Atmospheric pCO₂ and climate during late Eocene (36 ± 5 Ma) on the Indian subcontinent

B. P. Singh1 & Yong Il Lee2
1Department of Geology, Banaras Hindu University, Varanasi 221 005, India
2School of Earth and Environmental Sciences, Seoul National University, Seoul 151-747, Korea

This communication highlights the level of atmospheric CO₂ and the climatic conditions during Eocene (36 ± 5 Ma) based on measurements of stable carbon and oxygen isotopes of late Eocene soil carbonate (calcrites) occurring in the Himalayan foreland basin sequences. The atmospheric pCO₂ is estimated to be about 930 ppm V at high productivity and about 465 ppm V at low productivity. The covariance of δ¹⁸O and δ¹³C suggests that the higher atmospheric CO₂ may be responsible for higher temperature. Moderate weathering intensity (CIA value 70–82) of the host mudstones suggests warm climate associated with reasonable wetness that became dry-subtropical, resulting in calcrite development in the northern part of the Indian subcontinent during late Eocene. Wet subtropical climate demonstrates considerable rainfall at this time interval in the region long before the uplift of the Tibetan plateau. Alternatively, it can be suggested that uplift of the Tibetan plateau began much earlier than presently considered.

Keywords: Atmospheric carbon dioxide, Eocene, Himalayan foreland basin, Indian subcontinent, palaeoclimate.

GLOBAL warming resulting from increased CO₂ levels in modern times has heightened interest in the estimation of atmospheric CO₂ from the ancient climates. Geochemical modelling and field observations of modern soils indicate that a relationship exists between the δ¹³C of pedogenic carbonate and pCO₂ of the atmosphere, and δ¹³C can be used to infer the pCO₂ of the palaeoatmospheres. The estimated CO₂ levels of soil carbonates based on δ¹³C and the GEOCARB III model of Berner and Kothava are not in conformity with each other. Further, atmospheric CO₂ data from continental records are sparse for late Eocene and Oligocene times to verify their consequences for the Eocene warming. Additionally, there are conflicting views regarding the age of initiation/intensification of the monsoon-related rainfall on the Indian subcontinent and the uplift of the Tibetan plateau, which is considered as the major cause of the Asian monsoon initiation.

Climatic and tectonic history of the last ~58 m.y. is preserved in the Himalayan foreland basin sequences that contain thick packages of shallow marine (coastal) and continental deposits. This basin in the western part is envisaged as a marine basin from late Palaeocene to middle Eocene (57.9–43.6 Ma) and continental basin in younger times. The continental sedimentation began with the widespread occurrence of red beds in the Himalayan foreland basin that are exposed in the inner belt of the Sub-Himalaya from Pakistan in the west to northwest India in the east (Figure 1a). Details of outcrop belt and sampling locations are shown in Figure 1b. The age of initiation of the continental sedimentation in the Indian part of the Himalayan foreland basin has been assigned as late Eocene (36 ± 5 Ma) based on palaeomagnetic results. Identically, the earliest continental sediments of the Himalayan foreland basin from Pakistan occurring in strike continuity have been assigned the ages between 36 and 40 Ma based on ⁴⁰Ar–³⁹Ar dating method. The basal red beds contain calcrites as marker horizons within mudstone host (Figure 2). These calcrites are mainly nodular and form over a metre thick profile showing characteristics of Bk horizons. Also, these calcrites possess micromorphological features such as rhizoliths/rhizocretions, fungal filaments and borings, alveolar septal fabric, and micro-nodules (Figure 3). Therefore, essentially these are pedogenic and a fit case for atmospheric CO₂ estimation as suggested by Ekart et al., among others.

Nodular calcrite samples were collected from profiles that occur in reasonable thickness (>50 cm thick) and show horizonation. Detailed thin-section study of these samples was carried out and we identified six samples rich in fungal filaments and borings during the course of thin-section study. In all, seventeen samples were selected for stable isotope analysis, including six fungal filament-rich samples. The samples were sawed and polished from one side and the polished slabs were washed with dilute hydrochloric acid during processing. To avoid diagenetic overprinting, only micritic carbonate was drilled with the help of a dentist drill under continuous observation on a stereoscopic microscope and the carbonate powder was acid-digested according to the method suggested by Beinis et al. The liberated CO₂ was analysed for stable isotopes. The isotopic ratios are relative to PDBV standard with reproducibility of ± 0.05‰ for carbon and ± 0.1‰ for oxygen. Average δ¹³C value of fungal filaments poor calcrite samples was used for calculating pCO₂ as per equation of Cerling. Additionally, host mudstone samples were analysed for major oxides on an XRF and the chemical index of alteration was calculated from moles of aluminium, calcium, potassium and sodium oxides by the formula of Nesbitt and Young.

