

RESEARCH COMMUNICATIONS

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Isotopic fractionation of Ni⁶⁰/Ni⁶¹ in kerogen and bitumen samples

Dewakar^{†,***}, K. N. Mishra[†], Kuldeep Chandra[†], J. Arunachalam* and D. Karunasagar*

[†]KDM Institute of Petroleum Exploration, 9, Kaulagarh Road, ONGC, Dehra Dun 248 195, India

*Centre for Chemical Characterization of Material, Bhabha Atomic Research Center, ECIL Post, Hyderabad, India

Isotopic ratio of Ni⁶⁰/Ni⁶¹ has been studied in kerogen and bitumen samples from three geologically and geographically different Indian petroliferous basins. It is observed that the ratio shows significant variation in kerogen and bitumen samples, which is specific to a basin and also depends upon type and nature of organic matter. This can be useful in oil source correlation and oil exploration.

Ni and V distribution in crude petroleum has been widely studied for the purpose of their correlation, deposition environment and migration-related changes¹⁻⁴. These elements are derived from chlorophyll compounds from the source material and are transferred to oil after its generation from sedimentary organic matter, i.e. kerogen⁵. Bitumen is the soluble organic matter present in the rocks and is the remaining petroleum left in the source rock, after the expulsion of generated petroleum. There have been no data on the isotopic fractionation of various isotopes of these elements in kerogen, bitumen and petroleum.

An attempt has been made to determine isotopic ratio of Ni⁶⁰/Ni⁶¹ in kerogen and bitumen samples and their effect on generation potential. Samples were selected from three geologically and geographically different petroliferous regions, basin A in the West, basin B in the east and basin C in the south of India. The results

obtained are very encouraging to demonstrate the utility of such studies in petroleum exploration.

Ni has five isotopes, viz. Ni⁵⁸, Ni⁶⁰, Ni⁶¹, Ni⁶² and Ni⁶⁴. Ni⁵⁸ is interfered with Fe⁵⁸, Ni⁶² has interference by CaO and Ni⁶⁴ is interfered by Zn⁶⁴. Therefore these isotopes cannot be studied for isotopic ratios. Natural abundance of the isotopes studied, i.e. Ni⁶⁰ and Ni⁶¹ is 26.1 and 1.13%, respectively, and the ratio is 23.097. Bitumen was extracted from the rocks/well cuttings by first crushing them to fine powder and then by Soxhlet extraction of 100 g of powdered rock with chloroform for 48 h. Kerogen was then separated from the bitumen-extracted rock sample by first destroying the inorganic matrix by treatment with dilute HCl and HF and then filtered. From the residue, which contains pyrite and other minerals along with kerogen, the kerogen was isolated by gravity separation, as per the procedure given by Saxby⁶. The samples of kerogen and bitumen were digested with ultra-pure nitric acid at 200°C on a hot plate until all the matter is dissolved and the solution becomes clear. The samples were analysed on Inductively Coupled Plasma Mass Spectrometer (ICP-MS), VG PlasmaQuad 3, fitted with a temperature-controlled double pass Scott type chamber and a Meinhard concentric nebulizer for sample introduction, at CCCM, BARC, Hyderabad. The spray chamber was cooled to 3°C using a water recirculating chiller. The operating conditions are given in Table 1. A laboratory standard containing 5 ppb and 10 ppb of total Ni was used for quantitative estimation of Ni⁶⁰ and Ni⁶¹, and was analysed for precision and standard deviation (Table 2).

