

Redox structure of Vindhyan hydrosphere: clues from total organic carbon, transition metal (Mo, Cr) concentrations and stable isotope ($\delta^{13}\text{C}$) chemistry

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Trace metal concentration in black shales can hold valuable information regarding ancient deep-ocean redox state. The size of marine reservoir of redox-sensitive elements (particularly molybdenum and chromium) is principally controlled by the extent of anoxicity in marine conditions following the onset of oxidative weathering post Great Oxygenation Event (~2.5–2.3 Ga). Hence, it is considered that coupled analysis involving redox-sensitive element/s and primary organic productivity (total organic carbon) may provide a clue for redox behaviour of ancient deep ocean. Here, we use the redox behaviour of Mo and total organic carbon values of Vindhyan shales to show that the Vindhyan hydrosphere although initiated as a stratified sea with anoxic and sulphidic deep water as exemplified by the geochemical character of the Arangi Shale, the extent and veracity of anoxicity and euxinic was never pervasive. It further suggests that the Vindhyan hydrosphere developed euxinic deep water only during deposition of Arangi, Rampur and Bijaygarh black shale and was anoxic but certainly not euxinic during Koldaha and Rewa sedimentation. The low concentration of Mo and Cr, in general, in argillaceous intervals suggests that the Vindhyan Sea behaved as a moderate Mo and depleted Cr reservoir. The consistent low concentration of Cr within the Vindhyan shales also suggests restriction in the availability of Cr in the water column in the absence of any significant detrital supply of Cr at very low atmospheric oxygen level (<0.1% PAL; present atmospheric level).

Keywords: Hydrosphere, primary organic productivity, total organic carbon, transition metals, stable isotope chemistry.

BEGINNING with a bang, i.e. the Great Oxygenation Event (GOE) between 2.5 and 2.3 Ga, oxygenation of the atmosphere has played a pivotal role behind some profound

and irreversible changes in the earth's history that include oxygenation of the hydrosphere, and advent and diversification of multicellular life. From proxies, e.g. occurrence of detrital uraninite and pyrite, absence of red bed and mass-independent fractionation of sulphur isotope value in sulphides and sulphates, it is inferred that the early ocean–atmosphere system was reduced in nature. With the introduction of O_2 in the earth's atmosphere during the early Proterozoic (2.5–2.3 Ga), oceans started getting oxygenated on a global scale, though the oxic character principally remained restricted to the near-surface only¹. It is widely believed that the deep ocean remained anoxic² and/or euxinic for a fair part of the Proterozoic. This connotation, however, did not go without debate, particularly with regard to the scale of deep ocean euxinic and its extent in the basin-/global-scale. Record of redox-sensitive transition metals, viz. molybdenum and chromium from the Proterozoic chemical sedimentary record cast doubt on global-scale ocean anoxia³. Indeed, it is difficult to decipher hydrosphere redox structure in the absence of remnant seafloor and overlying sediment cover of the concerned time period since the onset of subduction as early as in the Eoarchean⁴.

Assessment of total organic carbon (TOC) from Proterozoic shale formations has received wide attention in recent times in connection with burial of organic matter vis-à-vis as a driving force for early oxygenation of atmosphere and hydrosphere. Sequestration of organic matter is considered as one of the most powerful positive feedback processes behind the increase of oxygen flux in the atmosphere by several times compared to its decrease by the decay of organic matter. In addition to the evaluation of scale of oceanic productivity, its variation through time, and TOC values also allow us to evaluate any argillaceous strata in terms of their hydrocarbon source rock potential. Extremely high positive $\delta^{13}\text{C}$ value (~10‰) in ~2.3 to 2.1 Ga carbonates (Lomagundi event)⁵ is interpreted as a signature of greatly enhanced organic matter burial in oceanic sediment in very low $p\text{O}_2$ condition that triggered significant increase in oxygen pressure

