CARBON ISOTOPE FLUCTUATIONS THROUGH THE NEOPROTEROZOIC-LOWER CAMBRIAN BIRMANIA BASIN, RAJASTHAN, INDIA

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ABSTRACT: The results of a carbon isotope study from a hitherto unexplored marine sediments from the Birmania basin, Northwestern India are reported, which documents significant isotope variation across the Precambrian-Cambrian boundary (Pc/C). An attempt has been made to identify carbon isotope chronostratigraphic marker for the Precambrian-Cambrian boundary in the sedimentay succession. The transition is marked by a negative excursion during phosphoritic activity at the base of the Birmania succession which is followed by a positive excursion close to the boundary and a swing back to less positive values in the Early Cambrian. The characteristics of the paleoenvironment during the transition interval is also discussed.

INTRODUCTION

The paleogeographic reconstruction of the end phase of Neoproterozoic assumes a significance due to the fact that the interactions between the biosphere and the atmosphere, hydrosphere and geosphere during this period of time strongly influenced the evolution of life and initiated a remarkable phase of organic evolution well documented in the rocks of this age (Banerjee and Majumdar 1999). Time related changes in these carbon reservoirs and processes during the end Proterozoic have played an important role in the evolution of the environment and of life (Des Marais 1997). Brasier (1992) discussed at length various factors that pushed shallow marine ecosystem of the late Neoproterozoic-Cambrian towards P-limitation and suggested that nitrate fixation, density stratification and massive removal of P in the sediments were responsible for the formation of phosphatic deposits within this time interval. East Gondwana assembly of continents provide fine examples of stratigraphic successions in which the ideas related to oceanic stratification, phosphate deposition, enhanced organic production and carbon isotope fluctuations can be verified and correlated from continent to continent (Banerjee and Majumdar 1999).

The Birmania basin is an oval shaped isolated remnant of the Marwar basin (Neoproterozoic-Early Palaeozoic) located in the heart of the Thar desert of western Rajasthan, India. It is underlain by Malani Igneous Suite of rocks which range in age
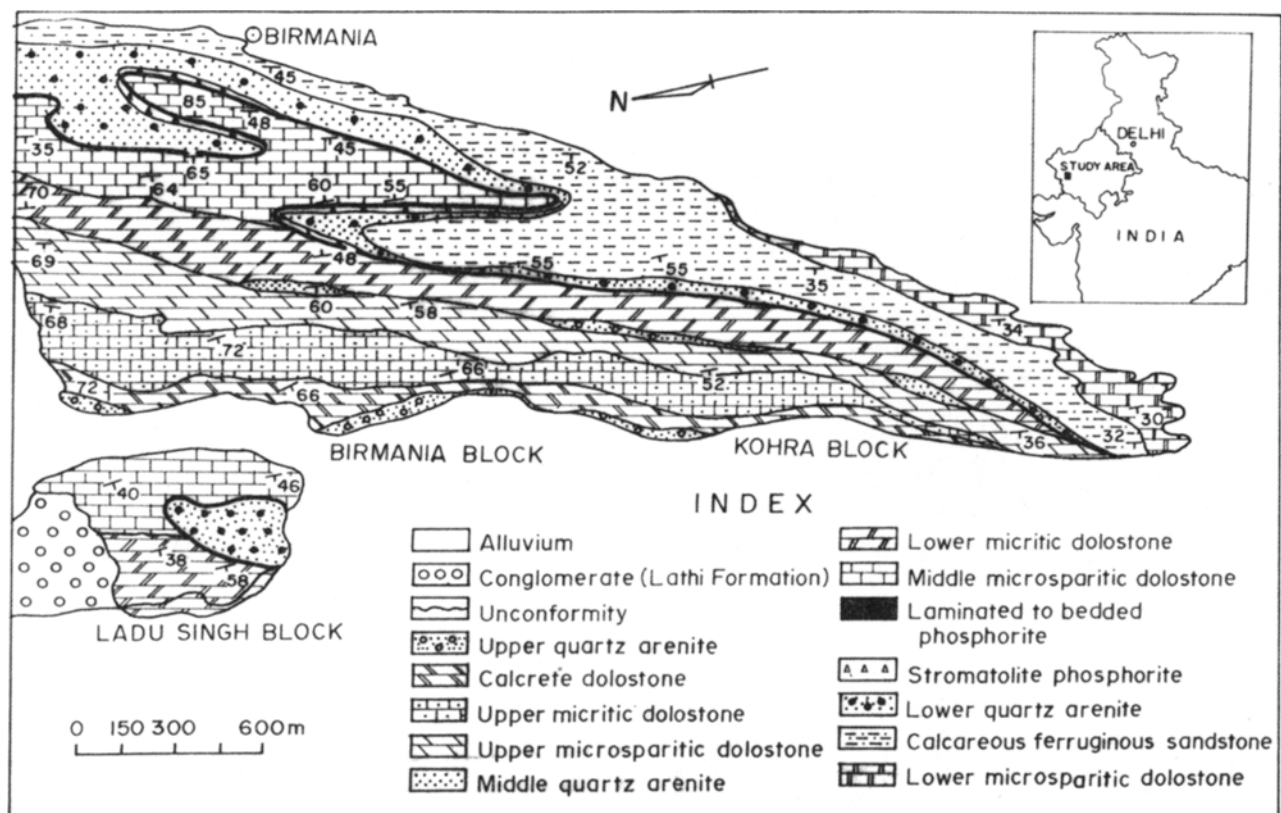