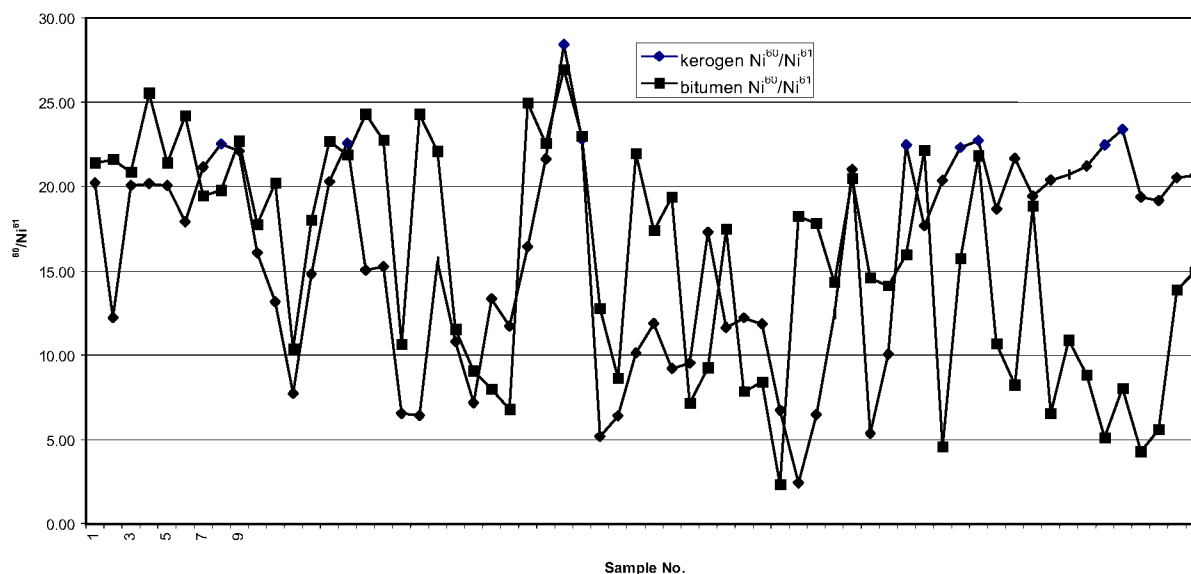
The distribution of Ni⁶⁰ and Ni⁶¹ is given in Table 3 and a plot of the ratio of Ni⁶⁰/Ni⁶¹ in kerogen and bitumen is shown in Figure 1. Sample nos 1 to 28 are from basin A, sample nos 29 to 45 are from basin B, and sample nos. 46 to 62 are from basin C. It is observed from the plot that in kerogen samples of basin C, the ratio is close to their natural abundance value (average value 20.76), but in bitumen the ratio is much less than the natural abundance value (average value 11.51). In basin B, both kerogen and bitumen samples show much lower values than their natural abundance values (average value, kerogen 9.97 and bitumen 13.63). In basin A, the samples show wide fluctuation in values, and in many of the samples the ratios are much lower than their natural abundance values (average value, kerogen 16.25, bitumen 19.44).

In basins A and B, there is positive syngenetic variation in the ratio between kerogen and bitumen. But in basin C this trend is reversed, i.e. there is negative sympathetic variation in comparison to basins A and B. The ratio in bitumen is higher when compared to its value in kerogen in basins A and B, except for a few samples. But in basin C, the ratio in bitumen is much lower than its value in kerogen.

***For correspondence.

Table 1. Operating conditions for the ICP-MS

ICP-MS system		Gas flow rates		Data acquisition conditions	
Instrument	VG PlasmaQuad 3	Coolant gas	13.4 l/min	Resolution	0.8
Torch type	Fassel	Auxiliary gas	0.83 l/min	Scan time per u	2 s
Forward power	1350 W	Nebulizer gas	0.43–0.63 l/min	Points per peak	3
Reflected power	<15 W	Sampler	1 mm Ni	Acquisition mode	Peak jump
		Skimmer	0.7 mm Ni		

**Figure 1.** Isotopic ratio of $\text{Ni}^{60}/\text{Ni}^{61}$ in kerogen and bitumen.**Table 2.** Precision and standard deviation in isotopic ratio measurement of $\text{Ni}^{60}/\text{Ni}^{61}$ in a standard sample

Concentration (ppb)			Ratio		
Ni	Ni^{60}	Ni^{61}	$\text{Ni}^{60}/\text{Ni}^{61}$		
5.0	1.142	0.050	22.710		
5.0	1.120	0.048	23.587	Average	24.293
5.0	1.136	0.044	25.583		
5.0	1.350	0.054	24.920	Standard deviation	
5.0	1.413	0.056	25.361		1.130
10.0	2.479	0.096	25.847		
10.0	2.461	0.108	22.896	Average deviation	
10.0	2.801	0.114	24.588		0.967
10.0	2.504	0.104	24.011		
10.0	2.385	0.102	23.428	Precision	3.979 (%)

It is also observed that the ratio in kerogen is higher in basin C when compared to basins A and B. In basin C, organic matter has been deposited in older formation, i.e. Mesozoics, while in basins A and B it has been de-

posited in Tertiary sediments. In general, organic geochemical studies indicate that organic matter in basins A and B is of better quality, and is considered good for hydrocarbon generation.

Ni and V in petroleum are present in porphyrins or between the asphaltene sheets. Ni and V are incorporated in porphyrins by replacing Mg or Fe present originally. This exchange takes place during early diagenesis of organic matter⁷. Isotopic fractionation of Ni^{60} or Ni^{61} in kerogen and bitumen is therefore taking place either due to their different natural abundance in different geological ages, e.g. Mesozoic and Tertiary, or due to thermodynamic stability of compounds they are associated with, or both. The fractionation in isotopes of Ni in kerogen and bitumen may also be dependent on the type of organic matter, which is quite different in basin C and is deposited in older rocks. It is also possible that isotopes of Ni in kerogen or bitumen are getting fractionated during formation of bitumen from kerogen, wherein one or the other isotope is either working as catalyst or compounds associated with one of the isotopes are decomposed preferentially.

