Carbon isotopic composition of fossil leaves from the Early Cretaceous sediments of western India

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Stable carbon isotope analysis of fossil leaves from the Bhuj Formation, western India was carried out to infer the prevailing environmental conditions. Compression fossil leaves such as *Pachypteris indica*, *Otozamite kachchhensis*, *Brachyphyllum royii* and *Dictyozamites* sp. were recovered from three sedimentary successions of the Bhuj Formation, Early Cretaceous in age. A chronology was established based on faunal assemblage and palyno-stratigraphy and further constrained by carbon isotope stratigraphy. The three sampling sites were the Karawadi river bank near Dharesi; the Chawad river bank near Mathal; and the Pur river section near Trambau village in Gujarat. The Dharesi sample was also analyzed to investigate intra-leaf $\delta^{13}C$ variability. The mean $\delta^{13}C$ of the leaf was $-24.6 \pm 0.4‰$ which implied negligible systematic change along the leaf axis. The Mathal sample was fragmented in nature and showed considerable variation in carbon isotopic composition. The Trambau sample considered to be the oldest, dating to the middle of Aptian (*ca.* 116 Ma), shows the most depleted value in $\delta^{13}C$ among all of them. The overall $\delta^{13}C$ trend ranging from mid Aptian (*ca.* 116 Ma) to early Albian (*ca.* 110 Ma) shows a progressive increase in $\delta^{13}C$ from -26.8 to $-20.5‰$. Based on these measurements the carbon isotopic composition of atmospheric carbon dioxide of the Aptian–Albian period is estimated to be between -7.4 and $-1.7‰$. The ratio of the partial pressure of carbon dioxide in leaf to that of the ambient atmosphere calculated based on a model is estimated to be similar to that of the modern plants. This indicates that the Early-Cretaceous plants adapted to the prevailing high carbon dioxide regime by increasing their photosynthetic uptake.

1. Introduction

The Earth has undergone several major environmental changes throughout the geological time. One of the most significant changes in the ocean atmosphere system that took place during the Cretaceous had imprints in both terrestrial and marine environments (Jemkyns 1980; Bralower *et al* 1994; Crane *et al* 1995; Littler *et al* 2011). Geochemical, paleobotanical and paleontological studies have provided valuable information about the environmental conditions of the Cretaceous. For example, the study of stomatal density in plant fossils provide an important means to estimate the past pCO_2 conditions (Retallack 2001). This has also been corroborated by stable carbon isotopic analysis of phytoplankton and pedogenic carbonates (Royer *et al* 2001). However, large uncertainties exist in

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quantifying one of the most important atmospheric parameters, the isotopic composition of carbon dioxide in the Cretaceous atmosphere. It is believed that δ^{13}C of atmospheric CO_2 during the Cretaceous was similar to the pre-industrial level of around $-6.5‰$ (Cerling 1991; Leuenberger *et al* 1992; Francey *et al* 1999; McCarroll and Loader 2004). But analysis of fossil plants indicates a somewhat enriched value. During the Aptian, Gröcke (2002) observed a large range in carbon isotopic composition of atmospheric CO_2 that varied between 0.5 and $-10‰$ and estimated an average δ^{13}C of atmospheric CO_2 in the order of $-3.0‰$. Since no single proxy record is able to provide this information with sufficient temporal and spatial resolution, it is thus essential to analyze fossil plants at various stratigraphic levels and at different geographic regions for a better estimate of atmospheric carbon isotopic composition. The study of fossil plant or plant mega fossil has certain advantages over the use of bulk terrestrial organic matter (TOM) that is widely used to establish correlation between the marine and terrestrial carbon cycle events through geological time (Grocke *et al* 2005). For example, the TOM can be sourced from a variety of floral components with varying abundances between samples and the TOM may be composed of floral components from different environments and thus varying isotopic signatures (*op cit.*). Plant mega-fossil representing a single species does not suffer from such limitations. It is also well established that the fossil plants typically retain their isotopic compositions (Degens 1969; Nambudiri *et al* 1978; Rigby *et al* 1981; Aucourt and Hillaire-Marcel 1993; Bocherens and Marootti 1998). So it is quite likely that the analysis of fossil plants from the Indian subcontinent would be useful in enhancing our understanding of the ancient atmospheric compositions, since carbon fixed by land plants reflects carbon isotopic fluctuations of atmospheric CO_2, and consequently, the isotopic behaviour of the ocean–atmosphere system (Hasegawa *et al* 2003). The Indian fossil plants have been extensively studied by paleobotanists to investigate the past vegetational and environmental conditions (Seward and Sahni 1920; Sahni 1928; Bose and Roy 1961; Roy 1967; Bose and Kasat 1972; Bose and Banerji 1984). But to our knowledge, no isotopic analysis of fossil leaves has ever been undertaken, especially from the Kachchh basin in Gujarat which is known to be a rich source of well preserved plant fossils belonging to the Mesozoic (Bose and Kasat 1972; Bose and Banerji 1984). Though in this context it may be mentioned that the isotopic analysis of benthic foraminifera from Kachchh helped to quantify the Palaeogene temperature that ranged between 22° and 32°C in this region (Saraswati and Ramesh 1992; Saraswati *et al* 1993).

