

376.43; C, 76.57; H, 6.43); IR: 1715 (C=O, ester), 1668 (C=O, acid), 1627, 1595 (C=C), 1255 (C=O, *str*); PMR (CDCl₃): δ 1.52 (6H, s, alicyclic), 2.27 (2H, s, alicyclic), 2.64 (2H, s, alicyclic), 3.76 (3H, s, -OMe), 7.35 (10H, s, aromatic).

The acid ester on saponification with 8% alc. KOH by refluxing for 8 h gave the diacid **4i** (5.0 g), crystallized by ethanol-water, m.p. 210°; (Found: eq. wt., 180.0; C, 75.89; H, 6.41. Required for C₂₃H₂₂O₄: eq. wt., 181.2, C, 76.22; H, 6.12); IR: 1674 (C=O, acid), 1620, 1592 (C=C), 1247 (C-O, *str*); PMR (CDCl₃): δ 1.33 (6H, s, alicyclic), 2.09 (2H, s, alicyclic), 2.50 (2H, s, alicyclic), 7.16 (10H, s, aromatic).

SC of dimethylcyclohexylidenesuccinate and benzophenone

Dimethylcyclohexylidenesuccinate **1e** (4.0 g) with benzophenone (3.2 g) in refluxing potassium *t*-butoxide (18 ml) for 1 h yielded the acid ester **4e** (5.2 g), and the crude product on saponification with 8% alc. KOH by refluxing for 8 h gave the diacid 3-carboxy-2,2-cyclohexylidene-4,4-diphenyl-3-butenoic acid **4i** (5.0 g), m.p. 210°.

Cyclization reactions⁵

The diacid **4i** on cyclization with PPA, conc. H₂SO₄ at 0°, acetyl chloride, and on internal Friedel-Craft's cyclization with anhydrous AlCl₃ yields the indenone with exocyclic double bond.

The present studies reveal a similar behaviour in dicondensation reactions. Cyclohexylidenesuccinate **1e** on Stobbe condensation with benzaldehyde at 100°C in potassium *t*-butoxide yields the acid ester **3a** in majority with endocyclic double bond, which on saponification gives subsequent diacid **3e** with endocyclic double bond. (The same reaction when carried out at room temperature gives the acid ester **4a** exclusively with exocyclic double bond⁶.) Also, Stobbe condensation of dimethylitaconate **1f** with cyclohexanone at 100°C in potassium *t*-butoxide yields the acid ester **3b** in majority with endocyclic double bond, which on saponification gives subsequent diacid **3e** with endocyclic double bond. (The same reaction when carried out at room temperature⁶ yields the acid ester **4b** with exocyclic double bond.) [In the present studies it has also been observed that the Stobbe condensation of cyclohexylidenesuccinate **1e** with anisaldehyde at 100°C in potassium *t*-butoxide yields the acid ester **3c** in majority with endocyclic double bond, which on saponification gives subsequent diacid **3f** with endocyclic double bond. (The same reaction when carried out at room temperature yields the acid ester **4c** with exocyclic double bond⁴.) Also, *p*-methoxyphenylitaconate **1g** on Stobbe condensation with cyclohexanone at 100°C in potassium *t*-butoxide gives the acid ester **3d** in majority with endocyclic double bond, which on saponification

yields subsequent diacid **3f** with endocyclic double bond. (The same reaction when carried out at room temperature⁶ yields the acid ester **4d** with exocyclic double bond.)]

Interestingly, the same double bond has been found to be quite stable in Stobbe reactions at 100°C in potassium *t*-butoxide when benzhydrylidenesuccinate **1b** was condensed with cyclohexanone or cyclohexylidenesuccinate **1e** condensed with benzophenone. [The Stobbe condensation of benzhydrylidenesuccinate with acetone and cyclopentanone gave the non-migrated products at room temperature (**4i**, R¹=R²=H and \square = Me₂ and \square). When the same reactions were done in reflux, the same acid esters and diacids were formed (m.p., m.m.p., and UV, IR and NMR spectra), indicating no bond migration in the five-membered cyclopentanone ring or the dimethyl group.] In these cases, the reaction products were exclusively the acid esters (**4e**, **4f**) and the diacid **4i** with exocyclic double bond. (Room-temperature reactions of these molecules always give the acid esters (**4e**, **4f**) and the diacid **4i** with exocyclic double bond⁷.) Thus no migration of double bond has been observed in the acid ester (**4e**, **4f**). This stability of the double bond is attributable to the presence of one more phenyl group in the benzophenone moiety that must be extending its pull over the conjugation in this particular butadienic system.

