Efficient transport of fossil organic carbon to the ocean by steep mountain rivers: An orogenic carbon sequestration mechanism

Robert G. Hilton12*, Albert Galy3, Niels Hovius3, Ming-Jame Horng4, and Hongey Chen5

1Laboratoire de Géochimie–Cosmochimie, Institut de Physique du Globe de Paris, 4 Place Jussieu, 75252, Paris Cedex 05, France
2Department of Geography, Durham University, Science Laboratories, South Road, Durham, DH1 3LE, United Kingdom
3Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom
4Water Resources Agency, Ministry of Economic Affairs, Hsin-Yi Road, Taipei, 10651, Taiwan
5Department of Geoscience, National Taiwan University, Roosevelt Road, Taipei, 10617, Taiwan

*E-mail: r.g.hilton@durham.ac.uk

ABSTRACT

Mountain building exposes fossil organic carbon (OCfossil) in exhumed sedimentary rocks. Oxidation of this material releases carbon dioxide from long-term geological storage to the atmosphere. OCfossil is mobilised on hillslopes by mass wasting and transferred to the particulate load of rivers. In large fluvial systems it is thought to be oxidised in transit, but in short, steep rivers that drain mountain islands, OCfossil may escape oxidation and re-enter geological storage due to rapid fluvial transfer to the ocean. In these settings, the rates of OCfossil transfer and their controls remain poorly constrained. Here we quantify the erosion of OCfossil from the Taiwan mountain belt, combining discharge statistics with measurements of particulate organic carbon load and source in 11 rivers. Annual OCfossil yields in Taiwan vary from 12 ± 1–
246 ± 22 tC km⁻² yr⁻¹, controlled by the high physical erosion rates that accompany rapid crustal shortening and frequent typhoon impact. Efficient transfer of this material ensures that 1.3 ± 0.1x10⁶ tC yr⁻¹ of OC_fossil exhumed in Taiwan is delivered to the ocean, with <15% loss due to weathering in transit. Our findings suggest that erosion of coastal mountain ranges can force efficient transfer and long-term re-accumulation of OC_fossil in marine sediments, further enhancing the role of mountain building in the long-term storage of carbon in the lithosphere.

INTRODUCTION

About 15x10¹⁵ tC of carbon is stored in rocks as fossil organic matter. This is almost 400 times the amount of carbon present in the atmosphere and oceans (Sundquist and Visser, 2004). The balance between the growth of this geological reservoir through burial of newly photosynthesised organic matter, and its decrease through oxidation of OC_fossil plays a crucial role in the long-term evolution of atmospheric CO₂ and O₂, and thus global climate (Berner, 1982; Berner and Canfield, 1989; Derry and France-Lanord, 1996; Hayes et al., 1999). It is commonly assumed that during mountain building, exhumed OC_fossil is completely converted to CO₂ by chemical weathering (Lasaga and Ohmoto, 2002; Bolton et al., 2006). OC_fossil can escape oxidation when physical erosion delivers it to the solid load of mountain rivers (Kao and Liu, 1996; Blair et al., 2003; Leithold et al., 2006; Hilton et al., 2008a). But when it enters large river systems (>100,000 km² area), up to 85% is oxidised in transport (Galy et al., 2008a; Bouchez et al., 2010). In contrast, short mountain rivers that drain to the ocean could deliver OC_fossil more efficiently to marine basins due to rapid transport in turbid waters (Dadson et al., 2005; Hilton et al., 2008b). Despite its potential importance, the transfer of OC_fossil from mountain islands has remained poorly constrained (Blair et al., 2003), due to both a lack of constraint of the source of particulate organic carbon (POC) in river sediments in these settings (Stallard, 1998; Lyons et
al., 2002) and its transport behavior over the large range of water discharges in steep mountain
catchments (Blair et al., 2003; Hilton et al., 2008a). To address this issue, we have determined
the source of POC and the relation between OC$_{\text{fossil}}$ transport and water discharge in rivers
draining the mountain belt of Taiwan.

