4. Schützendübel, A., Schwanz, P., Teichmann, T., Gross, K., Langenfeld-Heyser, R., Godbold, D. L. and Polle, A., Cadmium-induced changes in antioxidative systems, hydrogen peroxide content, and differentiation in Scots pine roots. *Plant Physiol.*, 2001, **127**, 887–898.
5. Davis, M. S., Effect of toxic concentrations of metals on root growth and development. In *Plant Root Growth – An Ecological Perspective* (ed. Atkinson, D.), Blackwell Scientific Publications, Oxford, 1991, pp. 211–227.
6. Poschenrieder, Ch. and Barceló, J., Water relations in heavy metal stressed plants. In *Heavy Metal Stress in Plants – From Biomolecules to Ecosystems* (ed. Prasad, M. N. V.), Springer-Verlag, Berlin, Heidelberg, 2004, 2nd edn, pp. 249–270.
7. Thakur, A. K. and Singh, K. J., Leaf temperature as thermal bio-indicator of heavy metal pollutants. *J. Agric. Sci. Technol. A*, 2012, **2**, 131–137.
8. Sievers, A. and Scott, T. K., Preface. *Planta*, 1997, **203**, S1.
9. Minchin, F. R. and Pate, J. S., Effect of water, aeration and salt regime in nitrogen fixation in nodulated legume – definition of an optimum root environment. *J. Exp. Bot.*, 1975, **26**, 60–69.
10. Turner, A. P., The responses of plants to heavy metals. In *Toxic Metals in Soil – Plant Systems* (ed. Ross, S. M.), John Wiley, West Sussex, England, 1994, pp. 153–187.
11. Chou, C. H. and Muller, C. H., Allelopathic mechanism of *Archtostaphylous glandulosa* var. *zazaensis*. *Am. Mid. Nat.*, 1972, **88**, 324–347.
12. Abdul-Baki, A. A. and Anderson, J. D., Vigour determination in soybean seed by multiple criteria. *Crop Sci.*, 1973, **13**, 630–633.
13. Kinraide, T. B., Identity of the rhizotoxic aluminium species. *Plant Soil*, 1991, **134**, 167–178.
14. Kuriakose, S. V. and Prasad, M. N. V., Cadmium stress affects seed germination and seedling growth in *Sorghum bicolor* (L.) Moench by changing the activities of hydrolysing enzymes. *Plant Growth Regul.*, 2008, **54**, 143–156.
15. Cooke, D. T. and Burden, R., Lipid modulation of plasma membrane bound ATPases. *Physiol. Plant.*, 1990, **78**, 153–159.
16. Munzuroglu, O. and Geckil, H., Effects of metals on seed germination, root elongation and coleoptile and hypocotyl growth in *Triticum aestivum* and *Cucumis sativus*. *Arch. Environ. Contam. Toxicol.*, 2002, **43**, 203–213.
17. Singh, A. K., Misra, P. and Tandon, P. K., Cadmium induced metabolic disorders in Pea (*Pisum sativum* L.). *J. Ecophysiol. Occup. Hlth.*, 2005, **5**, 185–188.
18. Di Salvatore, M., Carafa, A. M. and Carratù, G., Assessment of heavy metals phytotoxicity using seed germination and root elongation tests: a comparison of two growth substrates. *Chemosphere*, 2008, **73**, 1461–1464.
19. Lynch, J., Root architecture and plant productivity. *Plant Physiol.*, 1995, **109**, 7–13.
20. Aloni, R., Aloni, E., Langhans, M. and Ullrich, C. I., Role of cytokinin and auxin in shaping root architecture: Regulating vascular differentiation, lateral root initiation, root apical dominance and root gravitropism. *Ann. Bot.*, 2006, **97**, 883–893.
21. Audus, L. J., Plant geosensors. *J. Exp. Bot.*, 1979, **30**, 1051–1073.
22. Sievers, A. and Heyder-Caspers, L., The effects of centrifugal accelerations on the polarity of statocytes and on the graviperception of cress roots. *Planta*, 1983, **157**, 61–70.
23. Moore, R. and Evans, M. L., How roots perceive and respond to gravity. *Am. J. Bot.*, 1986, **73**, 574–587.
24. Perrin, R. M., Young, L.-S., Narayanamurthy, U. M., Harrisson, B. R., Wang, Y., Will, J. L. and Masson, P. H., Gravity signal transduction in primary roots. *Ann. Bot.*, 2005, **96**, 737–743.

Received 17 Mach 2014; revised accepted 25 July 2014

Geochemical characterization of Neoproterozoic heavy oil from Rajasthan, India: implications for future exploration of hydrocarbons

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The discovery of heavy oil in the Bikaner–Nagaur basin of Rajasthan in western India in reservoirs of Neoproterozoic age during the early nineties was one of the most significant events in the history of oil and gas exploration in India. Recently, discovery of heavy oil in the Punam Structure in the same basin has reconfirmed the hydrocarbon potential of the basin and has regenerated tremendous interest in exploration activities. Another significant factor that enhances exploration interest and hydrocarbon prospectivity of this basin relates to the fact that the Indian Mesoproterozoic and Neoproterozoic sedimentary basins share similar tectonic settings and depositional environments as their producing counterparts elsewhere (Oman, China, Siberian Platform, North Africa, Australia and so on). In this study, geochemical characterization of the heavy oil from Punam-X has been carried out for determining the source, maturity and extent of biodegradation using established biomarker ratios. Organic geochemical studies on the heavy oil from Punam-X indicate that the oil was generated in an anoxic hypersaline environment from marine clastic source rock. The oil is found to be generated from early mature source rock. Gas chromatograph analysis of the oil shows that it has also undergone some degree of biodegradation. Various similarities have been found between the Punam-X oil and other heavy oils of similar age found in Oman, Pakistan and in the adjoining areas in the Bikaner–Nagaur basin.

Keywords: Bikaner–Nagaur, Infra-Cambrian, neoproterozoic, petroleum geochemistry, Rajasthan basin.