The diacid **4i** on cyclization with polyphosphoric acid at 100°C, conc. H₂SO₄ at 0°C, acetyl chloride, or after internal Friedel-Craft's cyclization, did not show the migration of the double bond in the cyclized products⁵.

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Source and mechanism of carbon dioxide gas occurrences in water wells at and around Vidavaluru, South India

I. Radhakrishna

National Geophysical Research Institute, Hyderabad 500 007, India

Carbon dioxide (CO₂) gas in water wells at Vidavaluru near Nellore in Andhra Pradesh (South India), may have taken the lives of three agriculturists who were negotiating for water in water wells. I propose two

hypotheses to explain the source and mechanism of generation of such CO₂. (i) CO₂ could be generated through an interactive process between atmospheric oxygen (O₂) and organic matter (CH₂O). The generated CO₂ could migrate downward into the desaturated unconfined aquifer with empty pore space as a result of sequential droughts in the area. When the aquifer system is subjected to quick changes in the saturation levels as a result of flash rains, the recharged water displaces the gas filled in pore space, and allows its movement into open well structures and gets stacked. (ii) CO₂ could also be generated from the calcium-rich shell zone which occurs abundantly in the near surface aquifer zone. This zone could act like a heat chamber underground during periods of drought and high temperatures, and when quick recharge takes place due to flash rains, CO₂ could be released.

VIDAVALURU (Long: 80°04'09" and Lat: 14°34'17") is a small agricultural village located 25 km away from Nellore in the outfall region of Pennar delta and is about 10 km from the coast line. Intense agricultural practices could be seen all around the village. There are three big tanks (i) Vidavaluru tank, (ii) Mudivarthi tank, and (iii) Vavilla tank. These tanks, in the course of last few years, have been converted into agricultural lands. Tidal inlets and marshy lands appear further east of this village and these tanks.

In October 1987 three agriculturists died at Vidavaluru while working inside a dug cum bore well. The deaths are reported to have occurred due to poisonous/toxic gases at the well site. A few days later another incidence

took place at Mudivarthi village located south-east of Vidavaluru almost close to Pennar river. One farmer felt giddiness and suffocation on entering the well, but immediately came out of the well, remained unconscious for some time and regained full normalcy afterwards.

A team of scientists from National Geophysical Research Institute (NGRI) and National Environmental Engineering Research Institute (NEERI) visited the spot in December 1987, and collected 'gas' and 'water' samples from the well. The results of gas analysis and chemical analysis of water are shown in Table 1 and Table 2 respectively.

The gas was identified¹ by NEERI as 'carbon dioxide', and the report says that this could be generated through chemical fertilizers, such as super phosphate etc. The Agriculture Department, Government of Andhra Pradesh, conducted soil sample analysis and gave a negative opinion on the generation of carbon dioxide through chemical fertilizers. However, NEERI scientists feel the role of superphosphate fertilizers in generation of CO₂ cannot be ruled out particularly in the context of enough available CaCO₃ material in the vicinity. Measurements of gas samples carried out in different parts of the world established that CO₂ partial pressure of the soil atmosphere is normally higher than that of earth's atmosphere. CO₂ pressures are quite variable depending upon the variations of temperatures, moisture conditions, microbial activity and availability of organic matter. A detailed discussion on the occurrence and effect of CO₂ production is presented by Jakucs², and Trainer and Heath³. According to

Table 1. Analysis of gas samples.