**STUDY AREA, SAMPLING AND METHODS**

Located along the western edge of the Pacific Ocean, mountain building in Taiwan is
driven by collision between the Luzon Arc on the Philippine Sea plate and the Asian continental
margin since 7 Ma (Teng, 1990). Steep rivers draining Taiwan’s Central Range pass over narrow
coastal plains to the ocean (Dadson et al., 2003). Inside the mountain belt, they have incised
Mesozoic and Cenozoic siliciclastic and carbonate rocks, which have been metamorphosed up to
greenschist and amphibolite facies (Ho, 1986). These rocks contain on average 0.2% OC$_{\text{fossil}},$
mainly of marine origin (Hilton et al., 2010). The western flank of the Central Range comprises
Late Cenozoic turbiditic mudstones, sandstones and near-shore foreland sediments (Ho, 1986).
These lithologies contain on average 0.4% mainly terrestrial OC$_{\text{fossil}}$ (Hilton et al., 2010).
Metamorphic grade decreases from East to West across the Central Range and surface rocks
contain OC$_{\text{fossil}}$ of varying thermal maturity and structure, ranging from poorly organized
carbonaceous matter to polycrystalline graphite (Beyssac et al., 2007). Due to rapid crustal
shortening (Teng, 1990) and the prevailing subtropical cyclonic climate, rates of mass wasting
and physical erosion in river catchments of the Central Range are exceptionally high, averaging
$\sim$6 mm yr$^{-1}$ over the last four decades (Dadson et al., 2003), and Taiwan Rivers supply $384\times10^6$ t
yr$^{-1}$ of suspended sediments and $\sim120\times10^6$ t yr$^{-1}$ of river bed load to the ocean.

To determine the concomitant OC$_{\text{fossil}}$ transfer, we measured suspended sediment
concentration (SSC, mg L$^{-1}$), OC$_{\text{fossil}}$ concentration in the particulate load (POC$_{\text{fossil}},$ mg L$^{-1}$) and
water discharge \(Q_w, m^3 \text{ s}^{-1}\) in 11 main Taiwan Rivers over an 18 month period following established methods (Dadson et al., 2003; Hilton et al., 2008b; Hilton et al., 2010). The catchments ranged in size from 310 km² to 2,906 km² (covering a total area of \(9.6 \times 10^3 \text{ km}^2\), 27% of the islands surface) and were sampled 1–3 times per month over two typhoon seasons (March 2005–September 2006) to cover the dynamic range of \(Q_w\). All catchments drain more than one of the major geological formations, sourcing rocks with \(OC_{\text{fossil}}\) content ranging between 0.2% and 0.4% (Hilton et al., 2010). Determination of the source of POC in each sample has been described in detail elsewhere (Hilton et al., 2010). Briefly, an end-member mixing model was used to quantify the fraction of \(OC_{\text{fossil}}\) (\(F_f\)) in the total POC using measurements of the nitrogen to organic carbon ratio and the stable carbon isotopes of organic matter. \(F_f\) was tested against independent constraints from radiocarbon, and \(F_f\) average precision and accuracy are 0.09 and 0.05, respectively. \(POC_{\text{fossil}}\) for a suspended sediment sample is the product of SSC, total organic carbon concentration and \(F_f\).

To quantify river solid load yields we defined rating curves that link the \(Q_w\) measured at a station to the river load constituent concentration (SSC and \(POC_{\text{fossil}}, \text{mg L}^{-1}\)), and applied them to the continuous daily record of \(Q_w\) at that station to estimate the mass transfer of suspended load materials over the sampling period. Following common practice for small catchments, we used power law rating curves (Fig. 1a) with a least squares best fit to available data (Hilton et al., 2008b). Quoted errors on mass transfer estimates combine the rating curve exponent error (Fig. 1b) and the error in \(F_f\) (Hilton et al., 2010).

**FLUVIAL TRANSPORT OF \(OC_{\text{fossil}}\) AND ITS CHEMICAL ALTERATION**

In all rivers, \(OC_{\text{fossil}}\) was present in the suspended load throughout the sampling period. General, positive relationships between measured \(Q_w\), and SSC and \(POC_{\text{fossil}}\) in these rivers are
described well by power laws (Fig. 1a) with very similar least squares best fit exponents for SSC and POC$_{fossil}$ in a given catchment (Fig. 1b). The link between OC$_{fossil}$ and suspended sediment confirms their common rock source in mountain catchments (Leithold et al., 2006; Hilton et al., 2008a).

Following the observed relationship between POC$_{fossil}$ and Q$_w$ and the derived power law rating curves, OC$_{fossil}$ yields for all rivers ranged between 12 ± 1 and 246 ± 22 tC km$^{-2}$ yr$^{-1}$ over the gauged period (Fig. 2). These yields are significant natural transfers of carbon and two rivers had OC$_{fossil}$ yields >225 tC km$^{-2}$ yr$^{-1}$, greater than the highest total POC yield (fossil+non-fossil) previously reported for mountain rivers (Stallard, 1998; Lyons et al., 2002; Hilton et al., 2008a). The average OC$_{fossil}$ yield for the 11 studied catchments was 82 tC km$^{-2}$ yr$^{-1}$.

