

CHEMOSTRATIGRAPHY OF CARBONATE SUCCESSION OF THE VEMPALLE FORMATION, CUDDAPAH BASIN, INDIA: A STRATIGRAPHIC RECORD OF TERMINAL PALAEOPROTEROZOIC OCEAN-ATMOSPHERE-BIOSPHERE SYSTEM

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Abstract: A shallowing-upward succession of intertidal to subtidal stromatolitic dolomites of the upper Palaeoproterozoic (Orosirian) Vempalle Formation of Cuddapah basin, Peninsular India, is preserved in the Bramhanapalle area (14°25'15" N, 78°12'19" E), near Pulivendla, south India. The $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{V-PDB}}$ values of some selected stromatolitic dolomite samples from this succession vary from +1.25 to -5.74 per mil and from -5.42 to -18.25, respectively. These values are consistent with the global data during the upper Palaeoproterozoic time. A positive to negative $\delta^{13}\text{C}$ shift in the studied stratigraphic section is indicating (i) a gradual decrease in the biomass productivity during the deposition of Vempalle sediments (ii) the decline of stromatolite type carbonate rocks due to the volcanic activity during the deposition of the Vempalle sediments (iii) an advent of "snowball earth" - like condition in the Indian Peninsular region at the onset of Vempalle sedimentation.

Keywords: Palaeoproterozoic, Mesoproterozoic, Stromatolites, Concretions, Stable isotopes

1. INTRODUCTION

The Palaeoproterozoic time is marked by +ve excursion of $\delta^{13}\text{C}_{\text{carb}}$ between 2.40 and 2.06 Ma and this positive excursion is known as Lomagundi-Jatuli event, which is considered to be an unique isotopic event in terms of duration (> 300 Ma) and $\delta^{13}\text{C}$ enrichment (up to + 18 ‰) (Melezhic et al., 2005 and references therein). The end of this isotopic excursion is marked by the world-wide development of diagenetic carbonate concretions with negative $\delta^{13}\text{C}_{\text{carb}}$ values (Melezhic et al., 1999). However, $\delta^{13}\text{C}_{\text{carb}}$ values of the sedimentary successions deposited from the late Palaeoproterozoic to early Mesoproterozoic era record values near 0 ± 1 ‰ (e.g., Maheswari et al., 2005). The Vempalle Formation (~1.9 Ga) of Cuddapah basin in Peninsular India preserves a continuous thick succession of stromatolitic

dolomite (~1.5 km) during the upper Palaeoproterozoic (Orosirian) time. A detail chemostratigraphic study of the Proterozoic Cuddapah basin, the second largest intracratonic basin on Dharwar Craton (Ramakrishnan & Vaidyanathan, 2008), is not very robust (Chakrabarti et al., 2011) and also about the carbonate rocks from the upper Palaeoproterozoic Vempalle Formation is in infancy. Hence, the upper Palaeoproterozoic stromatolitic carbonates of the Vempalle Formation (~1.9 Ga old) of Cuddapah basin have been chosen in the present study to address the question of how far the chemostratigraphic data match the global chemostratigraphic curve in the Orosirian period. We also constrain the stable isotope signatures of the Vempalle marine carbonates, to understand the interaction of ocean-atmosphere system with sedimentation during the deposition of Orosirian Vempalle sediments.

2. GEOLOGY

The crescent-shaped Cuddapah Basin of Andhra Pradesh, south-eastern Peninsular India, is having a maximum width of 145 km (in the middle portion) and 440 km long, and exposed over an area of 44,000 sq. km. On the western margin of the basin the undisturbed Proterozoic sediments rest on an Archaean gneissic complex enclosing the greenstone belts of Kadiri, Veligallu and Gadwal (Nagaraja Rao et al., 1987) with a profound nonconformity. Its eastern margin has a thrust contact with both Archaean and Eastern Ghat Mobile belt.

