



## Stable isotope signatures of Ashoknagar crude oil

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### Abstract

Over half a century-long quest for oil and natural gas in the Indian sector of the Bengal Basin has ended after the recent discovery of the Ashoknagar oilfield, making Ashoknagar the only commercial exploratory oilfield in the basin. The stable isotope geochemistry of Ashoknagar crude oil is studied to understand the enigmatic occurrence of the oil. The stable isotope ratio of carbon ( $\delta^{13}\text{C}$ ), hydrogen ( $\delta^2\text{H}$ ) and sulfur ( $\delta^{34}\text{S}$ ) were analysed using an elemental analyser coupled with an isotope ratio mass spectrometer. The stable isotope signature of the crude indicates a marine deltaic source of the oil.

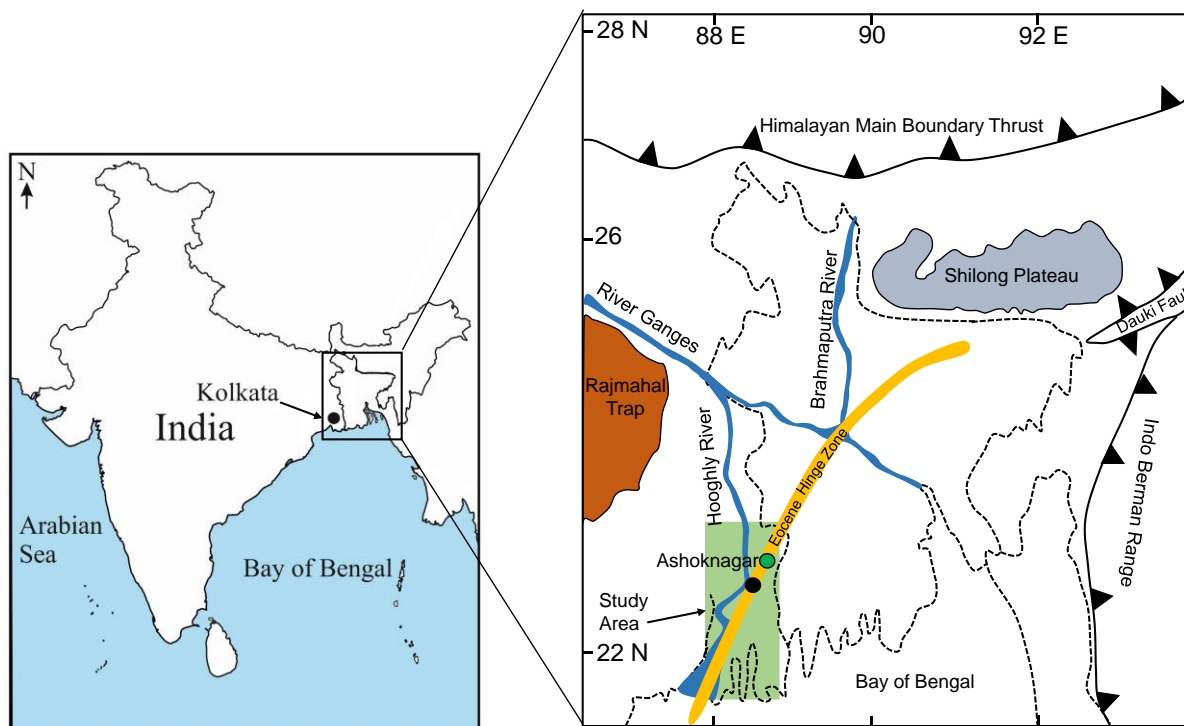
### Introduction

The Bengal Basin was formed synchronically with the rise of the Himalayas Mountain belt. A part of the basin falls in the east and northeast of India (West Bengal, Tripura and Assam), and the rest lies in Bangladesh. In the last few decades, several hydrocarbon explorations in the basin have been carried out. The recent discovery of oil in Ashoknagar, which is situated 40 km away from Kolkata, provides an opportunity to gain insight into the hydrocarbon system of the basin.

The carbon stable isotope ratio ( $\delta^{13}\text{C}$ ) is often used to study the organic matter (OM) source and depositional environment of oil (Ogbesejana et al., 2021). The variation in  $\delta^{13}\text{C}$  is also influenced by the maturation and migration of the hydrocarbon. The hydrogen stable isotope ratio ( $\delta^2\text{H}$ ) is used for oil-to-oil and source rock evaluation (Asif et al., 2011). Thermochemical sulfate reduction (TSR) and bacterial sulfate reduction (BSR) in source rock could be differentiated using the sulfur stable isotope ratio ( $\delta^{34}\text{S}$ ) (Cai et al., 2009). Behera et al. (2022) have reported a gradual change in the dominant OM source (terrestrial  $\text{C}_3$  plant to aquatic) and depositional environments from marsh (Miocene) to tidal flat (Pleistocene-Pliocene) using stable isotopes of organic carbon and nitrogen ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , respectively) and *n*-alkane analyses of Miocene-Pleistocene sediments from five ONGC wells in the Bengal Basin. The analysis of Ashoknagar oil offers a unique opportunity to study the stable isotope signatures of the crude and compare the data with the Mio-Plio-Pleistocene sediments analysed by Behera et al. (2022). The research objective was to study the OM source and depositional environment of the Ashoknagar crude using  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  and  $\delta^{34}\text{S}$ .