High OC$_{fossil}$ yields in Taiwan are closely linked to the yield of suspended sediment (Fig. 2) and are therefore controlled by physical erosion rate. This concurs with previous findings which suggest OC$_{fossil}$ is delivered to river channels by mass wasting, e.g., bedrock landslides (Hilton et al., 2008a), and gully erosion (Leithold et al., 2006), processes which can drive rapid physical erosion rates in mountain belts. Here, erosion of OC$_{fossil}$ must occur faster than its chemical alteration (Petsch et al., 2000), leading to incomplete oxidation in the weathering zone. The lack of substantial sediment storage in the bedrock channels of the Central Range implies that the fluvial transit time is very short (Dadson et al., 2005), further restricting alteration of OC$_{fossil}$ during transport, in notable contrast to large river systems (Galy et al., 2008a; Bouchez et al., 2010). OC$_{fossil}$ weathering may still occur within catchments, since sediment may reside for longer periods of time in regoliths and soils on hillslopes where the production of mineral surface area through physical erosion may enhance OC$_{fossil}$ weathering rates (Petsch et al., 2000; Bolton et al., 2006; Lasaga and Ohmoto, 2002).
OC_fossil oxidation in catchments can be quantified by comparing the measured fluvial export of OC_fossil to that predicted by eroding surface bedrock at known erosion rates. Measured fluvial exports imply a OC_fossil content of 0.35 ± 0.03% (±σ) in suspended sediments from Taiwan (Fig. 2). Surface rocks have an average organic carbon content of 0.24 ± 0.19% (±σ, n = 31) which varies between geological formations (Hilton et al., 2010). The highest average OC_fossil content of the main geological formations is 0.41%, which is similar to the +σ bound of all samples. If we assume little variability of OC_fossil content with grain size, demonstrated by previous work (Galy et al., 2008a; Bouchez et al., 2010; Hilton et al., 2010), this can be used to estimate that a maximum of 15 ± 7% of the exhumed OC_fossil is weathered prior to export (Fig. 2). This moderate weathering loss would correspond to a transfer of geological carbon to the modern hydrosphere and atmosphere of 12 ± 6 tC km⁻² yr⁻¹ in the sampled catchments. However, the measured average OC_fossil in rock precludes any weathering loss and is within one standard deviation of the OC_fossil content of suspended sediments (Fig. 2) making it difficult to estimate chemical alteration of OC_fossil by this method. We conclude that the bulk of exhumed OC_fossil is exported to the ocean from Taiwan in river sediment and that the magnitude of OC_fossil oxidation requires further investigation.

**DELIVERY OF OC_fossil TO THE OCEAN**

We estimate that the sampled mountain rivers delivered 0.9x10⁶ tC yr⁻¹ of OC_fossil to the ocean during the study period (Fig. 3). To quantify the OC_fossil transfer from the island over a longer period, we note that mean sediment yields in sampled catchments were 23,600 ± 6,800 t km⁻² yr⁻¹ (± standard error on the mean) during our study, and 21,700 ± 3,900 t km⁻² yr⁻¹ in the period 1970-1999 (Dadson et al., 2003) suggesting the measured OC_fossil yields are a natural feature of this mountain belt. On decadal timescales the spatial pattern of physical erosion in
Taiwan is set by the incidence of earthquakes and typhoons, and by bedrock erodability (Dadson et al., 2003), and this is likely also the case for the erosion of OC$_{fossil}$. We therefore combine the published decadal suspended sediment transfer (Dadson et al., 2003) with the average OC$_{fossil}$ concentration in the suspended load (0.35 ± 0.03% calculated by regression across 11 catchments; Fig. 2) to estimate a total fluvial export of 1.3 ± 0.1x10$^6$ tC yr$^{-1}$ of OC$_{fossil}$ to the ocean as suspended sediment. This equates to a normalized yield of 37 ± 3 tC km$^{-2}$ yr$^{-1}$ over the total area of Taiwan (35,980 km$^2$). Addition of bed load transport, assuming an average OC$_{fossil}$ content of 0.27 ± 0.12% (±σ) measured in 14 river catchments (Hilton et al., 2010), results in a total export of ~1.7x10$^6$ tC yr$^{-1}$. The suspended flux alone represents ~1% of the estimated 90-240x10$^6$ tC yr$^{-1}$ total POC (fossil+non-fossil) input to the oceans (Stallard, 1998; Lyons et al., 2002) from only ~0.02% of Earth’s landmass.