The Cuddapah basin was described as a rift basin resultant from crustal doming, erosion and subsidence (Drury, 1984; Jain et al., 1995; Acharya, 1997; Chakraborty, 2000) or by peripheral foreland basin based on geophysical investigation (Singh & Mishra, 2002). This basin consists of well-preserved Palaeoproterozoic-Neoproterozoic sedimentary and associated volcanic succession of ~ 12 km thickness. The Cuddapah Basin has been divided into two broad structural sectors divided by the Rudravaram Line (Meijerink et al., 1984) which is a structural divide (boundary fault) between folded Nallamalai Group of rocks occurring west of this line and the generally flat-lying Lower Cuddapah (Papaghni Group and Chitravati Group) and/or Kurnool Group of rocks occurring east of it. The arcuate belt east of the Rudravaram line is recognized as the Nallamalai Fold Belt (NFB) by Narayanswamy (1966). Granitic intrusions and mineralization are associated with the Rudravaram line.

The lithostratigraphy of the Cuddapah basin (Table 1) was established by King (1872), which composed dominantly of argillaceous and arenaceous sediments with subordinate calcareous sediments. Palaeoproterozoic is mainly dominated by ~ 1900 m thick Vempalle Formation of stromatolitic dolomite with subordinate mudstones, sandstones and cherts cropping out along the western and southwestern margin of the basin (Fig. 1), which overlies conformably on the basal siliciclastic Gulcheru Formation. Each of the three overlying groups viz, Papaghni Group, Chitravati Group and Nallamalai Group of the Cuddapah Supergroup are composed of quartzite at the base and a shale unit at the top, representing shallow-marine shelf succession with periodic transgressive and regressive events in the basin. Many workers like Dasgupta et al., (2005), Lakshminarayana (2008), Chakrabarti & Shome (2007, 2010, 2011) have studied the facies attributes of the basin and conclude an overall shallow marine shelf environment with individual sedimentary horizons

indicative of beach, littoral, tidal-flat and lagoonal environment. Chakrabarti et al., (2009) discussed the geochemistry of the Mesoproterozoic clastic sedimentary rocks of the basal Gulcheru Formation of the Cuddapah basin to highlight their provenance and weathering history. Chakrabarti & Shome (2010) described the microbial mat features within the inferred tidal deposits of the Gulcheru Formation, from Kottalu area, southwestern part of the Cuddapah basin near Pullivendla, Andhra Pradesh, India. Recently, Chakrabarti et al., (2011) further discussed the carbon and oxygen isotopic variation within stromatolitic dolomite, Vempalle Formation, Cuddapah basin. Contemporaneous igneous activity is represented by sills, volcanic flows and other intrusives along the western periphery of the basin (particularly in the Vempalle Formation) and the eastern part of the Nallamalai Group (Nagaraja Rao et al., 1987).

The Vempalle Formation, well-exposed in the Pulivendla area belonging to the Southwestern sector of the Cuddapah basin, which is represented by several litho-sections with a complete succession of stromatolitic dolomite, shale and volcanic rocks. The samples studied for stable isotope analysis are collected from the stromatolitic dolomitic limestone outcrops exposed in the upper portion of the Vempalle Formation in the vicinity of Bramhanapalle Asbestos Mine (14°25'15" N, 78°12'16" E), near the Pulivendla area (Fig. 1). Approximately, 50 m thick successions of stromatolitic limestone intercalated with black to grey chert are well-exposed in this region. At Bramhanapalle area, circular to oval-shaped closely-packed stromatolites, occur within continuous and well-defined zones, are less than one to few meters in thickness and less than 10 cm to more than 1 m in diameter (Schopf & Prasad, 1978). The spatial and temporal distribution of dome-shaped stromatolites along with profuse development of oolites seems to be indicative of shallow, marine, and probably intertidal to shallow subtidal depositional milieu (Schopf & Prasad, 1978, Chakrabarti et al., 2011).

3. AGE

Rb-Sr radiometric dating by whole rock analysis of the Pulivendla sills intruded into the lower Cuddapah supergroup has yielded an age of 1704 ± 112 Ma (Bhaskar Rao et al., 1995). Biotite and clinopyroxene minerals analyzed from two samples of the same sill gave an age of 1811 Ma and 1831 Ma, respectively, which may be an absolute upper age limit for sedimentation of the Papaghni and the Chitravati groups into which the sill intrudes (Murthy et al., 1987).

