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CORRESPONDENCE

C-isotope Composition of Carbonates from Indravati Basin, India: Implications for Regional Stratigraphic Correlation

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Abstract

The Indravati Basin represents an unmetamorphosed and unfossiliferous sequence and shows a broad similarity in lithological association with other Purana Basins of Central India. The carbonates belonging to Indravati Basin have on average, moderately positive $\delta^{13}C$ values (up to +4.5‰). Numerous successions reported from other parts of world, show similar $\delta^{13}C$ values and contain evidence to suggest that the latest Mesoproterozoic to early Neoproterozoic period may represent an isotopically recognizable interval globally. The elevated $\delta^{13}C$ values of Indravati Basin are also correlatable with other Purana Basins in India including Upper Vindhyan Supergroup.

Key words: Carbon isotopes, carbonates, Indravati Basin, Palaeoenvironment, correlation.

Introduction

In the absence of abundant fossils and environmentally sensitive sediments, perhaps the best way to understand the Precambrian period is to examine the geological records of the biogeochemical cycles linking the biosphere to the atmosphere, hydrosphere and lithosphere. The basic and more accessible of these cycles is the carbon cycle. It can be monitored by the carbon isotopic ratios ($^{13}C/^{12}C$) of carbonate and kerogen in marine sedimentary rocks, which reflect both the physiological fractionation of isotopes during photosynthetic CO_2-fixation and the relative burial rates of oxidized and reduced carbon (Broecker, 1970; Schidlowski et al., 1975). The secular trends in $^{13}C/^{12}C$ charted globally can be used to construct a chemostratigraphic model that mirrors the evolution of the carbon biogeochemical cycle. This approach has proved most productive in studies of Neoproterozoic biogeochemistry (e.g., Knoll et al., 1986; Magaritz et al., 1986; Kaufman et al., 1991; Kaufman and Knoll, 1995).

It is surprising that carbon isotopic data for the Mesoproterozoic are quite scarce compared with Neoproterozoic and Palaeoproterozoic. Buick et al. (1995) described the Mesoproterozoic, the era between 1.6 and 1.0 Ga as the dullest time in Earth's history. Available data indicate that late Paleoproterozoic to early Mesoproterozoic (>~1.3Ga) successions have average $\delta^{13}C$ values near 0 ±1‰ (Buick et al., 1995; Knoll et al., 1995; Frank et al., 1997; Xiao et al., 1997; Brasier and Lindsay, 1998). Based on such data sets, the Mesoproterozoic has been cited as a time of biogeochemical stasis (Buick et al., 1995; Brasier and Lindsay, 1998; Knoll and Canfield, 1998). The end of Mesoproterozoic era is however, reported to be marked by a change in atmospheric oxygen content (Des Marais et al., 1992; Canfield, 1999).

Recent studies indicate that the late Mesoproterozoic to early Neoproterozoic successions (1.3–0.85Ga) exhibit moderately positive average $\delta^{13}C$ values, with $\delta^{13}C$ ranging between about –2 ‰ and + 4 ‰ (Fairchild et al., 1990; Knoll et al., 1995; Kah et al., 1999, 2001; Bartley et al., 2001). The transition from a characteristically early Mesoproterozoic record of little $\delta^{13}C$ change to the moderate variability noted in the late Mesoproterozoic has not been reported frequently from any single succession.

The Proterozoic rocks of the Indravati Basin, Central India have been chosen under the present study for C- and O-isotope studies to address the Mesoproterozoic oceanic C-isotope evolution. No detailed geochronological data is available for this basin; however, based on field evidence, it is assumed that this basin was most likely deposited during the late Proterozoic period.

Indravati Group

The 'Purana' rocks defined a large spread of Middle to Upper Proterozoic platform cover deposits, which are preserved in several isolated basins in Peninsular India (Fig. 1). These sediments, despite their development in widely separated areas, show similarity of characters viz., unmetamorphosed nature, mostly unfossiliferous sequence and very little tectonic deformation. Interestingly the formations show a broad similarity in lithological association.

