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Characterization of C-isotope variability in the Delhi Supergroup, northwestern India and the Mesoproterozoic ocean

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Marine carbonate rocks of the Delhi Supergroup of northwestern India show little deviation in whole-rock δ^{13}Ccarb and δ^{18}Ocarb values, which generally are around 0 and –10‰ respectively. These narrow ranges and almost constant δ^{13}Ccarb values persist despite close sampling through long sections. The data suggest that the global rate of organic carbon burial was probably constant during deposition of the Delhi Supergroup. The nearly invariant C isotopic profile of the Delhi Supergroup is similar to C isotopic profiles of Mesoproterozoic carbonates older than 1.3 Ga, as reported from different parts of world. Carbonate units on the western margin of the Delhi Supergroup however, have on average moderately positive δ^{13}C values (from 2 to +4.96‰). These high δ^{13}C carbonates may represent the Mesoproterozoic–Neoproterozoic transition (from ~1.25 to ~0.85 Ga), a period characterized by high positive δ^{13}C values globally.

Keywords: carbon isotopes; carbonates; Mesoproterozoic; palaeoenvironment

Introduction

In the absence of abundant fossils and environmentally sensitive sediments, perhaps the best way to understand Precambrian geologic conditions is to examine the lithological record of biogeochemical cycles linking the biosphere to the atmosphere, hydrosphere, and lithosphere. The basic and most accessible of these cycles is the carbon cycle. It can be monitored by the 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). 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 ocean are quite scarce compared with Neoproterozoic and Palaeoproterozoic data. Buick *et al.* (1995) described the Mesoproterozoic, the era between 1.6 and 1.0 Ga, as the dullest

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time in Earth's history. Available data indicate that late Paleoproterozoic to early Mesoproterozoic (>~1.3Ga) successions have an average $\delta^{13}C$ values near 0 $\pm$1‰ (Pokrovsky and Vinogradov 1991; Buick *et al.* 1995; Knoll *et al.* 1995; Khabarov *et al.* 1996; Frank *et al.* 1997; Xiao *et al.* 1997; Brasier and Lindsay 1998). Based on such datasets, 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 the Mesoproterozoic is however, reported to be marked by a change in atmospheric oxygen content (Des Marais *et al.* 1992; Canfield 1999).

Recent studies indicate that late Mesoproterozoic to early Neoproterozoic successions (1.3–0.85Ga) exhibit moderately positive average $\delta^{13}C$ values, with $\delta^{13}C$ ranges between –2 and + 4‰ (Fairchild *et al.* 1990; Knoll *et al.* 1995; Podkovyrov and Vinogradov 1996; Podkovyrov *et al.* 1998; Kah *et al.* 1999, 2001; Bartley *et al.* 2001; Lindsay and Brasier 2000, 2002). 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.

In the present study, the Delhi Supergroup, Northwestern India, was chosen to address the C-isotope variability in the carbonates of this supergroup and its comparison with Mesoproterozoic oceanic C-isotope evolution.

Delhi Supergroup

The Delhi Supergroup constitutes the main edifice of the Aravalli Mountain range in Rajasthan, northwestern India (Figures 1 and 2). It occupies a narrow linear belt in central Rajasthan, and fans out considerably in the northeastern and southern directions where the Delhi rocks were deposited in several partially isolated basins (Singh 1982a). The rocks of Delhi Supergroup are traceable over a strike distance of about 450 km, with an outcrop width of about 150 km in the southwest and about 25 km in the northeast. The Delhi tectonostratigraphic cycle began with the development of linear grabens with intervening horsts. According to Singh (1982a,b, 1988), the basins initially formed in the northeastern part of Rajasthan, and later on the basins extended all along the axial zone of the Aravalli Mountains.

The lithostratigraphic package now being described for the Delhi Supergroup comprises a sequence of volcano-sedimentary rocks which were deposited during a number of sedimentary cycles (Figure 2). The Delhi Supergroup comprises dominantly quartzites, biotite schist, calc-schist, calc-gneiss, phyllite and marble with subordinate conglomerate and chert. Metavolcanics, granite, ultrabasics, amphibolite and gabbro occur as associated intrusives and extrusives. A narrow belt of mafic–ultramafic association is reported to be present in the southwestern part of the Delhi Supergroup and is described as the 'Phulad Ophiolite Belt'. Three distinct groups separated from each other by unconformities comprise the stratigraphic succession of the Delhi Supergroup (Singh 1988). The Ajabgrah Group (commonly pelitic with metavolcanics) is underlain by the Alwar Group (dominantly arenitic with metavolcanics), while the Rayanhalla Group represents the lower part (dominantly carbonate–metavolcanic–arenite association). The Rayanhalla carbonates are dolomitic in nature. The rocks of the Delhi Supergroup rest unconformably over the schists and gneisses of an older age (Heron 1917). The above stratigraphic succession has been erected mainly on the basis of field observations collected in the northeast part of Rajasthan.

