

Figure 4. Resonance spectra of 4-methyl-5,7-diethoxycoumarin (I).

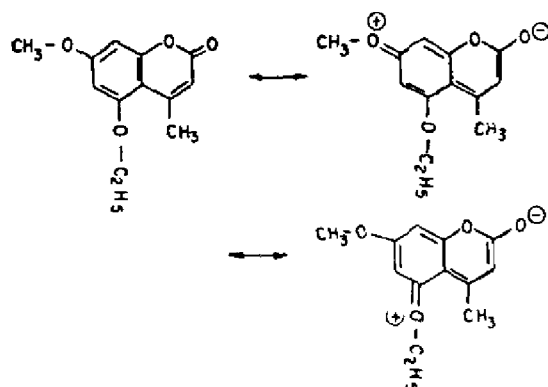


Figure 5. Resonance spectra of 4-methyl-5-ethoxy-7-methoxycoumarin (II).

xycoumarin is more than the value of 4-methyl-7-methoxycoumarin¹⁵.

Let us consider the data and graphs of coumarin III, it is clear that the wavelength shift plots are not straight lines (Figure 3). Therefore we could not calculate the change in dipole moment of 4-methyl-7, 8-diethoxycoumarin with the help of present solvatochromic methods. It appears as solute-solvent interaction and steric hindrance effects take place due to the substituents present at two adjacent positions. We had also observed the same problem in determining the excited state dipole moment of 4-methyl-6, 7-dimethoxycoumarin in an earlier work¹⁵.

Further, solvatochromic data can be used to identify the spectra, viz. $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, etc. It is noticed from the Table 1 that, with increase in the polarity of the solvent, the fluorescence emission peak undergoes a bathochromic shift, confirming a $\pi \rightarrow \pi^*$ transition. The shift of the fluorescence wavelengths towards longer wavelengths could be caused if the excited state charge distribution in the solute is markedly different from the ground state charge distribution and is such as to give rise to a stronger interaction with polar solvents in the excited state.

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Monsoon effect on isotopic composition of atmospheric carbon dioxide

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The Indian subcontinent and the adjoining seas (the Arabian Sea and the Bay of Bengal) experience seasonal reversal of wind systems and associated weather changes resulting from summer and winter monsoons. The monsoons are associated with significant changes in the oceanic and continental biosphere and are therefore expected to have considerable effect on the content and isotopic composition of atmospheric carbon dioxide. We have attempted to measure this effect in ground-level carbon dioxide samples collected in the city of Ahmedabad during 1990. The CO_2 content is in general agreement with values obtained elsewhere. The $\delta^{13}\text{C}$ value of air CO_2 shows a minor effect due to the increase of productivity on land during the southwest monsoon season. The $\delta^{18}\text{O}$ value of CO_2 is slightly enriched compared to northern high-latitude values owing to the equilibration of CO_2 with enriched leaf water expected in a tropical country like India.

The southwest monsoon brings a dramatic change in the climatic regime operating on the Indian subcontinent

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during June to September. The mean rainfall over the Indian plains in this period is 925 mm in contrast to a meagre 145 mm for the rest of the year¹. The lower level winds are southwesterly over the Arabian sea and the Bay of Bengal carrying prodigious amount of moisture picked up from the ocean. In contrast, the winter winds are northeasterly and composed mainly of dry continental air.