The Vindhyan Basin, having the largest spread among the Purana Basins covers Central India and Rajasthan. The other prominent Proterozoic Cuddapah Basin is in Andhra Pradesh. Kaldagi and Bhima are also two prominent Proterozoic basins of South India. The Purana rocks of Southeastern Madhya Pradesh and the adjoining part of Orissa State encompass Indravati, Chhatisgarh and several satellite basins viz., Albaka, Khariar, Sukma, Ampani, etc.

The Middle and Upper Proterozoic basins of Peninsular India present considerable problems for interbasinal correlation of different lithounits because of paucity of chronostratigraphic and biostratigraphic evidences. The recent advances on the stratigraphy of the Purana Basins and patterns of basin infilling with due recognition of regional unconformities permit broad correlation of all these basins. In the present work, an attempt would be made to compare the carbon isotope data of Indravati carbonates with those published for Vindhyan and other Purana Basins.

A sequence of undeformed and unmetamorphosed sedimentary rocks belonging to Indravati Group occupies a vast plateau around Jagdalpur, Baster district, Chattisgarh, India. The Indravati Basin covers an area of

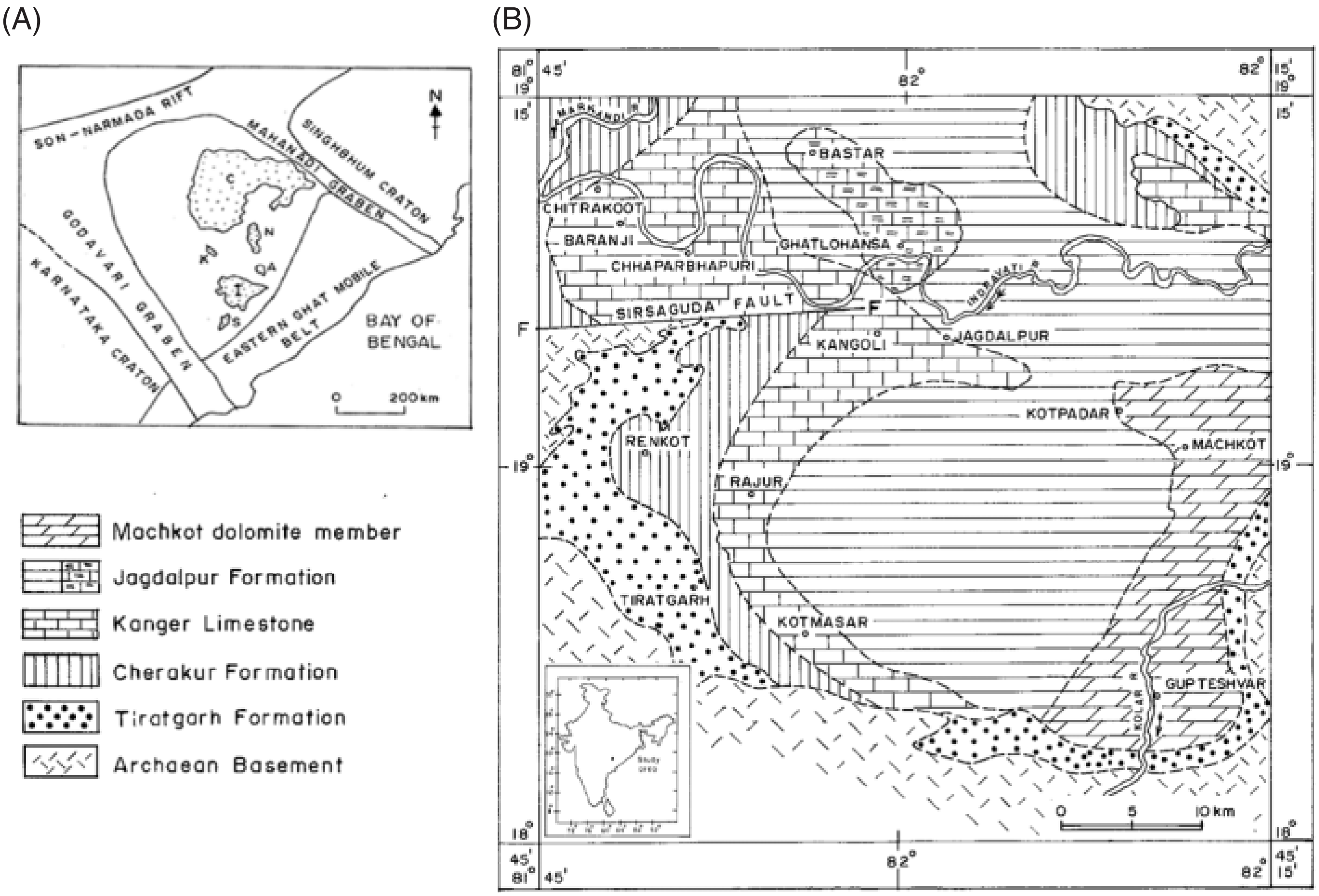

Fig. 1. (A) Position of Indravati Basin among Purana Basins of Central India (C–Chhatisgarh, N– Nawagarh Khariar, A–Ampani, I–Indravati, K–Keskal-Singarpur, S–Sukma) (B) Geological map of Indravati Basin, Central India.

9000 km^2 in Kanker-Baster-Dantewara districts of Chhatisgarh and Koraput district of Orissa (Fig. 1). The Indravati group rocks are underlain by lower Precambrian Gneissic Complex. Rocks of Indravati Group are essentially horizontally bedded with low dips from 5 to 20. The inward dips in basal sandstone indicate the nature of palaeoslope. No detailed work on Indravati basin rocks have been carried during