

FIG. 2. Difference spectrum of Lu(III)-Mb ($3.35\mu\text{M}$) + hemin ($3.35\mu\text{M}$) against Lu(III)-Mb ($3.35\mu\text{M}$) and hemin ($3.35\mu\text{M}$) in 0.1 M Tris-HCl buffer of pH 8.

In order to establish the structure of Lu(III)-Mb, the fluorescence emission spectra of fixed concentration of apomyoglobin in presence of various concentrations of Lu(III)-MP-IX were measured and shown in Fig. 3. The fluorescence of apomyoglobin is

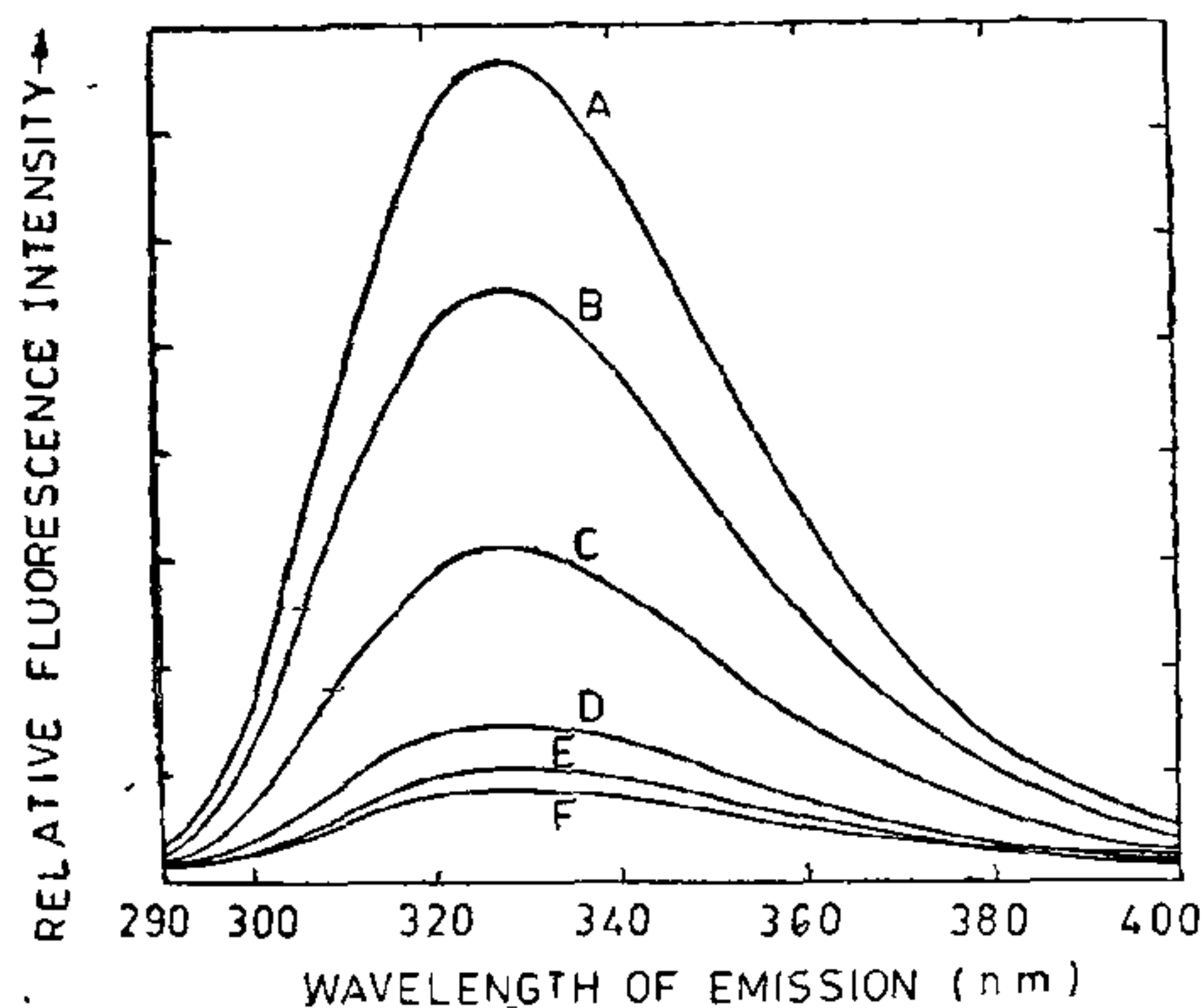


FIG. 3. Fluorescence emission spectra of apomyoglobin ($2.45\mu\text{M}$) in presence of $0.00\mu\text{M}$ (A), $0.63\mu\text{M}$ (B), $1.47\mu\text{M}$ (C), $2.31\mu\text{M}$ (D), $3.15\mu\text{M}$ (E), Lu(III)-MP-IX and $2.45\mu\text{M}$ (F) sperm whale metmyoglobin in 0.1 M Tris-HCl buffer of pH 8. Excitation wavelength was at 280 nm.

quenched with an increase in the concentration of Lu(III)-MP-IX. The fluorescence of protein is very weak when molar ratio of Lu(III)-MP-IX and apomyoglobin is 1.3 to 1. Thus, all apomyoglobin is

complexed in the presence of slight excess of Lu(III)-MP-IX. The amplitude of fluorescence in apomyoglobin is due to tryptophan and tyrosine⁷. The intensity of fluorescence of tryptophan and tyrosine depends upon the degree of quenching mediated by interaction with the metal porphyrin. The Lu(III)-MP-IX effectively quenches the fluorescence of tryptophan and tyrosine residues in the protein complex because of its central position and the overlap of its absorption spectrum with emission spectra of tryptophan and tyrosine. The protein fluorescence of Lu(III)-Mb is comparable with sperm whale metmyoglobin. Therefore they must have the same mean separation of the tryptophan and tyrosine fluorophores from metal porphyrin and thus have the same structures.⁸

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PREPARATION AND CHARACTERIZATION OF COPPER(II) NITRATE COMPLEXES WITH NICOTINIC ACID AND RELATED LIGANDS