Gas	10-12-1987		11-12-1987	
	Sample 1	Sample 2	Sample 1	Sample 2
CO ₂	Trace	Trace	1.2	1.4
O ₂	20.8	20.6	15.6	15.6
CO	Nil	Nil	Nil	Nil
H ₂	Nil	Nil	Nil	Nil
CH ₄ and C ₂ H ₆	Nil	Nil	Nil	Nil

All values are expressed in percentages.

Table 2. Chemical analysis of water samples.

pH	Conductivity (micromhos)	P-alkalinity as CaCO ₃	M-alkalinity as CaCO ₃	Total hardness as CaCO ₃	Calcium hardness as CaCO ₃	Magnesium hardness as CaCO ₃
8.2	2996	Nil	628	266	106	160
Alkaline hardness CaCO ₃	Nonalkaline hardness as CaCO ₃	Calcium as Ca	Magnesium as Mg		Chloride as Cl	Sulphate as SO ₄
362	260	42.4	38.8		370	425
Dissolved O ₂	Ammonical nitrogen		Nitrite (qualitative)		COD (Chemical oxygen demand)	
10:12:87:3.1					28	
11:12:87:2.1	Nil		Present			

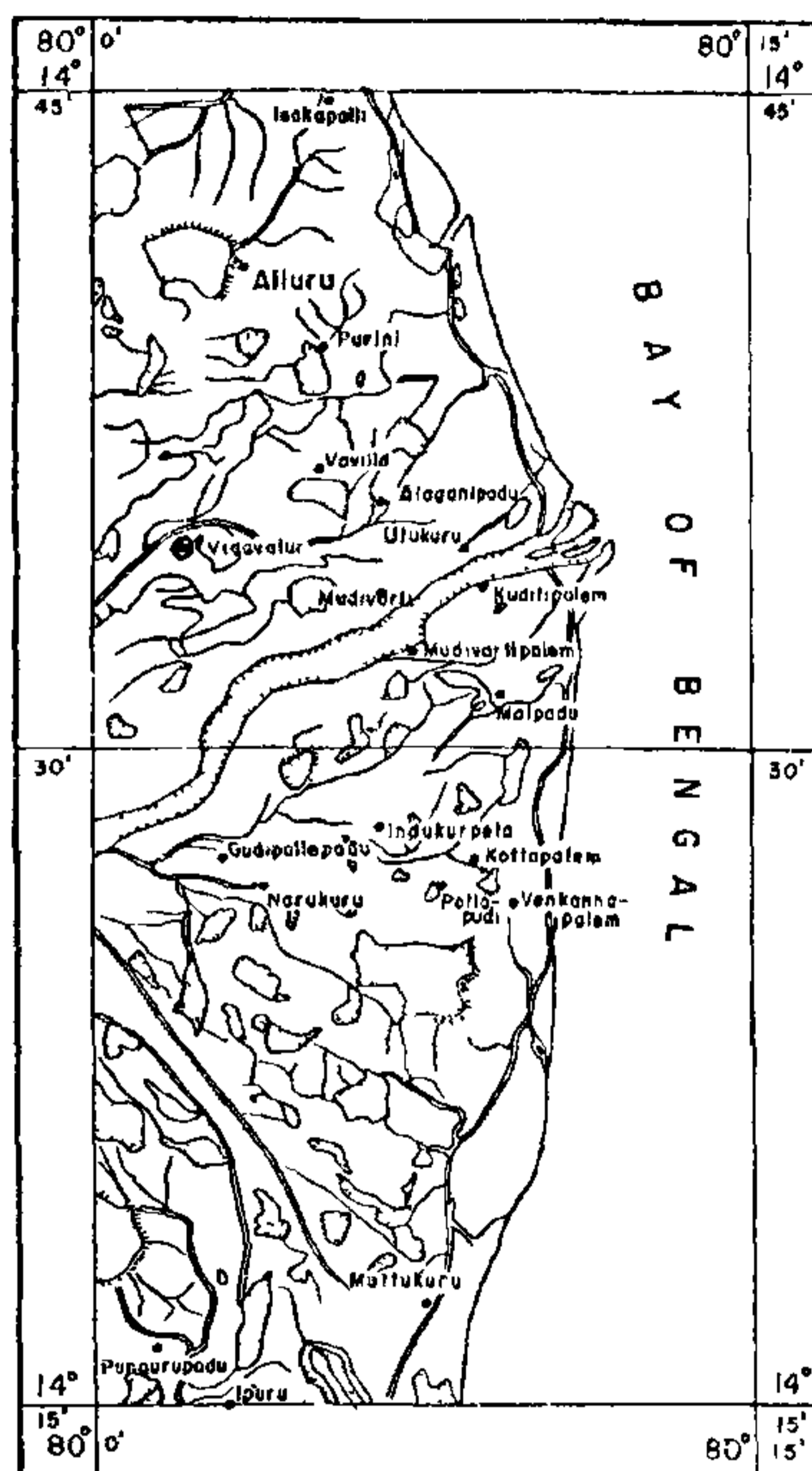
All values are expressed in mg/l except pH and conductivity.

