Organic carbon exhumation and global warming during the early Himalayan collision

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ABSTRACT

Organic carbon eroded and oxidized from marine sediments on the passive and active neo-Tethyan margins during the early Indian-Asian collision may have been sufficient to shift the carbon isotopic ratios of late Paleocene–early Eocene marine carbonates toward lighter values, and may have contributed to coeval global warming via the greenhouse effect. New limits on the timing of collision and the organic carbon content of Himalayan sedimentary sources and sinks allow us to estimate the net Paleogene flux. Our calculations suggest that continental collisions play a fundamental role in the global carbon cycle and climate through the exhumation as well as burial of organic carbon.

INTRODUCTION

Evaluation of recent hypotheses for feedback mechanisms between climate, biospheric chemistry, metamorphism, and collisional orogenesis (Fischer and Arthur, 1977; Molnar and England, 1990; Edmond, 1992; Burbank, 1992; Kerrick and Caldeira, 1993; Raymo, 1994; Selverstone and Gutzler, 1993) requires knowledge of both the nature and timing of continent-continent collisions. One logical place to investigate tectonic-climatic hypotheses for global change is the Himalayan-Tibetan region, because of its scale and the continually improving chronology data about its history. The present topographic and climatic expression of the region is easily appreciated, if not well understood (Molnar and England, 1990; Raymo, 1994). The possible isotopic and climatic effects of oceanic closure and initial continent-continent contact are controversial and less-well appreciated (Kerrick and Caldeira, 1993; Selverstone and Gutzler, 1993).

Following a review of global carbon sources and sinks, Kerrick and Caldeira (1993) proposed that volatilization of carbonate rocks during regional metamorphism in the Himalayan orogen may have been responsible for the marked early Cenozoic increase in temperature and, by inference, atmospheric CO$_2$. Selverstone and Gutzler (1993) challenged the notion that significant quantities of CO$_2$ are volatilized from carbonates during collisional metamorphism. They postulated that subduction of as little as 10$^{16}$ to 10$^{17}$ mol of carbon over 125 m.y. (flux $\sim 10^{11}$ to $10^{15}$ mol/m.y.) and its storage in metamorphic rocks during the Alpine-Himalayan orogeny have had a damping effect on global surface temperature during the Late Cretaceous and Cenozoic (Selverstone and Gutzler, 1993).

HYPOTHESIS

It is evident that a consensus regarding the net effect of early continental collision on the CO$_2$ content of the atmosphere and global temperature does not yet exist. Nonetheless, any tectonic mechanism for climate change involving the carbon cycle must be reconciled with the carbon isotopic composition of marine carbonates ($\delta^{13}$C$_{carb}$) (Shackleton, 1987) either directly or through additional, possibly independent, mechanisms. We investigate one of the more immediate consequences of continent-continent collisions: the exhumation of organic carbon (C$_{org}$) from strata at colliding active and passive margins.

We present evidence that (1) the timing of early Himalayan thrusting and exhumation of C$_{org}$ (kerogen, bitumen, and mobile hydrocarbons including methane) from neo-Tethyan strata above the north Indian shelf coincides with and is quantitatively compatible with the rapid decrease of $\delta^{13}$C$_{carb}$, near the Paleocene-Eocene boundary, and (2) collision-related C$_{org}$ fluxes are comparable to those of competing carbon-generating hypotheses for late Paleocene–early Eocene global warming (Kerrick and Caldeira, 1993; Selverstone and Gutzler, 1993; Beck et al., 1994).