The Rayanhalla Group comprises conglomerate, quartzite and basic volcanics, and it unconformably overlies the basement rocks. The oldest member of this group

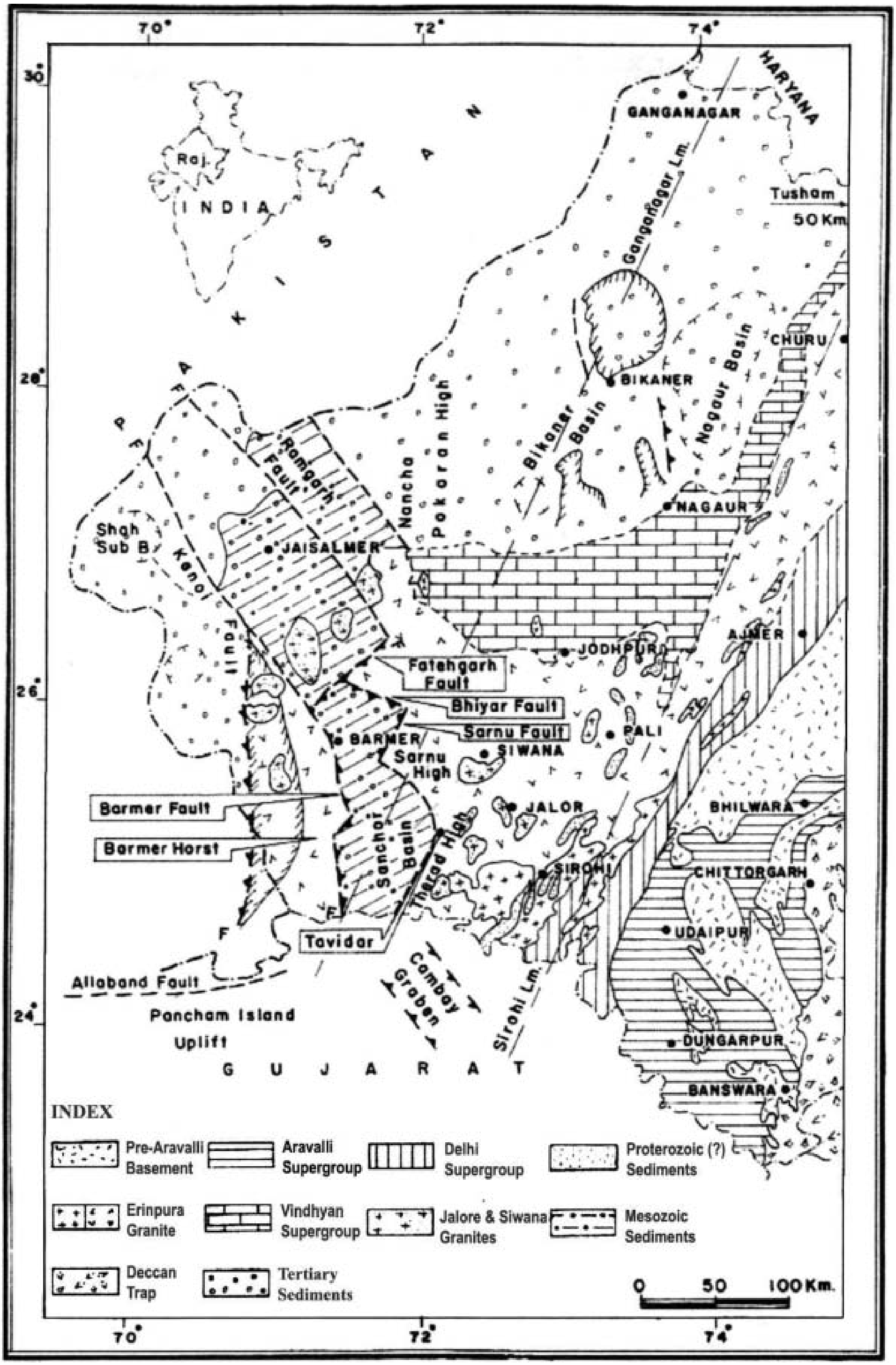

Figure 1. Regional geological map of western Rajasthan, India.