Leaf carbon isotope composition varies by 1–2‰ depending upon several factors including irradiance, height and aspect (Leavitt and Long 1986; Lockheart *et al* 1998; Heaton 1999; Turney *et al* 2002), but the intra-leaf carbon isotopic variability is no greater than that observed for bulk plant material. In this article, we report the preliminary observations on the carbon isotopic analysis of the compression fossil leaves from the Kachchh basin in Gujarat and discuss its implications in understanding the paleoenvironmental conditions prevailing during the Early Cretaceous.

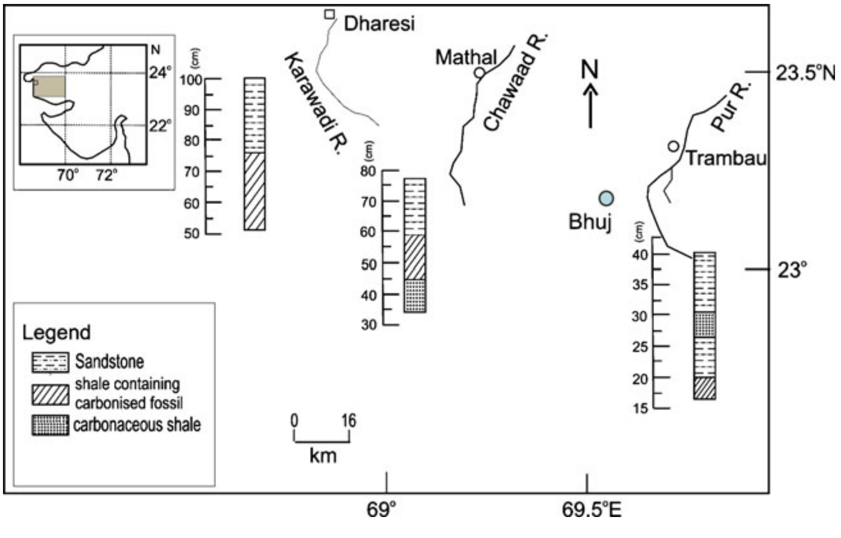

Figure 1. The sampling sites in the Kachchh basin of Gujarat. The grey area in the inset shows the sample location. Dharesi is marked by an open square. Other two sites, namely Mathal and Trambau are shown in the enlarged portion. The vertical scale for each of the site is also shown.

2. Materials and method

The plant mega fossils were collected from three localities belonging to the north western region of the Kachchh basin in Gujarat (figure 1). The first site is located near village Dharesi (23°41′N, 68°51′E) and the other two are from Mathal village of the Chawaad river section (23°30′N, 69°15′E) and Trambau village of the Pur river section (23°19′N, 69°44′E) (figure 1). All of the