them preparations of O₂ and CO₂ in soil gas differ from those in the atmosphere and concentrations of CO₂ of the order of 1% or higher (compared with an average of 0.03% in the atmosphere) are probably typical of most soils. Their studies also show increasing trends of percentages depth-wise in the soil zone. Zonn and Li Chin Kuei⁴ observed CO₂ concentrations of 6–8% or more during periods of high biological activities in a tropical region. They conclude that in the tropics where soil temperature is rather uniform throughout the year, the soil moisture controls CO₂ production, whereas in temperate regions, temperature and moisture together control the formation of CO₂ in soils. The CO₂ gas measurements from Indian soils are rather rare. It is only recently that such reports and their consequences have come to the limelight. CO₂ gas occurrences from Haryana are reported by Gupta and Mehta⁵, and several people died in the water wells. There could be several other places where CO₂ could accumulate in large quantities but are not reported. It is therefore considered worthwhile to look into the geohydrological situation in detail, which possibly could answer at least some of the questions, such as source of CO₂, its migration and possible mechanism.

Pennar delta area (Figure 1) received heavy rainfall of the order of 650 mm in December 1984 (flash rains) and again in October 1987 (flash rains) almost with the same intensity against an average normal annual rainfall of the order of 1050 mm. The intermediate period by and large is characterized by sequential droughts, and water levels in the upper aquifer have gone down by nearly 10 m in this particular patch. This means that the unconfined aquifer is more or less in a state of 'desaturation' during the above period.

A 3-m thick soil zone (black and variegated clays) is normally present in this track. This is followed by fine to medium sand zone from 3 m to 12 m. This is a saturated unconfined aquifer system with a high degree of porosity, but becomes desaturated during the periods of drought and nonmonsoon periods. This zone changes itself laterally into 'shell zone' (rich in CaCO₃) at many places towards the coast line. It is in this zone that 'carbon dioxide gas occurrences were reported. There is another clay layer below the sand zone with thickness ranging between 5 m and 8 m which is followed by another granular zone also running up to 40 m, which is a confined aquifer. A number of deep filter points and tube wells have come into existence in the confined zone recently because of scarcity of water in the first zone, particularly during summer months and drought periods.

The three traditional tanks which were existing in the area around Vidavaluru–Mudivarthi track could be repositories of rich organic matter and in course of time these tanks were gradually converted into agricultural fields. In addition the area around Vidavaluru is a very



I N D E X



Figure 1. Drainage map of Pennar delta area

good paddy-cultivated area and thus there is a considerable scope for accumulation of 'biomass' in the topsoil layer.

The carbon dioxide could be generated by decay of organic matter and by respiration of plant roots. Water that infiltrates through the soil zone is normally in contact with soil organic matter. O₂ consumption and CO₂ production could therefore be a widespread process in the near-surface environment.



The generated carbon dioxide could either escape into atmosphere or remain underground subject to the availability of pore space and open channels for its migration.