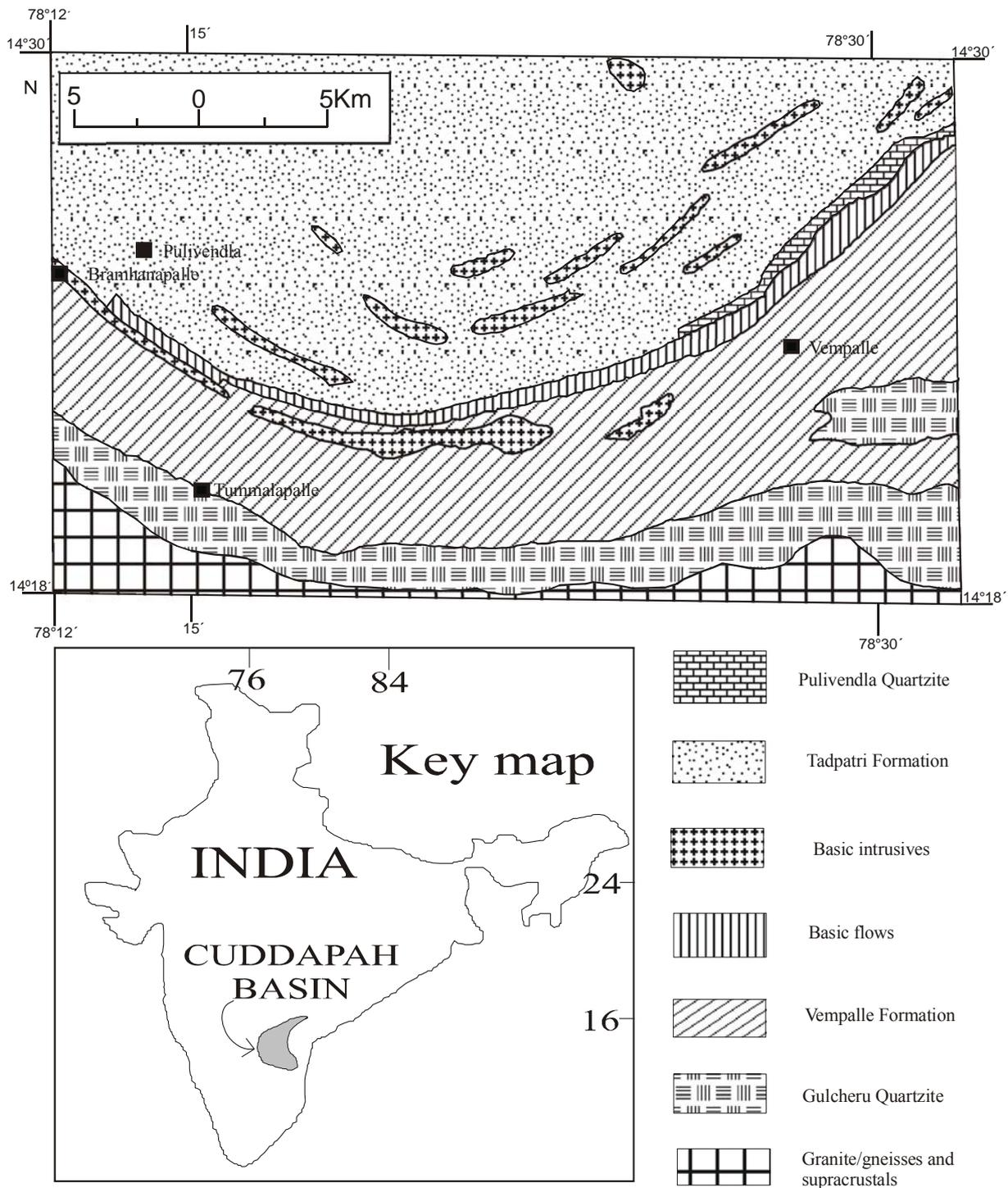


Figure 1. Geological map of the study area. Inset shows the location of the Cuddapah basin, India.

Zachariah et al., (1999) determined the Pb, Sr, and Nd, isotopic compositions on uranium mineralized and barren stromatolitic dolomite samples from the Vempalle and Tadpatri Formations. Their analysis (Zachariah et al., 1999) yielded a Pb-Pb age of 1756 ± 29 Ma, which is interpreted as the time of U - mineralization and as a minimum age for carbonate sedimentation and dolomitization. ^{40}Ar - ^{39}Ar laser-fusion determined on phlogopite mica, from the Tadpatri Formation mafic-ultramafic sill complex, constrain the

extension and volcanism in the initial phase of the Cuddapah basin at 1.9 Ga. (Anand et al., 2003). A recent high-precision U-Pb date of 1885 ± 4 Ma was obtained on a mafic sill from the Pullivendla region in the Cuddapah supergroup (French et al., 2008). According to Gururaja and Chandra (1987) the Vempalle and Tadpatri stromatolites were of Riphean age. However, a diverse mini-stromatolite assemblage of Palaeoproterozoic Era is also reported from the study area Vempalle Formation by Sharma & Shukla (1998).