Figure 1. Geological map of Birmania Basin, western India (modified after Mathur and Chauhan 1995).

from 780 to 680 Ma (Rathore et al. 1999). The Birmania basin comprises around 900 metre thick sedimentary sequence of siliciclastic, carbonate and phosphorite facies. These sequences are unconformably overlain by Lathi conglomerate of Jurassic age in northern flank of the basin (Fig. 1). Global Neoproterozoic glacial activity in the western Rajasthan is also reported and is represented by Pokaran Boulder Bed, few kms away from study area. The Pokaran Boulder Bed overlies the Malani Igneous Suite and is mainly consist of boulders and angular fragments of igneous rocks belong to Malani Suite (Srivastava 1992). In the present paper $\delta^{13}C$ and $\delta^{18}O$-values of 32 carbonate samples from Birmania Basin, Rajasthan, India is reported. The isotopic fluctuations along the Birmania succession is discussed and is correlated with carbon isotopic profiles as reconstructed from other Neoproterozoic successions of the world.

GEOLOGICAL FRAMEWORK

The sedimentary rocks of Birmania basin are broadly grouped into two formations viz: lower Randha Formation which comprises mainly siliciclastic facies and upper Birmania Formation which consists of repetitive sequences of siliciclastic, carbonate and phosphorite facies (Fig. 1). The sedimentary sequence of Randha Formation starts with brown to maroon coloured shale at the base which grades upward into fine grained shaly sandstone, siltstone and ferugenous sandstone. The sandstone shows development of small scale cross bedding and finally grades upward into creamish white, clean washed quartz arenite.

The base of Birmania basin is represented by the Malani Igneous Suite of rocks which range in age from 780 to 680 Ma (Rathore et al. 1999). The stratigraphic position of this succession is delineated on the basis of regional correlation with rocks of the Salt Range in Pakistan. Logical comparison of phosphorite beds of the Krol belt in the lesser Himalaya, Hazara in the salt range (Banerjee 1986) and Birmania in western Rajasthan (Hussain and Banerjee 1979) helps in identifying this closely connected continental mass as representing the end phase of the Neoproterozoic and the dawn of a new era.