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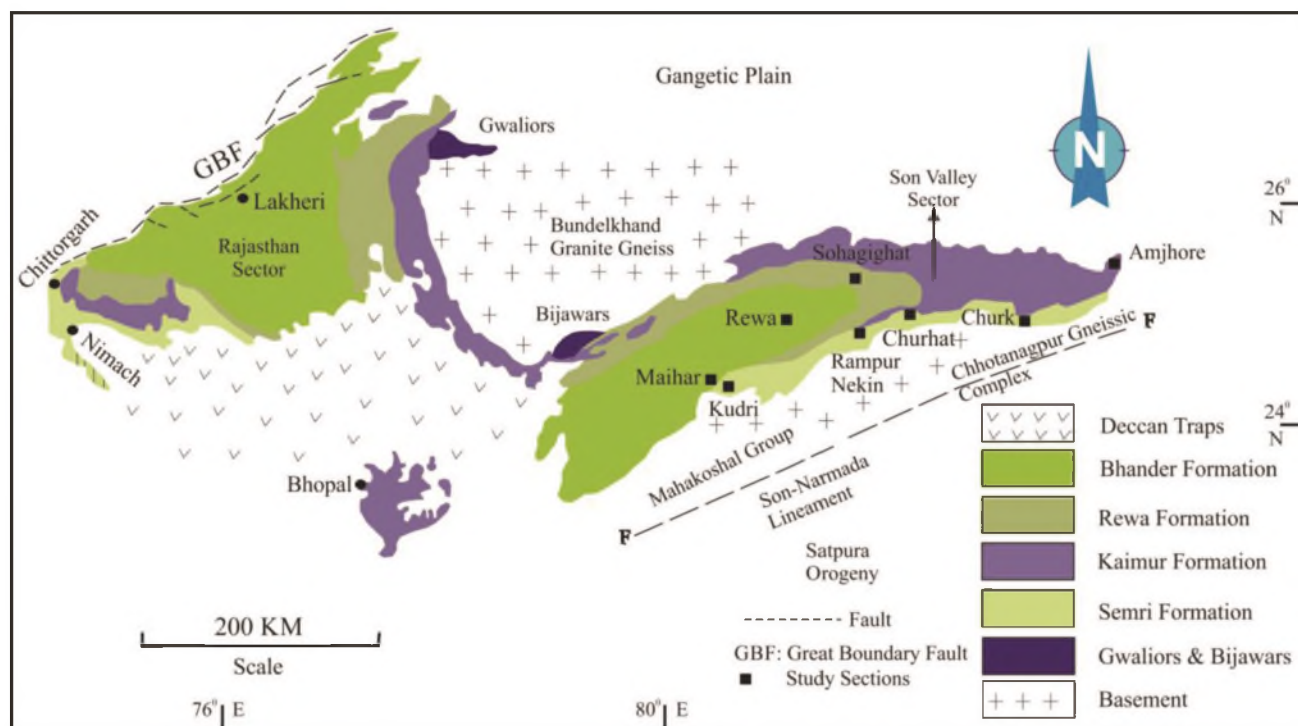


Figure 1. General geological map of the Vindhyan basin (modified after Krishnan and Swaminath⁴⁰) showing disposition of lithostratigraphic formations within the Son valley and Rajasthan sectors. Black squares represent locations of studied shale sections within the Son valley.

in the atmosphere. In this backdrop, the present study is aimed at understanding the scale of deep ocean anoxicity/euxinicity from a study of redox-element (Mo, Cr) geochemistry, organic matter stable isotope ($\delta^{13}\text{C}$) geochemistry and TOC values of Vindhyan shales deposited below storm wave base.

Background of the study area

Opening of the Vindhyan basin in riftogenic mode⁶, recurrent occurrence of thick shale successions, in some cases exceeding a thickness of ~150 m (refs 7, 8) (Figure 1) and presence of slide, slump and mass flows within Koldaha Shale, Sirbu Shale and Lakheri Limestone formations^{9,10} bear undoubted indication of discrete episodes of tectonic perturbation and basin subsidence through the depositional history of the basin. In addition, presence of thick porcellanite in the lower Vindhyan¹¹⁻¹³, kimberlite pipe intrusion within the Kaimur Formation and occurrence of volcanoclastics, though in subordinate volume, within the upper Vindhyan succession¹⁴ convey signature of thermal agility of the basin all through its depositional history. Occurrence of stromatolites and bountiful evidence of microbial mat proliferation from different stratigraphic levels through the basin succession^{15,16} amply support the contention of organic productivity in the basin and thereby, makes the basin lithopackage useful for understanding hydrosphere redox condition. As it is

widely believed that unlike modern open ocean basins, Proterozoic basins were epeiric/epicratonic in character¹⁷, we refer to the term 'deep sea' here as a part of the sea below storm wave base. Samples for the present study were collected from all argillaceous intervals, viz. Arangi, Koldaha, Rampur, Bijaygarh, Rewa and Sirbu and, in particular, from the facies variant of these shale intervals which represent distal shelf below storm wave deposition.