Table 1. Stratigraphy of the Cuddapah basin (GSI, 1981)

Supergroup	Group	Formation	Thick.(m)	Age	
C U D D A P A H S U P E R G R O U P	KURNOOL	Nandyal Shale	50-100	Neoproterozoic	
		Koilkuntala Limestone	15-50		
		Paniam Quartzite	10-35		
		Auk Shale	10-35		
		Narji Limestone	100-200		
	Banganapalle Quartzite	10-57			
			Unconformity		
	NALLAMALAI	Srisailam Quartzite	620(+)	Mesoproterozoic	
		Cumbum Formation	2000(+)		
		Bairenkonda(Nagari) Quartzite	1500		
			Unconformity		
	CHITRAVATI	Gandikota Quartzite	1200	Mesoproterozoic	
		Tadpatri Formation	4600		
		Pulivendla Quartzite	1-75		
	PAPAGHNI	Vempalle Formation	1500	Palaeoproterozoic	
		Gulcheru Quartzite	28-250		
			Unconformity		
		Archaean Gneissic Complex			

4. METHODOLOGY

The carbonate samples are sampled at close interval up-section from the exposed rock surfaces in the Bramhanapalle area, near Pulivendla (Fig. 1). A total number of 17 samples were selected for stable isotope analysis and petrographic study. The sample points are depicted in the litho-log (Fig. 2). The results are listed in table 2.

For the preparation of thin sections, samples were crushed into small slices. Sections perpendicular to bedding is commonly selected for the preparation of this section. Each sample is mounted on a glass slide after preliminary grinding. The sample is then further grounded and polished to bring to a thickness of 0.03 mm. The thin section is covered with a cover slip to avoid dust contamination and oxidation. The prepared thin sections are then photographed by using a high resolution polarizing microscope (Leica DMLP, Camera No. Leica DFC 320), under plane polarized light (PPL).

Carbon and oxygen isotopic compositions were determined at NEG-LABISE, Federal University of Pernambuco, Brazil, using the conventional digestion method (McCrea, 1950). Powdered samples were reacted with H₃PO₄ at 25⁰C to release the CO₂. Extended reaction period was preferred for dolomitic

or marl samples instead of increasing the reaction temperature. The δ¹³C and δ¹⁸O values were measured on cryogenically cleaned CO₂ (Craig, 1957) in a triple collector SIRA II mass spectrometer or in a DELTA V Advantage. The C and O isotopic data are presented (as ‰ 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 ± 0.1‰, in general. The values obtained for the standard NBS-20 in a separate run against BSC yielded δ¹³C_{V-PDB} = -1.05‰, and δ¹⁸O_{V-PDB} = -4.22‰. These results are in close agreement with the values reported by the US National Bureau of Standards (-1.06‰ and -4.14‰, respectively). The conversion of SMOW values to PDB standard have been attempted by using the following formula ¹⁸O_{calcite} (SMOW) = 1.03086 ¹⁸O_{calcite} (PDB)+30.86 (Friedman & O'Neil, 1977).

5. DEPOSITIONAL ENVIRONMENT

A brief description about the constituent facies in the study area is necessary to highlight the depositional environment of the studied lithostratigraphic succession.