The Birmania Formation comprises a mixed assemblage of siliciclastic, carbonate and phosphorite facies. This package of mixed assemblage has been divided into three distinct lithofacies associations i.g. the lower siliciclastic dominated, middle phosphorite dominated and upper carbonate dominated lithofacies association (Fig. 1). The lower lithofacies association comprises grey coloured microsparitic dolostones at the base which grades upwards into deep brown ferruginous sandstone, finally culminating into quartz arenite. These siliciclastic rocks show wavy to lenticular bedding and small- scale cross-bedding. The middle lithofacies association starts with stromatolitic phosphorite horizon. The stromatolites are domical to pseudocolumnar structures of 2.0 to 8 cm in height. They are composed of 2 to 3 mm thick,

moderate to steeply convex laminae of carbonate and phosphate. The stromatolitic phosphorite is followed by laminated to bedded phosphorite, which is composed of alternate laminations of carbonate and phosphate minerals. The upper lithofacies association starts with thickly bedded, dark grey microsparitic dolostones. It is followed by massive micritic dolostones which appears light grey in colour. The calcrete dolostone overlying micritic dolostone is a greyish brown massive hard rock. It shows gradational contact with the underlying micritic dolostones. The top of lithofacies association is represented by creamy white quartz arenite. This sequence of the Birmania Formation is unconformably overlain by conglomerate and sandstone of Lathi Formation of Jurassic age.

Petrographic, Geochemical & Environmental Attributes

The siliciclastic rocks of Birmania basin comprises 80 to 95 percent clean washed medium to coarse detrital quartz of unimodal nature (Mathur and Chauhan 1995). Heavy minerals present are tourmaline, zircon, sphene, garnet and magnetite. The phosphorite facies consisting of stromatolitic and bedded phosphorite is mainly composed of microcrystalline fluorapatite, calcite/dolomite and terrigeneous quartz. The stromatolitic phosphorite comprises columnar to pseudocolumnar structures in which each stromatolitic columns is composed of alternate laminations of phosphate and carbonate minerals often studded with detrital quartz grains. The intercolumnar spaces of the stromatolites are filled with quartz and phosphorite clasts which are in turn cemented by phosphate or carbonate minerals. The bedded phosphorite is composed of three types of laminations.

The microsparitic dolostone is composed of equant grains of dolomite/calcite showing xenotopic fabric with a few lenses of sparite. The micritic dolostones appears as structureless homogeneous dolomicrite mud at the bottom. It grades upward into a complex microsparitic mass consisting of clots of dolomicrite of 1.6 to 2.4 mm diameter. Calcrete dolostone represents three distinct textural patterns. Firstly, angular to subangular silt sized quartz coated by micrite. Secondly, spherical to ooidal carbonate bodies 0.64 to 2.3 mm in size, outlined by microsparite and micrite. Thirdly, bigger elongated, irregular carbonate bodies of 0.61 to 2.6 mm diameter. They also possess outer rim of micrite and internally composed of radial fibrous sparite.

The carbonate rocks of Birmania basin contain 28.77 to 33.70% CaO, 15.43 to 21.53% MgO with corresponding 1.3 to 2.05 CaO/MgO ratio (Mathur and Chauhan 1995). The carbonate rocks of Birmania basin may be defined as mainly calcitic dolostones (cf. Pettijohn 1969). P_2O_5 content of phosphorite of the area is as high as 29.37% (Mathur and Chauhan 1995). The CaO indicate positive correlation while SiO_2 and MgO show negative correlation with P_2O_5 contents.

This relationship corroborates with the petrographic studies of the phosphorite rocks of the area.

On the basis of stratigraphic, lithological, petrographic and geochemical data the siliciclastic, carbonate and phosphorite lithofacies association of Birmania basin, a relatively shallow water nearshore environment is proposed (Mathur 1995). The basal Randha siliciclastic facies, characterised by shale at the base grading upward into sandy shale, shaly sandstone, siltstone, ferrugineous sandstone and finally into quartz arenite, constitute a typical sequence coarsening upwardly. The sandy facies often show planar cross-bedding which display moderate variation in paleocurrent pattern. The overlying Birmania Formation is represented by different lithofacies association. The carbonate and siliciclastic facies form repetitive sequence while phosphorite facies form intermediate sequence with repetition of quartz arenite horizon only. It may be noted that each sequence starts with carbonate facies at the base and terminates in the form of quartz arenite at the top. This sort of vertical distribution of carbonates and siliciclastic facies signify repetitive events of sea level changes amounting to marine incursions followed by depositional regressions. Such a sequence is considered as shallowing upward cycle evolved due to repetitive transgressive events followed by carbonate sedimentation and influx of terrigeneous detritus representing regressive events (Mack and James 1986).