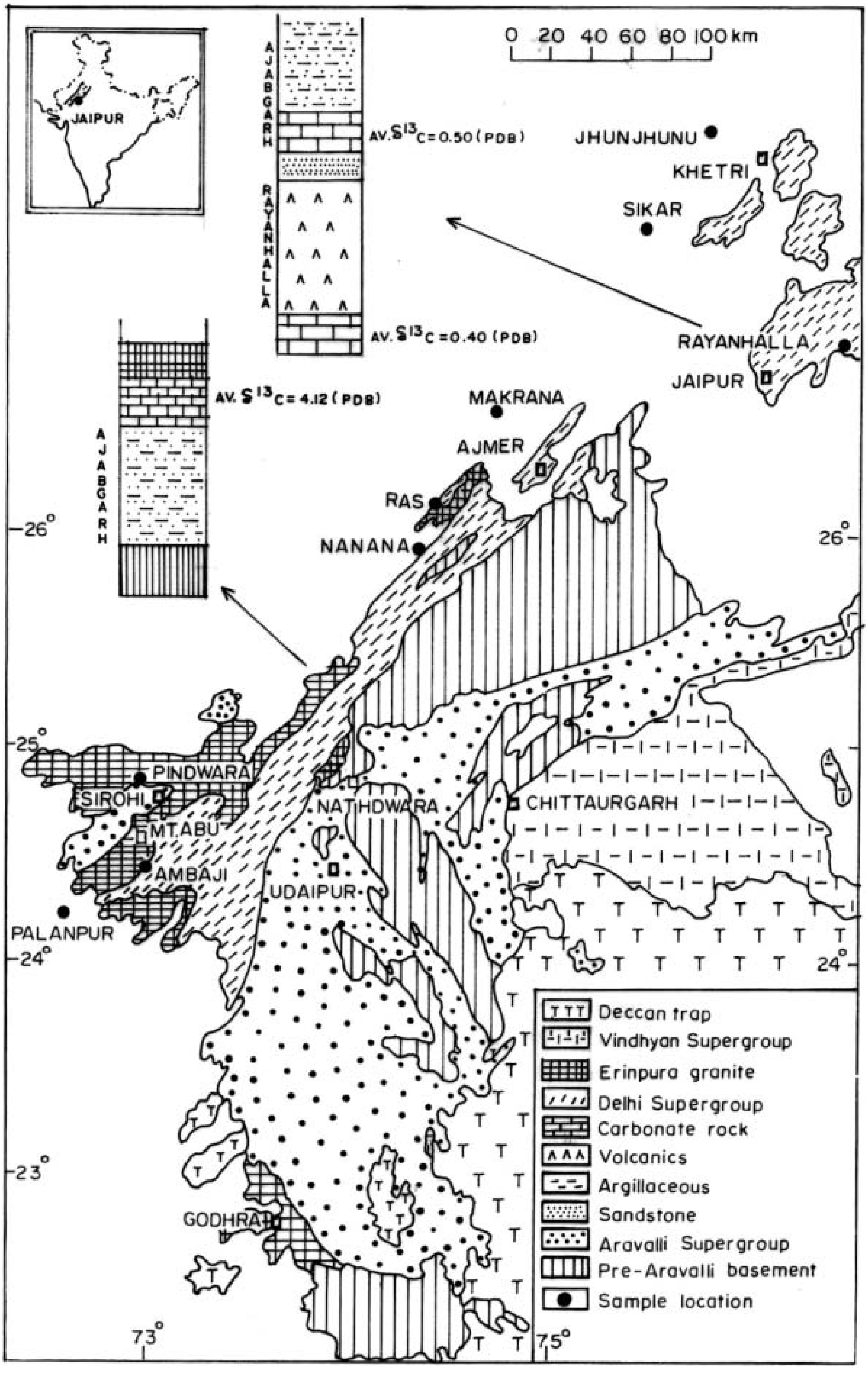

Figure 2. Location map for Delhi Supergroup carbonates, northwestern India.

is the Dogeta formation represented by carbonates, which was accumulated in shallow basins under stable conditions. The Alwar Group, underlain by the Rayanhalla Group, is represented by quartzite, conglomerate and sandstone. The sedimentary structures preserved in the form of current bedding and ripple marks suggest braided stream and subtidal to lower tidal-flat environment of deposition. The Ajabgarh sediments overlying the Alwar clastics with a disconformity are carbonate-rich on the lower portion, containing phosphorite lenses and interlayered basic volcanics (Das Gupta 1989). White quartzite, carbon phyllite and schist represent the middle and upper part of this group. The sedimentation was interrupted by subaqueous volcanism.

Carbonates have also been reported on the western limits of the Delhi Supergroup but are significantly calcitic in composition (Heron 1953). These calcitic carbonate occurrences exposed along NE–SW strike around Sikar, Jhunjhunu, Makrana, Ras, Pindwara, Ambaji and Palanpur are correlated with Rayanhalla carbonates, although these show a different stratigraphic setting compared to Rayanhalla carbonates and are exposed in between the Delhi Syncline and the Banded Gneissic Complex. The stratigraphic status of calcitic carbonates occurring on the western margin of Delhi Fold Belt and its correlation with carbonates from Rayanhalla Group has long been a matter of debate for researchers. Heron (1953) correlated the carbonates on the western margin of the Delhi Supergroup with Rayanhalla. Gupta *et al.* (1980) have showed that these carbonates are a part of the uppermost Ajabgarh Group. Sen (1983), on the other hand, suggests that these should belong to a younger sequence. Singh (1988) suggested that these carbonates constitute the Rayanhalla Group to the West of the 'main Delhi basin'. Roy and Sharma (1999) advocated for correlation of these carbonates with the younger Sirohi Group.

To resolve the correlation issue, besides representative sampling from Sikar, Jhunjhunu, Makrana, Ras, Ambaji and Palanpur (Figure 2), we have undertaken closed spaced sampling of a carbonate outcrop in Pindwara Abu region on the western margin of Delhi Supergroup. The study region is described as part of the Ajabgarh Group of the Delhi Supergroup by Coulson (1933). Gupta *et al.* (1980) classified these rocks as part of Basantgarh formation of the Kumbalgarh Group (Delhi Supergroup). The calcareous metasediments are represented by calcitic marbles, calc-gneiss and calc-schist. The exact stratigraphic status of Pindwara carbonate is not clear due to intermingling with the rocks of the Sirohi Group. The carbonates are calcitic marble with varying degrees of metamorphism. The metamorphic facies vary from lower amphibolite facies to granulite facies. Deb (2001) assigned a younger age of 987 Ma to the associated volcanogenic massive sulphide deposits within these rocks.