There is a significant change in the amount of biomass over the land and in the ocean associated with the summer monsoon. In the oceans the biomass increase takes place through nutrient recycling processes. For example, in several regions of the Arabian sea the low level monsoon winds cause intense upwelling, which brings up nutrient-rich deeper waters into the euphotic zone. This causes massive blooms of phytoplankton, algae and certain bacteria which, in turn, lead to an enhancement of the population of higher organisms in the water column. This increase in biological productivity in the Arabian sea has been clearly demonstrated by Nair *et al.*². Based on sediment trap experiments they showed that during June–September the flux of organic matter ($3.7 \text{ g m}^{-2} \text{ month}$) is about a factor of three higher compared to the flux during the rest of the year ($1.2 \text{ g m}^{-2} \text{ month}$). The estimated net primary productivity (NPP, in units of gC per year) over the oceanic region around India ($\sim 3.4 \times 10^{14}$), is much less compared to the NPP over the land ($\sim 14.3 \times 10^{14}$), the latter being composed of NPP's from forest (5×10^{14}), agriculture (6.7×10^{14}), grassland (1.4×10^{14}), culturable waste (0.8×10^{14}) and other minor sources (0.4×10^{14}) (ref. 3). The seasonal variations of NPP's of these carbon reservoirs are still not quantified accurately but estimates can be made using the available crop yield data, seasonal NPP data on some grasslands and seasonal carbon source-sink model of Box⁴. These considerations show that the ratio of total NPP (in units of gC per month) during the monsoon season over that of non-monsoon period is about 1.8 (Dadhwal, personal communication). There are two important consequences of this enhancement of biological productivity on the atmospheric CO_2 . First, a rapid rate of consumption of CO_2 to build the organic matter leads to a depletion of CO_2 content in air. For example, a reduction of CO_2 partial pressure in surface waters due to phytoplankton bloom results in enhanced draw-down of atmospheric CO_2 , causing local decrease in CO_2 content of air. Second, there are associated changes in the isotopic composition of carbon and oxygen in the atmospheric CO_2 . It is now well established that the process of photosynthesis (following two dominant modes designated as C_3 and C_4 path way) discriminates against the heavy isotope of carbon, ^{13}C . The C_3 photosynthesis leads to plants having average $\delta^{13}\text{C}$ value of -27% (w.r.t. PDB standard) whereas C_4 plants have average $\delta^{13}\text{C}$ value of

-13% (ref. 5). Therefore, the atmospheric CO_2 , which is characterized by the average $\delta^{13}\text{C}$ value of -7.8% (corresponding to the year 1990), will be relatively enriched when large amount of isotopically depleted CO_2 is removed by photosynthesis. The extent of the enrichment will depend on the amount of extra biomass generated and the rapidity of the change compared to regional mixing which tend to obliterate the seasonal effect. It is to be noted that this effect is not noticeable for marine air CO_2 since marine photosynthesis takes place from a large pool of dissolved CO_2 and not directly from CO_2 of atmosphere.

The oxygen isotopic composition of the atmospheric CO_2 is basically determined by the exchange of CO_2 with waters from various sources. The exchange rate, of course, differs from one process to another. For example, the dissolution of CO_2 in oceans or cloud water and its subsequent hydration hastens the exchange of oxygen isotopes between the gas phase (CO_2) and the liquid phase (H_2O), whereas any direct exchange between two gas phases (like CO_2 and O_2 or water vapour) occurs at a negligibly slow rate. Even the hydration reaction does not occur at a fast enough rate to explain the observed latitudinal variation in $\delta^{18}\text{O}$ of atmospheric CO_2 . Francey and Tans⁶ have recently proposed an important mechanism whereby hydration reaction inherent in photosynthetic activity is speeded up by about million times through the catalyst carbonic anhydrase. If this is true the large-scale change in biomass, associated with the monsoon in Indian sub-continent, is expected to introduce perturbation in the isotopic ratio of oxygen in the ground level CO_2 .

In view of the above-mentioned changes expected in air CO_2 and its isotopic composition for a monsoon-dominated region like India, it is of interest to know if we can identify and quantify such changes. Such a study will provide important inputs towards understanding the various exchange processes controlling the global budget of atmospheric CO_2 . This is especially significant in view of the growing concern over the increase of CO_2 due to fossil fuel addition and deforestation with its adverse effect on global temperature as stressed in the recent IGBP documents⁷. But till date there has not been any systematic measurement of the content and isotopic composition of CO_2 in India. We have, therefore, initiated a programme to study the effect of monsoon-induced changes on atmospheric CO_2 . First series of measurements were made on air samples collected from the roof top of the Physical Research Laboratory building (90 m above mean sea level), located in the city of Ahmedabad during March to November 1990.

Samples of air were collected in evacuated 2-litre flasks around 9–10 a.m. twice or thrice a week. The ambient temperature, relative humidity and wind direction were also noted. The CO_2 fraction was

separated from other gases in the flask (nitrogen, oxygen, water vapour and argon) immediately after collection using a vacuum line, where the air sample was pumped through three U-traps; the first trap was kept in a bath of alcohol cooled to -100°C by liquid nitrogen and the next two at -196°C liquid nitrogen temperature. The pumping was done slowly at a line pressure of 4–5 cm to ensure complete trapping of CO_2 . After initial separation, the CO_2 fraction was further purified from traces of water and its content was measured in a calibrated manometer. The oxygen and carbon isotopic ratios were measured in a VG Micromass 602D mass spectrometer with reproducibility of $\pm 0.05\text{‰}$ in each of them. The CO_2 content was corrected for relative humidity to express as ppmv of dry air and the isotopic values were corrected for the effect of minor amount of atmospheric N_2O (which also gets trapped with CO_2) by following standard procedures⁸.