The carbonate ion is typically inherited from biological respired CO₂ (e.g., organic decomposition and root respiration) rather than carbonate weathering or groundwater CO₂ because the rate of pedogenic carbonate formation is 10² to 10³ times slower than the rate of soil respiration. Also, transfer of carbon from its oxidized form, CO₂ in the atmosphere to the reduced organic forms (carbohy-
Figure 1. a. Map showing geographical distribution of different tectonic zones of the Himalaya, foreland sequences and the study area (in box) on the Indian subcontinent. Location of Thar Desert is also shown. b. Map showing locations of the calcite samples (1–17) analysed for stable isotopes in the outcrop belt of the Palaeogene sequences in western Himalaya.

Figure 2. Representative stratigraphic profiles of the late Eocene sequences in the western Himalayan foreland and stable carbon and oxygen isotope variation in the vertical profiles. a. Stratigraphic profile from extreme western end of the study area (Kalakot) shows multiple calcite horizons and vertical variation of isotopic values. b. Stratigraphic section from extreme east of the studied sections (Garkhal). This section shows two calcite profiles and variation of stable isotopes from one profile to the other and within a single profile. Note covariance of carbon and oxygen isotope values.

drake) in plants result in photosynthesis. During photosynthesis, when plant stomata are open, CO₂ diffuses inward, and O₂ and H₂O diffuse outward to the atmosphere, returning soil moisture to the atmosphere. Diffusion
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![Image of calcite photomicrographs showing Rhizolith (R) showing bifurcation and tapering end. Note spurtic carbonate filling in the root channel and micritic carbonate around it. Alveolar septal fabric (ASF) in the calcite. Note cross-cutting white layers of carbonate in micritic grey matrix. Root hair (Rh) and the fungal filament (F) association. Calcification of both root hair and filaments is observed. Fungal filaments (F) show a network around fungal borings (FB). Carbonate accumulation can be seen along the filaments.]

Table 1. δ¹³C and δ¹⁸O values (in ‰) relative to PDB V standard in calcite samples

<table>
<thead>
<tr>
<th>Sample nos</th>
<th>δ¹³C_VPDB</th>
<th>δ¹⁸O_VPDB</th>
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<tbody>
<tr>
<td>1</td>
<td>-9.41</td>
<td>-11.52</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>17</td>
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</tr>
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</table>

*Samples rich in fungal filaments and related features.

In the studied calcrites, the δ¹³C varies from -8.5 to -11.2‰, whereas δ¹⁸O varies from -8.5 to -13.1‰ (Table 1). Considering calcrites that are poor in fungal filaments and related features, the range of δ¹³C value reduces and comes down between -8.8 and -9.8‰ with an average value of -9.2‰. The negative δ¹³C and δ¹⁸O values in the studied calcrites demonstrate higher concentrations of lighter isotopes. Also, it is noted that calcrites rich in fungal filaments and associated biogenic features are enriched in lighter stable isotopes and show more negative values (Figure 4 and Table 1). The host mudstones on which calcite bands have developed are rich in silica and alumina compared to other major oxides and K₂O is more than Na₂O. Chemical index of alteration, an index of weathering intensity, ranges from 70 to 82 (Figure 5).

The atmospheric CO₂ commonly contributes to the soil carbonate and shows less negative δ¹³C as compared to the soil organic matter, which also includes carbon from roots respiration and plants decay in addition to atmospheric contribution. Further, mycorrhizal association with roots enhances uptake of many nutrients and increased uptake of phosphorous enhances the rate of photosynthesis, which results in fast fixation of carbon dioxide from the atmosphere by the host plants. On the other hand high soil productivity, inferred from the presence of fungal hyphae, may lead to greater oxidation and respiration of