The cause of the early to late Paleocene increase of $\delta^{13}$C$_{carb}$ (Fig. 1) is not known (Zachos et al., 1992). Organic carbon is strongly enriched in $^{13}$C by photosynthesis. Approximately 99.95% of all C$_{org}$ is stored in the sedimentary and metasedimentary reservoirs (Tissot and Welte, 1978). An increase in the size of the lithospheric C$_{org}$ reservoir would increase the $^{13}$C/$^{12}$C ratio of the minute oceanic and atmospheric reservoirs (Shackleton, 1987). Rapid fluctuations in sea level or erosion of the Trans-Himalayan arc (e.g., Raymo, 1994) during earliest collision that may have increased the nutrient flux and oceanic productivity, increased sedimentation rates and focused deposition (e.g., modern Mediterranean), and restricted circulation resulting in anoxia are all possible contributors to an increase in the apparent rate of C$_{org}$ burial (e.g., Calvert, 1987).

Conversely, a relative increase in the flux of C$_{org}$ to the biosphere could be responsible for the observed decrease in $\delta^{13}$C$_{carb}$ during isotopically and paleofloristically inferred late Paleocene to early Eocene increments of temperature ($T$) and the partial pressure of carbon dioxide (P$\text{CO}_2$) (Wolfe and Poore, 1982; Zachos et al., 1992; Sloan et al., 1992) (Fig. 1). If the C$_{org}$ source was imbricated Asian and Indian active- and passive-margin strata, a decline in $\delta^{13}$C$_{carb}$ should have begun after collision. As predicted by this hypothesis, the Cenozoic $\delta^{13}$C$_{carb}$ maximum that occurred during the
P5 *Morozovella velascoensis* subbiozone (Shackleton, 1987) preceeded massive exhumation during early Indian-Asian collision (Fig. 1) (Beck et al., 1995). The subsequent decrease in $\delta^{13}C_{\text{carb}}$ lasted ~4 m.y. (Shackleton, 1987) and coincided with vigorous erosion and oxidation of neo-Tethyan strata prior to deposition of overlying shallow-marine upper lower Eocene limestones and shales in northwestern Pakistan (Beck et al., 1995). The contemporaneous late Paleocene to middle Eocene positive excursion of $^{187}\text{Os}/^{186}\text{Os}$ values in marine clays has also been attributed to the erosion of Himalayan shales (Pegram, 1992).

Erosion and oxidation of sedimentary $C_{\text{org}}$ to CO$_2$ at the lithosphere-biosphere interface avoids the subducted carbonate volatilization controversy (Kerrick and Caldeira, 1993; Selverstone and Gutzler, 1993) and has previously been postulated to occur during eustatic sea-level falls (Broecker, 1982). However, the general upward trend of late Paleocene–early Eocene sea levels (Hallam, 1992) suggests that the apparent increase of $C_{\text{org}}$ erosion was not driven by eustatic sea-level fall.

**FLUX ESTIMATES**

Changes in the sedimentary $C_{\text{org}}$ reservoir must be compatible with the $\delta^{13}C_{\text{carb}}$ record. Shackleton's (1987) carbon isotope mass-balance calculations for the late Paleocene–early Eocene negative shift in $\delta^{13}C_{\text{carb}}$ values (~2.2‰) (Fig. 1) suggest a net decrease in the rate of $C_{\text{org}}$ burial of ~1.6 x $10^{18}$ mol/m.y., which was sustained for ~4 m.y. Thus, we have a standard against which to measure the feasibility of our hypothesis for the exhumation of $C_{\text{org}}$ during the Indian-Asian collision.

We used a simple sediment budget in combination with measured total $C_{\text{org}}$ (TOC) values from sedimentary sources and sinks to estimate the net quantity of early Himalayan $C_{\text{org}}$ exhumed. Our sediment/$C_{\text{org}}$ budget (Table 1) assumes that geometric cross sections of the Sumatran active margin (Hamilton, 1988) and the modern Atlantic passive margin (Grow, 1981) are reasonable analogs for the Himalayan segment of the neo-Tethyan accretionary prism and fore arc (Hamilton, 1988) and north Indian passive margin (e.g., Brookfield, 1993). We also assume that TOC values for shales of the Asian active margin and north Indian passive margin (Table 2) are representative of analogous strata along the suture (Meyers and Dickens, 1992; Karunakaran and Rao, 1976). Early erosion of most of the former Asian active and Indian outer passive-margin strata along the Himalaya is also a core assumption of our hypothesis. This assumption is supported in northwestern Pakistan by large quantities of reworked Jurassic pollen and dinoflagellates and Cretaceous chert and ultramafic clasts in late Paleocene–early Eocene strata that are securely dated on the basis of foraminifera as well as by