The soil, in general, has the capacity to generate

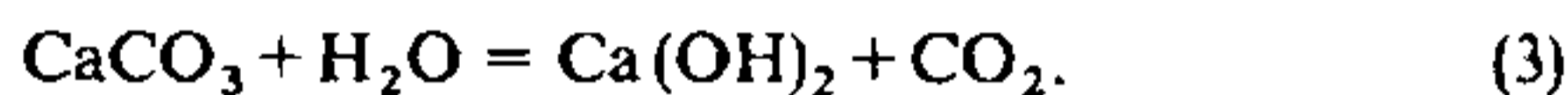
relatively large amounts of humic acid and consumes much or all of the available dissolved oxygen in water that infiltrates.



The area around Vidavaluru–Mudavarthi has all necessary required elements both for generation of CO_2 and its possible migration downward into the desaturated unconfined aquifer with empty pore space, as a result of sequential droughts in the area. As and when the system is subjected to quick changes in the saturation levels (rise in water levels) as a result of flash rains, the recharged water displaces the gas filled in pore space (without giving much scope for interaction/dilution) and consequently the displaced 'gas' moves into open well structures available in the area. CO_2 being a heavier gas than O_2 gets stacked in the lower part of the well and escapes into atmosphere during relatively warmer time periods.

The second possibility is generation of carbon dioxide from calcium-rich shell zone which occurs abundantly in the near-surface aquifer zone around this area. This zone is subjected to aeration and saturation during the periods of droughts and wet periods respectively.

During the periods of drought and high temperatures, this zone could act like a heat chamber underground and when quick recharge takes place due to 'flash rains', CO_2 could be released as expressed below:



The CO_2 generated through the above process could be of limited magnitude. More studies however are required to establish the applicability of the process in this area.

The above two processes could work either independently or jointly for production of 'carbon dioxide'. The first process could take place in alluvial sedimentary tracks where intensive cultivation and irrigation practices are in vogue, and where the near-surface aquifer system is subjected to overdraft situations followed by 'flash rains' and 'quick recharge'. In other words, whenever flash rains occur, after long dry spells in an intensely cultivated area, the chances of accumulation of ' CO_2 ' in well structures will be more.

Agriculturists should be advised not to go into the wells particularly in such situations as described above till such time the groundwater system reaches full saturation levels and the generated CO_2 either escapes into atmosphere or gets dissolved in water. The release of CO_2 cannot persist for a long time in a season, but can recur again in subsequent years if the conditions laid down above necessary for generation of CO_2 repeat. The presence of CO_2 could be tested by lowering a 'candle' or 'lantern' into the well, and in the event of presence of CO_2 in wells, rigorous pumping

should be carried out so that accumulated gas is flushed and escapes into atmosphere.

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Fossil cyanobacteria from the stromatolitic phosphorites of Udaipur, Rajasthan, West India

M. S. Sisodia

Department of Geology, University of Jodhpur, Jodhpur 342 001, India

Small spherical bodies identified as fossil cyanobacteria have been found within or in the vicinity of stromatolites in the Precambrian Aravalli phosphorites of Udaipur. These extremely rare fossils are elliptical to circular in section, 20 to 100 μm in diameter, and occur both singly and in massed colonies. They have a nucleus of carbonaceous material surrounded by a zone of very fine radiating needles of francolite or calcite. This outer zone is interpreted as francolite formed by transformation of assimilated phosphorus during early diagenetic alteration of the cells. These cyanobacteria could thus have been instrumental in accumulation of phosphorus in the Aravalli phosphorites.

THE Udaipur phosphorites are strictly confined to stromatolites which have been interpreted as accreting in subtidal, intertidal and supratidal environments¹⁻⁴. They are hosted by the dolomitic limestone unit of the Aravalli Supergroup. This supergroup has been assigned an age of 2000 million years (myr) (Aravalli orogeny)⁵. The petrography and geochemistry of the phosphate-bearing stromatolites of Udaipur have been described by several workers^{1-3,6,7}, who are also described some filamentous, cellular microfossils. In the present note we report the presence of cyanobacterial fossils and envisage a vital role for them in phosphogenesis.

Examination of stromatolites under high magnifica-