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 CO₂. Selverstone and Gutzler (1993) challenged the notion that significant quantities of CO₂ 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 $\sim 10^{14}$ 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 addi-

tional, 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 $\delta^{13}C_{earb}$ 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 ¹²C 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 ¹³C/¹²C 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 increases of temperature (*T*) and the partial pressure of carbon dioxide (*P*CO₂) (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



Figure 1. Values of δ^{18} O and δ^{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. ganserri* and being prior to end of P5 foraminiferal biozones (Beck et al., 1995). PLI.—Pliocene, PALEOC.— Paleocene, MA.—Maastrichtian.

P5 *Morozovella velascoensis* subbiozone (Shackleton, 1987) preceded massive exhumation during early Indian-Asian collision (Fig. 1) (Beck et al., 1995). The subsequent decrease in $\delta^{13}C_{carb}$ 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 ¹⁸⁷Os/¹⁸⁶Os values in marine clays has also been attributed to the erosion of Himalayan shales (Pegram, 1992).

Erosion and oxidation of sedimentary C_{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_{org} erosion was not driven by eustatic sea-level fall.

FLUX ESTIMATES

Changes in the sedimentary C_{org} reservoir must be compatible with the $\delta^{13}C_{carb}$ record. Shackleton's (1987) carbon isotope massbalance calculations for the late Paleocene–early Eocene negative shift in $\delta^{13}C_{carb}$ values (~2.2‰) (Fig. 1) suggest a net decrease in the rate of C_{org} burial of ~1.6 × 10¹⁸ 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_{org} during the Indian-Asian collision.

We used a simple sediment budget in combination with measured total Corg (TOC) values from sedimentary sources and sinks to estimate the net quantity of early Himalayan Corg exhumed. Our sediment/Corg 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

TABLE 1. ESTIMATES OF THE ORGANIC CARBON FLUX DURING THE INITIAL COLLISION OF INDIA AND ASIA	ss- Density Fraction Shale TOC Duration Fraction of TOC values Fraction of TOC values Net flux of Net flux of	ional (10 ¹⁵ deformed fraction values of of erosion sediment for sedi- sediment sediments organic carbon organic carbon	(km²) g/km³) and of strata pre- (m.y.) redepos- ments re- redeposited redeposited in released to from prism and	eroded collisional ited as deposited as marine marine shale atmosphere passive margin	strata red beds as red beds sediments (wt%) and hydrosphere (less eclogi <u>t</u> e	(10 ¹⁵ mol/m.y.) sink) (10 ¹⁵ mol/m.y.) sink) (10 ¹⁵ mol/m.y.) sink) (10 ¹⁵ mol/m.y.) mol/m.y.)	00 2.0 0.9 0.75 0.3 4 0.25 0.06 0.75 0.2 63	50 2.4 0.9 0.75 1.5 4 0.25 0.06 0.75 0.2 477	00 2.4 0.9 0.85 1.0 4 0.25 0.06 0.75 0.2 1050	50 2.4 0.2 0.65 1.5 4 0.25 0.06 0.75 0.2 9	1600 1550	0 tm TOC total accordion
FLUX D	on Fract	ion sedii) rede	itec	red		ō	0	0	0		
CARBON	Duratic	of erosi	(m.y.)				4	4	4	4		
DRGANIC C	<u>10C</u>	values of	pre-	collisional	strata	(wt%)	0.3	1.5	1.0	1.5		
S OF THE (Shale	fraction	of strata				0.75	0.75	0.85	0.65		rhon
ESTIMATE	Fraction	deformed	and	eroded			0.9	0.9	0.9	0.2		I organic ca
TABLE 1.	Density	c101)	g/km ³)				2.0	2.4	2.4	2.4		TOCtots
	Cross-	sectional	area (km [∠])				1600	450	1400	250		h = 2500 km
	Sedimentary organic	carbon source					Himalayan prism	Himalayan fore arc	N. Indian slope and rise	N. Indian outer shelf	Totals	Note: I enoth of orogen

Lithosome	Period, epoch or	No. of	Avg.	Location	Reference
	stage	samples	TOC		
			(wt%)		
Prism	Middle - Upper Cretaceous	51	0.3	Pakistan	This study
Slope	Neocomian	n.a.	1.0	NW Australia	Meyers and Dickens (1992)
Outer shelf	Carnian-Rhaetian	n.a.	1.5	NW Australia	Meyers and Dickens (1992)
	Oxfordian- Tithonian	n.a.	1.5	NW Australia	Meyers and Dickens (1992)
	Berraisian- Valenginian	n.a.	1.5	NW Australia	Meyers and Dickens (1992)
	Mid-Jurassic - Lower Cretaceous	n.a.	1.5	Nepal	Thurow et al. (1992)
Inner shelf	Jurassic- Cretaceous	42	0.82	Pakistan	This study
Flysch	Paleocene - early Eocene	68	0.18	Pakistan	This study
Molasse	Paleocene- Miocene	n.a.	0.06	India	Karunakaran and Rao (1976)

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_{org} contents (Thurow et al., 1992; Gaetani and Garzanti, 1991).

To determine the magnitude of the precollisional C_{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_{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 Corg-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 lowgrade 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_{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 CO₂ (e.g., Shackleton, 1987). TOC values for sandstones in the Indian shelf and slope and the molasse are low (<0.2wt%, 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_{org} sink. We assumed that 25% of all the eroded sediment (shale and nonshale fractions) was redeposited in the \leq 8-km-thick Paleogene red-bed facies (Karunakaran and Rao, 1976) (average TOC = 0.06 wt%) and the remaining 75% in the green-shale–rich marine flyschoid 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 ~30% of the total C_{org} 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 km³/yr, which is similar to the modern Himalayan value of 1.06 km³/yr (Summerfield and Hulton, 1994), and a C_{org} flux of $\sim 1.6 \times 10^{18}$ 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 $\delta^{13}C_{carb}$ values and may have driven Paleogene global warming by increasing the atmospheric concentrations of the greenhouse gases CH₄ and CO₂.

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