Sedimentation

A shallow water fluvial to marginal marine depositional environment has been envisaged for the sedimentary sequences of the Delhi Supergroup (Singh 1982a). The Rayanhalla Group forms the basal succession of the Delhi Supergroup and hosts a number of well preserved sedimentary structures (Patil 1998). The cross-laminations in the Alwar Group quartzites are mostly a torrential type with asymmetrical ripple marks. The calcareous sediments of the Ajabgarh Group contain well preserved, load casts and slump structures. Discontinuous small lenses of conglomerates at several stratigraphic levels indicate local minor pauses in sedimentation although lithostratigraphic units of the Delhi Supergroup grade into one another without a major stratigraphic break.

Sedimentation in the Delhi grabens attests to a significant proportion of volcanic compared to terrigenous clastic sediments. Deposits show a dominance of immature clastics derived from rapidly uplifted terranes supplying granite-derived sediments in the basal parts (Singh 1982b). The sedimentary successions of Delhi Supergroup are characterized by the dominance of calcitic marbles over dolomite and almost the absence of stromatolitic phosphorite horizon. The terrigenous sediments–olcanic association of the Delhi basins seems to match well with the 'Assembly II' of Condie (1982). This implies that the deposition of the Delhi sediments was predominantly in intracratonic rift basins. Basin-wise, the Delhi grabens are more linear in pattern, having well defined cleancut boundaries. Features providing evidence for a rift framework of sedimentation (Singh 1988) are: (1) thick accumulation of shallow water deposits; (2) the dominance of coarse clastics; (3) abrupt changes in thickness and in lithofacies association across the basin axis; (4) strong evidence of overlapping of lithofacies; (5) the presence of synsedimentary volcanics.

Metamorphism

Two distinct metamorphic facies have been recorded in the Delhi Supergroup: an andalusite–staurolite association with sporadic sillimanite near the post-Delhi granites characterizes the northeastern part, and the southwestern part shows a medium pressure, Barrovian metamorphism in which kyanite, sillimanite and staurolite are widespread (Gangopadhyay and Sen 1972). Ryanhalla carbonates, although showing sign of metamorphism, preserve sedimentary structures like cross-bedding, ripple marks, graded bedding and a variety of stromatolitic structures (Patil 1998). The Alwar Group is represented by magnetite quartzites, feldspathic quartzites with or without cummingtonite, and anthophyllite quartzites. The Ajabgarh Group is composed of Mica schists and phyllites containing andalusite $\pm$ staurolite, chlorite schists ($\pm$ garnet) and calc-silicate rocks with calcite and actinolite. Other index minerals in these rocks are garnet, biotite, gedrite, cummingtonite and cordierite.

Age

The age of the succession is not well constrained. Isotopic dates are reported from different parts of the Delhi basin. A critical analysis of these dates is necessary in order to have a meaningful correlation of the events with the geological evolution of the rocks of this basin. The oldest ages (ca. 1700 Ma) are reported from the detrital grains of zircon from the pelitic granulites and are considered as the maximum ages of the Delhi basin (Fareeduddin and Kroner 1998). Zircon from the tuffs rocks of the Saladipura indicates an age of 1850 Ma (Gupta *et al.* 1998). The age is conformable with the Rb–Sr isochron age of 1844 Ma (reported by Gupta *et al.* 1998) of the Jasrapura granite occurring in the North Khetri Belt, and 1849 ± 9 Ma of zircon from the Anasagar granite (Mukhopadhyay *et al.* 2000). All these ages suggest that granites and granite gneisses giving the Palaeoproterozoic ages formed the basement floor of the Delhi basin.

Gopalan *et al.* (1979) determined 1480 ± 40 Ma as the whole rock Rb–Sr isochron age of Saladipura and Udaipur granites. Choudhary *et al.* (1984) reported a similar Rb–Sr isochron age (1470 ± 90 Ma) for Seoli granite that occurs adjacent to the above granites. The age of Chapoli granites in the same region is 1340 ± 50 Ma (Choudhary 1984). Based on these age data, Roy (1990) suggested ca. 1450 Ma as the closing age of the Delhi orogenic cycle. Diorites, which intruded the Delhi rocks of the Ranakpur–Wikeria–Sai belt of the basin, yield an age of 1012 Ma (Volve and Macdougall 1990). This age is based on the whole rock isochron with an initial Nd isotopic composition similar to that of the bulk earth. Sm–Nd mineral isochron ages of the Ranakpur diorites are 838 ± 36, 835 ± 43 and 791 ± 43 Ma (Volve and Macdougall 1990). These younger ages reflect metamorphic re-equilibration of isotope compositions during widespread granite and granodiorite emplacemnt. Interpretation of Volve and Macdougall (1990) gets confirmation by the reports of pooled Rb–Sr isochron suggesting 850 ± 50 Ma for intrusive granites of Sendra, Sadri, Rankpur and Sai by Choudhary (1984) and Choudhary *et al.* (1984).