The variations of CO_2 content, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with time are shown in Figure 1. The values of CO_2 content lie within a range of 340 to 380 ppmv [neglecting four values which are too high (>390) and four values which are too low (<330)]. The simple average of the CO_2 content of 58 samples is 355 ppmv, which compares very well with 355.6 ppmv of CO_2 expected in mid nineties. The latter value is based on the content of 352.6 ppmv measured at Mauna Loa in January 1989 and a yearly increase of 2 ppmv during this period (i.e. a total increase of 3 ppmv from January 1989 to June 1990⁹). The pre-monsoon months and the month of June are characterized by higher values (~ 358 ppmv) whereas the CO_2 contents in July, August, September and October are significantly less (~ 350 ppmv). There is a scatter of values around this general trend which is probably due to admixture of small but variable amount of industrial and vehicular emissions expected in a city like Ahmedabad, where there is a large concentration of industries and a big thermal power plant.

The $\delta^{13}\text{C}$ value of CO_2 varies from about -7.7‰ to -9.6‰ with average of -8.3‰ . Keeling *et al.*⁹, based on extensive measurements at various latitudes over long periods, calculated globally averaged $\delta^{13}\text{C}$ of atmospheric CO_2 corresponding to various years. On the basis of these data the average $\delta^{13}\text{C}$ value in the northern hemisphere for the year 1990 is -7.9‰ . The values obtained in the present case are somewhat lower, indicating the effect of fossil fuel-derived component (characterized by $\delta^{13}\text{C}$ of -25‰). Despite the scatter in the data there is an increasing trend of the values with time (Figure 1). For example, the average bimonthly values are: March–April, -8.55‰ ; May–June, -8.37‰ ; July–August, -8.14‰ and September, -7.88‰ and $\delta^{13}\text{C}$ increase (Δ) from pre-monsoon (March–April) to monsoon (July–August–September)

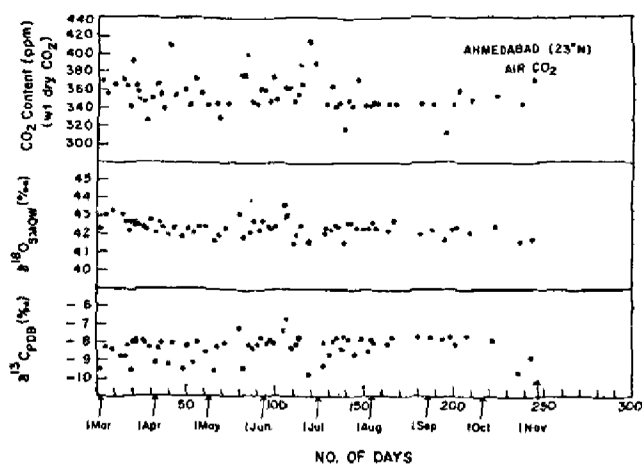


Figure 1. The content of atmospheric CO_2 and its oxygen and carbon isotopic composition during March to November 1990 plotted as function of number of days counted from 1 March 1990. See text for discussion.

season lies within 0.4 to 0.7‰. Assuming the depletion of 8 ppmv during monsoon season to be due to carbon fixation by C_3 photosynthesis (dominant vegetation in India) Δ can be derived by the following mass-balance equation:

$$358(-8.55) = 350(-8.55 + \Delta) + 8(-27) \\ \Delta = 0.4\text{‰}.$$

Considering the large scatter in $\delta^{13}\text{C}$ values the observed increase is reasonably close to the above calculated value.

The $\delta^{18}\text{O}$ value of CO_2 , on the other hand, does not show any systematic trend with time; the average value is 42.5‰ w.r.t. SMOW or 1.0‰ w.r.t. PDB. This value is about 0.7‰ higher compared to the $\delta^{18}\text{O}$ value of CO_2 in Mauna Loa, which is located at a comparable latitude of 20°N . Following the explanation of the latitudinal variation in $\delta^{18}\text{O}$ of CO_2 mentioned earlier we attribute this enrichment to the equilibration of the air CO_2 with leaf water. In a tropical country like India the leaf water is expected to be considerably enriched in ^{18}O . Since very few direct measurements of leaf water $\delta^{18}\text{O}$ exist one can make use of the available data on δD and $\delta^{18}\text{O}$ values of tree-ring cellulose. DeNiro and Epstein¹⁰ showed that the cellulose $\delta^{18}\text{O}$ (and δD) is primarily determined by that of the leaf water. Therefore, a comparison of $\delta^{18}\text{O}$ values of leaf water at various places can be made by comparing the corresponding $\delta^{18}\text{O}$ values of cellulose from trees in these places.

