

C- and O-isotopic characteristics of Neoproterozoic Sirohi Group meta-carbonates in NW India and their palaeoclimatic implications

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The low-grade meta-sedimentary sequence of the Sirohi Group comprises an ensemble of phyllite, schist and meta-carbonate rocks (including impure marble) and marks late Proterozoic tectonics in the NW Indian block. The $\delta^{18}\text{O}_{\text{V-PDB}}$ values for Sirohi meta-carbonates range from -20.2 to -101% , suggesting that the O-isotopic signatures have been variably affected by post-depositional alterations. The $\delta^{13}\text{C}_{\text{V-PDB}}$ fluctuate from marginally positive ($\sim 1.0\%$) to negative (-3.3%) values and represent primary sedimentary signatures. The Mn–Sr and Mg–Ca relationships further substantiate that the C-isotopic characteristics have not been significantly modified during the metamorphism. The $\delta^{13}\text{C}_{\text{V-PDB}}$ values are typical of normal carbonate sediments and suggest warmer climatic conditions during their deposition, most likely prior to the Neoproterozoic ‘snowball earth’. Evidence of glaciation in stratigraphically younger litho-units (occurrence of possible diamictite, glacial striations, etc. in the immediately overlying Sindreth Group and Marwar Supergroup) can be correlated with the worldwide glacial events during the Neoproterozoic.

Keywords: C- and O-isotopes, glaciation, meta-carbonates, palaeoclimatic implications.

THE Neoproterozoic has been heralded as one of the most dynamic periods in the history of the earth as it witnessed rapid movements of continental blocks, large-scale perturbations in the atmospheric oxygen and severe temperature fluctuations. It was also a period of amalgamation of continental blocks to form the supercontinent Rodinia (~ 1100 – 1000 Ma) and its later fragmentation (~ 800 – 750 Ma) that ultimately resulted in the Gondwana assembly at ~ 550 Ma. The Neoproterozoic has also been associated with worldwide glacial deposits, some of them at apparently low latitudes, implying severe cold climatic conditions^{1–3}. As an alternative explanation, rotation of the earth along a highly oblique axis was also proposed⁴.

The Neoproterozoic age (770–750 Ma) of Malani Igneous Suite (MIS) and coeval Sindreth Group in NW

India have been reasonably well studied in terms of geochronology, geochemistry and palaeogeography^{5–7}. However, not much is known about the meta-sedimentary package of the Sirohi Group which underlies the MIS. The Sirohi rocks were presumably deposited over a granitic ‘basement’, the latter conventionally described as the ‘Erinapura Granite’⁸. The contact relationships are not properly understood due to a tectonized contact between the two⁹. This communication focuses on the C- and O-isotopic characteristics of the Sirohi Group meta-carbonates, with an aim to infer the palaeoclimatic conditions during deposition. The results are discussed in terms of Neoproterozoic glaciation events observed in stratigraphically younger horizons (Sindreth Group, Marwar Supergroup).

Geological evolution of the NW Indian craton includes a 3.3–2.5-Ga-old Archean basement^{10–12} over which the Palaeoproterozoic Aravalli Supergroup and presumably the Meso–Neoproterozoic Delhi Supergroup supracrustal sequences were deposited (Figure 1). The Neoproterozoic stratigraphy of NW India is also summarized in Table 1.

The Sirohi Group and the overlying Sindreth Group were described as the youngest units of the Meso–Neoproterozoic Delhi Supergroup¹³. However, initially these rocks were correlated with the ‘Aravalli system’¹⁴. Some later workers^{9,15} consider the Sirohi Group to be stratigraphically younger than the Delhi Supergroup (Figure 1 and Table 1). The basement granites and gneisses define a tectonized contact with the Sirohi Group meta-sediments, while the Balda Granite shows an intrusive relationship^{9,13,16}. The Sirohi basin is a narrow, linear, sialic basin in the Sirohi–Ras–Makarana region, which presumably opened^{9,15,16} at 1 Ga, assuming a coevality with the regional 1 Ga mafic magmatism¹⁷. The age of the Sirohi sedimentation is still not properly constrained. However, rhyolitic flows from the overlying Sindreth Group have yielded a zircon U–Pb age⁶ of 761–765 Ma, which overlaps with the 770–750 Ma Malani Igneous Suite⁵. The Sirohi Group meta-sediments and the ‘basement granite and gneisses’ (also described as Erinapura Granite⁸) share a common deformation history adopted during the NW–SE directed crustal convergence¹⁸.