### Bengal Basin

The Bengal Basin is one of the world's largest fluvio-deltaic basins (~200,000 km<sup>2</sup>; Alam et al., 2003). The peripheral foreland basin is situated at the confluence of the Brahmaputra and Ganga rivers (Fig. 1). The Bengal Fan, the largest deep-sea fan complex on Earth (Rea, 1992), is further developed into the Bay of Bengal (Morgan and McIntire, 1959; Babu, 1976; Allison, 1998). The Indian craton, Indo-Burman ranges, Himalayan belt and Shilong massif surround the basin to the west, east and north. The basin extends into the Bay of Bengal to the south (Uddin and Lundberg, 1998). The Eocene Hinge Zone (EHZ) passes through Kolkata and Ashoknagar and separates the basin into two broad parts (a) the Stable shelf (Indian platform) to the northwest and west, and (b) the deeper part of the basin (Bengal Foredeep) to the south and east (Sengupta, 1966; Uddin and Lundberg, 1998; Mukherjee et al., 2009). Gondwana basement underlies the Bengal Basin sediments, and the thickness of the sediments varies between the foredeep (>16 km) and stable shelf (8 km).



**Figure 1.** Tectonic map of the Bengal Basin.

The formation of the Bengal Basin began during the late Jurassic. Major tectonic events, such as the Dauki fault and Naga thrust, occurred between the Late Cretaceous and Miocene, and the sea regression during the late Miocene and early Pliocene affected the basin formation (Sengupta, 1966) (Table 1). The Miocene Debagram and the Pandua Formations are characterised by claystone, siltstone, sandstone and shale (Banerji, 1984; Alam et al., 2003) (Table 1). The Pliocene and Pleistocene sequences in the Bengal Basin primarily belong to the Ranaghat Formation and mostly contain claystone, siltstone and pebbly sandstone. The Ranaghat Formation is characteristic of marginal marine with occasional interdeltic settings, while the Debagram Formation exhibits a mixed estuarine to marginal deltaic facies character (Banerji, 1984). The presence of planktonic and benthic foraminifera in the Pandua Formation indicates a short span of marine transgression during the Miocene (Banerji, 1984).

## Material and Methodology

### Sample

The MBA Basin of ONGC Limited provided the Ashoknagar crude oil sample. The sample was stored in an air-tight glass container in the dark before analysis.

### Stable isotope analysis

The total sulfur (TS) content of the whole crude was measured using an automated elemental analyser (EA). The elemental analyser (EA), coupled with Europa Scientific 20-20 isotope ratio mass spectrometer (IRMS), was used to analyse the  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  and  $\delta^{34}\text{S}$  of whole crude oil. The vanadium pentoxide catalyst was added to the sample prior to the TS and  $\delta^{34}\text{S}$  analyses. The results of the  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$  and  $\delta^{34}\text{S}$  analyses were calculated as follows:

$$\delta (\%) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$



**Table 1.** Stratigraphic succession of the Southwestern part of the Bengal Basin (Alam et al. 2003; Roy and Chatterjee 2015).

Age	Group	Formation	Lithological description	Environment of Deposition
Holocene		Alluvium	Sand, clay, gravel	Fluvial-alluvial and prograding delta-shelf
Pleistocene-Late Pliocene	Barind	Barind	Clay, minor sand	
Early Pliocene-Middle Miocene	Bhagirathi	Debogram/Ranaghat	Sandstone, siltstone and shale	Delta front to shelf and slope
		Pandua/Malta	Sandstone/mudstone	
Oligocene	Jayantia	Memari/Burdwan	Sandstone/mudstone	
Late Eocene		Kopili	Shale, mudstone, sandstone	
Middle Eocene		Sylhet Limestone	Limestone with sandstone	Carbonate platform
Paleocene		Jalangi	Sandstone, mudstone	Deltaic to outer shelf
Early to Late Cretaceous	Rajmahal	Ghatal	Sandstone, limestone, shale	Coastal to fluvial-alluvial
		Bolpur	Mudstone, sandstone, trapwash	
		Dhananjaypur	Grey shale	Subaerial lava flows
		Rajmahal Trap	Basalt, andesite, intertrappeans	
----- Basement: Precambrian Shield rocks along with the cover Gondwana coal-bearing formations -----				