NICOTINIC acid (NA), nicotinamide (NICA) and isonicotinamide (INA)—pyridine derivatives with a carboxyl or amido group in the ring—are important constituents of coenzymes which participate in various oxidation-reductions of physiological importance. Metal complexes of biologically important ligands are often more effective than the free ligands. This study describes the coordination compounds formed by the interaction of NA, NICA and INA with copper(II) nitrate which are likely to exhibit significant biological effects. Molar conductance, magnetic susceptibility, electronic and i.r. spectral studies down to 200 cm^{-1} have been carried out to elucidate

the mode of metal-nitrate bonding and the tentative stereo-chemistries of the compounds.

NA, NICA and INA were obtained from B.D.H. and used as such. The complexes were prepared by mixing together solutions of copper(II) nitrate and an excess of the corresponding ligand in ethanol. The mixtures were stirred on a water-bath and cooled. The complexes which crystallized out were suction-filtered, washed with ethanol, then ether and finally dried in an air oven at $\sim 70^\circ\text{C}$. Conductivity measurements were made on freshly prepared $\sim 10^{-3}\text{M}$ solutions of the complexes at 25°C with a Phillips conductivity bridge Model PR 9500. Electronic spectra were recorded as nujol mulls in the range $3300\text{--}6000\text{ cm}^{-1}$ on a Cary 14 spectrophotometer. The mulls were smeared on filter-paper and run against a reference consisting of a similar piece of filter-paper soaked in nujol. I.r. spectra of the uncoordinated ligands and of the complexes were recorded as nujol mulls on a Perkin-Elmer 621 spectrophotometer. Magnetic susceptibilities were measured at room temperature by the Faraday's method with a Cahn R.G. Electrobalance Model 7550. $\text{HgCo}(\text{NCS})_4$ was used as the magnetic susceptibility standard. Pascals' constants were used for diamagnetic corrections. Magnetic moments were calculated using the equation

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_{\text{M}}^{\text{corr}}}$$

Analytical data and characteristic i.r. bands and their assignments in uncoordinated ligands and the complexes are listed in Table I along with the electronic bands. The complexes are soluble in most of the common organic solvents. The assignments of the i.r. characteristic bands for the nitrate groups are reported in Table II. The conductivity measurement values are typical of the 1 : 2 electrolytes¹.