The meta-sediments of the Sirohi Group include a thick pile of argillites along with meta-carbonates and associated silicate rocks, with virtual absence of arenites and volcanics. The major rock units include phyllite, mica schist, marble and calc-silicate rocks. Mica schist is the most common lithology in the area. Presence of penetrative schistosity in the Sirohi metasediments makes these rocks clearly distinguishable from the those of the stratigraphically younger Sindreth Group.

The meta-carbonate rocks were sampled along a west-to-east transect (S-1 to S-15), north of Sirohi town (Figure 1). The meta-carbonate rocks and impure marble can be texturally described as (a) calc-silicate mylonite and (b) tremolite–actinolite-bearing calc-schist. These contain dolomite as the dominant carbonate mineral along with

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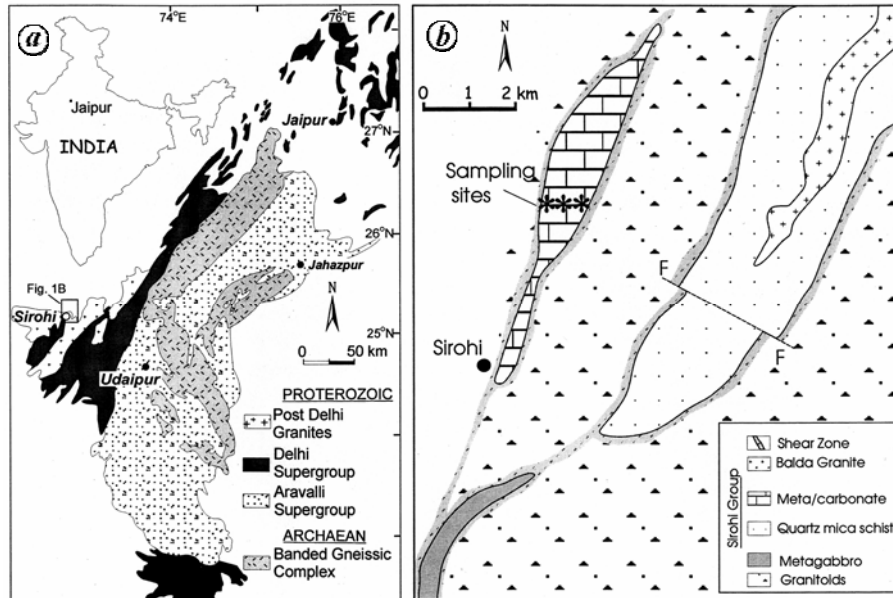


Figure 1. *a*, Simplified Precambrian geology of northwestern India (modified from Heron⁸ and Roy and Jakhar¹⁵). *b*, Geological map showing lithostratigraphy of Sirohi Group (adapted from Roy and Sharma⁹) and location of meta-carbonate samples (north of Sirohi town) along an east-west transect.

Table 1. Neoproterozoic stratigraphy of western Rajasthan, NW India (after Roy and Sharma⁹, Pandit *et al.*³⁰ and Pareek³¹)

Marwar Supergroup (Precambrian–Cambrian transition)	Nagaur Group	Tunklian sandstone Nagaur sandstone and evaporates
	Bilara Group	Pondlo dolomite Gotan limestone Dhanapa dolomite
	Jodhpur Group	Jodhpur sandstone/Pokaran sandstone Pokaran boulder bed (spread)
Unconformity		
Malani Igneous Suite (771–751 Ma) & Sindreth Group	Dyke swarms of Dhanta, Sankara and other places	
	Granites (Mirpur, Jalore, Siwana and other places) Felsic flows, ignimbrites and tuffs Mafic flows Basal conglomerates, grits and diamictites	
Unconformity		
Sirohi Group	Balda granite	
	Carbonaceous phyllite (Local) Calc silicate and marble Mica schist	
Unconformity		
Basement	Granitic gneisses, Biotite gneiss and granitoids	