Pb–Pb ages from Saladipura, Barotia and Deri–Ambaji ore bodies of the Delhi basin are available. These are 1800 Ma for the Saladipura, Barotia and Deri–Ambaji ore bodies of the Delhi basin (Deb *et al.* 1989). Deb (2001) reported 987 ± 6 and 986 ± 2 Ma U–Pb ages for the rhyolites from the Deri and Barotia Khurd areas from the Southern part of the Main Delhi basin. Deb and Thorpe (2004) indicated a tectono-thermal event 'Pindwara Orogeny' between 990 and 836 Ma in the Ambaji–Sendra belt. Choudhary (1984) and Choudhary *et al.* (1984) estimated a number of Rb–Sr isochron ages of granitoids from the Sendra, Sadri, Ranakpur and Sai regions from the Sothern part of basin. The age 850 ± 50 Ma is comparable to the 830 ± 30 and 820 ± 18 Ma ages of Neoproterozoic granitoids from Erinpura and Pali-Jhunjhunu respectively. Stratigraphic significance of these ages is indicated by the evidence of synkinematic emplacement of these granites along discrete shear zones within the undeformed and unmetamorphosed diorites of ca. 1012 Ma age in the Ranakpur-Sai region. A number of Rb–Sr mineral isochron ages are known from different parts of the Delhi basin (Choudhary *et al.* 1984). These include 840 and 875 Ma ages of the Seoli and Chapoli granites in the Khetri Copper Belt, between 750 and 700 Ma ages of Dadikar and ca. 740 Ma age of the Ajmer (Anasagar) granite.

Under the present study, we sampled carbonates belonging to the Rayanhalla Group and the Ajabgarh Group of the Delhi Supergroup exposed in the northeastern portion of Rajasthan, northwestern India for C-isotope studies. The carbonates were sampled around the town Rayanhalla and Ajabgarh, which are type areas for the Rayanhalla and Ajabgarh Groups respectively. The carbonates occurring on the western margin of the Delhi Supergroup were also sampled from different occurrences including Pindwara, Sirohi District. The isotope results are provided in Table 1.

Analytical methods, sampling and evaluating data quality

The whole-rock carbonate samples were sampled at close intervals along a stratigraphic profile from the Rayanhalla and Ajabgarh town, Northeastern Rajasthan, India. Representative samples were, however, collected from the different carbonate occurrences occurring on the western margin of the Delhi Supergroup and included in the ambit of the Rayanhalla Group. Closed spaced sampling was also carried out in carbonates from Pindwara, Sirohi District. 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 analysed 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, had a $\delta^{18}O$ value of –11.28 $\pm$ 0.004‰ PDB and $\delta^{13}C$ = $-$8.58 $\pm$ 0.02‰ PDB. The results are expressed in the notation δ‰ (per mil) in relation to international PDB scale.

C-isotope compositions of most carbonates probably do not change much during diagenesis because the volume of carbon within the carbonate rock is vastly greater than that in the pore-water reservoir and because the fractionation between calcium carbonate and water is relatively small at near-surface temperatures (Emrich *et al.* 1970; Scholle and Arthur 1980). Most metasedimentary carbonates in this study have suffered amphibolite facies of metamorphism. The Rayanhalla and Ajabgarh Group carbonates are dolomitic in composition, dolomite is generally considered as a diagenetic mineral. Nonetheless, there is growing evidence that precipitation of dolomite in the Precambrian was either coeval with calcite or that dolomitization was an early diagenetic phenomenon caused by waters isotopically comparable to that of seawater (e.g. Veizer and Hoefs 1976; Veizer *et al.* 1992a; Kah 2000).

Diagenetic methanogenic reactions can produce both high-$\delta^{13}C$ CO_2 and low-$\delta^{13}C$ CH_4, and may, therefore, produce elevated $\delta^{13}C$ values (Dix *et al.* 1995). However, mixing of early formed high-$\delta^{13}C$ CO_2 with CO_2 derived from the subsequent oxidation of low-$\delta^{13}C$–CH_4 commonly leads to the precipitation of carbonates with a wide range of both large positive and negative $\delta^{13}C$ values. This results in significant C-isotope heterogeneity and to subvertical trends on $\delta^{13}C$ versus $\delta^{18}O$ diagrams (De Giovani *et al.* 1974). In contrast, high $\delta^{13}C$ carbonates in study areas do not show significant scatter and do not show the range of highly negative $\delta^{13}C$ values that might be expected from diagenetic reactions with methane. Combined, these observations suggest that elevated $\delta^{13}C$ values for carbonates in this study probably reflect their original compositions, rather than subsequent processes.

The homogeneity in the $\delta^{13}C$ values in a sampled profile from the McCoy Creek Group suggests that the values are premetamorphic as it is difficult for $\delta^{13}C$ to homogenize in the carbonates at the highest metamorphic stage without oxygen being similarly affected (Wickham and Peters 1993).

The calcite-rich nature of most of amphibolite facies carbonates from western North America, means that they have undergone little or no decarbonation and that the $\delta^{13}C$ value of these carbonates was thus little affected by loss of CO_2 produced by metamorphic reactions (Wickham and Peters 1992). The high $\delta^{13}C$ values in calcite rich carbonates of the Delhi Supergroup show little variation in $\delta^{13}C$ values; however, the $\delta^{18}O$ values are significantly variable. The homogeneity of $\delta^{13}C$ values compared to $\delta^{18}O$ may also be observed in carbonates from the Rayanhalla and Ajabgarh groups.