current years but the previous work (Crookshank, 1963; Sharma and Atram, 1962; Dutt, 1963; Krupanidhi, 1962; Ramakrishnan et al., 1978; Mishra et al., 1988) incorporated the geological mapping of the basin. The generalized stratigraphic succession for the Indravati Group may be shown as follows:

	Jagdalpur Formation	Calcareous shales with purple and gray stromatolitic dolomite (Machkot dolomite member)
	Kanger Limestone	Purple limestone Grey limestone
Indravati Group	Cherakur Formation	Purple shale with arkosic sandstone and chert pebble conglomerate grit
	Tirathgarh Formation	Chitrakoot sandstone member quartz arenite Mendri member Subarkose and conglomerate
	------ Unconformity ------	
	Archaean	Granites and supracrustals

Age Considerations

The Middle and Upper Proterozoic basins of Peninsular India, including the Indravati, Chhattisgarh, Kurnool and Bhima Basins of Peninsula India present considerable problems for interbasinal correlation of different lithounits because of the paucity of chronostratigraphic and biostratigraphic evidences. On the basis of lithology and cyclic nature of sedimentation (Dutt, 1963; Kruezer, 1977; Murthi, 1987) these basins were considered as equivalent to the lower Vindhyans. The Indravati Basin has been correlated with lower Vindhyans or Kurnool by Bose (1900) Dutt (1963). Later research revealed that the sanstone member of Indravati Basin can be compared with the Chopardih Formation of Chhatisgarh Supergroup, which gives K-Ar age of 700–750 my (Kruezer, 1977). This age evidence is also supported by the presence of stromatolites in limestones and dolomites of Machkot area, which corresponds to late Riphean age (700–1100 my) as suggested by Walter (1976). Considering the available geochronological and field data, the Jagdalpur Carbonate Formation of the Indravati Basin may be correlated with Bhander limestone of Upper Vindhyan.