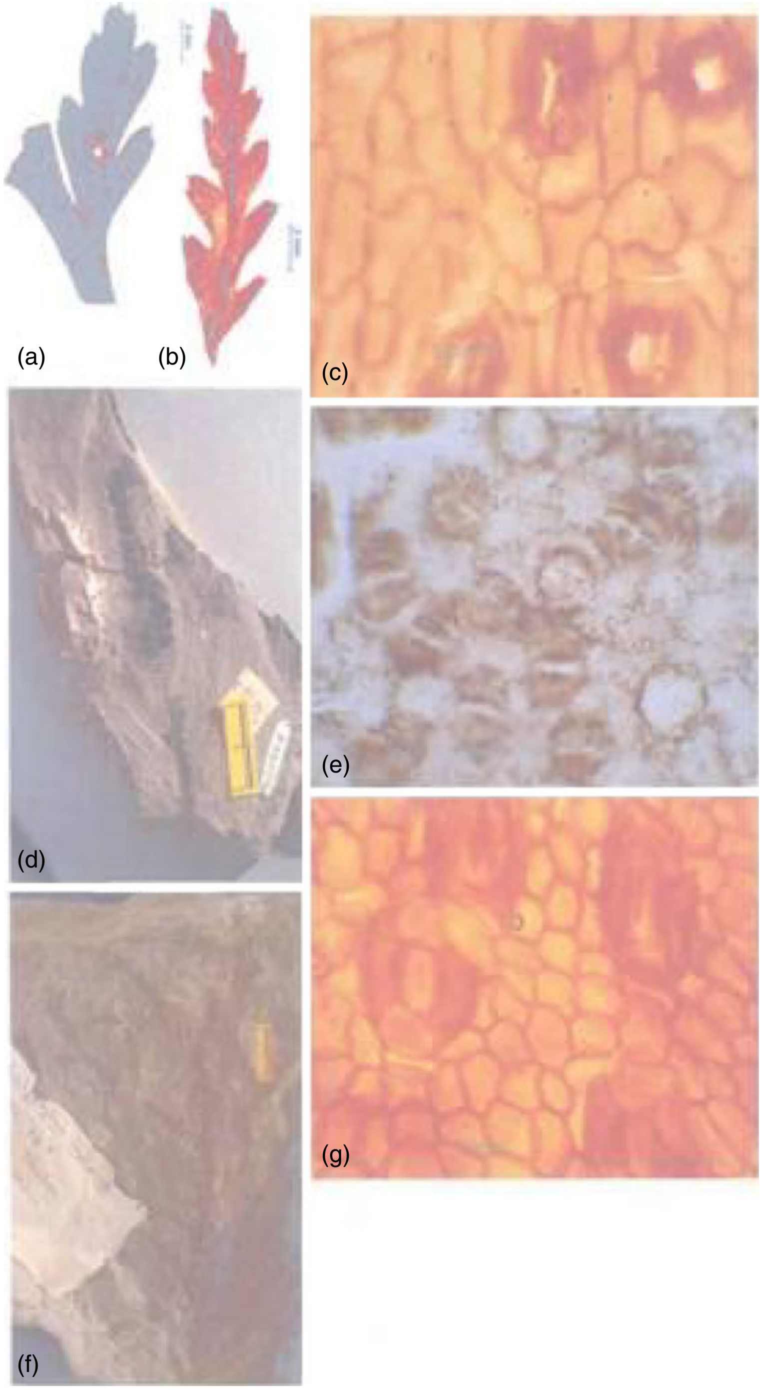

Figure 2. The fossil specimens used in this study. (**a** and **b**) A small twig of *Pachypteris indica* (No. B.S.I.P. 1/2679 C); at initial and final stages of maceration respectively; (**c**) a portion of stomatiferous surface of *P. indica* (No. B.S.I.P. 90/2411–1); (**d**) *Ottozamites kachchhensis* – preserved on bedrock. The missing portion at the middle of the fossil specimen was used for stable isotopic analysis. (**e**) Magnified part of stomatiferous surface of *O. kachchhensis;* (**f** and **g**) *Brachyphyllum royii.* (**f**) Branched leafy twigs of *B. royii* (No. B.S.I.P 32262) and (**g**) a magnified part of stomatiferous portion of *B. royii* (No. B.S.I.P. 84/2089c-1); (**h**) a leafy potion of *Dictyozamites* sp. (No. B.S.I.P. 29/6235), and (**i**) shows a part of stomatiferous pinnule surface (No. B.S.I.P. 29/62635–1); (**j**) leafy twigs of *Pagiophyllum morrissii* (No. B.S.I.P. 71/2679); and (**k**) stomatiferous portion of *P. morrissii* (No. B.S.I.P. 38/2676–1).