Nicotinic acid, nicotinamide and isonicotinamide possess two potential donor sites: (i) pyridine ring nitrogen and (ii) carbonyl oxygen in the case of NICA and INA or carboxyl oxygen in NA. As monodentate ligands bonding may take place through either the pyridine ring nitrogen or the carbonyl/carboxyl oxygen. Owing to the fixed orientation in space the two sites in INA cannot coordinate simultaneously to the same metal ion. However, one cannot rule out the possibility of the two coordination sites bonding to different metal ions (bidentate bridging ligand) resulting in polymeric structures. Significant absorption bands due to amide group in NICA and INA are νNH , νCO and νCN (Table I). In complexes of amides² and other carbonyl donors³ a significant negative carbonyl frequency shift takes place on coordination through the carbonyl oxygen. In the present study these frequencies remain either unperturbed or undergo slight positive shifts which clearly indicate the non-

participation of amido group in coordination. The carboxyl group vibrations of NA remain unperturbed in the i.r. spectrum of 1 : 2 copper(II) nitrate-NA complex thus excluding the possibility of metal-to-oxygen coordination. On the other hand, i.r. spectra of these complexes display appreciable perturbations in the fundamental frequencies of the pyridine part of the molecule. Absorption bands at ~ 1590 and $\sim 1550\text{ cm}^{-1}$ due to $\text{C} \cdots \text{C}$ and $\text{C} \cdots \text{N}$ stretching modes, respectively, in uncoordinated NA, NICA and INA and the pyridine ring vibrations of these ligands at ~ 990 , 605 and 405 cm^{-1} undergo significant positive shifts. These frequency shifts (Table I) indicate conclusively that coordination of the ligands occur *via* their pyridine ring nitrogen only⁴.

Comparison of the i.r. spectra of the copper(II) nitrate complexes with those of the corresponding uncoordinated ligand spectra and the halide complexes facilitated the assignment of bands due to coordinated nitrate groups. In addition to the six fundamental modes due to nitrate groups the nitrate combination modes in the range $1800\text{--}1700\text{ cm}^{-1}$ have been observed for all the copper(II) complexes reported here. The band positions are given in Table II. The assignments were made following those of earlier workers⁵⁻⁸. Data of representative mono- and bi-dentate nitrate ligands are given⁵.

I.r. spectroscopy has frequently been used in efforts to establish whether the coordinated nitrate group in metal-nitrate complexes is mono- or bi-dentate. It is, however, generally accepted that the splitting of the bands at $\sim 1360\text{ cm}^{-1}$ in the nitrate spectrum is not a good criterion for such purposes as the coordinated mono- ($-\text{ONO}_2$) and bi-dentate (O_2NO) groups have the same local site symmetry (C_{2v}). Curtis *et al.*⁸, suggested that the region $2300\text{--}2500\text{ cm}^{-1}$ can be utilized for the identification of the nitrate combination mode. They showed that a separation of $200\text{--}300\text{ cm}^{-1}$ between the combination modes in this region would indicate bidentate nitrate groups. Lever *et al.*⁹, suggested that the energy region $1800\text{--}1700\text{ cm}^{-1}$ provides a better choice for the identification of the nitrate combination mode. The combination bands appearing in this region are stronger than the bands in the region $2300\text{--}2500\text{ cm}^{-1}$. They suggested that an ionic nitrate shows only a single band in this region while mono- and bi-dentate nitrate ligands show two bands with a separation of $\sim 20\text{ cm}^{-1}$ for the mono- and $\sim 40\text{ cm}^{-1}$ for the bi-dentate nitrate ligands.