Quite a few geochemical and petrological parameters have been proposed to evaluate the degree of alteration of individual samples (Kaufman and Knoll 1995; Kah *et al.* 1999; Melezhik *et al.* 2001). Oxygen isotopes are sensitive indicators of alteration, with a marked decrease in $\delta^{18}O$ values if the system undergoes isotopic exchange with meteoric or hydrothermal fluids. In diagenetic environments, three orders of magnitude higher water/rock ratios are supposedly required to alter carbon isotope values compared to those of oxygen isotope values (Banner and Hanson 1990). The knowledge of the behaviour of Rb, Sr, Mn and Fe helps in selecting samples that have undergone little or no alteration. Among all the

Table 1. C- and O-isotopes and bulk chemical analyses of selected carbonate samples from the Rayanhalla and Ajabgarh Groups, Delhi Supergroup, NW India.

Sample	Locality	δO^{18}PDB	δC^{13}PDB	Stratigraphy (m)	CaO	MgO	Fe	Mn	Sr	Mg/Ca	Mn/Sr
S 3	Jhunjhunu	−14.89	4.3								
S 2	Sikar	−12.13	2.1		47.49	1.06	2420	207	91	0.01	2.27
21	Makrana	−13.5	3.3								
RM	Ras	−13.01	3.8		46.25	0.97	7670	152	2730	0.01	0.05
NM	Nannana	−12.23	2		47.08	4.28	5500	202	239	0.07	0.84
24	Ambaji	−20.21	4.3								
23	Palanpur	−8.02	3.9		64.72	4.24	980	12	210	0.03	0.05
RP 1	Pindwara	−10.30	4.06	0							
RP 2	Pindwara	−9.55	3.73	5							
RP 3	Pindwara	−9.53	3.64	10							
RP 4	Pindwara	−10.58	4.24	15							
RP 5	Pindwara	−10.48	4.08	20	48.41	1.69	5090	91	2473	0.02	0.03
RP 6	Pindwara	−9.27	4.16	25							
RP 7	Pindwara	−9.45	4.24	30	45.74	1.59	6580	127	2476	0.02	0.05
RP 8	Pindwara	−9.18	4.60	35							
RP 9	Pindwara	−9.51	4.96	40	45.50	1.61	7640	148	2699	0.02	0.05
RP 10	Pindwara	−11.30	3.83	45							
RP 11	Pindwara	−9.75	4.07	50							
RP 12	Pindwara	−9.57	4.33	55	38.89	2.09	11410	181	2148	0.04	0.08
RP 13	Pindwara	−8.61	4.64	60							
RP 14	Pindwara	−10.43	4.42	65	41.89	1.94	11930	230	2818	0.03	0.08
RP 15	Pindwara	−11.50	3.40	70	39.47	1.59	13680	291	2268	0.03	0.12
RP 16	Pindwara	−11.80	4.37	75							
RP 17	Pindwara	−8.73	2.90	80	47.46	1.40	7840	168	1761	0.02	0.09
RP 18	Pindwara	−11.24	3.63	85	48.28	1.68	7520	152	2088	0.02	0.07
RP 19	Pindwara	−9.68	4.46	90							
RP 20	Pindwara	−9.10	4.83	95							
AJB 4	Ajabgarh	−12.96	1.47	0							
AJB 7	Ajabgarh	−12.83	1.28	5							
AJB 8	Ajabgarh	−12.86	0.86	11	31.02	22.04	4700	272	19	0.59	14.31

Table 1. (*Continued.*)

Sample	Locality	δO^{18}PDB	δC^{13}PDB	Stratigraphy (m)	CaO	MgO	Fe	Mn	Sr	Mg/Ca	Mn/Sr
AJB 12	Ajabgarh	−15.58	-0.57	16							
AJB 13	Ajabgarh	−12.69	1.39	21							
AJB 15	Ajabgarh	−15.17	-0.32	25							
AJB 21	Ajabgarh	−11.9	0.22	30							
AJB 25	Ajabgarh	−11.86	-0.2	35							
AJB 28	Ajabgarh	−11.03	0.47	40							
AJB 30	Ajabgarh	−10.87	0.47	45							
RLO 1	Rayanhalla	−9.49	0.19	0							
RLO 2	Rayanhalla	−8.48	0.64	3							
RLO 3	Rayanhalla	−8.17	0.39	6							
RLO 4	Rayanhalla	−8.24	0.07	9							
RLO 5	Rayanhalla	−7.61	0.11	12	32.30	21.53	5300	243	12	0.55	20.25
RLO 6	Rayanhalla	−9.07	0.65	15							
RLO 7	Rayanhalla	−8.27	0.63	18							
RLO 8	Rayanhalla	−9.79	0.49	21							
RLO 12	Rayanhalla	−9.13	0.94	24							
RLO 17	Rayanhalla	−8.96	0.17	27							
RLO 18	Rayanhalla	−8.66	0.14	30							
RLO 21	Rayanhalla	−9.51	0.26	33							
RLO 22	Rayanhalla	−9.25	0.15	36							
RLO 24	Rayanhalla	−9.47	0.24	39							
RLO 26	Rayanhalla	−8.41	0.71	42							
RLO 27	Rayanhalla	−10.19	0.25	45							
RLO 29	Rayanhalla	−10.89	0.55	48							
RLO 30	Rayanhalla	−10.77	0.55	51							
RLO 33	Rayanhalla	−10.31	0.89	54							
RLO 36	Rayanhalla	−10.03	-0.26	57							
RLO 39	Rayanhalla	−11.34	0.64	60							
RLO 40	Rayanhalla	−9.4	0.64	63	23.86	16.46	5310	497	22	0.58	22.59