UNCONVENTIONAL oil and gas, including heavy oil is widely acknowledged as an important component of global petroleum resource. Current estimates indicate that these resources are several orders of magnitude more abundant than conventional oil. During the early nineties, the exploration for hydrocarbons in Bikaner–Nagaur basin in Rajasthan by Oil India Limited resulted in the discovery of heavy oil in Baghewala-1 well within Jodhpur sandstone of Neoproterozoic age. This was the first discovery of oil in rocks of late Proterozoic age in Indian sedimentary basins. Consequently, there was an increased interest in Baghewala and adjoining areas of Bikaner–Nagaur basin

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in terms of hydrocarbon prospectivity and exploration. Sustained exploration in the basin resulted in the discovery of heavy oil in Punam-X well in 2012 (ref. 1). The Punam structure, which is a fault closure, is about 10 km northeast of Baghewala discovery well (Figure 1). The well, Punam-X was drilled to a final depth of 1297 m within Malani volcanics. While drilling at a depth of 1231 m within Jodhpur sandstone, surface indications of heavy oil were obtained. The presence of heavy oil was established during wireline formation testing (MDT). The Punam-X well encountered 29 m gross thickness of Jodhpur sandstone and is correlatable with the wells of Baghewala. The objective of the study is to highlight the continued discoveries of heavy oil in the basin in new structures and the possibility of finding more deposits of conventional and unconventional oil through intensive exploration, by analogy with basins of similar geologic setting and age, and to the oils derived from carbonate–evaporite facies of the Infracambrian Huqf Group in the eastern flank province of southern Oman. This study is an attempt to achieve this objective by the application of organic geochemistry, particularly biomarker analysis of the heavy oil.

Rajasthan basin forms the eastern flank of the Indus Geosyncline and comprises the sedimentary tract to the west and northwest of Aravallis up to Indo-Pakistan border. This basin is classified as a Category-1 basin (onland) with established commercial oil and gas reserves. The total area of the basin is 126,000 sq. km and comprises three sub-basins namely Barmer–Sanchor (11,000 sq. km), Bikaner–Nagaur (70,000 sq. km) and Jaisalmer (45,000 sq. km).

Bikaner–Nagaur basin constitutes a Neoproterozoic–Early Palaeozoic basin in the northwestern (NW) part of Peninsular Indian Shield. The tectonic setting of Rajasthan shelf (Figure 2) comprises Bikaner–Nagaur, Jaisalmer and Sanchor basins. Structurally, Bikaner–Nagaur basin is bounded in the east by Delhi–Aravalli fold belt and in the south, southwest by Pokhran–Nachna High, separating Jaisalmer basin and to the northeast lies the Delhi–Sargodha Ridge (P. C. Misra *et al.*, unpublished). The basin slopes to north and northwest and merges with the Indus shelf. The Bikaner–Nagaur basin is probably an extension of the Proterozoic tectono-depositional system of Arabian basement highs trending meridonal to submeridonal faulting with longitudinal basin lows depositing maximum sediments of around 2100 m. The prominent east–west basement high trend acts as a structural trap for (a) clastic–carbonate system (Neoproterozoic–Cambrian) and (b) clastic dominant system (post-Devonian), in this basin. The synrift clastic–carbonate system is correlated to the Salt Range of Punjab Basin and Harmuz of Gulf.

A large number of oil and gas fields, including giant ones, have been discovered in the Neoproterozoic of the Siberian Platform and Oman[2]. Further, increasing attention is being given towards exploration of deeper and older plays in North Africa[3]. This emphasizes the need for more extensive hydrocarbon exploration in the Neoproterozoic of the Punjab Platform and Rajasthan basin. In 1958, the first exploratory well, Karampur-1 drilled in the Punjab Platform discovered heavy oil in Neoproterozoic. Karampur-1 heavy oil from Salt Range is interpreted to be geochemically similar to Baghewala oil[4,5].

The palaeogeographic reconstruction (Figure 3) for Neoproterozoic and Cambrian indicates that the restricted marine evaporite deposits (Salt Range) of NW India (Bikaner–Nagaur basin, Rajasthan), Pakistan and southern Oman (Huqf basin) were in close proximity to each other on a broad carbonate shelf along the northern margin of Gondwanaland during the Neoproterozoic[6].

In Bikaner–Nagaur basin, Jodhpur sandstone constitutes the principal reservoir facies, and is lithologically coarse-grained, cross-bedded and rippled; and was deposited in coastal plain channels oriented oblique to shoreline and tidal flat to coastal plain fine-grained sand–shale

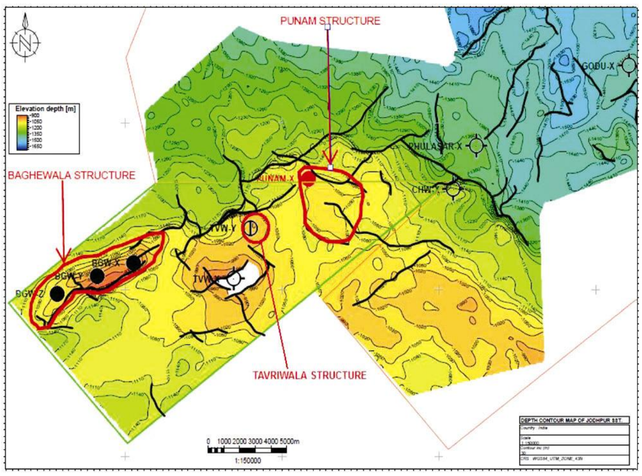

Figure 1. Location map of Punam structure (fault closure) in Bikaner–Nagaur basin.