Results and discussion

The marked concentration of iron formation in the Palaeoproterozoic era (>1.8 Ga) has been traditionally construed as a proxy for oxidation of deep ocean¹⁸. The idea is contested by Canfield and co-workers^{1,19-21} with the notion that the deep ocean became sulphidic instead of oxic with oxygenation of the atmosphere. Increase in continental weathering of sulphide minerals with a rise in atmospheric oxygen pressure led to the supply of more reactive sulphate ions in the marine realm, where sulphate-reducing bacteria responded with a reduction of sulphate (bacterial sulphate reduction, BSR) and formation of pyrite, thus stripping the seawater of iron. In fact, a stratified oxic-sulphidic ocean model (also referred to as 'Canfield' ocean)²⁰⁻²² was invoked in the post-1.8 Ga period that received support from studies involving oxygen-responsive C-S-Fe systematics, Mo and Cr isotope data and

biomarker signatures; an oxidized surface layer has been envisaged above deep sulphidic, euxinic layer^{1,19,23,24}. The model, though acknowledged by many, received rebuttal from some corners because of limited isotopic variability in sedimentary sulphides and suppressed isotopic fractionation at extremely low sulphate concentration (5%–15% of modern values). However, these models leave some questions unanswered, which include the degree and extent of anoxicity in Proterozoic oceans and its biological implication in terms of sequestration of redox-sensitive bioessential transition metals, viz. Fe and Mo, essential as micronutrients for life.

The strength of Mo as a tracer of oxygenation history is acknowledged because of its unique bimodal geochemical character. Primary supply of Mo in the ocean is as molybdate (MoO_4^{2-}) by riverine supply²⁵ and because of its long residence in oxygenated sea, its concentration becomes greater with time than any other transition element in seawater. One major sink of Mo in oceanic realm is sulphidic setting, where molybdate is converted to thiomolybdate ($\text{MoO}_x\text{S}^{4-x^{2-}}$) and gets removed by organic matter²⁶. A similar approach can be applied using other reduced metals such as Cr, which usually gets buried under anoxic conditions without any requirement of free sulphide. Chromium is promptly reduced from Cr(VI) to Cr(III) under the influence of ferrous iron in suboxic to anoxic condition and thereby becomes immobile and insoluble^{27,28}. Therefore, Mo and Cr concentrations in argillaceous facies, viz. shale may offer good proxy for anoxic/euxinic condition of deep sea and offer a defining perspective on the redox landscape of Proterozoic ocean. Since the Vindhyan Supergroup registers a depositional history exceeding 600 Ma (1631 ± 5 Ma; U–Pb zircon age from porcellanite in Lower Vindhyan and ~ 1000 Ma, U–Pb detrital zircon age from Upper Bhandar sandstone)^{13,29}, mapping of Mo, Cr and TOC data from argillaceous intervals through the entire basin succession is considered a unique opportunity to understand redox structure of the Vindhyan Sea through late Palaeoproterozoic–Mesoproterozoic time. Further, to substantiate inference on the basis of TOC and transition metal concentration, the study also examined carbon isotopic composition of organic matter from the shale intervals. Studies on carbon isotope ($\delta^{13}\text{C}$) composition of organic matter have established the role of environmental CO_2 and temperature on photosynthetic isotope effect³⁰ and thereby, potential of variability in organic matter $\delta^{13}\text{C}$ data as a tool to decipher relative oxygen pressure in the hydrosphere. Hence, to achieve the desired objective, the present study took into purview TOC, Mo and Cr analyses of all shale intervals of the Vindhyan lithopackage, viz. Arangi, Koldaha, Rampur, Bijaygarh, Rewa and Sirbu exposed in the Son valley, central India except poorly exposed Ganurgarh Shale of the Upper Vindhyan. In addition, carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) measurements were carried out on organic matter separated from shale intervals,

viz. Koldaha, Rewa and Sirbu shales. However, reproducible results could not be generated from organic matter of Rampur and Bijaygarh shales because of their high pyrite content and hence, are not reported here.