Note: Oxides are expressed in wt-% and trace elements in ppm.

parameters used for such an evaluation, the simplest and the most effective one is the Mn/Sr ratio (Kaufman and Knoll 1995). During marine as well as meteoric diagenesis of limestone, Mn increases and Sr decreases; therefore, the Mn/Sr ratio is generally considered a good indicator of alteration (Jacobsen and Kaufman 1999). Limestones or dolostones with low Mn/Sr usually retain near primary $\delta^{13}C$. As pointed out by Bekker *et al.* (2003), the greatest confidence in the preservation of primary isotopic trends comes from the consistency of the curves based on closely spaced samples collected in sequence stratigraphic framework from multiple sections within a given depositional basin. Palaeoproterozic carbonates, especially dolostones, are usually much more Fe- and Mn-enriched than Neoproterozic and Phanerozoic ones (Veizer 1992b). This may pose a problem in the use of the Mn/Sr ratio as in index of alteration. The Mn/Sr ratio is very low in the carbonates from the western margin of the Delhi Supergroup. The Mn/Sr ratio is usually higher than 10 in most of the analysed dolomites due to the high abundance of Mn in selected carbonate samples from the Rayanhalla and Ajabgarh Groups.

Results and discussion

The isotopic compositions of Mesoproterozoic Delhi carbonates are listed in Table 1. This table includes the data provided by Maheshwari *et al.* (2001, 2002) and the new data generated under the present study. As can be seen in an isotope stratigraphy (Figure 3), the spread of $\delta^{13}C$-values is narrow and mostly around $0 \pm 0.5‰$. Extreme values, however, reach a high of $+4.3‰$. The $\delta^{18}O$ is much more variable but most of the samples provide between –8 and –12‰ PDB. In the Delhi Supergroup, dolostones formed during early diagenesis probably possess isotopic ratios close to those of Mesoproterozoic seawater, as pore space in them was apparently occluded very soon after deposition, thus limiting subsequent fluid–rock interaction and attendant isotopic resetting. This is supported by the limited range of $\delta^{18}O$ values shown by most of studied carbonates (Table 1).

Marine carbonate rocks from the Delhi Supergroup of northwestern India show little deviation in whole rock $\delta^{13}C$carb values, which is generally around 0‰. This narrow range and almost constant $\delta^{13}C$carb values persist despite close sampling and through long sections. The data suggest that, in contrast to Neoproterozoic, the global rate of organic carbon burial was probably constant during deposition of the Delhi Supergroup, and perhaps generally during the Mesoproterozoic, as was the redox state of the atmosphere and hydrosphere. The nearly invariant C isotopic profile of the Rayanhalla Group and Ajabgarh Group exposed in the northeastern portion of Rajasthan, northwestern India, suggests that these groups of the Delhi Supergroup are older than any carbonates of the Delhi Supergroup. However, the observed pattern is similar to C isotopic profiles of Mesoproterozoic carbonates older than ca. 1.3 Ga as reported from different parts of world (Pokrovsky and Vinogradov 1991; Buick *et al.* 1995; Knoll *et al.* 1995; Xiao *et al.* 1997; Kah *et al.* 1999; Bartley *et al.* 2001). This observation supports an early Mesoproterozoic age for the Delhi Supergroup.

In contrast, the carbonates occurring on the western margin of Delhi Supergroup have, on average, moderately positive $\delta^{13}C$ values (from 2 to $+4.3‰$). The high $\delta^{13}C$ carbonates along the western limits of the Delhi Supergroup may, however, point to their deposition during the late Mesoproterozoic, a period characterized by such high positive $\delta^{13}C$ values globally (Kah *et al.* 1999, 2001; Bartley *et al.* 2001). The