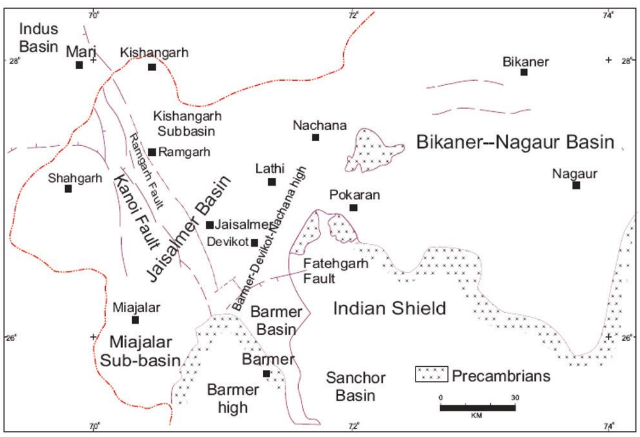

Figure 2. Structural map of western Rajasthan (after Misra *et al.*, unpublished).

Table 1. Generalized stratigraphy of Bikaner–Nagaur basin

Age		Formation	Thickness (m)	Lithology
Quarternary	Recent Pleistocene	Alluvium/Shumar	70–95	Fine to medium grained sand
Tertiary	Eocene Palaeocene	Palana and Marh	20–110	Clayey limestone and dark grey claystone
Mesozoic	Cretaceous	Parh equivalent	30–35	Dark grey claystone and sandstone
	Jurassic Triassic	Jaisalmer + Lathi	290–380	Red claystone and ferruginous sandstone with minor coal
Paleozoic	Permian	Bap and Badhaura	58–70	Red yellow and grey claystone and silts with conglomerate
	Marwar Super Group Neoproterozoic	Upper carbonate	250–600	Laminated dolostone and limestone with red claystone interbeds and occasional marl
		Nagaur	150–300	Mottled claystone with siltstone, fine-grained sandstone and minor dolostone
		Hanseran Evaporite Group	140–150	Anhydrite, halite, claystone and dolostone
		Bilara	50–120	Dolostone, fine-grained sandstone and reddish brown claystone

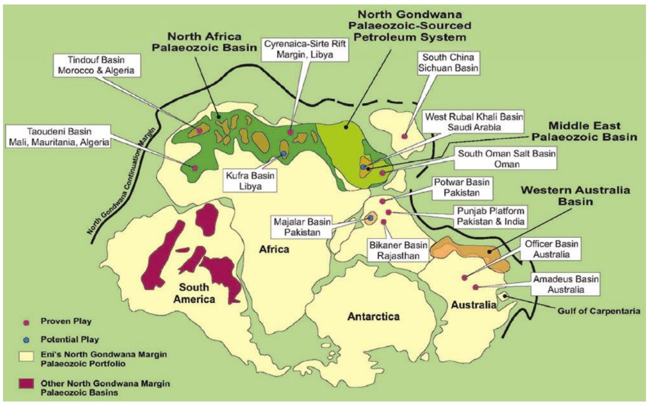

Figure 3. Gondwana margin Paleozoic and Neoproterozoic petroleum plays (reproduced with permission from J. Craig[3]).

alternations deposited along the shoreline[1]. The generalized stratigraphic succession for the Bikaner–Nagaur basin[1] is given in Table 1.

Thermal subsidence continued probably through the Neoproterozoic as indicated by the lagoon-tidal flat to restricted basin facies assemblage of Bilara and the Hanseran Evaporite Group (HEG)[1]. The HEG is characterized by thick and widespread halite deposits in lower part and mixed clastic–carbonate in upper part; whereas Bilara Group represents mixed carbonate and clastic sedimentary succession. In general, Jodhpur, Bilara and HEG have been deposited in fluctuating shoreline to low order regressive environment, controlled by tectonic topography in a range of coastal plain to tidal flat setting[1]. These successions have rich organic matter of high quality cyanophycean (stromatolites, acritarchs and filamentous algae) affinity that is proven to be high quality (Type I) source material for hydrocarbon generation[7].

A number of geochemical similarities for the Baghewala oil have been reported[4] with distinctive features of the Huqf-sourced oils, including a strong predominance of C_{29} steranes, diasteranes and monoaromatic (MA) steroids, a very negative stable carbon isotope ratio (–32‰), a low pristine/phytane ratio (0.9), low diasteranes, low API gravity (17.6°) and high sulphur (1.2%). The study concluded that Baghewala-1 oil is non-biodegraded, and thermal-maturation dependent biomarker ratios indicate generation from the source rocks within the early oil window[4]. Age-diagnostic and source-dependent biomarkers indicate that the oil originated from algal and bacterial organic matter with no higher plant input in Neoproterozoic, carbonate-rich Type II-S source rock deposited under anoxic marine conditions. These characteristics support a local origin of the Baghewala-1 oil from organic-rich laminated dolomites in the Bilara Formation.

An independent study[8] also concluded that the biomarker distribution and carbon isotope data in the present oil samples share good amount of resemblance to the patterns obtained from Oman Huqf oil and East Siberian oil.

The Huqf oils are those that have been correlated to known Huqf source rocks and are characterized by a strong C_{29} sterane predominance and very light carbon isotope[9]. Heavy oil and bitumen shows in Neoproterozoic and Cambrian reservoirs from few wells drilled in Punjab Platform have been reported and their presence may be attributed to the two possible explanations; firstly that organic matter has been converted to oil but not into lighter oil due to the absence of appropriate thermal regime; secondly, that oil generation takes place in close contact with reservoir[5]. Their study of vitrinite reflectance data indicates that Neoproterozoic was present in early oil generation window. Type II-S kerogen has an additional

Table 2. Crude oil properties of oil from western Rajasthan, Oman and Pakistan (data for Oman and Karampura-1 from Ahmed and Alam[14])

Crude properties	Baghewala wells	Punam-X	Oman	Karampura-1
°API	14–19	20	25–30	–
Resins + asphaltenes	22	46.8	–	–
Viscosity (cP) (at 50°C)	21,530–26,600	13,650	–	–
$\delta^{13}C/\delta^{12}C$ (‰)	–32	–33.7	–36.0	–36.0
Pr/Ph	0.9	0.68	<1	<1
C_{29} sterane	Predominant	Predominant	Predominant	Predominant

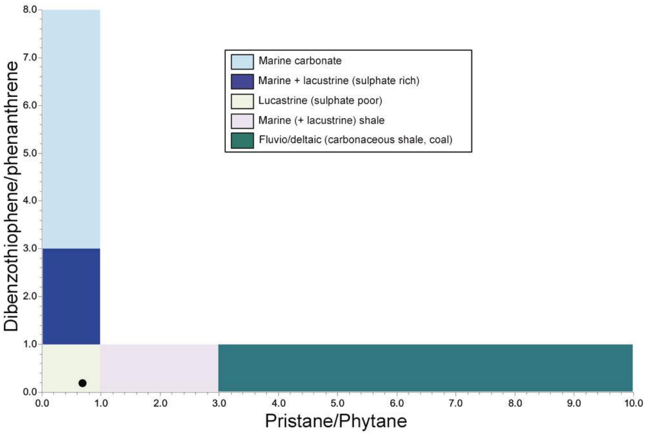

Figure 4. Bivariate plot of pristine/phytane versus dibenzothiophene/phenanthrene.