Geology of the Indravati Group

The Indravati group of rocks occupy low-lying plateaus and unconformably overlie the gneissic and granitic rocks of the Bengpal Group. Indravati Group comprises basal sandstone with intercalations of shales and glauconitic sandstone (Tirathgarh Formation) grading upward into a conformable sequence of shale (Cherakur Formation), horizontally laminated Kanger limestones, purple shales with stromatolitic dolomite (Jagdalpur Formation) in ascending order. The sedimentary rocks are essentially horizontally bedded and vertically and laterally merge into each other. The sediments in the Indravati Basin are considered to have been deposited in shallow marine, near shore tidal flat or lagoonal environment.

Tirathgarh Formation

A horizontally bedded sandstone with intercalations of conglomerate and grits overlying the older rocks represents the basal sandstone of Indravati Group. Conglomerate bed is best exposed around Dahikonga. Sandstone is greyish white to brown in colour, dominantly composed of quartz with feldspar and mica as an accessory minerals. Quartz grains are sub-rounded to rounded and cemented in a ferruginous matrix.

Cherakur Formation

The coarse-grained sandstone has been described as the “Cherakur Formation” by Ramakrishnan et al. (1978) as a marker horizon between the underlying Tirathgarh Formation and the overlying Jagdalpur Formation. The sandstone is invariably glauconitic and shows lateral variation into the shale. Mega ripples are observed in the Kapari section indicating the shallow water conditions of deposition. The sandstone is essentially horizontally bedded and dark brown in colour. The quartz grains are subangular to subrounded, cemented in a ferruginous matrix. Intercalations of shales are seen as a lateral variation and overlying the basal sandstones. Shales are purple and khaki colour and grade into hard and compact pyritiferous indurated rock (tuff ?). Ripple marks are also noticed in shales exposed around Mungapadar. Shales are fine-grained, well laminated and contain cubes of pyrite in certain areas.

Kanger Limestone

The shaly members of Cherakur Formation grade inwards into fine calcareous shales and limestones. Southwestern part of the area is occupied by dark coloured limestones. The limestone is exposed around Chapka and Markandi River section. In the cultivated areas, limestone has been intersected in the boreholes and wells. Limestone is horizontally bedded and shows typical elephant skin weathering. At places it contains pyrite crystals and traversed by calcite veins.

Jagdalpur Formation

The Jagdalpur Formation is the youngest unit of Indravati Basin. It is mainly represented by purple buff shales and stromatolitic dolomite. The shale is poorly exposed while stromatolitic dolomite is confined to Bastar Machkot section only. The Jagdalpur shale overlies stromatolitic dolomite. The stromatolitic dolomite is exposed near Basta (Village Junaguda), Raykera Nala, Kotpadar, Machkot, Tikripadar Nala, Tiria and Gupteshwar area. The purple-gray stromatolitic dolomite forms small hills 30 to 50 ft high near Machkot and derives its name as Machkot member. It looks like "crocodile skin" due to differential weathering. Ramakrishnan and Balagopalan (1968) and Schnitzer (1977) identified stromatolites as reef complexes and described them as SH and LLH types. Near Village Kotpadar, at railway cuttings, intraformational conglomerate with flat pebble shale is exposed. The shale is chertified and contains detrital quartz, biotite, chlorite, etc.

Analytical Methods and Sampling

The whole-rock carbonate samples were sampled at close interval along two stratigraphic profile (a) Chitrakoot-Jagdalpur section (b) Bastar-Machkot section of the Indravati Basin. Samples were taken from exposed rock surfaces along both the sections. A total of 30 carbonate samples were collected. Selected samples were analyzed for major and trace elements on an RIX-3000 XRF spectrometer using fused beads. Fused beads were prepared using lithium fluoride and lithium tetraborate. For C- and O-isotopic determinations, CO_2 was extracted from powdered carbonates in a high vacuum line after reaction with orthophosphoric acid at 25°C, and cryogenically cleaned, according to the method described by Craig (1957). CO_2 gas released by this method was analyzed for O and C isotopes in a double inlet, triple collector SIRA II mass spectrometer, using the reference gas BSC (Borborema Skarn Calcite) that calibrated against NBS-18, NBS-19 and NBS-20, has a $\delta^{18}O$ value of -11.28 ± 0.004 ‰ PDB and $\delta^{13}C = -8.58\pm0.02$ ‰ PDB. The results are expressed in the notation δ‰ (per mil) in relation to international PDB scale.