of ¹²CO₂, a lighter molecule is more rapid in plant tissues than that of ¹³CO₂, which composes about 1.1% of atmospheric CO₂. Also inside the leaf, ribulose bisphosphate carboxylase has a higher affinity for ¹²CO₂ resulting in more ¹³CO₂ to enter into the leaf than ¹⁵CO₂ in a given period of time and as a consequence, the organic matter has very negative δ¹³C (-28‰)⁹,¹¹.
soil material and greater oxidation and respiration may result in more negative soil carbonate δ13C values2. Here, we interpret that the more negative δ13C values in the calcrete that preserve fungal hyphae are likely attributed to high soil productivity and oxidation of soil organic matter, rather than increased fixation of atmospheric CO2 in them. Additionally, mycorrhizae provide 100 times more surface area and 10,000 times more length of absorbing organs as a consequence of its 100 times smaller size than the associated root hairs12. Therefore, the higher absorbing capacity of the fungal hyphae may be responsible for the lighter δ18O values in the calcretes rich in them.

Assuming that pedogenic carbonate forms in isotopic equilibrium with soil gas throughout the soil profile, CO2 palaeobarometer equations of Cerling3 allows to estimating atmospheric CO2 from δ13C of soil carbonates and δ18O of soil organic matter1. The isotopic values for determining pCO2 in the soil carbonates depend upon types of vegetation using C3, CAM and C4 photosynthetic pathways, temperature, soil porosity and depth of soil development and atmospheric pCO2 can be estimated only in cases of C3-dominated photosynthesis7. The range of δ13C from −8.5 to −11.2‰ in the present case suggests that the C3 plants composed of trees, shrubs and some grasses dominated the floral community during late Eocene. Commonly, the carbon isotopic composition of the soil organic matter from C3-dominated Eocene paleosols is about −24‰ and the difference between coexisting soil organic matter and pedogenic carbonate in their carbon isotopic composition is 14–16‰, as a result of equilibrium fractionation between carbon isotope species and the diffusive gases7. In the present study, soil organic matter δ13C value of −24‰ is taken as a reference for the pCO2 estimation and a difference of 14.9‰ on an average is found between the carbon isotopic composition of the soil organic matter and the soil carbonate.

In the pCO2 estimation, the soil temperature plays a pivotal role in respiration rate and productivity and the rates of respiration are not exactly known for the geological past5. As a consequence, soil resired CO2 equals to 10,000 ppm V with high productivity in warm conditions (temperature = 25°C) and soil resired CO2 equals to 5000 ppm V with low productivity in cool conditions (temperature = 15°C)5. In the present case, the pCO2 is calculated both at high respiration rate as well as low respiration rate and the average values are 930 and 465 ppm V respectively (Figure 6). Hence, atmospheric pCO2 is estimated to be a maximum of 930 ppm V during late Eocene (~36 Ma) on the low latitude region of the Indian subcontinent. This value of atmospheric carbon dioxide is much lower than that estimated from 45 Ma soil carbonates of Clarion, Utah (1950 ppm V) and even lower than that estimated from 25 Ma Salla (Bolivia) soil carbonates (1470 ppm V) by Ekart et al.1. The low atmospheric CO2 demonstrates that there was a period of low atmospheric CO2 around 36 Ma in between 45 and 25 Ma. This may be true as a result of cyclic variations in the levels of atmospheric carbon dioxide of the geological past.

Pedogenic calcretes form in dry subtropical climatic zones between 10 and 30° latitudes, and the dry subtropical palaeoclimatic zone is characterized by low annual precipitation and seasonal differences in temperature13. Palaeomagnetic data13 indicate that the northern part of the Indian subcontinent was located between 10 and 20°N before 35 Ma. Therefore, the latitudinal position favoured calcrete formation on this part of the continent. Pedogenic calcrete forms by the carbonate accumulation after the end of rainy season (after July–August in the modern Indian summer monsoon) in the Thar Desert and during

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**Figure 4.** Bivariate plot showing distribution of δ18O and δ13C in calcretes of the Himalayan foreland. Values of less mature calcrete are shown with filled circles and calcretes possessing biogenic features with open quadrangle. Both δ18O and δ13C show high negative values, δ18O is higher in the samples in which δ13C is higher and vice versa with few exceptions.