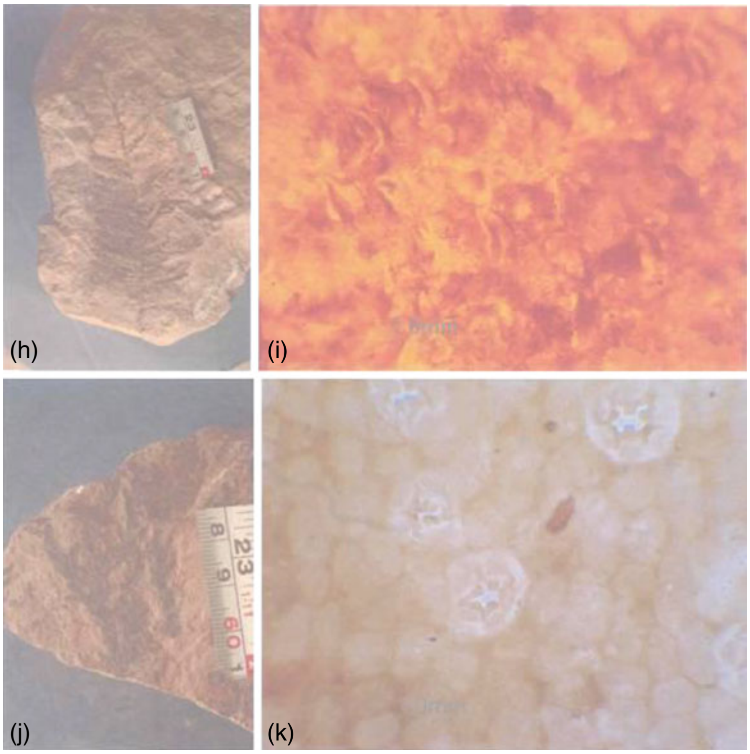

Figure 2. *(Continued).*

sites show well exposed mid-to-lower Cretaceous sedimentary successions. The sedimentary deposits mainly consist of gravel, sandstone and carbonaceous shale.

The Dharesi site is situated about 120 km northwest of the town of Bhuj and 40 km east of the lake, Narain Sarovar. The fossiliferous section under study was exposed on the northern bank of the river Karawadi and located *ca.* 1.5 km northwest of Dharesi village. One mega fossil was collected from this site that yielded almost entire portion of a leaf. A total of eight samples were collected from the other two sections; these were fragments of different portions of fossil leaves belonging to four genera. The physical characteristics of the fossils as well as the taphonomic analysis (Bose and Banerji 1984) suggest that the deposits were original leaf carbon and no secondary deposits were present.

The village Trambau is situated *ca.* 11 km northeast of the town of Bhuj. The fossiliferous beds in this area are exposed mainly along the northern and southern banks of the Pur River. The carbonized fossils were recovered from a section that was 2.5 km northwest of the village Trambau.

The Mathal and Trambau samples are relatively older than the Dharesi sample. The geologic timescale in this area was estimated from palynostratigraphy and faunal assemblages (Bose and Banerji 1984). Three to four lithofacies were found in these sections. For example, Dharesi is characterized by sandstone and carbonaceous shale, both containing fossil leaves. Other two sections have poorly stratified sandstone facies, carbonaceous shale and siltstone/claystone facies dominated by carbonized organic matter.

Of these localities, well preserved compression fossils were mainly found at Trambau in Pur River site and Mathal in Chawad River site. On the contrary, the fossils from Dharesi are relatively ill preserved. This particular fossiliferous section (Dharesi) is more weathered. But the fossils of Trambau and Mathal sections are less weathered and are overlain by huge layers of other strata in Trambau. Figure 2 shows the fossil specimens used in this study; (a) and (b) show a small twig of *Pachypteris indica* at initial and final stages of maceration; other images from (c) to (k) have been described in the figure.

For isotopic analysis the fragmentary organic matter was carefully separated from the host rock by gently scraping with knife and scalpel. The samples were treated according to the methodology of Gröcke *et al* (1999) but with minor modifications. They were treated with dilute (2 M) hydrochloric acid to remove carbonates and then with mild alkali and acid in sequence. The samples were thoroughly rinsed with de-ionized water and dried overnight in an oven (40°C).

The leaf sample (*ca.* 10 mg) was combusted at a temperature of 800°C in a quartz tube attached to a vacuum system (dimensions; 150 mm long × 8 mm bore) in the presence of copper (II) oxide (500 mg) and silver wool for approximately 3 hours (Sofer 1980; Minagawa *et al* 1984). Following the cryogenic separation of water, CO_2 was dynamically transferred to a calibrated volume to determine the yield and finally collected and sealed in a glass ampoule. Subsequently, the ampoules were taken to the Physical Research Laboratory, Ahmedabad for mass spectrometric measurements on a Europa GEO 20–20 isotope ratio mass spectrometer. The isotopic values were reported in δ notation, relative to VPDB and expressed in permil (‰). The measurement precision based on the replicate analysis of a standard was 0.1‰ while the overall analytical precision was 0.33‰. In most cases, the small sample sizes prevented the repeat analysis of leaf material.