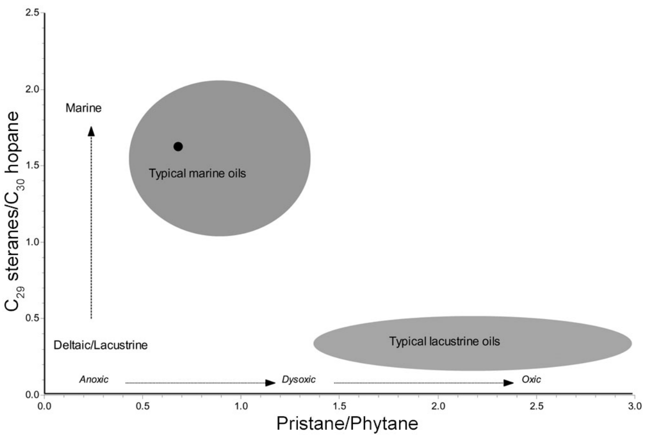

Figure 5. Plot of pristine/phytane and steranes/hopane for oil from Punam-X.

complement of weak bonds association with bound sulphur[10]. The preferential cleavage at weak sulphur linkages tends to produce larger fragments, leading to high initial amounts of asphalts, resins and sulphur-rich aromatics together with smaller amounts of saturated hydrocarbons.

A sample of heavy oil obtained during production testing was used for the analysis. Saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes were separated from a typical crude oil of 31° API, using medium pressure liquid chromatography (MPLC) method of Radke *et al.*[11].

A volume of 1 μl of 1% Punam-X oil was injected to a Agilent 6890N Gas Chromatograph (GC) equipped with a 30 m × 0.25 mm × 0.25 μm RTX1 fused silica capillary column. 1 μl of 1% crude oil solution in dichloromethane was injected to the GC. The GC was programmed as constant injector temperature at 300°C with 4.206 : 1 split ratio, column temperature programmed from 80°C with 1 min hold time to 300°C with 5 min hold time at 20°C/min. heating rate, detector temperature was kept at 300°C. Total time of analysis was 17 min.

For the GC–MS analysis, 1 μl of 1% Punam-X oil (saturated hydrocarbons or aromatic hydrocarbons fraction) was injected to a Thermo Trace Gas Chromatograph connected to a Thermo DSQ mass spectrometer. The GC column used was RTX-1 (60 m × 0.25 mm i.d., 0.25 μm film thickness) and the oven temperature program was 50°C (3 min) to 100°C at 25°C/min (0.0 min) again from 100°C to 300°C (20 min) at 2°C/min. The GC conditions were: split injector 300°C; split flow 20 ml/min; split ratio 20 : 1; carrier gas He at constant flow; transfer line 300°C, carrier flow rate 1 ml/min. The MS operating conditions were: ion source 200°C; SIM mode. Total time of analysis: 130 min.

The Punam-X oil is characterized by a saturate, aromatic, resin and asphaltene contents of 26.4%, 26.8%, 12% and 34.8% respectively. Biomarkers present in the heavier and middle fraction of oil have been used to determine the depositional environment and the source input for the source rocks from which the oil is derived.

Pristane to phytane (Pr/Ph) ratio is a commonly used parameter for depositional environment. Pr/Ph ratios >3.0 have been described for terrestrial input deposited under oxic conditions and low Pr/Ph ratios, i.e. < 1 indicate anoxic/hypersaline or carbonate environment, whereas Pr/Ph ratio 1 to 3 has been associated with marine oxic/dysoxic conditions[12,13]. The pristane/phytane ratio for the oil is less than 1 (0.6) implying that the oil has been generated from source rock deposited under anoxic condition. Selected crude oil parameters[14] comparing the Rajasthan, Oman and Karampura-1 crude oil is presented in Table 2.

The ratio of dibenzothiophene to phenanthrene (DBT/P) is an indicator of source rock lithology. The DBT/P ratio >1 indicates a carbonates type facies, whereas DBT/P ratio <1 indicates a marine shale type lithology[15]. DBT/P was measured from GC–MS analysis of the aromatic fraction whereas Pr/Ph ratio was determined from GC analysis of crude oil. The Pr/Ph ratio < 1 and DBT/P < 1 for Punam-X oil indicate anoxic hypersaline (lacustrine) depositional environment with marine shale type lithology of source rock (Figure 4).

The oil has high steranes/hopane ratio (1.68), which is an indicator of marine depositional environment[16]. A cross-plot of Pr/Ph and steranes/hopane (Figure 5) shows that the oil has been generated from a marine source rock deposited under anoxic environment.

Presence of significant quantities of gammacerane in the oils indicates that the source rock for the oil was deposited under highly reducing, hypersaline conditions[17,18]. The gammacerane index (gammacerane/hopane) for the oil is 0.1. Thus, the oil has generated from a marine source rock that was deposited under reducing, saline conditions. Presence of C_{30} steranes in oils in unequivocally linked to their marine origin[16]. C_{30} sterane has been identified to be present in this oil confirming its marine origin. Distribution of C_{29}, C_{30} and C_{31} hopanes (Figure 6) also shows that the oil is derived from marine shale[19].