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**Figure 1.** Values of $\delta^{18}O$ and $\delta^{13}C$ for marine Cenozoic carbonate strata (Shackleton, 1987) vs. timing of initial Indian-Asian collision with consequent erosion of organic carbon-bearing north Indian slope, outer shelf, south Asian fore arc and accretionary prism. Initial collision is determined as postdating *G. gansseri* and being prior to end of P5 foraminiferal biozones (Beck et al., 1995). PLI—Pliocene, PALEOC.—Paleocene, MA.—Maastrichtian.
upper lower Eocene strata, which unconformably overlie klippen of Indian slope and Asian accretionary-prism strata (Beck et al., 1995). Remnants of the active and passive margins provide lower limits on their original C\textsubscript{org} contents (Thurow et al., 1992; Gaetani and Garzanti, 1991).

To determine the magnitude of the precollisional C\textsubscript{org} source, we subdivided two-dimensional cross sections of the active- and passive-margin analogs to estimate more precisely the relative proportion of shale and nonshale rocks, their densities, and respective TOC values. The cross-sectional areas were multiplied by the length of the Himalayan mountain chain (2500 km) to estimate their precollisional volumes. Representative densities were taken from analogs determined by seismic, well-bore, and gravity data (Hamilton, 1988; Grow, 1981). Average shale contents were estimated from published data on Himalayan outcrops (Sinha and Upadhyay, 1990; Meissner et al., 1975) or analogous strata from similar tectonic environments (Seuss et al., 1987) (Table 1). We multiplied the resulting mass of shale in each subdivision (Table 1) by average TOC values from Himalayan strata, strata with which they were once continuous, or analogous strata (Table 2) to obtain the mass of C\textsubscript{org} stored in each subdivision.

The north Indian passive margin and the northwest Australian margin with which it was once continuous are remarkable for the abundance of C\textsubscript{org}-rich strata they contain (Gaetani and Garzanti, 1991; Meyers and Dickens, 1992; Thurow et al., 1992). Permian, Triassic, Jurassic, and Cretaceous outer shelf shales in northern India (Gaetani and Garzanti, 1991) and Nepal contain 1–2 wt% TOC or more (Meyers and Dickens, 1992), despite at least low-grade metamorphism (Gaetani and Garzanti, 1991). We included only shale-dominated strata of the active margin, the north Indian slope, and 20% of the outermost shelf in our C\textsubscript{org} source estimates.

The constant Paleogene carbonate compensation depth (CCD) (Rea, 1993) suggests that calcium and magnesium carbonates were redeposited with little or no effect on oceanic carbon isotope ratios or atmospheric CO\textsubscript{2} (e.g., Shackleton, 1987). TOC values for sandstones in the Indian shelf and slope and the molasse are low (<0.2 wt%, this study). Thus, for the sake of simplicity, we made the conservative assumption that the nonshale fraction of pre- and postcollisional sedimentary material had a TOC value equal to 0 wt%.

TOC data (Table 2) were also used to estimate the magnitude of the syndeformational sedimentary C\textsubscript{org} sink. We assumed that 25% of all the eroded sediment (shale and nonshale fractions) was redeposited in the ≥8-km-thick Paleogene red-bed facies (Karunakaran and Rao, 1976) (average TOC = 0.06 wt%) and the

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**Table 2. Total Organic Carbon Data for Precollisional Strata**