Mo and Cr concentration and TOC values measured from shale intervals are plotted using horizontal bars in Figure 2, along with Mo/TOC values (Tables 1 and 2). Low Mo (0.2–76.6 ppm), low Mo/TOC (0.34–17.67 ppm per wt% TOC) and low Cr (54–159 ppm) characterize Vindhyan shales, irrespective of their stratigraphic status. Although most Mo values are below 20 ppm, samples from Bijaygarh Shale (three samples analysed) and Rampur Shale recorded comparatively high Mo (>15 ppm, up to 56 ppm) and Mo/TOC values (9–17 ppm Mo per wt% TOC). It is worth mentioning that samples with higher Mo values show presence of pyrite. Also, the generated data were collated against the available literature data from Proterozoic black shale successions around the globe (refs 3, 31 and references therein) (Figure 3 a and b). Figure 4 illustrates a comparative view on $\delta^{13}\text{C}_{\text{org}}$ values (Table 3) obtained from organic matter in Koldaha, Rewa and Sirbu shales. Whereas $\delta^{13}\text{C}_{\text{org}}$ values in organic matter from the Koldaha and Rewa shales range from -28.5‰ to -32.9‰ and from -32.1‰ to -32.9‰ respectively; values obtained from organic matter of Sirbu Shale are significantly enriched and vary between -23.19‰ and -25.30‰ . A clear $\sim 3\text{‰}$ enrichment in $\delta^{13}\text{C}_{\text{org}}$ values can be observed within organic matter from the Sirbu Shale.

In order to draw inference from the obtained data on degree and extent of anoxicity/euxinic in the deeper part of the Vindhyan Sea, clue is sought from modern examples so as to reverse engineer and draw correlation with hydrosphere redox structure that prevailed during the Proterozoic. In contrast to the existence of numerous euxinic basins in geological records from where black shales, often with pyrite, are reported, there are only a few examples of euxinic basins today; the Black Sea and Caraico basin (Venezuela) are two major modern examples. It is observed from modern basins that Mo removal in the presence of organic matter and other reduced substances is faster than that of oxygenated water column by a factor of 200–5000 (ref. 3). This is exemplified by depletion of Mo in the water column of the Black Sea and low Mo/TOC value compared to other oxygenated ocean basins³². In sulphidic ocean, preferential removal of Mo by organic matter and sulphide phases as thiomolybdate or tetra-thiomolybdate cause its stripping from ocean water column resulting in relatively high Mo content within marine shales. Considering sulphidic condition as the major cause behind persistent ocean euxinic, it may be conceived that low Mo and low Mo/TOC values in shales are signals that non-sulphidic deep ocean condition was dominant in depositional history of the Vindhyan Sea. However, according to Scott *et al.*³, the concentration of dissolved Mo in Proterozoic ocean remained less than