Table 3. Distribution of Ni⁶⁰ and Ni⁶¹ along with their ratio in kerogen and bitumen

Serial no.	Sample no.	Basin	Concentration (ppm)				Ratio	
			Kerogen		Bitumen		Kerogen	Bitumen
			Ni ⁶⁰	Ni ⁶¹	Ni ⁶⁰	Ni ⁶¹	Ni ⁶⁰ /Ni ⁶¹	Ni ⁶⁰ /Ni ⁶¹
1	C1	A	25.38	1.26	22.01	1.03	20.19	21.40
2	C2	A	2.25	0.18	9.29	0.43	12.20	21.59
3	C3	A	1.83	0.09	2.73	0.13	20.04	20.84
4	C4	A	1.57	0.08	1.58	0.06	20.16	25.52
5	C5	A	8.31	0.41	8.17	0.38	20.04	21.38
6	C6	A	6.35	0.36	6.18	0.26	17.89	24.18
7	C7	A	9.92	0.47	18.75	0.96	21.13	19.44
8	C8	A	3.68	0.16	2.11	0.11	22.51	19.76
9	C9	A	7.81	0.35	24.33	1.07	22.09	22.68
10	C11	A	1.03	0.06	1.28	0.07	16.04	17.74
11	C12	A	7.25	0.55	3.10	0.15	13.14	20.19
12	C13	A	2.15	0.28	0.62	0.06	7.70	10.37
13	C14	A	2.83	0.19	1.02	0.06	14.79	17.99
14	C15	A	16.93	0.84	20.28	0.89	20.27	22.67
15	C16	A	9.20	0.41	5.39	0.25	22.57	21.88
16	C17	A	14.93	0.99	12.95	0.53	15.02	24.28
17	C18	A	10.74	0.71	6.30	0.28	15.23	22.74
18	C19	A	1.36	0.21	0.27	0.03	6.52	10.62
19	C20	A	2.58	0.40	4.35	0.18	6.39	24.26
20	C21	A	13.99	0.90	9.13	0.41	15.54	22.07
21	C22	A	4.23	0.39	4.81	0.42	10.77	11.51
22	C23	A	3.44	0.48	4.07	0.45	7.15	9.04
23	C24	A	6.18	0.46	9.27	1.17	13.32	7.95
24	C25	A	3.21	0.27	2.74	0.40	11.70	6.76
25	C26	A	14.67	0.89	36.91	1.48	16.41	24.94
26	C27	A	18.64	0.86	54.66	2.42	21.61	22.56
27	C28	A	23.59	0.83	85.53	3.18	28.41	26.93
28	C29	A	17.32	0.76	9.13	0.40	22.80	22.97
29	A1	B	4.46	0.86	0.81	0.06	5.16	12.74
30	A2	B	0.50	0.08	0.18	0.02	6.37	8.62
31	A3	B	1.19	0.12	2.06	0.09	10.11	21.94
32	A4	B	1.39	0.12	0.41	0.02	11.85	17.37
33	A5	B	2.95	0.32	2.99	0.15	9.19	19.36
34	A7	B	1.64	0.17	0.99	0.14	9.51	7.11
35	A8	B	1.45	0.08	0.70	0.08	17.29	9.24
36	A9	B	2.61	0.22	1.04	0.06	11.61	17.45
37	A10	B	4.45	0.37	0.19	0.02	12.18	7.83
38	A11	B	5.87	0.50	0.68	0.08	11.82	8.38
39	A12	B	38.43	5.73	0.06	0.02	6.71	2.28
40	A13	B	0.07	0.03	1.02	0.06	2.40	18.23
41	A14	B	3.52	0.55	0.45	0.03	6.45	17.79
42	A15	B	1.05	0.08	0.90	0.06	12.42	14.30
43	A16	B	0.36	0.02	0.52	0.03	20.99	20.45
44	A17	B	17.32	3.25	0.98	0.07	5.33	14.56
45	A19	B	1.05	0.10	0.38	0.03	10.02	14.09
46	K1	C	13.47	0.60	10.31	0.65	22.45	15.94
47	K2	C	13.89	0.79	56.53	2.56	17.66	22.12
48	K3	C	7.20	0.35	0.94	0.21	20.34	4.53
49	K5	C	7.31	0.33	5.70	0.36	22.30	15.71
50	K6	C	10.75	0.47	55.04	2.52	22.71	21.81
51	K7	C	10.17	0.55	3.03	0.28	18.65	10.65
52	K8	C	11.46	0.53	2.79	0.34	21.64	8.21
53	K10	C	11.14	0.57	26.59	1.41	19.41	18.83
54	K11	C	9.71	0.48	2.23	0.34	20.37	6.52
55	K13	C	8.71	0.42	1.23	0.11	20.69	10.86
56	K15	C	5.45	0.26	1.65	0.19	21.19	8.81
57	K16	C	7.90	0.35	1.62	0.32	22.45	5.08
58	K17	C	8.69	0.37	1.41	0.18	23.37	8.01
59	K18	C	4.68	0.24	2.97	0.70	19.34	4.26
60	K19	C	4.56	0.24	0.09	0.02	19.15	5.57
61	K21	C	16.52	0.81	2.78	0.20	20.51	13.85
62	K22	C	8.51	0.41	1.35	0.09	20.63	14.93
Average ratios:			Basin A	Basin B	Basin C			
Kerogen			16.25	9.97	20.76			
Bitumen			19.44	13.63	11.51			