ANALYTICAL METHODS AND SAMPLING

Carbonates were sampled at close interval around Birmania and Kohra town in the Birmania basin. A total of 32 carbonate samples were collected. CO_2 was extracted from carbonates in a high vacuum line after reaction with phosphoric 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 V.G. ISOTECH 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 $\delta^{13}C = 8.58\ 0.02$ ‰ PDB. The results are expressed in the notation δ ‰ (per mil) in relation to international PDB scale.

RESULTS AND DISCUSSION

The carbon isotopic composition of Phanerozoic marine carbonates is complicated by the vital effects of skeletal organisms and pervasive bioturbation. Proterozoic carbonates are not plagued with these problems (Hoffman et al. 1998). The palaeontologic information necessary for characterizing the boundary interval in Birmania formation is absent however, it is now widely accepted that the isotope age curve provides a useful tool for stratigraphic analysis and correlation, particularly for unfossiliferous successions. The Birmania succession is represented by phosphorite horizon and number of carbonate formations. The carbon and oxygen

isotope profiles of the Birmania succession are presented here and their implication for the Precambrian-Cambrian (Pc/C) boundary interval have been explored.

A global review of carbon isotopic composition of Proterozoic carbonates (Veizer et al. 1992) and organic matter (Strauss et al. 1992) indicates that 'redox events' were episodic during this transition. The observed episodic records of markedly positive δ^{13}Ccarb excursions in these carbonates indicate that relative rates of organic burial increased dramatically concomitant with rise of O_2 level in the atmosphere (Karhu and Holland 1996). A global positive δ^{13}Ccarb event during the interval 590-550 Ma is accompanied by high $^{87}Sr/^{86}Sr$ values (Derry et al. 1992) which helps to infer that this geochemical event triggered an enhanced rate of continental erosin which was sustained through the Pan-African uplift (Asmerom et al. 1991). Consequently, it is believed that the absolute rates of organic sedimentation were accelerated during the closing phase of Neoproterozoic and the atmospheric oxygen levels markedly increased (Kaufman and Knoll 1995). The end-Neoproterozoic isotope event accompanied the first well demonstrated occurrence of multicellular life (Kaufman and Knoll 1995; Brasier 1990). Both carbon isotopic and accompanying biological events are consistent with an increase in atmospheric O_2 level (Knoll and Holland 1995; Des Marais 1997) at this juncture of the earth history. The carbon isotopic records of Neoproterozoic sections from China, Iran, Lesser Himalaya and Rajasthan in India, Oman and a general review by Ripperdan (1994) demonstrate an overall consistency in the variation pattern. The terminal Neoproterozoic carbonates in these sections are characterised by positive δ^{13}Ccarb value with negative excursions due to presence of phosphorite beds sandwiched between normal dolomites.

We have obtained δ^{13}C values for 32 carbonate samples collected through the Birmania basin around Birmania and Kohra town. These data have been provided in Table 1 and plotted in figure 2 along the lithocolumn. The primary Birmania basin carbonates appeared to underwent early fabric-retentive dolomitization, rendering them relatively impermeable. The carbonates of Birmania basin sampled for present study have neither suffered deep burial nor alteration. Consequently, Birmania carbonates may provide pristine status of the C cycle at the time of their deposition and these values can, therefore, be useful in inter-regional correlations.

The carbon isotope composition of the Birmania basin carbonates are provided in Table 1. The isotope profile of Birmania succession is shown in Fig. 2. The base of Birmania Formation is represented by stromatolitic phosphorite. The carbonate interlayers associated with phosphorite are characterised by negative δ^{13}C (upto - 3.56 PDB ‰). The lower microsparitic dolostone underlying to stromatolitic phosphorite provide negative δ^{13}C value around Kohra block. The middle microsparitic dolostone, lower & upper micritic

Table 1. Carbon-isotope ratios of Birmania carbonates.