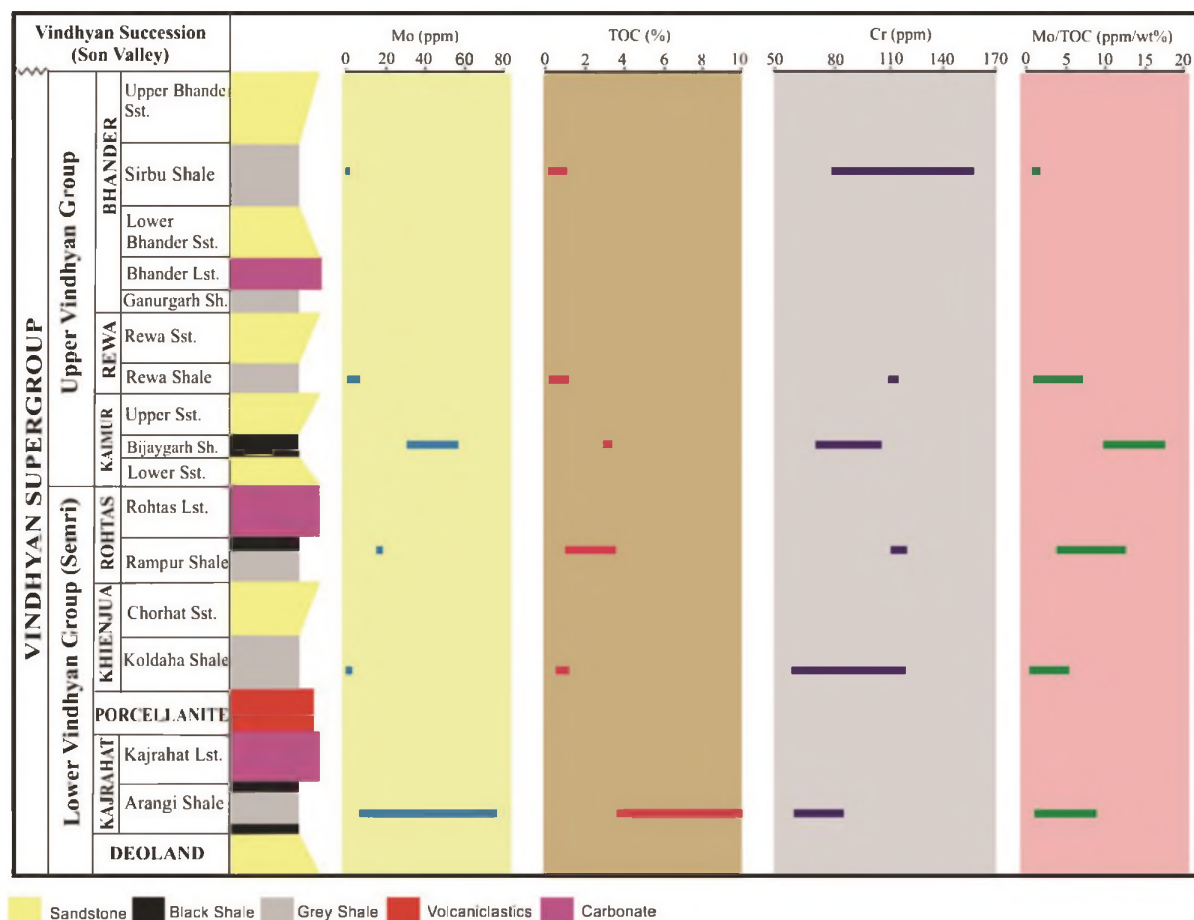


Figure 2. A composite stratigraphy of the Vindhyan Supergroup exposed at the Son valley. Compositional ranges (horizontal bars) of Mo, TOC, Cr and Mo/TOC ratio within the studied shale formations are also shown. Note consistent low concentration of Mo, Cr and low Mo/TOC ratio, but high TOC values within black shale units.

Table 1. Mo (ppm), TOC (%) and Mo/TOC (ppm/wt%) concentration of Vindhyan shales

Formation	Sample	Mo	TOC	Mo/TOC
Sirbu Shale	N7-28	0.6	0.67	0.88
	N8-29	0.2	0.55	0.36
	N9-29	0.6	0.36	1.66
	SBS-6	0.6	0.72	0.83
	SBS-8	0.8	1.07	0.74
Rewa Shale	PS-3	0.5	0.55	0.90
	PS-4	6.2	0.84	7.38
	PS-5	0.3	0.68	0.44
Bijaygarh Shale	BGS-1	56.1	3.20	17.52
	BGS-2	54.6	3.08	17.67
	BGS-3	30.64	3.15	9.72
Rampur Shale	BS-1	15.1	3.62	4.16
	BS-2	18.2	1.45	12.5
Koldaha Shale	KSK-1	0.8	0.86	0.92
	KSK-2	0.2	0.57	0.34
	KSK-3	2.4	0.44	5.39
	KSK-4	0.5	0.48	1.02
Arangi Shale	B-30	76.6	8.43	9.08
	B-31	10.5	8.18	1.28
	B-33	7.17	4.4	1.62
	B-36	16.64	6.9	2.41

10–20% of the modern ocean value for ~800 My following initiation of Mo cycling with GOE and hence, poor Mo concentration may not be entirely because of sulphidic deep ocean condition but because of low supply by the river system. Assessing the degree of iron pyritization, Raiswell *et al.*³³ suggested that only 10% increase in sulphidic pore water is sufficient for depletion of ocean Mo reservoir by 90% in ~200,000 years. In this backdrop, the overall low Mo and low Mo/TOC values in Vindhyan shales (Figure 3 *a* and *b*) corroborate well with the global trend and go against the view of extensive sulphidic deep ocean in the Proterozoic, as proposed by Canfield and co-workers^{1,19–21}. Only the Arangi Shale, Rampur Shale and Bijaygarh Shale formations, where relatively high Mo concentration, high TOC and incidence of sulphide mineral pyrite are recorded, bear undoubted indication of development of deep-basin anoxicity vis-à-vis sulphidic condition with coupled burial of Mo and organic carbon.