OC$_{fossil}$ transported through the modern erosion system can be re-buried in long-lived marine sediments (Dickens et al., 2004; Galy et al., 2008a). Locally this can alter the geochemical record of the organic matter because OC$_{fossil}$ has a variable isotopic signature (Hayes et al., 1999; Hilton et al., 2010). If OC$_{fossil}$ re-burial is globally significant then it will influence the residence time of carbon in the lithosphere and our understanding of the long-term cycles of carbon and oxygen (Berner and Canfield, 1989; Galy et al., 2008a), while also influencing our interpretation of the isotopic mass balance of carbon in the oceans (Derry and France-Lanord, 1996; Hayes et al., 1999). In large river systems with long transport pathways and significant sediment storage, only refractory graphitic OC$_{fossil}$ is resilient to chemical weathering and physical attrition during transport (Galy et al., 2008a). In the case of the Madeira floodplain of the Amazon, >85% of the eroded OC$_{fossil}$ may escape geological storage to the atmosphere (Bouchez et al., 2010). In contrast, the steep mountain rivers of Taiwan export...
OC\textsubscript{fossil} eroded from rocks with a range in thermal maturity (Hilton et al., 2010), with little
OC\textsubscript{fossil}-loss across the island irrespective of its graphitization state (Fig. 2).

The fate of OC\textsubscript{fossil} exported from Taiwan is not well constrained, but several
observations suggest that a significant proportion is re-buried in marine sediments. First, by its
nature OC\textsubscript{fossil} is associated with mineral surfaces, and this has been shown to enhance organic
carbon burial efficiency (Hedges and Keil, 1995). Second, offshore Taiwan rapid accumulation
of clastic sediment is likely to optimize organic carbon preservation (Canfield, 1994).

Hyperpycnal sediment discharge in very turbid river plumes, and deposition of turbidites may be
especially important in this process (Hilton et al., 2008b). Hyperpycnal discharge represented
30\%–42\% of the sediment export from Taiwan to the ocean in 1970–1999, and may be even
more important on longer time scales (Dadson et al., 2005). Accounting for bed load transport,
and assuming full preservation of hyperpycnal OC\textsubscript{fossil} on long time scales, this results in a re-
burial flux of 0.5–0.7x10\textsuperscript{6} tC yr\textsuperscript{-1} in basins around Taiwan. The closest constraint on the fate of
OC\textsubscript{fossil} comes from the Images core MD012403 collected from the Okinawa Trough to the NE
of Taiwan (Fig. 3). There, the radiocarbon age of bulk organic carbon in sediments is offset by
~7,000 years from the age of planktonic foraminifera, throughout the Holocene (Kao et al.,
2008). Assuming a binary mixture of radiocarbon-dead OC\textsubscript{fossil} and contemporaneous organic
matter, the authors estimate that of the ~0.7\% organic carbon in sediments at this site, ~0.3\% is
OC\textsubscript{fossil}. If this material is present even at a site ~150km from Taiwan’s coastline and with
limited hyperpycnal input, then our re-burial estimate of 0.5–0.7x10\textsuperscript{6} tC yr\textsuperscript{-1} is likely to be
conservative.

**WIDER IMPLICATIONS AND CONCLUSIONS**
To assess their wider significance, our findings can be compared to observations from a much larger orogenic system. Erosion of the Himalaya is thought to have resulted in re-burial of 0.3–0.5x10^6 tC yr^{-1} of OC_{fossil} in the deep marine Bengal fan (Galy et al., 2008a). Averaged over the source area, the OC_{fossil} re-burial flux in the Bengal fan represents 0.2–0.3 tC km^{-2} yr^{-1}. The equivalent re-burial flux estimated here for Taiwan is 14–19 tC km^{-2} yr^{-1} which is likely to represent a lower bound as discussed previously. This large discrepancy is due in part to a lower OC_{fossil} content in Himalayan surface rocks, typically <0.20% (Galy et al., 2008a), associated with older, higher-grade Proterozoic to Early Paleozoic meta-sediments. The discrepancy is also related to erosion rates which are 2–3 times higher in Taiwan (Galy and France-Lanord, 2001; Dadson et al., 2003). However, these factors cannot explain the factor ~70 difference in the normalized OC_{fossil} re-burial flux. Its main cause is the transit length and time of OC_{fossil} in the terrestrial environment. While fluvial entrainment and delivery of sediment to the ocean typically occur within a single flood event in steep rivers of Taiwan (Dadson et al., 2005; Hilton et al., 2008b), Himalayan sediment is routed through the Gangetic plain, with a large capacity for sediment storage and subsequent OC_{fossil} alteration (Galy et al., 2008b), as such only the most refractory components of OC_{fossil} persist at the river mouth (Galy et al., 2008a).