These observations are yet to be correlated with other geochemical data, but the study certainly indicates a relationship between nickel isotopic ratio, geological history and type of organic matter.

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Coral bleaching and mortality in three Indian reef regions during an El Niño southern oscillation event

Rohan Arthur

Centre for Ecological Research and Conservation, 3076/5, IV Cross, Gokulam Park, Mysore 570 002, India

The 1997–1998 El Niño Southern Oscillation (ENSO) event, which elevated Sea Surface Temperatures (SSTs) of tropical oceans by more than 3°C, was one of the most extreme ENSO events in recent history. Such increases in SSTs above the seasonal average can trigger widespread bleaching in coral reefs. This study examined bleaching in three Indian coral reef regions in relation to SSTs using quantitative rapid assessment methods between April and July, 1998. The Gulf of Kutch reefs showed an average of 11% bleached coral with no apparent bleaching-related mortality. In contrast, bleached coral comprised 82% of the coral cover in lagoon reefs of Lakshadweep and 89% of the coral cover in the Gulf of Mannar reefs. Bleaching-related mortality was high – 26% in Lakshadweep and 23% in Mannar. The coral mass mortality may have profound ecological and socio-economic implications and highlights the need for sustained monitoring for coral reef conservation in India.

ECOLOGISTS have long been concerned and fascinated with large-scale disturbances that affect coral reefs. Storms and unusually prolonged low tide events, crown-of-thorns starfish (*Acanthaster planci*) outbreaks, coral

disease epidemics, and elevated seawater temperatures often cause dramatic reductions in coral populations and have far-reaching consequences for their coral reef environments^{1,2}.

The El Niño Southern Oscillation (ENSO) warm water ocean current system of 1997–1998 created a nearly pan-tropical band of warm water and brought in its wake a spate of global climatic and ecological changes. The magnitude of the ENSO event, perhaps the most severe on record³, is implicated as the primary cause of mortality of coral in reef ecosystems across the world⁴.

Elevated Sea Surface Temperatures (SSTs) caused by ENSO are known to cause coral stress and mortality through a phenomenon known as bleaching^{1,5}. Bleaching is a rapid loss of pigmentation of coral, leading to a whitening of the colony. This is a generalized stress response of scleractinian coral, caused by the expulsion of photosynthetic symbiont zooxanthellae by the polyp, or by a severe reduction in the photosynthetic activity of resident zooxanthellae⁶. Bleaching is often a normal, non-lethal response to seasonal variation in water temperatures⁷, and coral regain photosynthetic algae when conditions improve. If bleaching is severe and prolonged, however, the coral may die, often due to secondary stresses⁸. While elevated SSTs have been implicated as the main agent of coral bleaching, increased irradiance, reduced salinity, bacterial infection, and decreased water temperatures have also been known to induce similar responses in coral^{5,9}.

Mass bleaching was first recorded on Pacific coral reefs in 1984 (ref. 10) and has since also been noticed in other tropical reefs. It appears to be well correlated with changes in SSTs and, in El Niño years, the frequency of bleaching events in coral reefs increases dramatically^{11,12}. The 1998 ENSO resulted in varying degrees of coral bleaching and mortality in reefs throughout the Indo-Pacific tropics and several programmes have been set up to monitor reef degradation and recovery processes.

Indian coral reefs have not received the same attention because of the lack of field research in coral reefs of the country. Major reef areas exist in India in the Gulf of Kutch, the Lakshadweep, Gulf of Mannar, and the Andaman and Nicobar islands^{13,14}. Ravindran and others¹⁵ surveyed some of these reef areas and report heavy bleaching of coral in the Andamans (in July 1998), but their surveys of Lakshadweep reefs (between April 1996 and February 1998), did not record high bleaching. This survey, conducted when abnormal sea surface temperatures had begun to affect Indian reef areas, was specifically geared towards rapidly assessing the impact of the 1998 El Niño event on the Gulf of Kutch, Lakshadweep, and Gulf of Mannar. I looked for differences in the effects of bleaching on various benthic components and different lifeforms of coral. *In situ* stud-

e-mail: arthur@ncf-india.org