The inference, however, not in tandem with very low to low Cr concentration, points to lower than the average crustal value (Figure 5), recorded in its shales (Table 2). Subject to availability of Cr(VI) in the water column,

Table 2. Cr (ppm) and Ti (ppm) content of Vindhyan shales units

Formation	Sample	Cr (ppm)	Ti (ppm)	Formation	Sample	Cr (ppm)	Ti (ppm)
Sirbu Shale	N-1/28	146	5698.61	Rampur Shale	BGS-7	70	6523.41
	N-2/28	109	5623.63		RN1	116.48	5398.68
	N-3/28	105	4573.88		RN2	117.55	2924.28
	N-4/28	88	5023.77		RN3	118.47	3899.05
	N-5/28	82	4198.97		RN4	115.89	4498.90
	N-6/28	112	5548.65		BS1	114	2324.43
	N-7/28	80	4723.85		BS2	112	5323.70
	N-8/28	80	5023.77		BS3	117	4348.94
	N-9/28	101	4948.79		RS1	116	5923.55
	N-10/28	95	4423.92		RS2	112	6223.48
Rewa Shale	SS-1	131	4273.96	Koldaha Shale	RS3	110	6148.50
	SS-2	78	4948.79		KSK1	116.66	5848.57
	SS-3	86	5473.66		KSK2	114.02	6673.37
	SS-4	93	5248.72		KSK3	114.72	6673.37
	SS-5	97	5398.68		KSK4	114.02	6823.34
	SBS-3	83	5098.76		KSK5	114.43	6223.48
	SBS-4	101	4948.79		KS1	110.23	4648.86
	SBS-5	139	4798.83		KS2	112.32	6748.35
	SBS-6	124	5248.72		KS3	114.52	6673.37
	SBS-7	84	5398.68		KS4	115.62	6898.32
Bijaygarh Shale	SBS-8	91	4873.81	GS1	84	3974.03	
	SBS-9	99	5173.74	GS2	58	4049.01	
	SBS-10	159	4648.86	GS3	56	3974.03	
	PS1	113.25	5398.68	GS4	54	3899.05	
	PS2	109.35	6223.48	GS5	56	3749.08	
	PS3	112.6	7798.10	GS6	67	3974.03	
	PS4	112.5	7198.25	GS7	57	4049.01	
Bijaygarh Shale	PS5	111.76	9372.72	GS8	74	4049.01	
	PS6	113.47	9297.73	KDS0	86	3824.07	
	JS1	113.12	9522.68	KDS1	85	3974.03	
	BGS-1	106	5473.66	KDS2	104	3899.05	
	BGS-2	89	5998.54	KDS3	103	4049.01	
	BGS-3	85	5698.61	Arangi Shale	B31	61	2056.46
BGS-4	102	5548.65	B32		70	3081.75	
BGS-5	84	5398.68	B34		85	2593.73	
BGS-6	79	6073.52	B35	79	2408.74		

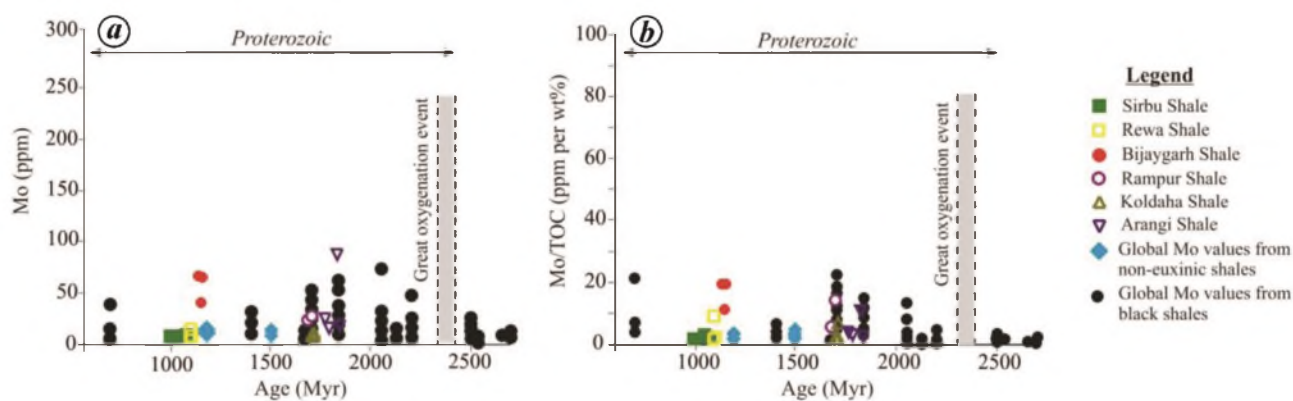


Figure 3. (a) Mo and (b) Mo/TOC values of Vindhyan shales in the backdrop of corresponding values from euxinic organic-rich shales (black circles) reported from different parts of the globe during the Proterozoic era³. Note consistent low Mo and low Mo/TOC values in the Vindhyan shales except for some samples from the Arangi and Bijaygarh shales. The shaded area refers to the Great Oxygenation Event as defined by sulphur isotope data. Ages of Vindhyan shales are approximated based on available geochronologic dates from the basin.