<table>
<thead>
<tr>
<th>Lithosphere</th>
<th>Period, epoch or stage</th>
<th>No. of samples</th>
<th>Avg. TOC (wt%)</th>
<th>Location</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prism</td>
<td>Middle-Lower Cretaceous</td>
<td>51</td>
<td>0.3</td>
<td>Pakistan</td>
<td>This study</td>
</tr>
<tr>
<td>Slope</td>
<td>Neocomian</td>
<td>n.a.</td>
<td>1.0</td>
<td>NW Australia</td>
<td>Meyers and Dickens (1992)</td>
</tr>
<tr>
<td>Outer shelf</td>
<td>Campanian-Turonian</td>
<td>n.a.</td>
<td>1.5</td>
<td>NW Australia</td>
<td>Meyers and Dickens (1992)</td>
</tr>
<tr>
<td></td>
<td>Oxfordian</td>
<td>n.a.</td>
<td>1.5</td>
<td>NW Australia</td>
<td>Meyers and Dickens (1992)</td>
</tr>
<tr>
<td>Tithonian</td>
<td></td>
<td>n.a.</td>
<td>1.5</td>
<td>NW Australia</td>
<td>Meyers and Dickens (1992)</td>
</tr>
<tr>
<td>Baramanian-Valeianian</td>
<td>n.a.</td>
<td>1.5</td>
<td>Nepal</td>
<td>Thurow et al. (1992)</td>
<td></td>
</tr>
<tr>
<td>Mid-Jurassic-Lower Cretaceous</td>
<td>n.a.</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inner shelf</td>
<td>Jurassic-Cretaceous</td>
<td>42</td>
<td>0.82</td>
<td>Pakistan</td>
<td>This study</td>
</tr>
<tr>
<td>Flysch</td>
<td>Paleocene - Early Eocene</td>
<td>68</td>
<td>0.18</td>
<td>Pakistan</td>
<td>This study</td>
</tr>
<tr>
<td>Molasse</td>
<td>Paleocene-Miocene</td>
<td>n.a.</td>
<td>0.06</td>
<td>India</td>
<td>Karunakaran and Rao (1975)</td>
</tr>
</tbody>
</table>

Note: Source of variables discussed in text. TOC—total organic carbon.
remaining 75% in the green-shale–rich marine flysch facies. New TOC analyses ($n = 68$) distributed vertically through the Paleocene to middle Eocene marine flysch facies yield an average TOC value of 0.2 wt%. Accordingly, our budget suggests that $\sim 30\%$ of the total TOC in the active and passive margins was reburied by its own detritus (Table 1).

The rate of India-Asia convergence and the geometry of the colliding margins will determine the rate at which sedimentary $C_{org}$ is uplifted and eroded. To estimate $C_{org}$ fluxes, we must know the duration of this presumably diachronous process. Initial collision is determined as pre–earliest Eocene (pre–56 Ma) (Beck et al., 1995) for the western one-third of the Himalayan suture, and recent field work in south Tibet indicates that contraction commenced in the Paleocene, and it is attributed to the approach of the Indian continental margin (Burg and Chen, 1984; Einsele et al., 1995).

We estimate a duration of 4 m.y. ($\sim 60–56$ Ma) for the closure of the Himalayan segment of neo-Tethyan remnant ocean basins and the initial stages of Indian-Asian collision. Between 600 and 800 km of convergence would have occurred during this interval (Dewey et al., 1989). This implies a sediment flux of $1.97 \text{ km}^3/\text{yr}$, which is similar to the modern Himalayan value of $1.06 \text{ km}^3/\text{yr}$ (Summerfield and Hulton, 1994), and a $C_{org}$ flux of $\sim 1.6 \times 10^{18} \text{ mol/m.y.}$, which is comparable to the apparent decrease in $C_{org}$ burial predicted by Shackleton (1987). We conclude that organic carbon exhumed from the early Himalayan active and passive margins may have depressed late Paleocene–early Eocene $\delta^{13}C_{\text{org}}$ values and may have driven Paleogene global warming by increasing the atmospheric concentrations of the greenhouse gases $\text{CH}_4$ and $\text{CO}_2$.

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