Values of the magnetic moments of these complexes, $1.7\text{--}2.2\text{ B.M.}$, suggest negligible magnetic interactions in these complexes (Table I). In tetrahedral copper(II) complexes with triplet ground state one should theoretically expect magnetic moments above 2.0 B.M. but rarely one does because distortion almost

TABLE I
Analytical, magnetic moments, electronic bands and partial i.r. spectral data (cm^{-1})

Compound	μ_{eff} (B.M.)	Electronic band	Metal Found	Nitrate (Calc.) %	νNH	νCO^*	$\nu\text{C}\equiv\text{C}$ $\nu\text{C}\equiv\text{N}$	νCN	Ring vibrations
NA						1685 s	1585 m		989 m 610 m 387 m
NICA					3330 s 3120 m	1680 m	1580 m 1570 m	1120 m	990 m 605 m 396 m
JNA					3372 m 3192 s	1660 m	1592 m 1548 s	1115 m	991 m 603 m 406 m
$\text{Cu}(\text{NA})_2(\text{NO}_3)_2$	1.79	13330	15.1 (14.6)	29.5 (28.6)		1700 m	1625 m 1600 m		1027 m 640 m 416 m
$\text{Cu}(\text{NICA})_4(\text{NO}_3)_2$	2.20	14285	9.7 (9.4)	10.7 (10.3)	3316 m 3212 m	1700 m	1600 m	1140 w	1026 m 630 m 440 m
$\text{Cu}(\text{JNA})_2(\text{NO}_3)_2$	1.70	14705	15.3 (14.7)	29.5 (28.7)	3300 m 3221 m 3104 w	1705 m	1600 m	1130 m 1117 m	1019 m 632 m 433 m

* νOCO for nicotinic acid.

TABLE II
Coordinated nitrate bands (cm^{-1})

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	Combina- tion mode	Reference
$\text{Cu(NA)}_2(\text{NO}_3)_2$	(a) 1316 s	1008 w	710 w	1434 s	736 w	814 m	1754 w 1736 w	This work
$\text{Cu(NICA)}_4(\text{NO}_3)_2$	(a) 1332 s	1012 m	716 w	1465 s	740 w	818 m	1780 w 1762 w	This work
$\text{Cu(INA)}_2(\text{NO}_3)_2$	(b) 1466 s	1056 w	750 w	1300 s	711 w	818 m	1786 w 1756 w	This work
$\text{Cu}(\rho_x)_2(\text{NO}_3)_2$	(a) 1306	1026	730	1408	718	820		10
$\text{Cu}(\rho_y)_2(\text{NO}_3)_2$	(b) 1474	1024		1282		814		10

(a) Monodentate nitrate ligands ($-\text{ONO}_2$); (b) Bidentate nitrate ligands ($=\text{O}_2\text{NO}$).

invariably removes the degeneracy of the ground state. On the other hand, copper(II) complexes with no triplet ground state moments above 1.7 B.M. are achieved by mixing of excited orbitally degenerate term with the ground state term¹⁰. The process of mixing is directly proportional to the spin-orbit coupling constants [very large for copper(II)] and inversely proportional to the energy separation between the ground state and excited state terms. For different stereochemistries variations are observed in the energy separation between the ground state and excited states. Further, it is necessary to see whether the difference between the two ligands is real but in the present study it seems as though INA causes a larger decrease in spin-orbit coupling than caused by NA and NICA.

The d^9 configuration of copper(II) with D^2 term is split in a regular octahedral field into a lower doublet E_g level and an upper triplet T_{2g} level and only one spin-allowed transition should result. However, the crystal field theory predicts larger distortion for cubic symmetry for the octahedral complexes of copper(II)¹¹. Hence the d^9 ground state being Jahn-Teller unstable shows further splitting of the E_g and T_{2g} levels so that even in a complex with six identical donors a regular octahedral configuration is not achieved.

Electronic spectrum of the 1:2 copper nitrate-NA complex shows a broad single band at 13330 cm^{-1} consistent with the pseudotetrahedral structure¹² for the complex. The $d-d$ bands of highly distorted, virtually planar complexes^{7,13,14} occur in the range $14000-18000 \text{ cm}^{-1}$. Distortion of the planar struc-

ture towards a tetrahedral structure lowers the band frequencies. Bands at $7000-10000 \text{ cm}^{-1}$ and $12000-13000 \text{ cm}^{-1}$ have been assigned¹² from the frequencies and relatively low intensity to crystal field transition of the copper(II) in a pseudotetrahedral environment. Hence the observed band for the NA complex strongly supports a pseudotetrahedral structure.