An estimate of cellulose $\delta^{18}\text{O}$ for the tropical part of India can be made by using the δD – $\delta^{18}\text{O}$ relation given by Ramesh *et al.*¹¹, and the measured average δD value of cellulose from teak trees in Maharashtra¹². The average cellulose $\delta^{18}\text{O}$ value for these trees is about 33‰ , which is indeed higher compared to the values for

trees taken from higher latitudes, e.g. Wisconsin (lat. $\sim 45^\circ$ N) trees have average $\delta^{18}\text{O}$ value of about 26‰ and British Columbia (lat. $\sim 55^\circ$ N) trees have average value of about 23‰ (ref. 13). Therefore the enriched value of $^{18}\text{O}/^{16}\text{O}$ ratio in air CO_2 from Ahmedabad can probably be ascribed to equilibration of CO_2 with enriched leaf water expected in the tropical part of India. The enrichment in CO_2 is less than that of the leaf water due to the rapid mixing of air on a global scale.

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Precambrian–Cambrian boundary in the Tal Formation of Garhwal Lesser Himalaya: Rb–Sr age evidence from black shales underlying phosphorites

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The recently reported faunal evidence for placing the Precambrian–Cambrian boundary within the main phosphorite unit of the Chert–Phosphorite Member of the Tal Formation, Garhwal Lesser Himalaya, is supported by the present report of 626 ± 13 myr for the whole-rock Rb–Sr isochron age of the black shales directly underlying the phosphorite band.

THERE is considerable international effort to recognize the Precambrian–Cambrian boundary in sedimentary records worldwide. The Working Group on Precambrian–Cambrian boundary of the International Commission on Stratigraphy has recommended that this boundary be placed in stratigraphic units showing the earliest appearance of diverse small shelly fossils¹ and selected three stratotype candidates for this boundary in present-day eastern Siberia (Aldan River), southern China (Meishucun) and eastern Newfoundland (Burin Peninsula). In this connection, the recent discovery of small shelly faunas close to the base of the Tal Formation in Garhwal Lesser Himalaya^{2–6} has great significance for Lesser Himalayan stratigraphy and Precambrian–Cambrian boundary research. The candidate for the boundary stratotype in the Garhwal section is a 3-m-thick phosphorite band (Figure 1) from the Surkhet Block of the Maldeota phosphorite quarry, 14 km from Dehra Dun. The shelly faunas in this band include *Anabarites trisulcatus*, *Protohertzina anabarica*, *P. robusta*, *P. unguiformis*, *Fomitchella infundibuliformis*, *Mongolodus platybasalus*, *Hyolithellus* spp., *Spirellus columnaris*, etc. and are highly correlatable with those of zone I of Meishucunian stage in southern China, Pre-Tommotian Manykian stage from the Siberian Platform and Yukon Territory of Canada^{2,4}. According to the presently available palaeomagnetic reconstruction of the geography of the early Cambrian⁷, faunal similarities between India and China are expected to be very strong.

The age of the Precambrian–Cambrian boundary has been inferred from isotopic dating of suitable sedimentary or igneous rocks temporally close to the boundary⁸. The

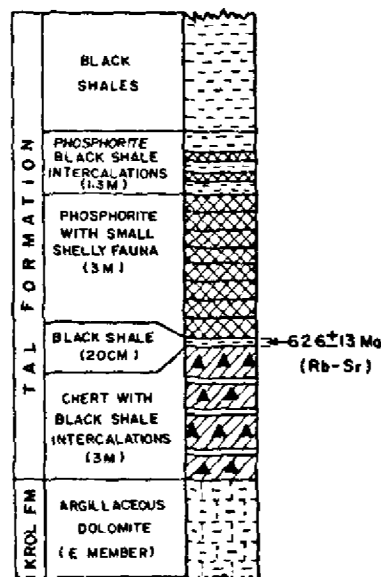


Figure 1. Vertical section across the Precambrian–Cambrian boundary at Surkhet Block, Maldeota Phosphorite Mine, Garhwal Lesser Himalaya.