Sample No. Birmania	Sample No. Kohra	Stratigraphic Unit	delta13C PDB Birmania	delta13C PDB Kohra	delta18O PDB Birmania	delta18O PDB Kohra
	A1	lower microsparitic dolostone		-2.11	n.a.	-6.08
	A2	lower microsparitic dolostone		-2.11	n.a.	-6.1
B3	A3	stromatolitic phophorite	-3.03	-3.37	-6.65	-6.78
B4	A4	stromatolitic phophorite	-3.56	-3.31	-6.95	-6.73
B5	A5	bedded phosphorite	-1.76	-3.05	-6.28	-6.19
B6	A6	bedded phosphorite	-1.72	-3.36	-6.1	-6.74
B7	A7	middle microsparitic dolostone	3.07	1.27	-2.31	-2.64
B8	A8	middle microsparitic dolostone	3.06	1.27	-2.34	-2.65
B9	A9	lower microsparitic dolostone	1.33	2.5	-3.49	-1.84
B10	A10	lower microsparitic dolostone	1.34	2.51	-3.47	-1.87
B11	A11	upper microsparitic dolostone	3.21	3.86	-1.91	-0.88
B12	A12	upper microsparitic dolostone	3.19	3.87	-1.97	-0.98
B13	A13	upper micritic dolostone	2.22	0.69	-3.51	-2.75
B14	A14	upper micritic dolostone	2.21	0.66	-3.52	-2.76
B15	A15	greyish dolostone	2.07	2.27	-1.96	-0.92

dolostone and calcrete dolostones overlying the phosphorites are represented by positive $\delta^{13}C$ values upto +3.87‰ PDB. A swing to less positive $\delta^{13}C$ values may be observed in uppermost carbonates of study sequence. Oxygen isotopic composition of carbonates are very much prone to alteration during diagenesis. However, the carbonates of Birmania succession show very high oxygen isotopic composition and may be taken to represent compositions close to the original values. This further indicates that the carbon isotopic signals preserved in this succession are primary and not affected by diagenesis.

The widespread occurrence of phosphorite during late Neoproterozoic-early Cambrian time interval demands global synchronicity of events like movement of continents in environmentally conducive latitudes, development of large scale rifting, oceanic turnover, development of upwelling cells, shallowing of the basin and carbon burial, oxidation and reduction. This period of phosphate accumulation was closely linked with periods of continental extension and rifting (Bond et al. 1984) which resulted into creation of many shallow epicontinental seaways at low latitudes (Cook and McElhinny 1979) in which phosphorites formed in substantial quantity. The late Neoproterozoic-Early Cambrian phosphogenesis is therefore, an expression of geological and geochemically activities commencing around ~800 Ma when large scale organic matter burial took place leading to O_2 buildup in the contemporary atmosphere. The carbon reservoirs of the contemporary oceans and continents will be drastically affected by such environmental changes expressed in the form of considerable increase followed by a sharp decrease of $\delta^{13}C$ in the marine carbonates and phosphates deposited during this time. The phosphogenic event was either triggered by, or the result of transformation of soft-bodied organisms into mineralised skeletons closely connected to the increasing pCO$_2$ level which can be safely linked to continental rifting. During the late Neoproterozoic and beginning of the early

Cambrian the prevailing stagnancy in the ocean basin was interrupted by a well marked phase of ventillation, concomitant with a sharp negative swing in the carbon isotope value. Continental rifting at this period of time enhanced the possibility of phosphate deposition by providing shallow water locales in the lower latitudes (Cook and Shergold 1984). The logical comparison of phosphorite beds of Birmania in western Rajasthan with Krol belt in lesser Himalaya and Hazara in the Salt Range (Banerjee 1986) indicate as representing the end phase of the Neoproterozoic and dawn of a new era.