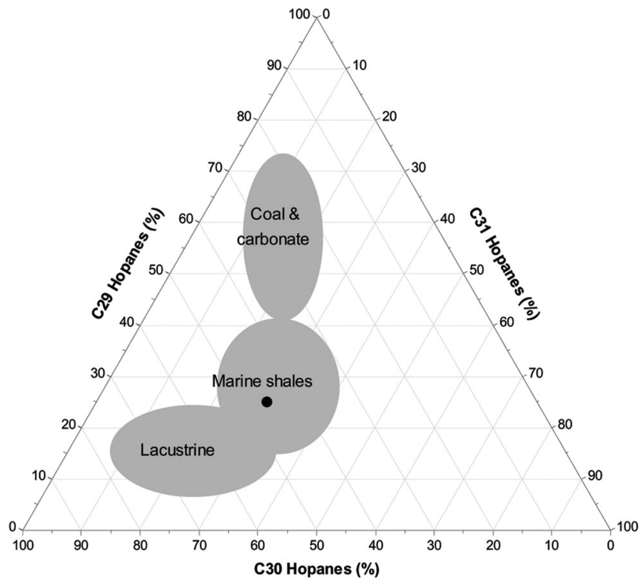

Figure 6. Distribution of C_{29}, C_{30} and C_{31} hopanes for oil from Punam-X.

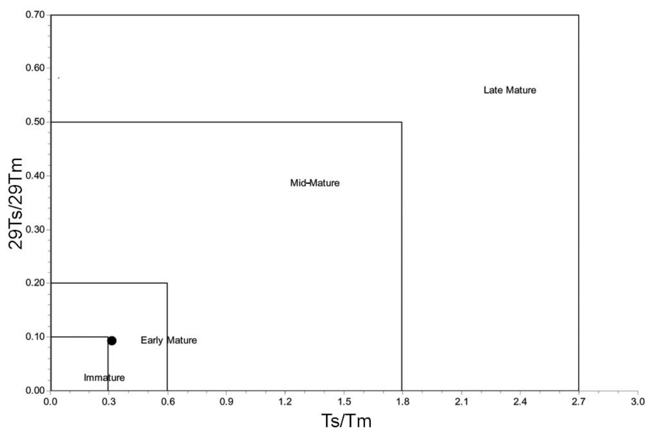

Figure 7. Plot of Ts/Tm and C29 Ts/Tm for oil from Punam-X.

The maturity of oil was determined using biomarkers present in the heavier fraction of oil. Ts/Tm is a maturity parameter based on the ratio of isomers of C_{27} hopanes, viz. C_{27} trisnorneohopane (Ts) and C_{27} trisnorhopane (Tm). This ratio is applicable from low maturity to peak maturity to high maturity of oils[20,21]. Similarly, C_{29} Ts/Tm ratio is based on C_{29} norneohopane (C_{29} Ts) and C_{29} norhopane (C_{29} Tm) and has a similar applicability[22]. A bivariate plot of Ts/Tm versus C_{29} Ts/Tm (Figure 7) shows that the Punam-X oil is in early mature stage.

With increasing maturity, C_{30} moretane is converted to C_{30} hopane and C_{29} normoretane is converted to C_{29} norhopane. The ratios hopane/(hopane + moretane) and norhopane/(norhopane + normoretane) are useful maturity parameters in immature to early mature range[23,24]. The values for these maturity parameters are 0.87 and 0.88 for hopane/(hopane + moretane) and norhopane/(norhopane + normoretane) respectively, which implies that the oil is in early mature stage (Figure 8).

The ratio 22S/(22S + 22R) C_{32} hopane is a maturity parameter applicable for immature to early mature range[24]. This ratio is 0.58 for Punam-X oil indicating that the oil is in early mature stage.

The maturity parameters based on isomers of C_{29} sterane, 20S/(S + R) and iso/(iso + reg) steranes are very reliable maturity parameters that are widely used. They are applicable in immature to peak mature range[25,26]. A bivariate plot of these parameters shows that the Punam-X oil is in early mature stage (Figure 9).

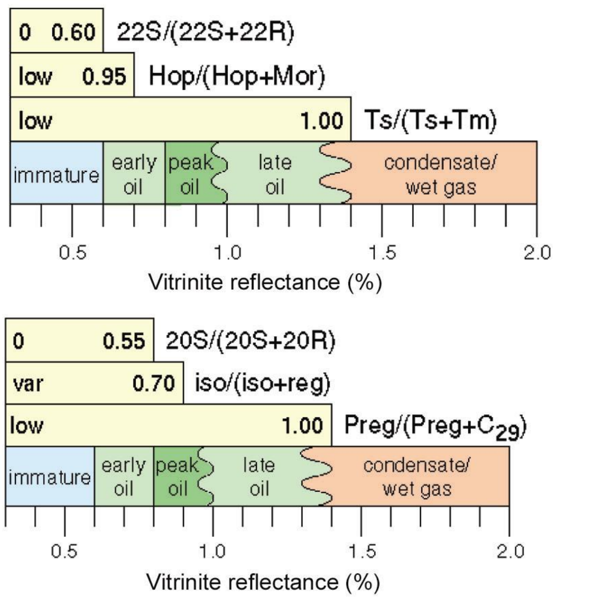

Figure 8. Maturity equivalence for hopane and sterane maturity parameters.

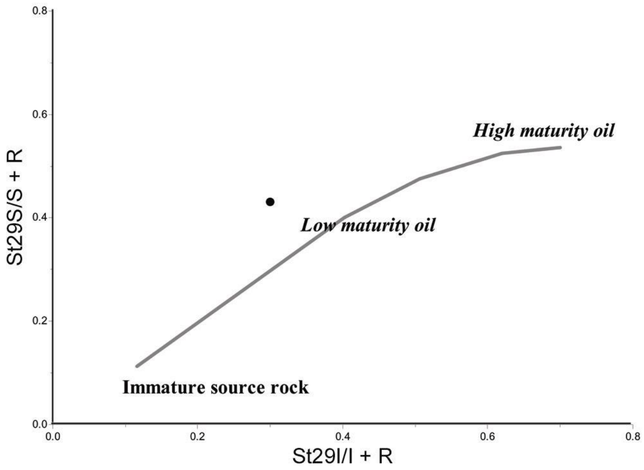

Figure 9. Plot of C_{29} iso/(iso + reg) and 20S/(20S + 20R) steranes for oil from Punam-X.