Constraints on Postdepositional Diagenesis

Carbonates from the Indravati Basin have high positive $\delta^{13}C$ values that could have potentially developed during initial carbonate deposition or diagenesis. The possibility that these high $\delta^{13}C$ values have been developed during meteoric diagenesis is unlikely, as these processes typically lower, or do not significantly reset $\delta^{13}C$ values (Saltzman et al., 1998). Moreover studies of Proterozoic carbonates suggest that diagenetic shifts in $\delta^{13}C$ carb values are markedly smaller (<1 ‰) than in Phanerozoic equivalents (Kaufman et al., 1991; Strauss et al., 1992). Diagenetic methanogenic reactions produce both high-^{13}C CH_4, and may therefore produce elevated $\delta^{13}C$ values. However, mixing of early formed, high ^{13}C CO_2 with CO_2 derived from the subsequent oxidation of low-^{13}C CH_4 commonly leads to the precipitation of carbonates with a wide range of both large positive and negative $\delta^{13}C$ carb values. This results in significant carbon isotope heterogeneity, that are not seen in present dataset.

During post-depositional diagenesis, carbonate rocks typically show more negative $\delta^{13}C$ and $\delta^{18}O$ values accompanied by increased Mn and Fe concentrations and decreased Sr concentrations. In the absence of HCO_3 -rich fluid migration, carbon isotopic values are typically buffered by initial dissolution and recrystallization of the carbonate phase, resulting in little alteration of primary $\delta^{13}C$ compositions (Kaufman et al., 1991). Even post-depositional thermal alteration of organic matter often preserves primary carbon isotopic signatures in carbonate phases (Wickham and Peters, 1993). In contrast, oxygen isotopic depletion, which results from addition of isotopic depleted fluids or temperature increases during burial, is typically large, given roughly equal fractions of oxygen in water and carbonate rock reservoirs (Banner and Hanson, 1990). The Indravati Basin samples preserve a narrow range of $\delta^{13}C$ (0.5 to 1‰) accompanied by much greater variation in $\delta^{18}O$ (–5.73 to –10.53‰), suggesting that primary $\delta^{13}C$ has been retained by Indravati carbonates.

Post-depositional alteration and evaporative effects can significantly change the C- and O-isotopic compositions. The likely alteration trends (Burdett et al., 1990; Gurrera et al., 1997; Melezhik et al., 2001) have been superimposed onto the $\delta^{13}C$ –$\delta^{18}O$ cross plot (Figure not given). The post-depositional alterations lead to simultaneous depletion in $\delta^{13}C$ and $\delta^{18}O$ and the evaporative process would result in variable and unrelated enrichment in $\delta^{18}O$. The inverse correlation between C- and O-isotopic ratios, rules out the possibility of any post-depositional modifications in Indravati carbonates.

Partial major and trace element concentrations and some significant elemental ratios for representative carbonate samples of the Indravati Basin, India have been provided in table 1. The extent of postdepositional diagenesis can be approximated by examining geochemical trends that result from the significantly different chemistries of marine and diagenetic waters. Therefore representative samples were subjected to elemental analysis to determine Fe, Mn, and Sr abundances. In particular, the elemental ratio of Mn to Sr is commonly used as a diagenetic indicator; during meteoric diagenesis, Mn is commonly incorporated into sedimentary carbonates, whereas Sr is flushed from the carbonate lattice (Veizer, 1983; Derry et al., 1992). Empirical evidence suggests that retention of primary carbon isotopic values is favored by the rapid stabilization of carbonate sediments during early marine diagenesis, and that carbonates with Mn/Sr <10 generally retain primary carbon isotopic compositions (Kaufman and Knoll, 1995).