sequestration of Cr is likely in anoxic water in the form of immobile Cr(III). The low Cr concentration in Vindhyan shales despite inferred anoxic character of deep wa-

ter may possibly be because of low Cr availability in the water column. Verification of the contention has been made from the mutual relation between Cr and Ti;

Vindhyan shales, irrespective of their stratigraphic position, record lack of any linear relationship between Cr and Ti (Figure 5); Cr/Ti values range from 1.19×10^{-2} to 4.90×10^{-2} , with an average of 2.12×10^{-2} . A linear relationship between Cr and Ti enrichment in marine sediments is interpreted as proxy for detrital input^{31,34} and signature of soluble Cr(VI) oxyanion release by oxidation of terrestrial, soil-bound Cr(III) in the presence of Mn oxide and free atmospheric O₂. Low Cr concentration and lack of Cr–Ti relationship in Vindhyan shales rule out any significant detrital Cr influx in the course of Vindhyan sedimentation; instead, observed Cr values are interpreted as a result of authigenic enrichment (cf. Cole³⁵).

Sarkar *et al.*²⁴, on the basis of heavy $\delta^{34}\text{S}$ values ($25.5 \pm 8.7\text{‰}$; $n = 42$) in sedimentary pyrites from the

Bijaygarh Shale Formation, surmized stratified water column for the Vindhyan Sea with anoxic and sulphidic deep water. Trace element (Mo) geochemistry and TOC analysis carried out in the present study strengthen the contention for the periods of Arangi, Rampur and Bijaygarh Shale deposition. At the same time, the present data raise a big question on extending the hypothesis to the entire Vindhyan sedimentation history and considering it as over-generalization. Low Mo (Koldaha, 0.2–2.4 ppm; Rewa, 0.3–6.2 ppm), absence of sulphide mineral and relatively low TOC content in Koldaha Shale (0.44–0.86%) and Rewa Shale (0.55–0.84%) bear clear indication of deposition under non-euxinic basinal condition. Further, very low Mo concentration, low TOC sequestration and $\sim 3\text{‰}$ enrichment in average $\delta^{13}\text{C}$ value of Sirbu

Table 3. $\delta^{13}\text{C}_{\text{org}}$ concentration (‰) of organic matter from Koldaha, Rewa and Sirbu shales

Formation	Sample code	$\delta^{13}\text{C}_{\text{org}}$ (‰)
Sirbu Shale	N-1/28	-25.30
	N-2/28	-24.10
	N-3/28	-22.75
	N-4/28	-23.74
	N-5/28	-24.98
	N-6/28	-25.12
	N-7/28	-24.43
	N-8/28	-25.11
	N-9/28	-24.45
	N-10/28	-24.92
Rewa Shale	SS-1	-24.54
	SS-2	-24.18
	SS-3	-23.20
	SS-4	-23.75
	SS-5	-23.82
	SBS-3	-25.03
	SBS-4	-23.19
	SBS-5	-23.35
	SBS-6	-23.68
	SBS-7	-23.80
Koldaha Shale	SBS-8	-25.08
	SBS-9	-24.86
	SBS-10	-23.83
	PS-3	-32.1
	PS-4	-32.9
	PS-5	-31.2
	KSK-1	-32.9
	KSK-2	-32.4
	KSK-3	-32.2
	KSK-4	-32.0
GS-1	-31.2	
GS-2	-31.3	
GS-3	-31.4	
GS-4	-31.6	
GS-5	-29.9	
GS-6	-32.0	
GS-7	-30.0	
GS-8	-32.4	
KDS-0	-28.5	
KDS-2	-30.3	
KDS-3	-29.5	