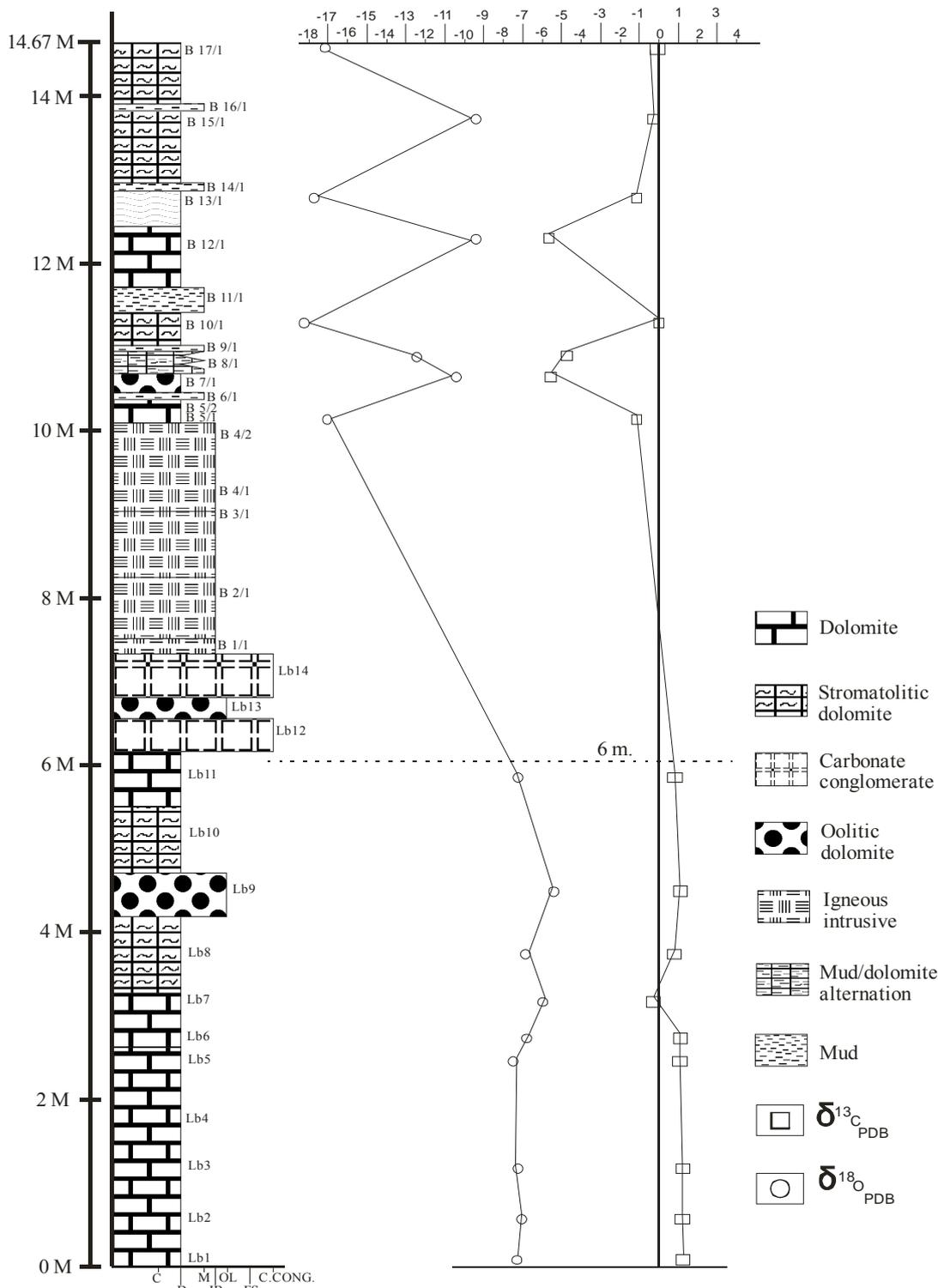


Figure 2. Litholog, sample points and temporal variation of stable isotope data from Bramhanapalle area, Cuddapah basin, India Please write the explanation on the inside of figures with similar 10 Times New Roman!.

The Vempalle Formation in the study area is represented by four distinct lithofacies viz i) heterolithic facies ii) oolitic grainstone facies (iii) columnar stromatolite facies, and (iv) domal stromatolite facies (Chakrabarti et al., 2011, 2012). Heterolithic facies consisting of small domal and microdigitate stromatolites interbedded with micritic

limestone, occasionally concretions are common.

The mudcracks within the heteroliths indicate occasional emergence while the syneresis cracks within the dolomite indicates either shrinkage and swelling in a soft substrate as a result of salinity change in a marine or lacustrine condition or due to seismic shaking.