fine-grained calcite and minor diopside, talc and wollastonite. Tremolite–actinolite calc-schist/gneiss occurs in the central part of the meta-carbonate outcrop. Most of the mineral grains show flattening parallel to the foliation. Calc-silicate mylonites have paper-thin lamellae and down-dip lineations. Intense shearing seems to have obliterated all the primary features; however, some relict

calcite, diopside, talc and wollastonite can be recognized under the microscope. Tremolite–actinolite calc-schist is banded in appearance and shows thin, alternate carbonate and silicate mineral-rich bands.

The C- and O-isotopic analyses of Sirohi Group meta-carbonate rocks were done at the NEG-LABISE, Federal University of Pernambuco, at Recife, Brazil, following

the conventional digestion method¹⁹. Powdered samples were reacted with H₃PO₄ at 25°C to release the CO₂. An extended reaction period (3 days) was preferred for slow-reacting dolomites, instead of increasing the reaction temperature. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were measured on cryogenically cleaned CO₂ in a triple collector SIRA II mass spectrometer. The C- and O-isotopic data are presented (as $\delta\%$ deviation with reference to V-PDB and V-SMOW respectively) in Table 2. Borborema Skarn Calcite (BSC), calibrated against international standards, was used as the reference gas and reproducibility of the measurements was better than $\pm 0.1\%$, in general. The values obtained for the standard NBS-20 in a separate run against BSC yielded a $\delta^{13}\text{C}_{\text{V-PDB}} = -1.05\%$, and $\delta^{18}\text{O}_{\text{V-PDB}} = -4.22\%$. These results are in close agreement with the values reported by the US National Bureau Standards (-1.06 and -4.14% respectively).

Four samples of the Sirohi meta-carbonate rocks were also analysed using X-ray fluorescence spectroscopy for major and some trace elements; the data are presented in Table 3.

A number of post-depositional processes, beginning with the early diagenesis and dolomitization, can potentially alter the original isotopic signatures of carbonate rocks. It is therefore desirable to assess the data before attempting any interpretation on depositional conditions. Although a number of geochemical parameters have been suggested for evaluation of the degree of preservation of primary isotopic signatures²⁰⁻²², none of them is independently conclusive. Enrichment in Fe and Mn and depletion in Sr have been recognized as useful parameters in evaluating the diagenetic history in successor phases²². The Mn/Sr ratio has been regarded as a reliable indicator for assessing the degree of alteration and post-depositional modifications²³. Although samples with Mn/Sr ratio < 3 are considered to be well-preserved and unaffected by

post-depositional alterations²⁴, values as high as ten are also acceptable, being little affected by post-depositional processes²⁰. The MnO concentration of the analysed Sirohi meta-carbonate samples ranges from 0.04 to 0.2% and the Mn/Sr ratio from 2.81 to 4.26, except one sample with an anomalous high value of 12.63, which can be related to its high MnO content (Table 3). A nonlinear Mn/Sr – $\delta^{13}\text{C}_{\text{V-PDB}}$ (Figure 2a) relationship indicates that the samples are generally unaffected by post-depositional alterations, which would have otherwise resulted in depletion in $\delta^{13}\text{C}$ and a corresponding increase in the Mn/Sr ratio²⁵. Mg/Ca ratio is another useful parameter and a simultaneous increase in the Mg/Ca and Mn/Sr ratios can be attributed to the alteration process²⁵. A nonlinear relationship between the two parameters in the Mn/Sr–Mg/Ca cross-plot (Figure 2b) precludes any notable alteration effect. A positive correlation of Mg/Ca with both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Figure 2c and d) is also consistent with unaltered isotopic and geochemical signatures²⁶.