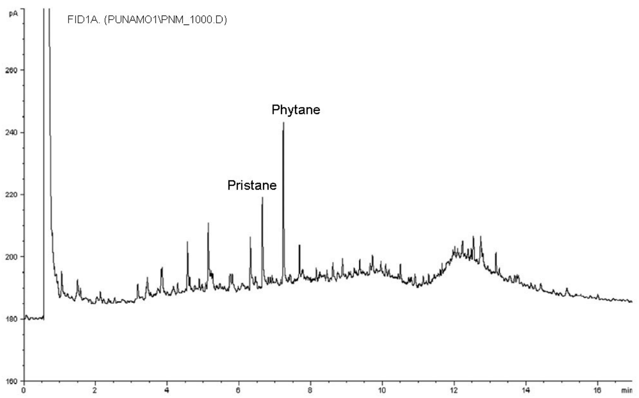

Figure 10. GC fingerprint of Punam-X oil.

The maturity of oil can also be determined using aromatic compounds present in the middle fraction of oil. Methyl phenanthrene index (MPI) is a very reliable parameter that is applicable over a wide range of maturity. The correlation between MPI and equivalent vitrinite reflectance of the source rock at the time of generation of oil is also well-developed[27]. The equivalent vitrinite reflectance (Rc) for Punam-X oil is 0.71 which again confirms that the oil is in early mature stage. Low maturity oils are heavier and more viscous than high maturity oils. The fact that early maturity oil can be heavy is well-acknowledged[28]. However, in the Proterozoic successions in China[29], hydrocarbon formed early is heavy oil with low maturity, a large proportion of which is 'self-storage'. It, therefore, follows that there could be significant deposits of autochthonous heavy oil within the source rocks in the Bikaner–Nagaur basin. In a study of heavy oils and tar sands in China[30], for oils having the same specific gravity, the viscosity of low maturity heavy oil is higher than high maturity heavy oil. However, based on limited data from two wells, there seems to be a contrary trend for oils from the Bikaner–Nagaur basin (Table 2). Further studies are being undertaken for a better understanding on the generation and post-depositional changes related to heavy oil in the basin.

The presence of heavy oils in reservoirs is mostly related to the secondary processes such as biodegradation, water washing and phase separation. A number of commonly used parameters have been used to assess the extent/level of biodegradation in Punam oil. GC analysis of saturated part of Punam-X crude oil shows presence of only isoprenoid compounds (Figure 10) with substantial unresolved complex mixture (UCM). This indicates that this oil has been biodegraded and the remaining fraction has become enriched by the high molecular weight of unresolved components.

Since isoprenoids such as pristane and phytane are still present and biomarkers such as sterane and hopane have been preserved, the oil is moderately biodegraded, equivalent to 4 on a biodegradation scale of 1 to 10 developed by Peters *et al.*[16].

In conclusion, organic geochemical studies on the heavy oil from Punam-X indicate that the oil was generated in an anoxic hypersaline environment from marine clastic source rock. The oil is found to be generated from early mature source rock. GC analysis of the oil shows that the oil has also undergone some degree of biodegradation. Various similarities have been found between the Punam-X oil and other heavy oils of similar age found in Oman, Pakistan and in the adjoining areas in the Bikaner–Nagaur basin.

The Neoproterozoic–Cambrian rift basins in western India, Pakistan, southern Oman and South China were in close proximity during the Neoproterozoic. The existence of proven Neoproterozoic–Cambrian petroleum systems in South China, Oman, Pakistan and Western India and the fact that there are petroleum systems with giant and supergiant fields in some of these provinces provides a major source of encouragement and optimism for intense exploration for conventional as well as unconventional oil in such basins in India.

Three key elements[31] appear to be important for the development of effective Neoproterozoic–Cambrian petroleum systems, viz.

- Relative tectonic stability since deposition of the Neoproterozoic–Cambrian succession.
- Relatively late phase of hydrocarbon maturation and generation.
- Presence of an effective seal (typically evaporites).

The Bikaner–Nagaur basin is characterized by the presence of all the above key elements. Further, the possibility that commercial prospects for unconventional hydrocarbon resources such as shale oil and autochthonous heavy oil preserved in the source units could exist in this basin as well as other Proterozoic basins of India, provide incentives for aggressive and intensive exploration for oil and gas in the Neoproterozoic basins of India. The hydrocarbon prospects of Indian Proterozoic basins is fairly well-documented. According to Ojha[32], the Infracambrian petroleum system appears to be prevalent throughout Gondwanaland and not just confined to the 'Northern Rim' of defragmented Gondwanaland. In peninsular India, the Bikaner–Nagaur, Vindhyan, Cuddapah, Chattisgarh, Bastar, Bhima and Kaladgi are the most important Proterozoic basins that have thick Neoproterozoic successions, in addition to the Palaeoproterozoic and Mesoproterozoic strata[7]. These successions have rich organic matter of high quality cyanophycean (stromatolites, acritarchs and filamentous algae) affinity that is recognized as high quality source material for hydrocarbon generation[7]. In various surface geochemical surveys, encouraging surface manifestations of hydrocarbons have been recorded[33–36]. While it is clear that Proterozoic basins, in general, appear to have favourable characteristics that warrant detailed exploration efforts for finding conventional and unconventional fossil fuels, a detailed discussion on this aspect is beyond the scope of this communication.