A non-linear relationship in the values of $\delta^{13}C$ and Mn/Sr indicates that the samples under study are unaffected by post-depositional alterations. Mn/Sr ratios of samples are less than 4.00, well within the range of accepted values for "little-altered" carbonates. The low Mn/Sr ratios may be attributed to high Sr concentration in these samples. Sr values fall significantly with increasing Mg content (Sathyanarayan et al., 1987; Carpenter et al., 1991). Low Mn/Sr ratios may therefore rule out the possibility of diagenetic dolomitization in studied samples. Low Mg/Ca ratios in Indravati carbonates further rule out the possibility of dolomitization. A non-linear correlation between Mn/Sr and Mg/Ca further rules out the possibility of metamorphic dolomitization in the study samples.

Results and Discussion

The isotopic compositions of the Indravati Basin carbonates along two sections, namely Chitrakoot-Jagdalpur and Baster-Machkot section, are listed in table 1. As can be seen in an isotope stratigraphy (Fig. 2) of both the sections, the spread of $\delta^{13}C$-values is narrow and mostly around 3.0 to 4.50 ‰. The broad positive excursion of $\delta^{13}C$ reaches a maximum of 4.52‰ in the upper parts of sequence in the Baster-Machkot section. One of the samples

Table 1. C-, O-isotopes and bulk chemical analyses of selected carbonate samples from the Indravati Basin, Central India.

Sample	Locality	δO^{18}PDB	δC^{13}PDB	CaO	MgO	Fe	Mn	Sr	Mg/Ca	Mn/Sr
Chitrakoot-Jagdalpur Section										
CB 1	Badanji	–8.67	3.04							
CB 2	Badanji	–6.06	2.95	45.70	0.98	3290	614	269	0.01	2.28
CB 3	Badanji	–5.73	3.47							
CB 4	Badanji	–5.83	3.55	46.15	0.63	2760	467	298	0.01	1.56
CB 5	Badanji	–5.81	3.31							
CB 6	Badanji	–5.85	3.39							
CB 7	Takraguda	–7.06	2.37							
CB 8	C.Bhanpuri	–6.06	3.64							
CB 9	C.Bhanpuri	–6.21	3.64							
CB 10	C.Bhanpuri	–7.42	3.16							
CB 11	C.Bhanpuri	–8.81	3.86							
CB 12	C.Bhanpuri	–7.79	3.30							
CB 13	C.Bhanpuri	–9.49	3.81	39.95	1.14	12420	401	202	0.02	1.98
CB 14	Nalla section	–8.69	1.94	12.76	2.07	37110	248	294	0.15	0.84
CB 15	Kangoli	–9.3	3.12							
CB 16	Kangoli	–9.13	3.66	37.06	1.02	12480	295	159	0.03	1.85
CB 17	Kangoli	–9.69	3.82							
CB 18	Kangoli	–9.16	3.63							
Bastar-Machkot Section										
CB 19	Balenga	–8.42	3.08							
CB 20	Balenga	–831	3.13	25.17	1.84	30140	550	252	0.06	2.18
CB 21	Bastar	–9.02	3.36	32.17	1.59	21590	354	115	0.04	3.07
CB 22	Ghatlunga	–10.53	3.26	34.79	1.55	16900	601	151	0.03	3.98
CB 23	Ghatlunga	–10.51	3.17							
CB 24	Kotpadar	–8.69	1.94	40.96	1.68	9990	209	200	0.03	1.04
CB 25	Kotpadar	–10.05	–2.57	29.51	3.14	17150	319	83	0.09	3.84
CB 26	Tikripadar nala	–6.13	4.33	39.45	1.01	13120	225	132	0.02	1.70
CB 27	Tiria	–10.02	3.48							
CB 28	Tiria	–7.74	4.20							
CB 29	Gupteshwar	–7.68	4.52							
CB 30	Gupteshwar	–7.29	4.23							