The C-isotopic data on Sirohi meta-carbonates can be considered to be pristine and representative of the original isotopic ratios. Dolomitization has been identified as the early diagenetic phenomenon in the Proterozoic rocks involving transformation of still-preserved metastable aragonite and/or Mg-calcite into dolomite²⁷. Therefore, the isotopic signatures can be considered as representative of the sea water. Preservation of isotopic signatures depends upon the water/rock ratio for a given element at the time of diagenetic recrystallization²⁸. The reported sequence of water–rock interaction is O > Sr > C, which means that the C-isotopic values are the least modified.

Table 2. C- and O-isotopic composition of Sirohi Group meta-carbonates represented as standard $\delta\%$ notation relative to V-PDB

Sample no.	$\delta^{18}\text{O}_{\text{V-PDB}}$	$\delta^{13}\text{C}_{\text{V-PDB}}$
S-1	-15.6	1.3
S-2	-14.6	-0.9
S-3	-17.3	-0.8
S-4	-20.2	-2.6
S-5	-10.1	0.2
S-6	-15.9	-2.8
S-7	-13.8	-3.5
S-8	-12.3	-2.6
S-9	-13	-3.3
S-10	-14.3	-2.2
S-11	-15.4	1
S-12	-13.6	-0.1
S-13	-15.8	-0.3
S-14	-14.2	-1.9
S-15	-12.1	0

Table 3. Partial whole-rock geochemistry (X-ray fluorescence) of Sirohi Group metacarbonates (major oxides as wt% and trace elements in ppm)

Sample no.	S-4	S-8	S-12	S-15
SiO ₂	23.3	29.9	11.8	47.6
Al ₂ O ₃	1.2	0.85	0.9	6.8
Fe ₂ O ₃	1.1	1.2	1.6	2.8
MgO	10.25	17.4	18	14.4
CaO	33.2	23.9	29	14.7
Na ₂ O	0.5	0.25	0.15	0.9
K ₂ O	0	0.1	0.4	0.3
TiO ₂	0.03	0.04	0.03	0.3
P ₂ O ₅	0.01	0.04	0.01	0.04
MnO	0.2	0.04	0.05	0.1
Total	69.79	73.72	62.94	87.94
Si	108,733	139,533	54,979	222,133
Ca	23.56	17	20.6	10.45
Mn	1756	336	430	996
Mg	6.11	10.4	10.88	8.4
Sr	139	87	153	234
Rb	2	6	23	32
Fe	6997	8061	10,509	18,998
Ba	n.d	n.d	n.d	n.d
Mg/Ca	0.26	0.61	0.53	0.8

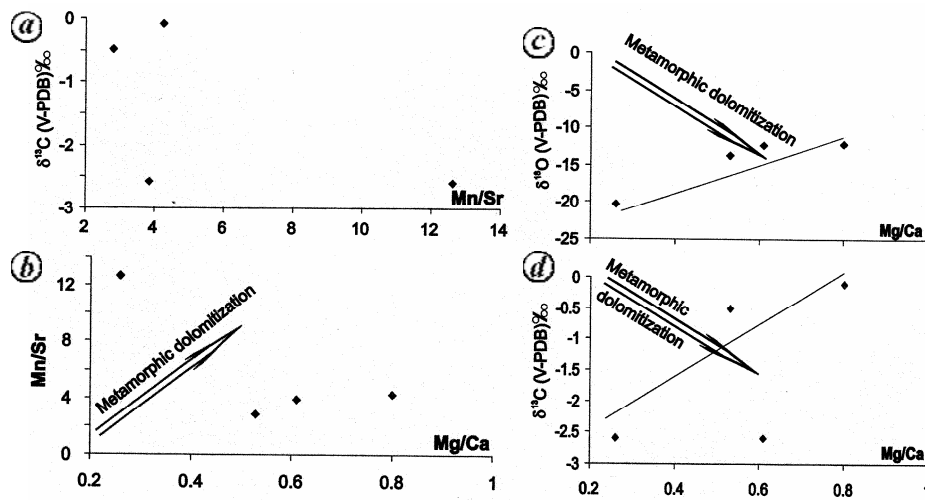


Figure 2. Variation in some diagnostic geochemical parameters and C- and O-isotopic characteristics of Sirohi meta-carbonates, indicating that the geochemical and isotopic signatures have not been significantly modified during post-depositional processes. Known trends of metamorphic dolomitization³⁰ have also been superimposed. *a*, Mn/Sr– $\delta^{13}\text{C}$ variation; *b*, Mg/Ca–Mn/Sr variation; *c*, *d*, Mg/Ca variation against $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ respectively.