**Figure 5.** A-CN-K diagram exhibiting relative fields and CIA values of river-suspended sediments from the glaciated terrain (A) (after Singh et al.2), Ganga River sediment (B) (after McLennan3) and late Eocene mudstones of the host calcretes (C).
the time period of carbonate accumulation (October–March), soil temperatures vary from 22–32°C at a depth of 30–50 cm in the Thar Desert. Temperature of carbonate formation, precipitation intensity, source of moisture and shifts in seasonality can be inferred from δ¹⁸O of pedogenic carbonates. The range of δ¹⁸O value from −8.5 to −13.1 suggests that the studied calceretes were precipitated under the influence of fresh water after the rainy season. Their precipitation might be associated with high surface temperatures also, Andrews et al. found positive correlation between δ¹⁸O and δ¹³C and argued that temperature was dependent on level of soil respired CO₂ in Quaternary pedogenic calceretes of the Thar Desert. In the studied calceretes, the covariance of δ¹⁸O and δ¹³C suggests that high levels of atmospheric/solr respired CO₂ was, in turn, related to high surface temperature during the precipitation of them. This analogy also exists in the present climatic system where anthropogenic contribution towards increase in atmospheric CO₂ level is resulting global temperature rise. Hence, we predict that higher value of atmospheric CO₂ than the present day value led to elevation in surface temperature during late Eocene times.

Continental sedimentation in the Himalayan foreland basin is correlated with the proto-(Main Central Thrust) formation at about 35 Ma. It may be related to a sea-level change in the late Eocene and/or a warm climatic condition associated with soil formation and low supply of the detritus from the hinterland. Mathur has recorded the dominance of palm and poor occurrence of angiosperms and ferns from the late Eocene succession of the Himalayan foreland basin and suggested an open coastal environment during the late Eocene period. Chemical Index of Alteration (CIA), a measure of weathering intensity, is an important index of climatic conditions around the hinterlands from where the sediments are supplied to the depositional basin. CIA values of about 45–55 indicate virtually no weathering, whereas 100 indicates an intense weathering with complete removal of alkali and alkaline earth metals. CIA in a glaciated river catchment of Himachal Pradesh, which experiences cold climate throughout the year, is reported between 41 and 54 and CIA value of the Ganga River suspended sediment is 66. In Figure 5, the range of CIA in the host mudstones (70–82) is higher than the Ganga River sediment value, the catchment area of which experiences a range of summer temperatures from 30 to 50°C and largely summer monsoon-related rainfall. Therefore, the CIA range of the host mudstones suggests that the weathering was moderate as a result of high temperature and high rainfall during late Eocene. The occurrence of calceretes suggests arid/semi-arid climates during intervening periods when soil carbonates accumulated during low supply of sediment in the Himalayan foreland basin, when the atmospheric CO₂ was less than 930 ppm V.

It is considered that uplift of the Tibetan plateau had significant influence on the Asian monsoon system and the uplift of the Tibetan plateau to its present elevation is suggested to have taken place around 15 Ma. Later around 11 Ma, largest change in the planktonic foraminiferal assemblages in the Indian Ocean was linked to closing of Indonesian seaway and this may be related to intensification of the Indian monsoon. Similarly, −10‰ δ¹³C value of soil carbonates from the Himalayan foreland basin sequences demonstrates Asian monsoon intensification at ~10.5 Ma with a clear onset of another monsoon intensification at 6 Ma. Large negative values of δ¹³C in the studied calceretes suggest a warm condition during late Eocene times, in conformity with the oceanic record, which demonstrates that the Eocene was warmer than the Palaeocene as well as the younger times. Most modern subtropical climates are seasonal, experiencing monsoon related rainfall. On the Indian subcontinent, the warmer phase was linked with sufficient rainfall contributing moderately weathered denudation products (muddy...
sedi
tment) to the depositional basin. Therefore, the host mudstones deposited during warm and wet climate phases and the calcretes developed during drier phases. This suggests that substantial rainfall began long before the uplift of the Tibetan plateau. Alternatively, it can be suggested that the Tibetan plateau was uplifted even in late Eocene.

$\delta^{13}C$ values of soil carbonates suggest that the level of atmospheric $CO_2$ was about 930 ppm V in late Eocene on the Indian subcontinent. The moderate weathering conditions under warm and wet climate during the deposition of host mudstones and intervening drier phases during the development of calcretes demonstrate fluctuations in the climate. Elevated levels of atmospheric $CO_2$ may be responsible for warmer phase resulting in lighter oxygen isotopes ($\sim-10\%$) in the late Eocene calcrete samples. The warm and wet climate during mudstone sedimentation may be related to seasonal climatic conditions that existed even during late Eocene. This also suggests that the Tibetan plateau was uplifted much earlier than the previously inferred times of its uplift.


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