To check the accuracy of the method, the IAEA C_3 cellulose international standard was also analyzed in the same way. The mean δ^{13}C value of -25.03 ± 0.33‰, $n = 10$ was in good agreement with the consensus value of -24.91 ± 0.49‰ (3-σ error) (Rozanski 1991; Rozanski *et al* 1992) and similar to other reported values; -24.60 ± 0.10‰, $n=50$ (Knöller *et al* 2005) and the recently recommended value of -24.72‰ (Coplen *et al* 2006).

Table 1. *Dharesi sample showing the intra-leaf variability in δ^{13}C.*

Leaf portion	δ^{13}C (‰)
Top	−24.8
	−24.9
Middle	−24.8
	−24.7
	−24.8
	−24.2
Base	−23.9

3. Results

The isotopic data of the Dharesi sample are given in table 1, while table 2 compiles the same for all three sites. Table 1 shows the intra-leaf variability in δ^{13}C.

The δ^{13}C of the base of the leaf is found to be slightly enriched (−23.9‰) relative to its top (−24.8‰). The total variation is *ca.* 1.0‰ and the mean value is -24.58 ± 0.38‰ ($n = 7$). It seems that the intra-leaf variability in δ^{13}C of fossil plants from this region is about 1‰ and that the leaf samples represent C_3 type of plant.

4. Discussion

In order to interpret the isotopic data it is essential to know whether there was any diagenetic alteration of the sample. Indirect evidence shows that diagenetic alteration was minimal in this case. Firstly the cellular details of these fossil leaves were carefully studied under microscope and no sign of alteration was found attesting excellent preservation. Secondly, the isotopic values obtained in these cases are in good agreement with that of the plants belonging to the same period from different geographical locations. For example, fossil plants analyzed from the Flat Rocks in Australia of the Aptian age gave a mean δ^{13}C of -23 ± 1‰ (Gröcke 1998). Popp *et al* (1989) reported δ^{13}C of the terrestrial organic matter from the Cenozoic and Mesozoic to be around −26‰. Cerling (1991) also used a value of −26‰ for the organic matter for the Mesozoic. The carbon isotopic values of the fossil leaves obtained in this study are well within this range, which suggests that there was no significant diagenetic alteration of the leaf material.

There is considerable evidence which suggests that the ocean–atmosphere system underwent substantial changes during the Jurassic and Cretaceous time. Weissert and Erba (2004) presented a composite Late Jurassic–Early Cretaceous Tethyan

Table 2. *The measurement of the carbon isotopic composition of the fossil plants studied in this paper.*

Laboratory no.	Sample identification	Sample site	δ^{13}C (‰)	Approximate geological age
Dharesi (mean) 84/2511	*Dictyozamites* sp.	Dharesi	-24.58 ± 0.38	Early Albian (*ca.* 110 Ma)
82/2411C	*Pachypteris indica*	Mathal	−20.50	
100/2411B	*Pachypteris indica*	Mathal	−23.64	
31/2891A	*Ottozamites kachchhensis*	Mathal	−24.55	
2/2679C	*Pachypteris indica*	Mathal	−26.02	
135/2411B	*Pagiophylluim morrisii*	Mathal	−26.19	
90/2411C	*Pachypteris indica*	Mathal	−26.24	
84/2411C	*Pachypteris indica*	Mathal	−26.63	
32262	*Brachyphyllum royii*	Trambau	−26.83	Mid Aptian (*ca.* 116 Ma)

bulk carbonate carbon isotope plot that showed significant perturbations in the global carbon cycle. As mentioned earlier the approximate ages of these samples are made available from palynostratigraphy and faunal assemblages (Bose and Banerji 1984), that is Early Createaceous. Since Wiessert and Erba's (2004) bulk carbonate plot represents isotopic variation of the global carbon cycle, it is expected that the carbon isotopic composition of the contemporaneous vegetation would closely resemble this curve. So we compare the carbon isotopic values of our fossil leaves with the carbon isotopic record of the Tethyan bulk carbonate δ^{13}C plot of Weissert and Erba (2004). Figure 3 shows the δ^{13}C of the bulk carbonate (grey dots) and the fossil leaves (filled circles and rectangles). It is quite apparent from this figure that the pattern of variation of fossil leave δ^{13}C is quite similar to that of the Tethyan bulk rock carbon isotopic variation. Based on this comparison, we further constrain the chronology of our fossil leaves that range from Mid-Aptian to Early Albian. The approximate numerical ages of the end members were estimated to be *ca.* 116 and 110 Ma respectively based on the Weissert and Erba (2004) curve.