(CB 25) in Baster-Machkot section however show negative $\delta^{13}C$ (–2.57‰) value. The $\delta^{18}O$ values are not much variable in both the sections and range between –6‰PDB and –10.5‰PDB. Average $\delta^{18}O$ values, approximately –6‰ are not unusual for Proterozoic sediments (Veizer and Hoefs, 1976; Veizer et al., 1992). It has been proposed that such values record stabilization in isotopically light marine waters, whereas heavier $\delta^{18}O$ values reflect locally evaporitic conditions (Burdett et al., 1990).

The C-isotopic record of the post-2.0 Ga Proterozoic can be conveniently subdivided into three parts (Kah et al., 2001, 2003). The first, comprising the late Proterozoic and early Mesoproterozoic (2.0–1.25 Ga), is characterised by C-isotopic values near 0 ±1%, and records an unprecedented interval of long-term C-isotopic stasis which began ca. 2.0 Ga (Brasier and Lindsay, 1998). The second interval, spans the Mesoproterozoic-Neoproterozoic transition (from ~1.25 to ~0.85 Ga) and is recognised by moderately positive average $\delta^{13}C$ values (up to + 4‰). The third interval begins after 0.85 Ga and contains large, rapid variation in $\delta^{13}C$, with a generally elevated baseline (~+ 5‰; Kaufman and Knoll, 1995).

Following Kah et al. (2001), carbon isotope data of Indravati Basin carbonates indicates that these carbonates appears to be deposited during the Mesoproterozoic-Neoproterozoic transition (~1.25 to ~0.85 Ga), a period characterized by moderately positive $\delta^{13}C$ values (~4‰). The possible contemporaneous evolution of Vindhyan and other Purana Basins including the Indravati Basin permit us to compare the carbon isotope variation of these basins. Numerous other Purana Basins are characterised by more positive carbon isotope values, with $\delta^{13}C$ typically 3.5±0.5‰. Purana successions showing elevated $\delta^{13}C$ values include the Upper Vindhyan Supergroup (Ray et al., 2003); the Raipur (Schidlowski et al., 1975; Murthi and Aswathanarayana, 1982); Kurnool (Schidlowski et al., 1975); and Badami and Bhima (Sathyanarayan et al., 1987). In addition, worldwide numerous other sedimentary basins are also characterised by more positive carbon isotope values, with $\delta^{13}C$ typically 3.5±0.5‰ and contain evidences supporting their deposition during latest Mesoproterozoic to earliest Neoproterozoic (Kah et al., 1999).

Among the Purana Basins, the Vindhyan Supergroup is well studied for its $\delta^{13}C$ stratigraphy and geochronology e.g., Friedman and Chakraborty (1997); Sarkar et al. (1998), Kumar and Schidlowski (1999); Kumar et al. (2002); Ray et al. (2002, 2003); Rasmussen et al. (2002). The Lower and Upper Vindhyan Supergroup carbonates