1. Boruah, K. and Deb, S. S., Heavy oil discoveries in Bikaner–Nagaur Basin: opportunities and challenges. *APG J.*, 2012, **3**, 40–43.
2. Bois, C., Bouche, P. and Pelet, R., Global geological history and distribution of hydrocarbon reserves. *Bull. AAPG*, 1982, **66/9**, 1248–1270.
3. Craig, J., Grigo, D., Rebora, A., Serafini, G. and Tebaldi, E., From Neoproterozoic to Early Cenozoic: exploring the potential of older and deeper hydrocarbon plays across North Africa and the Middle East. In Petroleum Geology Conference Series. Geological Society of London, 2010, vol. 7, pp. 673–705.
4. Peters, K. E., Clark, M. E., Das Gupta, U., McCaffrey, M. A. and Lee, C. Y., Recognition of an Infracambrian source rock-based on biomarkers in the Baghewala-1 Oil, India. *AAPG Bull.*, 1995, **79**(10), 1481–1493.
5. Hasany, S. T., Aftab, M. and Siddiqui, R. A., Refound exploration opportunities in Infracambrian and Cambrian sediments of Punjab Platform, Pakistan. In PAPG Annual Technical Conference, Islamabad, Pakistan, 2007.
6. Singh, A. K. and Tewari, P. K., Infracambrian hydrocarbon systems and emerging hydrocarbon potential in Bikaner–Nagaur and Jaisalmer (Miajlar Subbasin), Rajasthan, India. GEO-India Conference, New Delhi, 12–14 January 2011.
7. Ram, J., Neoproterozoic successions in peninsular India and their hydrocarbon prospectivity. *Geol. Soc. London*, *Spec. Publ.*, 2012, **366** (abstract).
8. Dutta, S., Bhattacharya, S. and Raju, S. V., Biomarker signatures from Neoproterozoic-early Cambrian oil, Western India. *Org. Geochem.*, 2013, **56**, 2013, 68–80.
9. Grantham, P. J., Lijmbach, G. W. M. and Posthuma, J., Geochemistry of crude oils in Oman. *Geol. Soc. Spec. Publ.*, 1990, **50**, 317–328.
10. Orr, W. L., Kerogen/asphaltenes/sulfur relationships in sulfur-rich Monterey oils. *Org. Geochem.*, 1986, **10**(1–3), 499–516.
11. Radke, M., Wilsch, H. and Welte, D. H., Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Anal. Chem.*, 1980, **56**, 2538–2546.
12. Didyk, B. M., Simoneit, B. R. T., Brassell, S. C. and Eglinton, G., Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature*, 1978, **272**, 216–222.
13. ten Haven, H. L., de Leeuw, J. W., Rullkotter, J. and Sinninghe-Damsté, J., Restricted utility of the pristane/phytane ratio as a palaeoenvironmental indicator. *Nature*, 1987, **330**, 641–643.
14. Ahmed, W. and Alam, S., Organic geochemistry and source rock characteristics of Salt Range Formation, Potwar Basin, Pakistan. *Pak. J. Hydrocarb. Res.*, 2007, **17**, 37–59.
15. Hughes, W. B., Holba, A. G. and Dzou, L. I. P., The ratios of dibenzothiophene to phenanthrene and pristane to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochim. Cosmochim. Acta*, 1995, **59**, 3581–3598.
16. Peters, K. E., Walters, C. C. and Moldowan, J. M., *The Biomarker Guide*, Cambridge University Press, Cambridge, 2005, vols. 1&2, p. 1155.
17. Moldowan, J. M., Seifert, W. K. and Gallegos, E. J., Relationship between petroleum composition and depositional environment of petroleum source rocks. *Am. Assoc. Petrol. Geol. Bull.*, 1985, **69**, 1255–1268.
18. Mello, M. R., Telnaes, N., Gaglianone, P. C., Chicarelli, M. I., Brassell, S. C. and Maxwell, J. R., Organic geochemical characterisation of depositional palaeoenvironment of source rocks and oils in Brazilian marginal basins. In *Advances in Organic Geochemistry 1987*, Proceedings of 13th International Meeting on Organic Geochemistry, Venice (eds Mattavelli, L. and Novelli, L.), Oxford, Pergamon Press, 1988, pp. 31–46.
19. Killops, S. D. *et al.*, Predicting generation and expulsion of paraffinic oil from vitrinite-rich coals. *Org. Geochem.*, 1998, **29**, 1–21.
20. Moldowan, J. M. *et al.*, Rearranged hopanes in sediments and petroleum. *Geochim. Cosmochim. Acta*, 1991, **55**, 3333–3353.
21. Moldowan, J. M., Sundararaman, P. and Schoell, M., Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. *Org. Geochem.*, 1986, **10**, 915–926.
22. Hughes, W. B., Holba, A. G., Miller, D. E. and Richardson, J. S., Geochemistry of Greater Ekofisk crude oils. In *Petroleum Geochemistry in Exploration of the Norwegian Shelf* (eds Thomas, B. M. *et al.*), Graham and Trotman Ltd, London, 1985, pp. 75–92.
23. Peters, K. E. and Moldowan, J., Effects of source, thermal maturity, and biodegradation on the distribution and isomerization of homohopanes in petroleum. *Org. Geochem.*, 1991, **17**, 47–61.
24. Seifert, W. K. and Moldowan, J. M., The effect of thermal stress on source rock quality as measured by hopane stereochemistry. In *Advances in Organic Geochemistry 1979*, Proceedings of 9th International Meeting on Organic Geochemistry, Newcastleupon-Tyne EAOG (eds Douglas, A. G. and Maxwell, J. R.), Pergamon, Oxford, 1980, pp. 229–237.
25. Seifert, W. K. and Moldowan, J. M., Paleoreconstruction by biological markers. *Geochim. Cosmochim. Acta*, 1981, **45**, 783–794.
26. Seifert, W. K. and Moldowan, J. M., Use of biological markers in petroleum exploration. In *Biological Markers in the Sedimentary Record* (ed. Johns, R. B.), Elsevier, Amsterdam, 1986, pp. 261–290.
27. Radke, M. and Welte, D. H., The Methylphenanthrene Index (MPI): a maturity parameter based on aromatic hydrocarbons. In *Advances in Organic Geochemistry 1981* (eds Bjorøy, M. *et al.*), John Wiley, 1983, pp. 504–512.
28. Khavari-Khorasani, G., Dolson, J. C. and Michelsen, K., The factors controlling the abundance and migration of heavy vs. light oil, as constrained by data from Gulf of Suez. Part I. The effect of expelled petroleum composition, PVT properties and petroleum system geochemistry. *Org. Geochem.*, 1998, **29**(1–3), 255–282.
29. Zhang, M., Ou, G.-X., Li, L.-Q., Zhang, J.-F. and Qui, L.-F., Study on reservoir fluid and the history of hydrocarbon migration and accumulation in the middle-upper Proterozoic system in the west Liaoning-North Hebei area. *Bull. Min. Petrol Geochem.*, **28**(1), 2009, 19–23.
30. Niu Jiayu and Hu Jianyi, Formation and distribution of heavy oil and tar sands in China. *Mar. Petrol. Geol.*, 1999, **16**(1), 85–95.