Table 2. C and O-isotope data for the Vempalle carbonates, Cuddapah Basin, India

Sample #	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VSMOW)	Precision for C- isotope ratio measurements (12 cycles)	Precision for O- isotope ratio measurements (12 cycles)
B17/1	-0.03	-17.17	13.16	0.007	0.007
B15/1	0.27	-9.41	21.16	0.005	0.008
B13/1	-1.17	-17.75	12.56	0.003	0.007
B12/1	-5.74	-8.19	22.42	0.004	0.006
B10/1	-0.24	-18.25	12.05	0.006	0.009
B8/1	-4.73	-12.43	18.04	0.006	0.009
B7/1	-5.56	-10.41	20.44	0.006	0.013
B5/1	-1.13	-17.05	13.29	0.005	0.004
LB1	1.25	-7.28	22.80	0.003	0.013
LB2	1.20	-7.10	23.54	0.016	0.016
LB3	1.22	-7.22	22.88	0.012	0.017
LB5	1.07	-7.50	23.60	0.008	0.010
LB6	1.09	-6.79	23.31	0.005	0.002
LB7	-0.29	-5.99	24.02	0.008	0.011
LB8	0.81	-6.84	23.62	0.005	0.009
LB9	1.09	-5.42	24.68	0.006	0.014
LB11	0.83	-7.26	22.78	0.006	0.010



Figure 3. Columnar stromatolites showing partially linked and branching columns, Bramhanapalle area, Cuddapah Basin, India.



Figure 4. Domal stromatolites from Vempalle Formation, Bramhanapalle area, Cuddapah Basin, India

Stromatolitic dolomites form when the sediments shoaled into the upper subtidal and intertidal zone. Columnar stromatolites (Fig. 3) formed in the

zone of greater wave agitation than did domal stromatolites (Fig. 4) (Riding, 1991, Grotzinger, 1986).

The abundance of unconformities, rare channeling, presence of ooids, siltstone / dolopackstone couplets are consistent with the deposition in subtidal to intertidal set-up (Sumner and Grotzinger, 2004). Thin beds of intraformational carbonate conglomerate composed of equant fragments etc. indicate synsedimentary seismic shock (Pratt, 2001). Abundant algal stromatolites, mud cracks and ripple marks are representing a shallow marine environment for the deposition of sediments (Roy et al., 1990; Dhana Raju et al., 1993).

6. ISOTOPE COMPOSITION

The overall range of stable isotope composition for the Vempalle stromatolitic dolomites from the studied sedimentary succession is shown in table 2. The $\delta^{13}\text{C}_{\text{carb}}$ values of the Vempalle Formation vary from +1.25 to -5.74 per mil, whereas the $\delta^{18}\text{O}_{\text{V-PDB}}$ values vary from -5.42 to -18.25‰. One dolomite sample (B17/1) shows near 0 value (-0.03) of $\delta^{13}\text{C}$. A cross-plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ (Fig. 5) shows low positive correlation (correlation coefficient value $r = 0.25$, number of samples $n = 17$). This poor correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data indicates that at least some of the $\delta^{13}\text{C}$ of these stromatolitic dolomites are representative of the original signatures (Armstrong-Altrin et al., 2009, 2011).

Following major C- and O-isotopic trends have been noticed in the studied succession (Fig. 2).

(a) Low positive C-isotopic values have been observed in the first 6 m of the studied succession.

- (b) Significant moderate negative c-isotope values have been observed for the remaining part of the studied succession.
- (c) Moderately depleted low negative O-isotopic values have been observed in the first 6 m of the studied succession.
- (d) Significantly depleted high negative O-isotopic values have been observed for the remaining part of the studied succession.

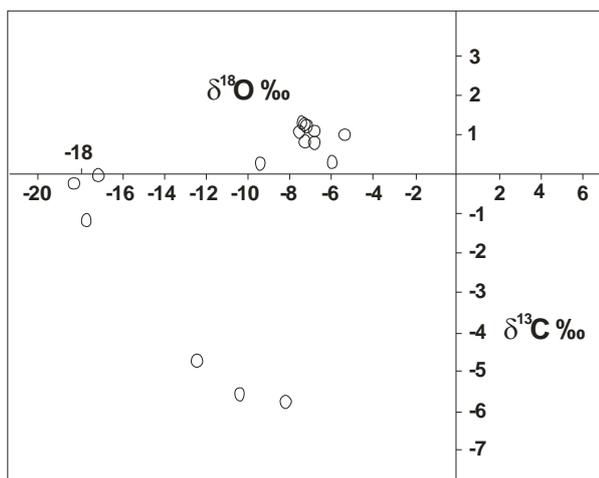


Figure 5. $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ plot for the Vempalle Formation stromatolitic dolomites, Bramhanapalle area, Cuddapah basin, India.