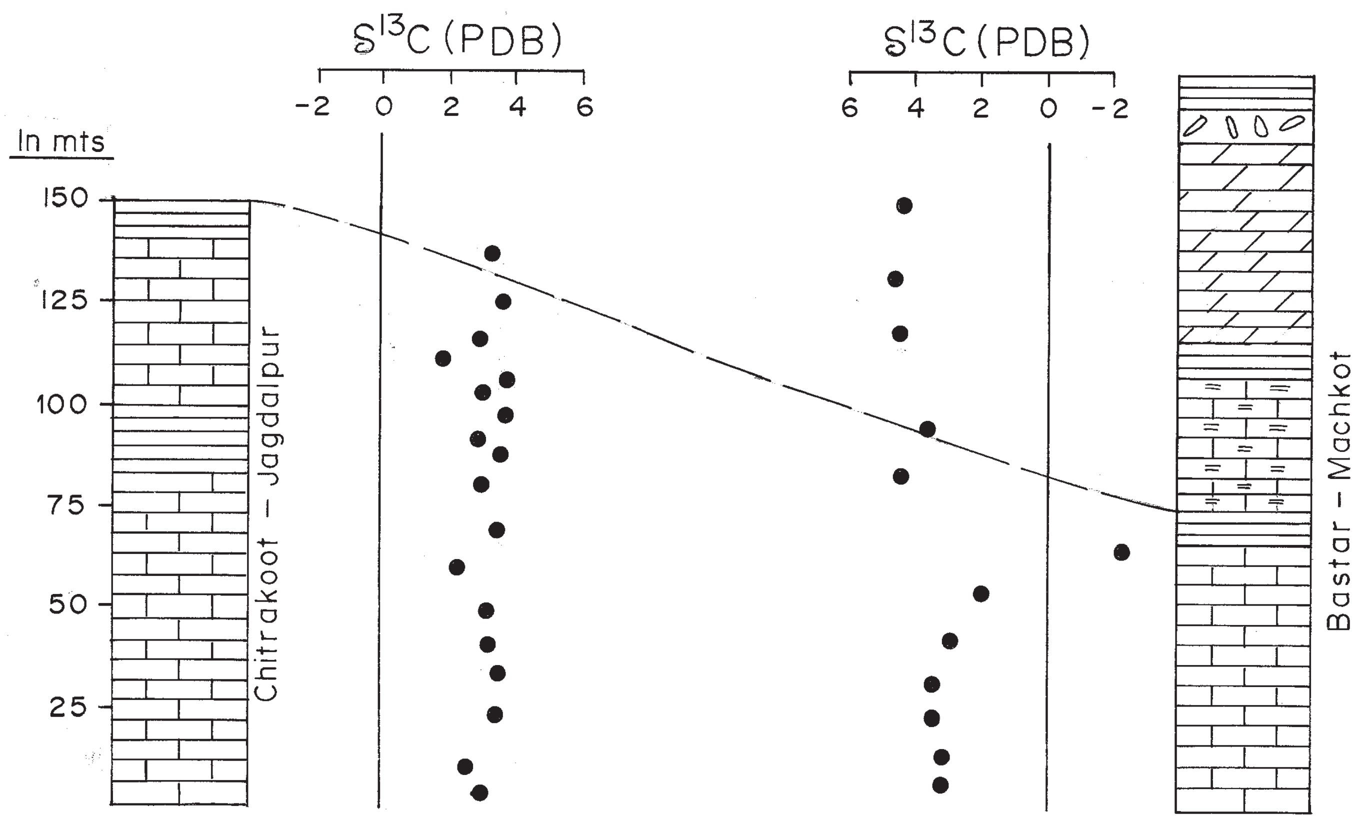

Fig. 2. Secular variations in $\delta^{13}C$ of carbonates from Indravati Basin. Lithologic unit symbols are same as in figure 1.

are characterised by an average $\delta^{13}C$ values of 0±2 and 3±2‰ (Ray et al., 2003). An age of 1601±130 (Ray et al., 2002, 2003; Rasmussen et al., 2002) have been assigned to Lower Vindhyan Supergroup. Sr isotope stratigraphy of carbonates from the Upper Vindhyan Supergroup suggests a mid-Neoproterozoic (750–650 Ma) age for these formations (Ray et al., 2003). The $\delta^{13}C$ values of Indravati carbonates are comparable with the Bhander limestone unit of Upper Vindhyan Supergroup. More Purana Basins studies are however required for a proper definition of this isotopically recognizable interval in Indian subcontinent and to further undertake stratigraphic correlation of all these Purana Basins in India.

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