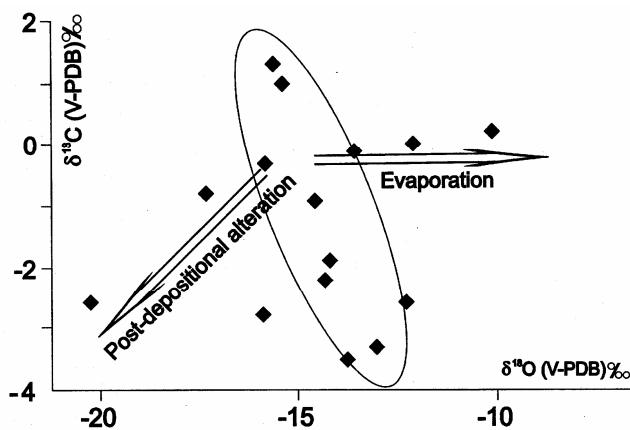


Figure 3. $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ cross-plot for Sirohi Group meta-carbonate rocks showing a general inverse correlation in a majority of the cases. Trends of metamorphic alteration and evaporative processes have also been superimposed onto the diagram.

Oxygen isotopes are generally more likely to get affected by circulating meteoric waters at elevated temperatures during metamorphism. Carbonates with the $\delta^{18}\text{O}$ range of -10 to -5‰ can be considered as primary, being close to the ‘best-preserved’ $\delta^{18}\text{O}$ value of $-7.5 \pm 2\text{‰}$, reported for most of the Proterozoic–Early Cambrian carbonate rocks²⁹. The $\delta^{18}\text{O}$ values for Sirohi meta-carbonates range from -20.2 to -10.1‰ , suggesting that the O-isotopic signatures have been variably modified. The C- and O-isotopic characteristics of Sirohi Group meta-carbonates are illustrated in the conventional $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ cross-plot (Figure 3). A narrow range of $\delta^{18}\text{O}$ (-17.3 to -12.1‰ , except two extremely enriched and depleted samples, -10.1 and -20.2‰ respectively) and $\delta^{13}\text{C}$ (-3.5

to 1.3‰) values indicate a more or less homogeneous dataset. Most of the samples define a moderate inverse relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Figure 3). The likely post-depositional alteration trend²⁵ has been superimposed onto the cross-plot, which indicates that only two samples seem to show some alteration effect. Post-depositional alteration would result in simultaneous depletion in both the parameters, while evaporative processes would result in a variable and unrelated enrichment in the $\delta^{18}\text{O}$ values.

The carbon isotopic signatures of the Sirohi Group meta-carbonate rocks are significantly different from the end-Neoproterozoic Bilara Limestone (Marwar Supergroup); the latter shows considerable fluctuations in the isotopic record and documents significantly negative $\delta^{13}\text{C}$ excursions³⁰, indicating cold and intervening warmer climatic conditions prevalent during the Neoproterozoic–Cambrian transition.

An inverse correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ indicates well-preserved primary signatures in the Sirohi meta-carbonate rocks. Late diagenesis and low-grade metamorphism, and deformation would result in a corresponding lowering in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values due to devolatilization reactions. While the C-isotopic signatures in the Sirohi meta-carbonates can be considered as primary, the O-isotopic signatures seem slightly lower. The $\delta^{13}\text{C}$ values close to zero ($\pm 2\text{‰}$) indicate warmer climatic conditions during deposition of the Sirohi Group carbonate rocks. The Sirohi Group is overlain by a volcano-sedimentary assemblage of the Sindreth Group which has been dated⁶ at ~ 760 Ma. The contact between the Sirohi and Sindreth Groups is marked by a polymictic conglomerate comprising unsorted angular cobbles, boul-



Figure 4. Field photograph of suspect Sindreth diamictite showing highly unsorted nature and variation in clast size and shape.