Table 2 shows the mean carbon isotopic values of the Dharesi sample as well as those of individual Mathal and Trambau samples. The samples have been arranged in sequence according to their approximate geological ages. The lowermost sample represents the Mid-Aptian (*ca.* 116 Ma) while the top sample (Dharesi) belongs to the Early Albian (*ca.* 110 Ma), approximately covering a period of 6 Ma. This exercise also helped us to assign an approximate age model of the individual samples based on their locations on the sedimentary horizon and assuming linear sedimentation rates. The lowermost sample shows the most ^{13}C depleted value of -26.8‰ whilst the topmost samples from Mathal is enriched by more than 6‰ having a δ^{13}C value of -20.5‰. Out of the eight samples, five samples (filled circle in figure 3) are *P. indica*, whilst the other three samples (filled rectangle) are *Otozamite kachchhensis, Brachyphyllum royii,* and *Dictyozamites* sp., respectively. It may be noted that the variance of δ^{13}C of all the samples is significantly higher than the intra-leaf variability of 1‰ (table 1) and hence the variability is unlikely due to inter species differences (Leavitt and Newbery 1992). There is, however, no direct evidence that this variability is due to environmental change and not due to taxonomy. However, from figure 3 we see that the pattern of carbon isotopic composition of all the species (except the Dharesi sample which comprises many fragments of a single leaf) and the pattern of δ^{13}C variation of *P. indica* only, are more or less the same. Since *P. indica* is a single species and hence its isotopic values would be affected only by environmental parameters, our interpretation will not be affected even if the other three samples (*Otozamite kachchhensis, Brachyphyllum royii,* and *Dictyozamites* sp.) show species dependent carbon isotopic variability.

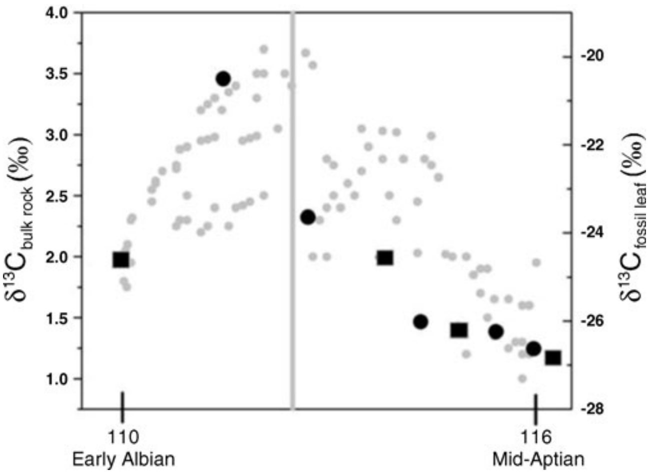

Figure 3. Comparison of the fossil leave δ^{13}C with that of the bulk rock carbon that represented the ocean atmospheric changes of carbon cycle during the Cretaceous (Weissert and Erba 2004). The grey dots represent the bulk rock carbon isotopic composition while the filled circles and rectangles are that of fossil leaves δ^{13}C of this study. The vertical axis on left shows the isotopic values of the bulk rock while the right axis represents that of the fossil leaf. The x-axis is the geological age and the numerical values were based on the Weissert and Erba (2004) plot. The vertical grey line shows the boundary between Aptian and Albian.