Electronic spectra of the NICA and INA complexes are characterized by the presence of strong bands at 14235 and 14705 cm^{-1} , respectively, with shoulders at 11500 cm^{-1} characteristic of distorted octahedral (C_{4v}) coordination¹⁵. In this symmetry three bands are expected¹⁶. The broad high energy main band may be assigned to the superimposed transition ${}^2B_1 \rightarrow {}^2B_2$ and ${}^2B_1 \rightarrow {}^2E$ and the other band or shoulder to the ${}^2B_1 \rightarrow {}^2A_1$ transition. One could expect the main band at higher energies in the NICA than INA complex provided the effect of distortion from octahedral symmetry and steric hindrance in both the complexes is comparable. From the position of the bands (14705 cm^{-1} vs. 14285 cm^{-1} in NICA) the INA complex seems to be more distorted than NICA complex. Furthermore, the i.r. bands due to coordinated nitrate groups (Table II) indicate clearly the presence of terminally bonded monodentate nitrate ligands in the NA and NICA complexes and bidentate chelating nitrate ligands in the case of INA complex. Based upon the considerations of magnetic moments, electronic and i.r. spectral data the geometries proposed are: monomeric pseudotetrahedral for the 1:2 copper(II) nitrate-NA complex and six-coordinated

distorted octahedral structures for the 1:4 copper(II) nitrate-NICA and 1:2 copper (II) nitrate-INA complexes in the solid state.

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Sr⁸⁷/Sr⁸⁶ RATIOS IN VEMPALLE DOLOMITIC LIMESTONES FROM PULIVENDLA

THE study of Sr⁸⁷/Sr⁸⁶ in carbonates makes a definite conclusion regarding the nature and conditions of their formation. The higher values of Sr⁸⁷/Sr⁸⁶ (0.7059–0.7104) in the Vempalle dolomitic limestones than the average value (0.7035) for carbonatites confirm that they are sedimentary in nature and not carbonatites as suggested by Narasimharao *et al.*¹

The Vempalle formation comes under Papaghni Group of Cuddapah Supergroup (Proterozoic period) and forms an important stratigraphic unit because of asbestos, baryte and steatite mineralization.

In recent years much attention has been made to revise the Cuddapah Supergroup. Narasimharao *et al.*¹ attributed volcanoclastic origin to every formation in the Cuddapah Supergroup and considered the Vempalles as carbonatites. An attempt has been made here to confirm that the Vempalle dolomitic limestones (near Pulivendla 14° 25' : 78° 14') are not carbonatites, based on strontium isotope study.

Sr⁸⁷/Sr⁸⁶ values for eight dolomitic limestones are determined (Table I) following the procedure adopted by Vizer and Compston². The samples of about 30 mg weight are dissolved in 0.1 N HCl, the strontium centrifuged, traces of 84 Sr and 85 Rb added, then Rb and Sr extracted in cation exchange columns for mass spectroscopy. From Table I it is clear

TABLE I

Strontium isotope data of Vempalle dolomitic limestone

Sample No.	Sr ⁸⁷ /Sr ⁸⁶
100	0.7059 ± 3
101	0.7108 ± 2
102	0.7071 ± 4
103	0.7068 ± 3
104	0.7079 ± 4
105	0.7104 ± 3
1250	0.7066 ± 7
1255	0.7108 ± 1

that the Sr⁸⁷/Sr⁸⁶ values for dolomitic limestones are higher than the average value (0.7035) for carbonatites^{3–5} and are comparable to values given for normal marine dolomites and limestones^{6,7} (0.706–0.709). The sedimentary origin of the dolomitic limestones is further evidenced by the nature, occurrence of stromatolites and oolites, chemical study and identification of the sedimentary features and structures of the overlying (Pulivendla quartzite) and underlying (Galcheru quartzite) stratigraphic units. The variations