7. DISCUSSION

The Precambrian secular curve for $\delta^{13}\text{C}_{\text{carb}}$ has two major peaks at c. 2.3-2.2 Ga and at c. 0.65 Ga. In between these two peaks, the curve is essentially flat. The $\delta^{13}\text{C}_{\text{carb}}$ peak at c. 2.3-2.2 Ga is commonly called Lomagundi-Jatuli event and during this time $\delta^{13}\text{C}_{\text{carb}}$ values reach as high as +18 per mil (Melezhic et al., 2005 and references therein). The conspicuously bimodal nature of the secular C-isotopic curve indicates step-wise increase of oxygen in atmosphere as a result of episodic burial of carbon (Lindsey & Brasier, 2002, Nagarajan et al., 2008, Ader et al., 2009). Global Supercontinent cycles are also thought to be related to this Palaeoproterozoic isotopic excursion (Karhu, 1993, Bekker et al., 2003). This type of strongly positive $\delta^{13}\text{C}$ in carbonates characterizes pre glacial successions, while negative $\delta^{13}\text{C}$ anomalies occur in all “cap carbonates” over Neoproterozoic glacial sediments. However, it is quite enigmatic that the end of the Palaeoproterozoic C-isotopic excursion at c. 2.3-2.2 Ga is not marked by any recognized global glacial phenomenon. Rather, the end of the Lomagundi-Jatuli event is marked by diagenetic carbonate concretions with negative $\delta^{13}\text{C}_{\text{carb}}$ values. This may be the first reliable evidence of oxygenic material being recycled during diagenesis under oxic conditions (Melezhic et al.,

1999). These diagenetic carbonate concretions are abundant in c. 2 Ga sedimentary successions and are associated with other diagenetic products like phosphatic nodules. After this, there was little carbon burial and the interaction with biosphere was minimal, which leads to biogeochemical stasis during the period from 1.8-0.8 Ga (Kah et al., 2001).

With this framework in mind, the isotopic value of the analyzed samples from Vempalle dolomites in Bramahanapalle area is evaluated. Available age data indicates that the Vempalle sedimentation began at ~ 1.9 Ga, i.e., at the upper part of Palaeoproterozoic Era (Orosirian), which is characterized by C-isotopic values near 0 ± 1 per mil (Bartley et al., 2007). The Proterozoic carbonate sequences in the Jixian section, Tianjin, China also preserve secular variation of $\delta^{13}\text{C}$ values of sea-water from 1700 Ma to ca. 800 Ma. In the Changchengian of upper Palaeoproterozoic the $\delta^{13}\text{C}$ values are mostly negative ones from -4.9 per mil to -2.6 per mil (Xuelei et al., 2004). Hence, the $\delta^{13}\text{C}$ data of this study ($\sim +1.25$ to -5.74 ; Table 2) is almost consistent with the global data. Since there is no correlation between C-and O-isotope values ($r = +0.25$), the possibility of post-depositional modifications has been ruled out. The petrographic study of these carbonates further shows that they preserve primary fabric like oolites (Fig. 6), stromatolitic laminae (Fig. 7) and micrite cement. So the isotopic signatures are considered to be unaltered and remain with primary and pristine characteristics (Aharon et al., 1987). Furthermore the stable isotope values and the petrographic characteristic of the Vempalle carbonates indicating a depositional medium with increased productivity of stromatolitic microbial communities, which preferentially fixes ^{12}C in the form of organic C (C_{org}) leading to ^{13}C enrichment in carbonate carbon (Schidlowski, 2000). The $\delta^{13}\text{C}$ in the lower part of the Vempalle succession shows positive excursion and this is likely to be the result of increased rate of organic matter burial in a shallow stromatolitic carbonate platform. A positive to negative $\delta^{13}\text{C}$ trend (from bottom to up) may possibly reflect a gradual decrease in the biomass productivity. If we consider the model (Melezhic et al., 1999) of restricted basin with the high bio-productivity for Vempalle sedimentation, the negative carbon isotope values indicate the contribution of CO_2 or bicarbonate derived from oxidation of organic matter (Botz et al., 1988) as it is evident from high level of bio-productivity marked by the occurrence of abundant stromatolites. Another point also needs to be mentioned here is that the Vempalle Formation is the only stratigraphic unit of the Cuddapah basin, which contains a sequence of lava flows (Anand et al.,