The carbon isotopic composition of C_3 plants ($\delta^{13}C_{\text{plant}}$) is controlled by the concentration and δ^{13}C values of atmospheric carbon dioxide, stomatal conductance and the carbon assimilation rate according to the following relation (Vogel 1980; Farquhar *et al* 1982a):

$$\delta^{13}C_{\text{plant}} = \delta^{13}C_{\text{air}} - a - (b - a)\,(C_i/C_a), \tag{1}$$

where a is the discrimination caused by diffusion of CO_2 through the stomata and b is the discrimination resulting from CO_2 fixation by ribulose-1, 5-biphosphate carboxylase-oxygenase and are considered constants. The term C_i/C_a is the ratio of the partial pressures of intercellular CO_2 to atmospheric CO_2 and is a function of stomatal conductance and carbon assimilation rate. This ratio is sensitive to environmental parameters, such as water stress, humidity, light levels, temperature, nutrients and pCO_2 (McCarroll and Loader 2004).

Arens *et al* (2000) have compiled a large database (n=394) to assess the effect of C_i/C_a and $\delta^{13}C_{\text{air}}$ on plant δ^{13}C. They found that when some of the environmental parameters, such as light condition, nutrients and temperature are low, the C_i/C_a ratio increases resulting decrease in

$\delta^{13}C_{\text{plant}}$. On the other hand, water stress and low relative humidity, osmotic stress decrease the C_i/C_a ratio, thereby increasing the plant $\delta^{13}C$. Over geological timescales, when the atmospheric CO_2 concentration varies significantly, the dominant control on $\delta^{13}C_{\text{plant}}$ is the carbon isotopic ratio of the atmospheric CO_2 (*op cit.*). Although Gröcke (1998) has observed an inverse relationship between $\delta^{13}C_{\text{plant}}$ and pCO_2, Arens *et al* (2000) demonstrate that 90% of plant $\delta^{13}C$ variations can be accounted for, by the isotopic composition of the atmospheric CO_2. Hence they establish the following relationship between $\delta^{13}C_{\text{air}}$ and $\delta^{13}C_{\text{plant}}$:

$$\delta^{13}C_{\text{plant}} = 1.10 \times \delta^{13}C_{\text{air}} - 18.67. \qquad (2)$$

In deriving this equation the authors did not use fossil plants, rather plants were grown in chambers that simulated the past atmospheric conditions. The air $\delta^{13}C$ was varied between −6 and −10‰ while pCO_2 had a range of 98 to 1300 ppmV. The $\delta^{13}C_{\text{plant}}$ was observed to have varied from −20 to −36‰. According to Arens *et al* (2000) this equation can be applied in the case of fossil plants, when the pCO_2 was significantly higher than today, to estimate the past value of atmospheric $\delta^{13}C_{\text{air}}$. Until recently it is believed that the atmospheric CO_2 concentration during the Early Aptian was about 1470 ppmV (Berner and Kothavala 2001). However, a recent study reports that the atmospheric pCO_2 was in the range of 1130 ppmV (Fletcher *et al* 2008) in the Early Cretaceous (*ca.* 100 Ma ago). This value lies within the pCO_2 range of 98–1300 ppmV used by Arens *et al* (2000) to derive equation (2). Hence we use this equation to determine the atmospheric $\delta^{13}C$ using the fossil leaf $\delta^{13}C$ values.

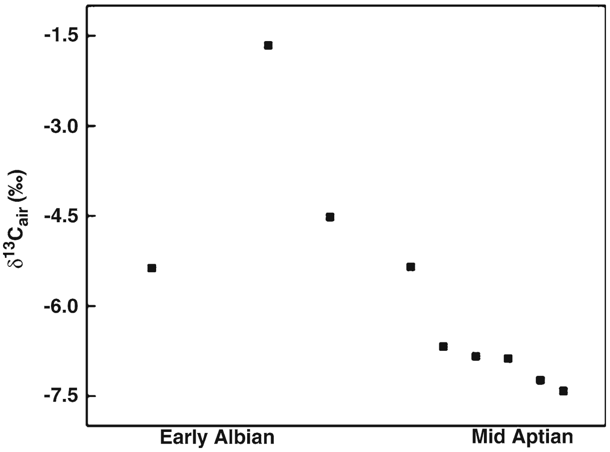

Figure 4. Determination of the atmospheric $\delta^{13}C$ based on the carbon isotopic composition of the fossil leaves from the Kachchh basin during the Aptian–Albian using the equation derived by Arens *et al* (2000). Method of calculation is given in the text.