The reference material IA-R005 (beet sugar,  $\delta^{13}\text{C}_{\text{V-PDB}} = -26.03 \text{ ‰}$ ) was used for  $\delta^{13}\text{C}$  analysis. The check samples of IA-R006 (cane sugar,  $\delta^{13}\text{C}_{\text{V-PDB}} = -11.64 \text{ ‰}$ ) and IA-R071 (cane/beet sugar mix,  $\delta^{13}\text{C}_{\text{V-PDB}} = -19.26 \text{ ‰}$ ) were analysed along with the samples as quality control checks. IA-R005, IA-R006 and IA-R071 have been calibrated against and are traceable to IAEA-CH-6 (sucrose,  $\delta^{13}\text{C}_{\text{V-PDB}} = -10.43 \text{ ‰}$ ), distributed by the International Atomic Energy Agency.

For  $\delta^2\text{H}$  analysis, the reference material IA-R002 (mineral oil,  $\delta^2\text{H}_{\text{V-SMOW}} = -111.2 \text{ ‰}$ ) was used. The IA-R002, IAEA-CH-7 (polyethylene foil,  $\delta^2\text{H}_{\text{V-SMOW}} = -100.3 \text{ ‰}$ ) and IA-R072 (mineral oil,  $\delta^2\text{H}_{\text{V-SMOW}} = -148.61 \text{ ‰}$ ) were measured along with your samples as quality control check samples. IA-R002 and IA-R072 have been calibrated against and are traceable to NBS-22 (mineral oil,  $\delta^2\text{H}_{\text{V-SMOW}} = -118.5 \text{ ‰}$ ). International Atomic Energy Agency distributed the NBS-22 and IAEA-CH-7 inter-laboratory comparison standards.

The reference material IA-R061 (barium sulfate,  $\delta^{34}\text{S}_{\text{V-CDT}} = +20.33 \text{ ‰}$ ) was used for sulfur isotope analysis. The in-house standards IA-R061, IA-R025 (barium sulfate,  $\delta^{34}\text{S}_{\text{V-CDT}} = +8.53 \text{ ‰}$ ) and IA-R026 (silver sulfide,  $\delta^{34}\text{S}_{\text{V-CDT}} = +3.96 \text{ ‰}$ ) were used for calibration and correction of the  $^{18}\text{O}$  contribution to the  $\text{SO}^+$  ion beam. The in-house standards were calibrated against and traceable to NBS-127 (barium sulfate,  $\delta^{34}\text{S}_{\text{CDT}} = +20.3 \text{ ‰}$ ) and IAEA-S-1 (silver sulfide,  $\delta^{34}\text{S}_{\text{V-CDT}} = -0.30 \text{ ‰}$ ). The check samples namely, IAEA-SO-5 (barium sulfate,  $\delta^{34}\text{S}_{\text{V-CDT}} = +0.50 \text{ ‰}$ ) and IA-R069 (tuna protein,  $\delta^{34}\text{S}_{\text{V-CDT}} = +18.91 \text{ ‰}$ ) was used for quality control. IA-R069 is an in-house standard calibrated against and traceable to NBS-127 and IAEA-SO-5. NBS-127, IAEA-S-1 and IAEA-SO-5 are inter-laboratory comparison standards distributed by the International Atomic Energy Agency (IAEA) with internationally accepted  $\delta^{34}\text{S}$  values. The analyses were performed at the Iso-Analytical Limited in the UK.

## Result and Discussion

The  $\delta^{13}\text{C}$ ,  $\delta^{34}\text{S}$  and  $\delta^2\text{H}$  values of Ashoknagar crude are  $-24.77 \text{ ‰}$ ,  $9 \text{ ‰}$  and  $-110 \text{ ‰}$ , respectively. Crude oils from terrigenous OM sources show a lighter  $\delta^{13}\text{C}$  signature than the marine source (Craig, 1953; Silverman, 1965; Ogbesejana et al., 2021). The  $\delta^{13}\text{C}$  values ( $-28 \text{ ‰}$  to  $-23.5 \text{ ‰}$ ) of low sulfur ( $<0.5 \%$ ) rich oils indicate the marine deltaic source (Chung et al., 1992). The oil generated from carbonate source rocks shows a lighter  $\delta^{13}\text{C}$  and heavier  $\delta^2\text{H}$  signature than the shale-sourced oils (Barrie et al., 2018). Furthermore, the  $\delta^{13}\text{C}$  signature of oil becomes heavier with increasing maturation (Clayton, 1991). The  $\delta^{13}\text{C}$  value of Ashoknagar crude ( $24.8 \text{ ‰}$ ) falls within the  $\delta^{13}\text{C}$  range of marine sourced oil ( $-24 \text{ ‰}$  to  $-27 \text{ ‰}$ ) and is heavier than the  $\delta^{13}\text{C}$  values of non-marine oil ( $-30 \text{ ‰}$  to  $-32 \text{ ‰}$ ) (Table 2). The low TS content ( $0.03 \%$ ) of the Ashoknagar oil indicates a marine deltaic source.