The Precambrian-Cambrian Transition

The Precambrian-Cambrian transition was a geological interval characterised, most discernibly, by profound changes in the biosphere, with the evolution of many new metazoan groups and the development of bio-mineralisation (Cowie and Brasier 1989). Certainly, the changes in the biosphere were also associated with changes in the other related domains, such as atmosphere, hydrosphere, cryosphere and lithosphere. Evidence indicates that there was a glacial epoch at or near the Precambrian-Cambrian boundary reaching down to low latitudes. The terminal Precambrian glacial climate was replaced by warm Cambrian climate with melting of glaciers and rise in sea level (Tucker 1992) and the Precambrian-Cambrian boundary appears to straddle an interval between cool ice-house and warm greenhouse conditions (Brasier 1992). It has been found that at many places the transitional Precambrian-Cambrian beds contain phosphorite (Brasier 1992; Tucker 1992) and their proper interpretation and evaluation may lead to profound implications for the Precambrian-Cambrian transitional regime. It appears that the period of Precambrian-Cambrian transition was a time of global change, with increased plate movements and opening oceans and a climate progression from late Precambrian glaciation to Cambrian global warming.
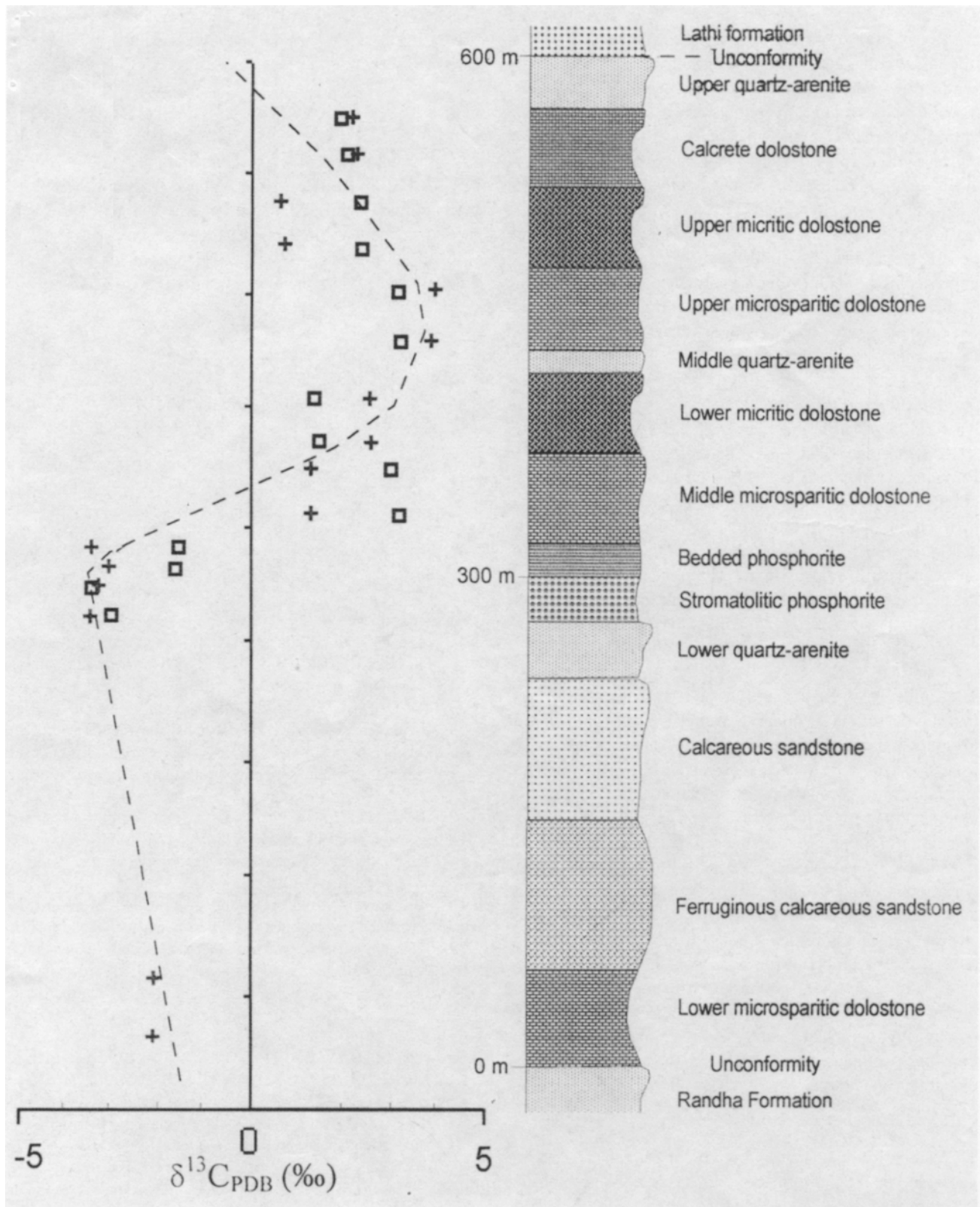
Figure 2. Secular variations in δ³C of carbonates through the Birmania Basin. + Kohra Block sample; □ Birmania Block sample