31. Bhat, G. M., Craig, J., Hafiz, M., Hakhoo, N., Thurow, J. W., Thusu, B. and Cozzi, A., Geology and hydrocarbon potential of Neoproterozoic–Cambrian Basins in Asia: an introduction. *Geol. Soc. London*, *Spec. Publ.*, 2012, **366**, 1–17.
32. Ojha, P. S., Precambrian sedimentary basins of India: an appraisal of their petroleum potential. *Geol. Soc. London*, *Spec. Publ.*, 2012, **366**, pp. 69–74.
33. Vishnuvardhan, C., Panicker, C. K. and Kumar, B., Comparison of Proterozoic basins of India with similar basins of the world: implications to hydrocarbon resource prospects. In Proceedings of Petroleum Geochemistry and Exploration in the Afro-Asian Region (eds Digang Liang, Darui Wang and Zhenxili), 2008.
34. Kalpana, M. S., Patil, D. J., Dayal, A. M. and Raju, S. V., Near surface manifestations of hydrocarbons in Proterozoic Bhima and Kaladgi Basins: implications to hydrocarbon resource potential. *J. Geol. Soc. India*, 2010, **76**, 548–556.
35. Dayal, A. M. and Raju, S. V., Discovery of hydrocarbon in Proterozoic Vindhyan basin, East India, using geochemical signatures. In Proceedings of Goldschmidt Conference, Davos, Switzerland, 2010.
36. Kalpana, G., Madhavi, T., Patil, D. J., Dayal, A. M. and Raju, S. V., Light gaseous hydrocarbon anomalies in the near surface soils of Proterozoic Cuddapah basin: implications for hydrocarbon prospects. *J. Petrol. Sci. Eng.*, 2010, **73**(1), 161–170.

ACKNOWLEDGEMENTS. We thank the anonymous reviewer whose insightful comments enabled to improve the article. We also thank Mr J. K. Borgohain, Group General Manager (Rajasthan Project), Oil India Limited, for providing the oil sample and geological data.

Received 30 August 2013; revised accepted 1 August 2014

Impact of rainfall variability on groundwater resources and opportunities of artificial recharge structure to reduce its exploitation in fresh groundwater zones of Haryana

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Climate change likely to impact rainfall patterns leading to higher uncertainty and difficulties in management of both water scarcity and flood events. Temporal trends of rainfall and its variability of Karnal district, representing fresh groundwater zones of Haryana, were analysed by non-parametric Mann–Kendall (MK) test and Sen's slope approaches. Analysis of long-term rainfall data (1972–2010) indicated that Karnal receives a mean annual rainfall of 757.6 mm with a high degree of variation (CV = 34.3%). Categorization of monsoon rainfall based on long-period average (LPA) and its CV indicates that during the last decade (2001–2010) Karnal received deficit rainfall in 6 years (18–57% lower than LPA), normal rainfall in 2 years and excess rainfall (9–70% higher than LPA) also for 2 years. The rainfall and rainy days during the last decade (2000–2010) decreased by 13% and 20% respectively, over long-term (1972–2010) averages. The MK and Sen's slope approach applied to pre- and post-monsoon groundwater levels indicated significant declining trend emphasizing the need to augment groundwater by artificial groundwater recharge (AGR) system. AGR through recharge wells installed by CSSRI at village Nabiabad in Karnal districts resulted in 2.32 m and 3.16 m rise in water table during 2009 and 2010 respectively. Installation of artificial groundwater recharge in low lying areas has proven highly effective in enhancing groundwater and improve its quality.

Keywords: Artificial groundwater recharge, Karnal, Mann–Kendall, rainfall.

SCIENTIFIC evidence has demonstrated that the Earth is moving towards a point of no return, where imbalances brought about by climate change will have serious ecological impacts. Climate change is no more an environmental concern. It has emerged as the biggest developmental challenge for the planet. Throughout the 21 century, India and other countries in southeast Asia are projected to experience warming above the global mean. India will also begin to experience greater seasonal variation in temperature, with more warming in winter than summer[1]. The longevity of heat waves across India has extended in recent years, leading to warmer temperatures at night and hotter days and this trend is set to continue[2]. These heat waves will lead to increased variability in summer monsoon precipitation, with drastic effects on the agricultural sector in India[3].

Rainfall is a climate parameter that affects the way and manner in which mankind survives. Apart from the beneficial aspects, rainfall can also be destructive by playing a major role in natural disasters such as floods and landslides. Long-term trends of Indian monsoon rainfall for the country as well as for smaller regions have been studied by several researchers. It has been reported that the monsoon rainfall is without any trend, being highly random in nature over a long period of time[4]. However, on a spatial scale, existence of trends was noticed[5,6]. Using the network of 306 stations and for the period 1871–1984, areas having increasing or decreasing trends of monsoon rainfall were identified[6].

Karnal district lies in the Upper Yamuna Basin and 70% of the net irrigated area is irrigated by groundwater. Despite greater use of new varieties and fertilizers, the current productivities of rice and wheat in Indo-Gangetic plains are showing stagnating trends[7]. Changes in the onset of monsoon and lack of contingency planning further complexes the farming process and ultimately affects its

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