinson 1993). The similar PAAS normalized REE patterns of both microseepage-affected and unaffected sediments in the study area indicate their derivation from the same provenance. The particular importance of the normalized REE pattern is the positive Eu anomaly. Eu anomaly is primarily controlled by the presence of plagioclase feldspar due to Eu’s compatibility with plagioclase (Rollinson 1993). Consequently, a positive Eu anomaly indicates presence of plagioclase feldspar in the sediments, which is also confirmed from the XRD spectra. Though REEs were originally presumed to be immobile, Nesbitt (1979) showed that CO$_2$ and organic matter bearing waters could remove the REEs from the surface soils and deposited in the deeper soil horizons (Aide and Aide 2012). As hydrocarbon microseepage environments are dominated by CO$_2$, it is feasible that REEs are leached by the CO$_2$-rich water and deposit in the deeper soil horizons. The leaching of the REEs is reflected in the low concentrations of the REEs in the microseepage-affected sediments. Positive correlations between REEs and Al$_2$O$_3$, Fe$_2$O$_3$, TiO$_2$ and K$_2$O indicate that the REEs may be controlled by clay, iron minerals and rutile. On the other hand, the poor correlation of REEs with SiO$_2$ suggests that silica does not typically control the REE distribution in the sediments.

One important observation on the results of the above studies is that the statistical difference of mineralogical and geochemical characteristics between the hydrocarbon-affected and unaffected sediments is not very high. This may arise due to:

(a) the development of weak microseepage systems and/or (b) the effect of abundant rainfall in the area. Presence of several commercial oil and gas fields shows that reservoirs are ample in the basin. Being located in a tectonically active convergent accretionary prism setting with highly deformed terrains and ample neotectonic activities, the cap as well as the overlying rocks may have been affected with abundant faults and micro-fractures, which can serve as good conduits for microseepages of hydrocarbons. Numerous surface oil and gas macroseepages support leaking of reservoirs in the basin. It is therefore, microseepages should be well developed in the basin. Hence, the role of surface/groundwater may be considered as an important parameter on the microseepage system. Asadzadeh and de Souza Filho (2020a) pointed out that mass transfer into or out of the microseepage systems may occur by groundwater in proportion to the flow gradient and their distribution patterns. The mass transfer of minerals and elements by surface/groundwater may have some effects on the mineralogical and geochemical characteristics of the sediments.

6. Conclusions

The study documents mineralogical and geochemical characteristics of hydrocarbon microseepage-induced sediments of Assam–Arakan Fold Belt dominated by warm humid climate utilizing reflectance spectroscopy and geochemical analytical techniques. Microseepage-bearing sediments are enriched in illite clay and deficit in goethite as revealed by the reflectance spectroscopy. Geochemically, the altered sediments are characterized by high Al$_2$O$_3$ and K$_2$O and low Na$_2$O and SiO$_2$ contents. Geochemical indices such as Al, Si, and MIAI reflect that the microseepage-affected sediments have undergone a little higher degree of alterations. Microseepage-affected sediments in the area are enriched in trace elements such as V, Cu, Zn, Ga, Zr, and Mo which are typically found in hydrocarbon microseepage environments. REE deficiency in the affected sediments indicates leaching effects in response to microseepages.

In view of the limited number of sample analysis, the study may be considered as a pioneering study to characterize microseepage-affected sediments using diffuse reflectance spectroscopy and geochemistry in the basin, which will help in filling the knowledge gap in the subject. Future works should
focus on analyzing more surface as well as drill cutting samples from producing wells to characterize the microseepage-induced sediments in detail. Additionally, the study of groundwater flow patterns vis-à-vis hydrocarbon traps in the microseepage areas may help us understand the role of groundwater in the microseepage system.

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Author statement

SG: Conceptualisation of work, field data collection and analysis, interpretation of results, drafting original and revised manuscript. DM: Conceptualisation of work, supervision of analysis and interpretation of results, drafting original manuscript. PD: Analysis and interpretation of data, supervision of draft and revised manuscript.

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