The carbon isotopic records of the Pc/C transition are available only from shallow-marine carbonates. Carbon isotope determinations of carbonates from stratigraphically continuous sedimentary successions have yielded well-defined records of $\delta^{13}C$ variations during the time interval immediately preceding the appearance of shelly metazoans at the base of Cambrian. Carbon isotope profiles are now available from boundary sections of many parts of world including Siberia, Iran, India, China, Morocco and South Australia (see Brasier et al. 1990 for references). There are remarkable similarities in the patterns of $\delta^{13}C$ variations imprinted in the shallow marine carbonate sequences in spite of their wide geographic distribution. In all cases the trend comprises negative-low positive values in the terminal Proterozoic (Vendian) to markedly positive values in the Nemakit-Daldynian, followed by a swing back to negative-less positive values in the early Tommotian strata (Kaufman and Knoll 1995; Aharon and Liew 1992; Brasier 1992; Tucker 1992; Ripperdan 1994). The pattern of $\delta^{13}C$ variations in Birmania Basin (Fig. 2) is very similar to as observed from different carbonate sequences of world. Dissimilarities between the $\delta^{13}C$ records are related to the rates of shift, the amplitude of the isotope excursions, and the exact position of the negative $\delta^{13}C$ offset with respect to the Pc/C boundary. It has been suggested that the $\delta^{13}C$ positive excursion prior to the Pc/C boundary lasted for a time interval not exceeding 7 m.y. (Aharon and Liew 1992).

The similarity of the carbon isotope records across the Pc/C transition in different boundary sections, in spite of their wide geographic distribution, implies that the causes of the isotope excursions must be related to some global events and the excursion is of chronostratigraphic significance and may be used as an aid to correlation (see Brasier et al. 1990). This contention is strengthened by the fact that the transition is also marked by changes in sea level, pCO_2, atmosphere, nutrient content of seawater (manifested by phosphorite deposits) and temperature. All these changes may be related to the climatic change from ice house-cold house to greenhouse condition during the Precambrian-Cambrian boundary interval associated with large-scale, global extensional tectonic regime during the transition leading to opening of oceans. These global environmental changes taking place during the transition were likely to affect organic matter production, oxidation and burial resulting in the observed isotope excursions.

The carbon isotopic pattern observed in Birmania succession appears to be similar to that observed in the well-established Precambrian-Cambrian boundary sections of the world (Kaufman and Knoll 1995; Aharon and Liew 1992; Aharon et al. 1987; Friedman and Chakraborty 1997). The Birmania succession is apparently unfossiliferous resembling the Precambrian-Cambrian boundary in Oman where also the strata lack Cambrian body fossils (Burns and Matter 1993). A worldwide phase of phosphogenesis (Cook and Shergold 1984) at or near, the Pc/C boundary supports the inference

(Tucker 1986; Lambert et al. 1987) of biological controls driven by ocean fertility changes and acting on the marine carbon reservoir.

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