ders and pebbles of carbonaceous phyllite, quartz, mica, schist, quartzite and granite (drawn from the Sirohi Group and granitoids), cemented in a siliceous and ferruginous matrix (Figure 4). Fine- to medium-grained lithic matrix is also seen in a few cases. Unsorted nature and sub-angular character of pebbles suggest a close proximity to the provenance. Presence of a wide range of poorly sorted, angular to well-rounded clasts supported by a typically clayey matrix, suggests a possible glacial origin for the conglomerate. Although the basal part of the Sindreth Group falls within the time window of the snowball earth (750–580 Ma), the ‘glacial origin’ of these basal conglomerates (possible diamictite) needs to be established through further evidence.

The basal unit of the overlying Marwar Supergroup is the Pokaran Boulder Bed (spread), which marks an erosional unconformity with the basement rocks of the MIS³¹. The boulder spread comprises a cluster of isolated pebbles, cobbles and boulders without any matrix³². Cold climatic conditions during the initial phases of deposition of the Marwar sediments are indicated by glacial striations on the cobbles and boulders³², presumably correlated with the Gaskiers carbonates on top of the 580-Ma-old diamictites. The diagnostic C-isotopic characteristics (fluctuations in isotopic trend and prominent $\delta^{13}\text{C}$ depletions) of the overlying Bilara Group limestone have been described to represent the Neoproterozoic–Cambrian transition in this region³⁰.

The ‘normal’ (sedimentary) C-isotopic signatures of the Sirohi meta-carbonates and absence of any glacial deposits indicate warmer conditions during Sirohi Group sedimentation. Marginally negative $\delta^{13}\text{C}$ values, observed in some cases, can be attributed to the metamorphic effects which tend to lower these values. It can be concluded that the Sirohi Group carbonates were deposited outside the ‘snowball’ time window and may be older than presumed by some other workers¹³. Evidence of glacial events in younger rocks can be correlated with the glo-

bally recognized Neoproterozoic glaciation events and provide possible evidence for the snowball earth from the NW Indian block.

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Episodes of phosphorus accumulation in the Cauvery Basin, South India: implications on palaeoclimate, productivity and weathering

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The Barremian–Danian strata of the Cauvery basin, exposed in the erstwhile Tiruchirapalli district, record three positive excursions of phosphorus, namely, during Albian, Cenomanian and Maastrichtian respectively, and a negative excursion across the Cretaceous–Tertiary boundary. Corroboration of the depositional history of the strata and comparison with the trends of relative sea level, Si, Sr and C_{Org} revealed that while the Albian episode was related with reduced inflow of siliciclastics and prevalent oxygen minimum owing to the sea-level highstand, the other two positive excursions resulted from sea-level lowstand and concomitant redistribution of intraformational sediments. The negative excursion across the Cretaceous–Tertiary was due to higher faunal turnover.

Keywords: Palaeoclimate, phosphorus, positive and negative excursion, weathering.

CHEMOSTRATIGRAPHY involves the application of elemental and isotopic geochemistry for the characterization of sedimentary sequences¹. This tool is based on the sedimentary record of changes in certain elements with time². Many studies^{3–6} have utilized this tool for stratigraphic correlation, fixation of geological boundaries and petroleum exploration. This communication documents the trends of phosphorus in sedimentary rocks of Barremian–Danian strata of the Cauvery basin to decipher causative factors.

A more or less complete Upper Cretaceous–Palaeocene succession is exposed in the Ariyalur–Pondicherry depression of the Cauvery basin⁷ (Figure 1). The Cauvery basin was initiated during Lower Cretaceous and continued to evolve till the end of Tertiary through rift, pull-apart, shelf sag and tilt phases, during which many episodes of transgression, regression, erosion and deposition took place to fill the basin⁸. Sea-level curve of this basin based on foraminiferal data documented the presence of six third order glacio-eustatic global cycles^{9,10}. Sea-level curve constructed based on lithofacies data is also similar to the curves based on foraminiferal data, excepting the addition of fourth-order sea-level cycles (Figure 2) of

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