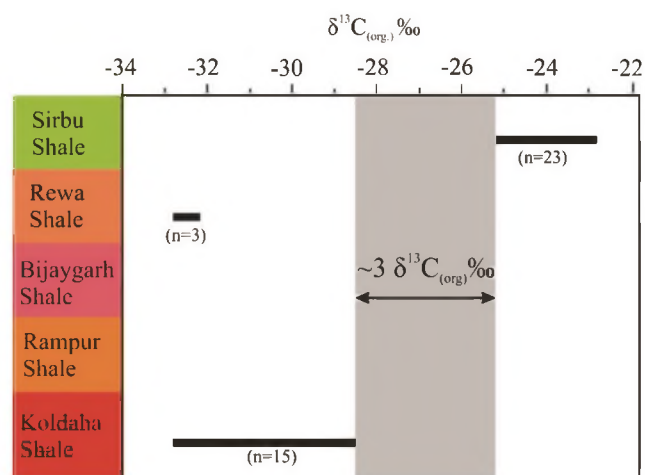


Figure 4. Range of $\delta^{13}\text{C}_{\text{org}}$ values (horizontal bars) obtained from organic matter of Koldaha, Rewa and Sirbu shales. Note a significant $\sim 3\text{‰}$ enrichment of $\delta^{13}\text{C}_{\text{org}}$ value in organic matter from the Sirbu Shale.

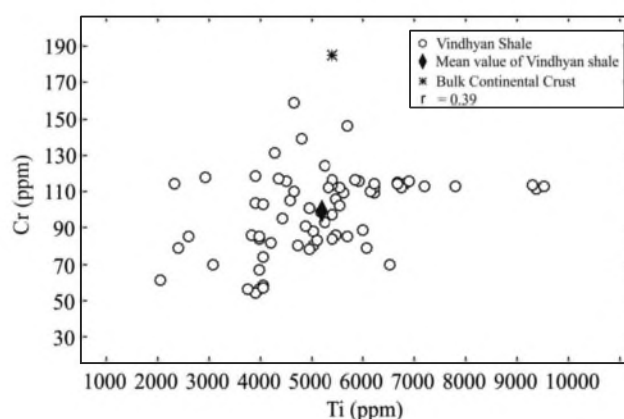


Figure 5. Scatter plot involving Cr (ppm) and Ti (ppm) from Vindhyan shales (open circles), irrespective of their stratigraphy. Mean concentration and concentration in bulk continental crust are shown as black diamond and asterisk. Note consistent, very low Cr concentration, lower than the concentration in bulk continental crust (BCC)⁴¹ and poor correlation ($r = 0.39$) between Cr and Ti.

Shale organic matter in comparison to organic matter of Koldaha and Rewa Shale formations bear indication for near-oxic hydrosphere condition at the time of Sirbu Shale deposition. Several studies have demonstrated isotope fractionation and change in bulk carbon isotope composition during oxidation of organic matter^{36,37}. Preferential removal of ¹²C by bacterial and inorganic oxidation processes lead to increase in ¹³C content of residue to the tune of 2–3‰, as observed in the weathering profile by Clayton and Swetland³⁸. Similar changes in organic matter $\delta^{13}\text{C}_{\text{org}}$ values along with decline in TOC and hydrogen index were also noticed by Talbot and Livingstone³⁹, along subaerial exposure surfaces of basinal sequence. Hence, it is tempting to relate ~3‰ enrichment in $\delta^{13}\text{C}_{\text{org}}$ value of Sirbu Shale organic matter with its oxidation history in near-oxic water column.

Conclusion

The study concludes that the Vindhyan Sea initiated as a stratified sea with anoxic and sulphidic deep water (Arangi Shale), although the extent and veracity of anoxicity and euxinicity were never very high and pervasive, as evident from Mo concentration, TOC value and Mo/TOC ratio of argillaceous intervals through the Vindhyan lithopackage. While the present dataset corroborates the idea of euxinic deep water during Arangi, Rampur and Bijaygarh Shale deposition, it contradicts the idea of extending similar hydrosphere redox structure during Koldaha and Rewa Shale sedimentation. Despite being partly anoxic, as evident from the occurrence of black shale, the basin certainly was not euxinic in the course of Koldaha and Rewa Shale sedimentation. Possibly, the Vindhyan Sea turned near-oxic by the time of Sirbu Shale sedimentation. Mo and Cr data from the shale intervals suggest that the Vindhyan Sea acted as a moderate Mo, but depleted Cr reservoir. Consistent low concentration of Cr within shale intervals, irrespective of stratigraphic status and basin anoxicity, bears indication of the limitation in availability of Cr in the water column in the absence of any significant detrital supply. With high (>2% up to 8%) TOC content and anoxic/euxinic deep water condition in course of deposition, the Arangi and Bijaygarh Shales have good potential as hydrocarbon source rocks. However, organic matter type (humic/sapropelic) and degree of maturation need to be assessed to take a final decision in this regard.

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