Figure 4 plots the atmospheric carbon isotopic composition during the Early Cretaceous. The atmospheric $\delta^{13}C$ increased from −7.4‰ from lower Aptian to about −1.7‰ in the upper Aptian. During this time the atmospheric pCO_2 value decreased from 1500 ppmV to about 1300 ppmV (Royer *et al* 2001). The atmospheric $\delta^{13}C$ values derived here agree with the estimates of Berner (1991), except one of the Mathal samples that had $\delta^{13}C$ of −1.7‰; this is in contrast to the values given by Gröcke (2002) who estimated an average atmospheric $\delta^{13}C$ to be in the order of −3‰ during the Aptian.

We have also estimated the C_i/C_a ratio for these plants using equation (1) and time series of atmospheric $\delta^{13}C$ were generated for a set of values of C_i/C_a (ranging from 0.6 to 0.7) and are shown in figure 5 assuming that this ratio remained constant throughout the Early Cretaceous. This assumption is justified since within reasonable limits plants tend to maintain a constant C_i/C_a ratio to optimize their assimilation rate. This was demonstrated for some modern plants which maintained a nearly constant C_i/C_a ratio despite a moderate increase in atmospheric pCO_2 (Francey and Farquhar 1982). The values of a and b (in equation 1) are taken to be 4.4 and 27%, respectively. These values are typical for C_3 plants (Farquhar *et al* 1982b). The lowermost curve in this figure correspond to $C_i/C_a = 0.6$ and the uppermost curve to 0.7. The plot corresponding to $C_i/C_a = 0.65$ closely resembles the values reconstructed earlier using equation (2) (grey line in figure 5). The value 0.65 is comparable to

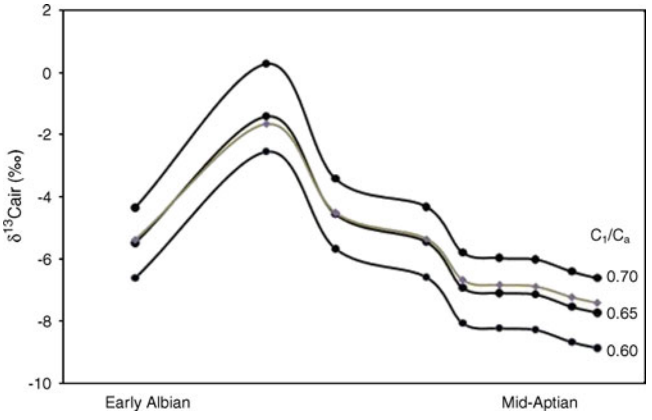

Figure 5. Numerical estimation of $\delta^{13}C$ of the Aptian air based on the fractionation model of Farquhar *et al* (1982a) for C_3 plants (equation 1 in the text). Time series of air $\delta^{13}C$ were generated using the plant isotopic values and for given values of C_i/C_a, i.e., 0.6, 0.65 and 0.7, respectively (bottom to top). Then these time series were compared with the air $\delta^{13}C$ derived using equation (2), represented by grey line in this figure. Air $\delta^{13}C$ time series with $C_i/C_a = 0.65$ appears to have good match with the observed data.

that of many modern C_3 plants that are characterized by a value of 0.7 (Evans *et al* 1986; Polley *et al* 1993). This implies that the (Early Cretaceous) plants modulated their C_i in response to a high C_a value at that time (the average pCO_2 during the Aptian was ∼1100–1200 ppmV, i.e., Fletcher *et al* 2008) probably by increasing their photosynthetic rate aided by the prevailing higher temperature since photosynthetic capacity of a plant increases with temperature (Amthor 1995; Beerling 1996).

5. Conclusions

The carbon isotopic composition of plant fossils from the western India is used to estimate the isotopic composition of atmospheric carbon dioxide during the Aptian–Albian using a recently established empirical model. The $\delta^{13}C$ of the fossil leave showed similar pattern of variation with that of the bulk rock carbon isotopic composition that represented the carbon cycle perturbation in the ocean atmospheric system. The atmospheric $\delta^{13}C$ progressively increased from *ca.* −7.4 to about −1.7‰ and then reduced to *ca.* −5.4‰ from the Mid Aptian to Early Albian. This result accords well with the decreasing trend in pCO_2 observed over this period and with the estimate of Cerling (1991). Based on a leaf CO_2- $\delta^{13}C_{air}$ fractionation model, the plant C_i/C_a ratio of C_3 plants during the Aptian–Albian is estimated to be similar to that of the modern plants. This indicates that the Early Cretaceous plants seem to have adapted themselves to the prevailing high pCO_2 regime by increasing their photosynthetic uptake.

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