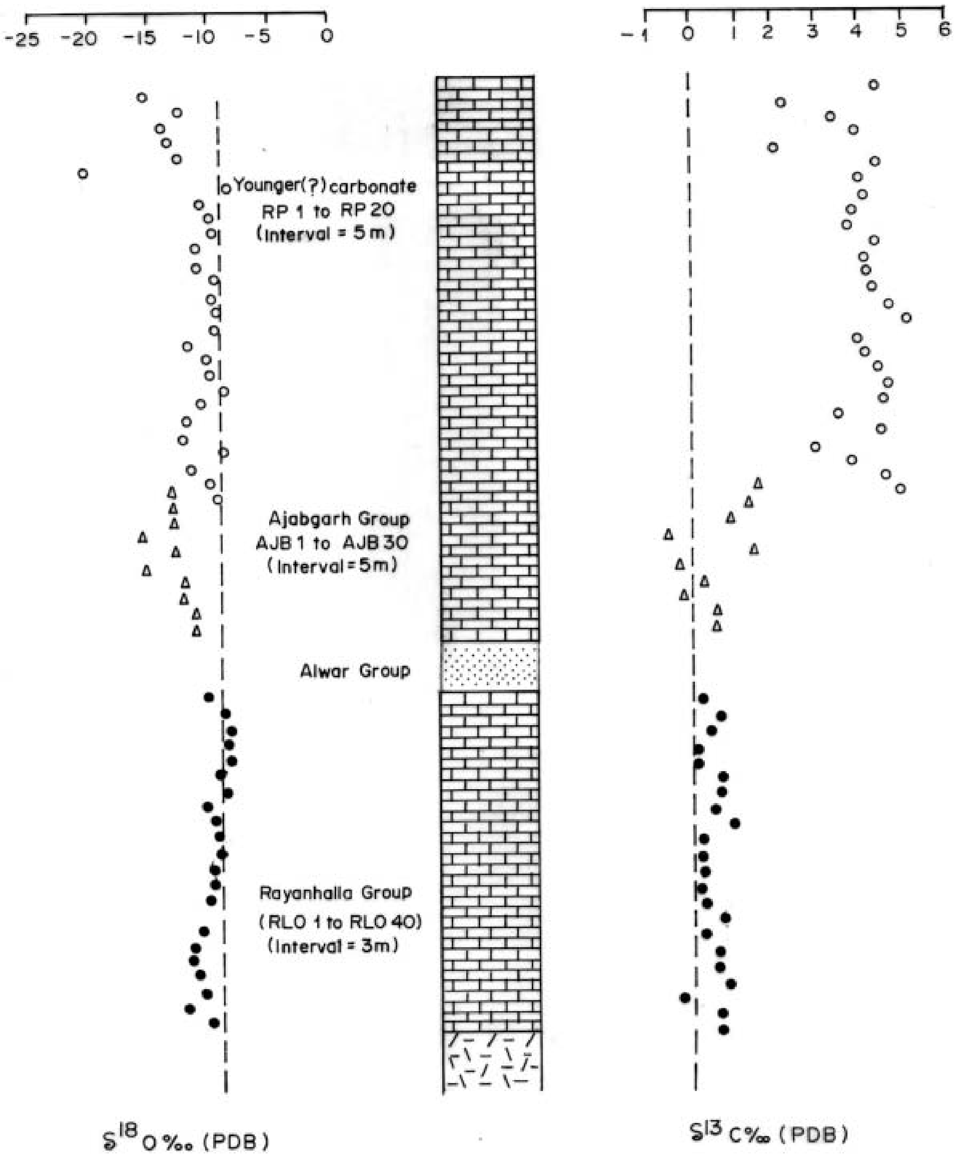

Figure 3. Secular variations in $\delta^{13}C$ and $\delta^{18}O$ along the composite sequence of carbonates, Delhi Supergroup, India. ●: Rayanhalla Group; Δ: Ajabgarh Group; ○: Younger Sirohi carbonates.

positive $\delta^{13}C$ values in the metamorphosed carbonates are assumed to represent C-isotope composition of the carbonate protoliths, since there is no known process to enrich carbonate in ^{13}C during regional metamorphism. $\delta^{13}C$ is much more difficult to change than $\delta^{18}O$ in a rock system, as the relative masses of C in rock versus diagenetic fluids is typically such that $\delta^{13}C$ compositions will be buffered to rock values. As such, oxygen isotopic compositions of the carbonate will be altered upon diagenesis at a much quicker rate than carbon isotopic compositions.

Evolution of carbonate $\delta^{13}C$ to more positive values reflects increased biomass and/or increased proportional burial of isotopically light organic matter, potentially attributable to one of several tectonic forcing mechanisms. The observed changes in the character of the global C isotopic curve in the later part of the Mesoproterozoic likely record changes in the character of global biogeochemical cycling, and are plausibly linked to the assembly of the supercontinent Rodinia (Bartley *et al.* 2001).

As data accumulate from successions worldwide, our understanding of Mesoproterozoic seawater evolution improves, changing incrementally with each new dataset (Bartley *et al.* 2001). The C isotopic record of the post-2.0 Ga Proterozoic can be conveniently subdivided into three parts (Kah *et al.* 2001). The first, comprising the late Proterozoic and early Mesoproterozoic (2.0–1.25 Ga), is characterized by C isotopic values near $0 \pm 1\%$, 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 recognized 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 (about +5‰; Kaufman and Knoll 1995).

Conclusion

Delhi Supergroup carbonates are characterized by $\delta^{13}C$ values similar to those measured for Mesoproterozoic carbonates worldwide. It may, therefore, be inferred that Rayanhalla and Ajabgarh carbonates of the Delhi Supergroup were deposited during early Mesoproterozoic time, representing the 2.0–1.25 Ga interval, as proposed by Kah *et al.* (2001). Carbonates occurring on the western margin of the Delhi Supergroup, however, have on average moderately positive $\delta^{13}C$ values (from 2 to +4.96‰). These high $\delta^{13}C$ carbonates point to the Mesoproterozoic–Neoproterozoic transition (from ~1.25 to ~0.85 Ga), a period characterized by high positive $\delta^{13}C$ values globally.

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