**Table 2.** Carbon stable isotope ratio of published marine and non-marine oils.

	Area	$\delta^{13}\text{C}$ (‰)	
Marine Oil	Gulf of Mexico, offshore	$-26.5 \pm 0.7$	Chung et al., 1992
	Gulf of Mexico, onshore	$-26.9 \pm 0.6$	
	Gulf of Mexico, onshore	$-25.7 \pm 1.0$	
	Gulf of Mexico, onshore	$-24.8 \pm 0.6$	
	Scotian basin	$-25.6 \pm 0.1$	
	Avalon basin	$-25.6 \pm 0.1$	
	North Slope, Alaska	$-29.6 \pm 0.4$	
	North Slope, Alaska	$-30.4 \pm 0.4$	
	California	$-22.8 \pm 0.4$	
Non-Marine Oil	Crude oil-Duchesne field Utah	$-30$ to $-31$	Silverman et al., 1958
	Crude oil-Red Wash field, Utah	$-31.0$	
	Crude oil-Brennan Bottom field, Utah	$-30.6$	
	Crude oil-Flat Mesa field, Utah	$-31.7$	

The hydrogen stable isotope ratio is used for establishing oil-oil co-relationships and source rock evaluation, although hydrogen isotope exchange with surrounding environments during diagenetic and catagenetic processes influences the  $\delta^2\text{H}$  signature of oil. The hydrocarbon fraction shows a heavier  $\delta^2\text{H}$  signature due to thermal maturation (Ogbesejana et al., 2021). Further, the  $\delta^2\text{H}$  values of marine and non-marine source-derived oil show a range of  $-85\text{‰}$  to  $-252\text{‰}$  and  $-141\text{‰}$  to  $-163\text{‰}$ , respectively (Table 3). The  $\delta^2\text{H}$  value of Ashoknagar crude ( $-110\text{‰}$ ) falls within the  $\delta^2\text{H}$  signature of the marine sourced oil. The  $\delta^{34}\text{S}$  values of marine sourced crude oil vary between  $-12.5\text{‰}$  to  $14.7\text{‰}$ , whereas the  $\delta^{34}\text{S}$  value of non-marine crude oil is  $25\text{‰}$  (Table 4). The Ashoknagar crude oil  $\delta^{34}\text{S}$  value falls in the marine crude oil range.

**Table 3.** Published  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values of marine and non-marine oils (Yeh and Epstein, 1981).

	Location	$\delta^2\text{H}$ (‰)	$\delta^{13}\text{C}$ (‰)
Marine Oil	Choctaw, AL	-85	-25.0
	Mobile, AL	-88	-23.3
	Cook Inlet, AK	-132	-28.7
	Cook Inlet, AK	-137	-30.4
	N. Cook Inlet, AK	-130	-30.5
	Swanson River, AK	-133	-30.7
	North Slope, AK	-132	-29.9
	Kenai, AK	-252	-27.9
	Kern, CA	-132	-26.5
	San Joaquin, CA	-153	-29.7
	Los Angeles, CA	-132	-23.8
	Ventura, CA	-123	-23.1
	San Miguel, CO	-92	-28.8
	Fremont, CO	-144	-28.9
	Washington, CO	-144	-27.3
	Hendry, FL	-103	-27.4
	Hamilton, IL	-119	-29.5
	Bridgeport, IL	-125	-30.4
Non-Marine Oil	Uinta, UT	-149 to -163	-31 to -32
	Duchesne, UT	-141 to -156	-30 to -32

\*AL- Alabama, AK- Alaska, CA- California, CO- Colorado, FL- Florida, IL- Illinois and UT-Utah.

**Table 4.** Sulfur stable isotope signature of published marine and non-marine oils.

	Location	$\delta^{34}\text{S}$ (‰)	References
Marine Oil	Alabama and Mississippi (onshore)	-12.5 to 14.7	Wei et al. (2012)
Non-marine Oil	Uinta Middle Green River	28.2	Thode H. G. (1958)

## Conclusion

The  $\delta^{13}\text{C}$ ,  $\delta^2\text{H}$ , and  $\delta^{34}\text{S}$  signatures of Ashoknagar crude indicate a marine deltaic source of the oil. Further analyses are required to know the biodegradation level, source rock's origin and the depositional environments.



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