2003). The thickest lava flow occurs in the southern part of the Cuddapah basin at Pulivendla, Vempalle, and Animala (~ 50 m thick) areas. Basic lava flows conformably overlies the Vempalle Formation stromatolitic dolomites marking roughly the end of the Vempalle sedimentation in Papaghni sub basin.



Figure 6. Broken oolites (seen under plane polarized light) identified from the oolitic grainstone facies of the Vempalle Formation, Bramhanapalle area, Cuddapah Basin, India. Scale bar = 200 μm.

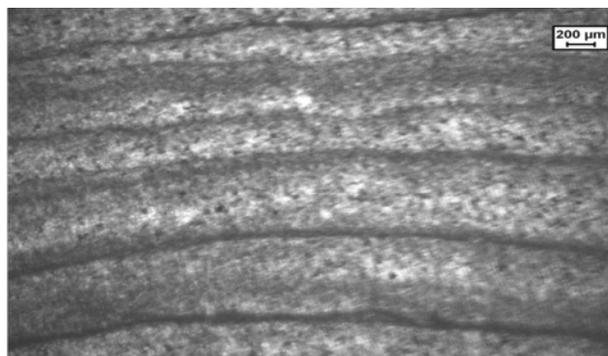


Figure 7. Banded microstructure (stromatolitic laminae seen under plane polarized light) from columnar stromatolite facies, Bramhanapalle area, Vempalle Formation, Cuddapah Basin, India. Scale bar = 200 μm.

During volcanism, due to enormous heat production, most of the bacteria disappeared and tends to decline the stromatolite carbonate platform. This leads to the decrease in biological ^{12}C uptake from the inorganic C-pool, which results an increase in ^{12}C in surface water and probably caused the negative $\delta^{13}\text{C}_{\text{carb}}$ shift in marine carbonate precipitates. Alternatively, they may reflect the first appearance of isotopically light diagenetic carbonate concretions linked to the emergence of “modern-style” recycling of organic matter (Melezhic et al., 2005). Such diagenetic concretions are observed in the study area (Fig. 8). Usually, the post glacial marine cap carbonates are also associated with negative C isotopic excursions (~ -5 ‰) (Hoffman et al., 1998 and references therein). Hence, we also do not gainsay the possibility of the impact of terminal period of Huronian glaciation or may be an advent of “snowball earth” - like condition in the Indian Peninsular region at the onset of Vempalle

sedimentation. However, voluminous stable isotope analyses of carbonate rocks may require to address the aforesaid postulate.



Figure 8. Diagenetic concretions in dolomites from the Vempalle Formation, Bramhanapalle area, Cuddapah Basin, India.

8. CONCLUSIONS

(a) The $\delta^{13}\text{C}_{\text{carb}}$ values of the marine stromatolitic dolomites of the upper Palaeoproterozoic Vempalle Formation, of Cuddapah Basin, south India vary from +1.25 to -5.74 per mil while the $\delta^{18}\text{O}_{\text{V-PDB}}$ values vary from -5.42 to -18.25.

(b) The poor correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data for the Vempalle carbonates reveals that they are not significantly affected by post-depositional alterations.

(c) Available age data indicates that the Vempalle sedimentation began at ~ 1.9 Ga (upper part of Palaeoproterozoic era) and characterized by C-isotopic values near 0 ± 1 per mil (Bartley et al., 2007). Hence, the $\delta^{13}\text{C}$ data of this study is consistent with the global data during this period.

(d) A positive to negative $\delta^{13}\text{C}$ shift in the studied stratigraphic section is indicating (i) a gradual decrease in the biomass productivity during the deposition of the Vempalle sediments (ii) the decline of stromatolite type carbonate rocks due to volcanic activity during the deposition of Vempalle sediments (iii) an advent of “snowball earth” - like condition in the Indian Peninsular region at the onset of Vempalle sedimentation.

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