Our data suggest that where sedimentary bedrock is prevalent and clastic sediment yields exceed 3,000 t km^{-2} yr^{-1} (Fig. 2), OC_{fossil} should be present in river sediments. These conditions are met throughout the mountainous islands of Oceania, and on active margins throughout the world (Milliman and Syvitsky, 1992). If our findings from Taiwan apply more widely to those settings, then one effect of mountain building on the organic carbon cycle may be felt through the repeated exhumation, erosion and re-burial of previously sequestered CO_{2} and the inhibition of its reflux to the atmosphere. This effect is likely to be governed disproportionately by re-burial
of OC\textsubscript{fossil} in basins adjacent to steep, coastal mountain ranges. At present, the combined OC\textsubscript{fossil}
re-burial flux in the Taiwanese and Himalayan source-to-sink systems is at least 0.8–1.2x10\textsuperscript{6} tC
yr\textsuperscript{-1}, accounting for >1\% of the present day total organic carbon burial in marine sediments
(Berner, 1982; Schlünz and Schneider, 2000). Globally, this flux is presently unaccounted for in
models of carbon cycling and atmospheric evolution (Berner and Canfield, 1989; Derry and
France-Lanord, 1996; Lasaga and Ohmoto, 2002; Bolton et al., 2006;), yet should be sustained
during orogenesis and contribute to geological storage of carbon derived from the atmosphere.

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Suspended sediments were collected by the 1\textsuperscript{st}, 3\textsuperscript{rd}, 4\textsuperscript{th}, 6\textsuperscript{th}, 7\textsuperscript{th}, 8\textsuperscript{th}, and 9\textsuperscript{th} regional offices of
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REFERENCES CITED

473.


Beyssac, O., Simoes, M., Avouac, J.P., Farley, K.A., Chen, Y.-G., Chan, Y.-C., and Goffe, B.,
2007, Late Cenozoic metamorphic evolution and exhumation of Taiwan: Tectonics, v. 26,


Figure 1. Relationships between water discharge \( Q_w \) (\( \text{m}^3 \text{s}^{-1} \)) and fossil particulate organic carbon concentration \( \text{POC}_{\text{fossil}} \) (mg L\(^{-1} \)) and suspended sediment concentration \( \text{SSC} \) (mg L\(^{-1} \)) in Taiwan Rivers. (a) Direct measurements of \( Q_w \), SSC and \( \text{POC}_{\text{fossil}} \) for the Chenyoulan River in Taiwan. Whiskers show error in concentration where large than the point. Power law rating curves for SSC (black line) and \( \text{POC}_{\text{fossil}} \) (gray line) were determined by a least squares best fit with exponents \( \Sigma \) and \( \Phi \), respectively. (b) Power law rating curve exponent between \( Q_w \) and solid load constituents (\( \Sigma \) and \( \Phi \)) for 11 Taiwanese rivers determined by a least squares best fit. Whiskers are errors on the fit. Solid line show linear regression through the data \( y = (0.93 \pm 0.06)x + 0.01 \pm 0.06; R^2 = 0.97, P<0.0001 \) and dashed lines 95% confidence intervals.
Figure 2. Relationship between suspended sediment yield (t km\(^{-2}\) yr\(^{-1}\)) and fossil organic carbon (OC\(_{\text{fossil}}\)) erosion yield (tC km\(^{-2}\) yr\(^{-1}\)) in Taiwan Rivers. A linear regression of the data (y = (0.0035 ± 0.0003)x - 1 ± 10; R\(^2\) = 0.94 P<0.0001), dashed gray showing 95% confidence intervals, implies an average OC\(_{\text{fossil}}\) concentration of 0.35 ± 0.03% in suspended sediments and that clastic sediment transfer is the dominant control on OC\(_{\text{fossil}}\) yield. Shaded region (gray) indicates the predicted range of OC\(_{\text{fossil}}\) yields for the measured suspended sediment yields using the OC\(_{\text{fossil}}\) concentration measured in rock samples from the major geological formations in Taiwan (Hilton et al., 2010).
Figure 3. Fossil organic carbon (OC$_{\text{fossil}}$) export (ktC yr$^{-1}$) to the ocean from Taiwan over the sampling period. The sampling locations and gauging stations (black circles), their catchment area (black line) and main rivers (blue line) are overlain on topography bathymetry. The relative magnitude of the OC$_{\text{fossil}}$ yield is indicated by the circles (gray).