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Publisher: GSA
Journal: GEOL: Geology
Article ID: G30608

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ABSTRACT

The two long-term sources of atmospheric carbon are CO_2 degassing from metamorphic and volcanic activity, and oxidation of organic carbon (OC) contained in sedimentary rocks, or petrogenic organic carbon (OC_{petro}). The latter flux is still poorly constrained. In this study, we report Particulate Organic Carbon (POC) content and ^{14}C-activity measurements in Amazon River sediments, which allow for estimates of the OC_{petro} content of these sediments. A large

decrease of OC_{petro} content in riverine sediments is observed from the outlet of the Andes to the mouth of the large tributaries. This loss reveals oxidation of OC_{petro} during transfer of sediments in the floodplain, and results in an escape of ca. 0.25 MtC/yr to the atmosphere, which is on the same order of magnitude as the CO_2 consumption by silicate weathering in the same area. Raman microspectroscopy investigations show that graphite is the most stable phase with respect to this oxidation process. These results emphasize the significance of OC_{petro} oxidation in large river floodplains in the global C cycle.

INTRODUCTION

CO_2 degassed from Earth's interior is partly scavenged by chemical reactions occurring during weathering of silicate rocks and subsequent carbonate precipitation in the ocean (Garrels et al., 1976). It is also consumed by photosynthesis followed by burial of organic matter in marine sediments (Hayes and Waldbauer, 2006). These two mechanisms have respectively built up the two major carbon reservoirs of Earth's surface: limestones (50×10^6 GtC), and ^{14}C-free organic matter disseminated in sedimentary rocks, or petrogenic OC (OC_{petro}, 12.5×10^6 GtC; Berner, 1990). The oxidation of petrogenic OC is a source of CO_2 to the atmosphere (Berner, 2004). However, quantifying the modern rates of OC_{petro} oxidation remains a challenge for understanding and modeling the geological carbon and oxygen cycles. Although a few studies based on soil profiles have attempted to determine rates of OC_{petro} oxidation (e.g., Keller and Bacon ; 1998, Petsch et al., 2000), budgets of fossil organic carbon oxidation at river catchment scale have not received much attention (e.g., Galy et al., 2008b ; Hilton et al., 2008).

The dissolved and particulate load transported by rivers derive from chemical weathering of rocks and physical erosion of soils and rocks. This includes organic material, which consists in a mixture of recent biospheric carbon (OC_{recent}), and OC_{petro} (Blair et al., 2004 ; Komada et al.,

2004 ; Leithold et al., 2006). The oxidation of OC transported in rivers is thought to mostly affect OC_{recent} and to have no effect on the geological budget of atmospheric CO_2. In their study on the Amazon river, Hedges et al. (1986) showed that the organic material transported by the Amazon river mostly consists in OC_{recent} derived from the highly productive lowland ecosystems. During fluvial transport, the oxidation of this dissolved and particulate organic matter results in the escape of ca. 500 MtC/yr to the atmosphere (Richey et al., 2002). Most of this oxidation derives from OC_{recent} (Mayorga et al., 2005) and has therefore no impact on the long-term regulation of atmospheric CO_2. However, a significant fraction of particulate organic matter can be of petrogenic origin. Distinguishing between OC_{petro} and OC_{recent} in rivers is thus of prime importance because only the oxidation of OC_{petro} represents an input of C to the active reservoirs at Earth's surface.

In this study, we report POC (Particulate Organic Carbon) and ^{14}C activity measurements in river sediments collected throughout the Amazon River system. Sediments were collected along river depth-profiles in order to capture the whole range of granulometric spectrum of erosion products. Concentrations of OC_{petro} were measured in these sediments, and coupled with structural characterization of OC_{petro} by Raman microspectroscopy. This allows us to estimate the first order of carbon input to the atmosphere by OC_{petro} oxidation during transfer of sediments in the floodplains of the Amazon Basin, and gives a lower bound on the estimate of CO_2 release to the atmosphere by the oxidation of OC_{petro} in the Amazon Basin.

SETTING, SAMPLING AND ANALYTICAL METHODS

The Amazon is the world largest river in terms of drainage area and water discharge to the ocean (Meybeck and Ragu, 1997). Isotopic studies (Allègre et al., 1996) have clearly shown that most of the Amazon River sediments are derived from the Andes. There, Amazon tributaries

drain extensive outcrops of easily erodible sedimentary and meta-sedimentary rocks, such as black shales in the Bolivian Andes.

We sampled the two main tributaries of the Amazon, the Solimões and the Madeira rivers, at their mouth, as well as the Amazon mainstream at Obidos, in June 2005 and March 2006 (Fig. 1). The Beni River, which supplies most of the sediments to the Madeira River, has been sampled at the outlet of the Andes, near Rurrenabaque, where it enters the Madeira floodplain, in February 2001. At each location, river water was sampled at various river depths along vertical profiles, from channel surface to bottom, and filtered at 0.22 µm porosity; bed sediments were also dredged. Within the channel of large rivers, granulometric sorting induces important variations of chemical composition of river sediments from the surface to the bottom (Galy et al., 2008a). The sampling technique used here allows us to characterize the whole range of erosion products in terms of grain size distribution and mineralogy.

POC content was determined using a modified Eurovector EuroEA3028-HT elemental analyzer coupled to a GV Instruments IsoPrime continuous-flow isotope mass spectrometer at the CRPG, Vandoeuvre-lès-Nancy, France (Galy et al., 2007). ^{14}C activity was determined by Accelerator Mass Spectrometry at LMC14 National Facility, Saclay, France, after off-line organic matter combustion and CO_2 cryogenic purification. Samples were decarbonated before combustion (Galy et al., 2007). ^{14}C values are given after correction for ^{13}C fractionation (normalization to a $\delta^{13}C$ of –25‰), and expressed as pMC (percentage of Modern Carbon) comparatively to 95% of the ^{14}C activity of the oxalic acid standard OXI. Petrogenic carbon was characterized by Raman microspectroscopy using a Renishaw InVia Raman micro-spectrometer at the Laboratoire de Géologie, Ecole Normale Supérieure, Paris, France (Bernard et al., 2008). Raman spectra were obtained directly on raw sediments, and on thin sections for bedrocks.

RESULTS: ^{14}C AGE OF OC_{recent} AND OC_{petro} CONTENT

In depth-profile sediments, ^{14}C content shows a wide range of variation, between 37.5 and 86.2% pMC (Tab. 1). A first-order positive relation between pMC and POC is observed, the coarser bed sediments being the most depleted in both OC and ^{14}C.

In river sediments, OC can be interpreted as a binary mixture of OC_{petro} and OC_{recent} with distinct ^{14}C content (e.g., Blair et al., 2004). Following the approach of Galy et al. (2008b) we plot our results in a diagram of POC * pMC (or Modern C) as a function of POC (Fig. 2). Depth-profiles from different sampling locations define linear trends, at 95% confidence level, regardless the sampling period. These correlation indicate that samples from a given depth-profile have rather constant absolute OC_{petro} concentration and ^{14}C activity of the OC_{recent} component (see appendix for details). The values of OC_{petro} content in the samples and ^{14}C-age of the OC_{recent} pool can be both determined from the slope and intercept of each line (Tab. 1). Similar observations were made on the Ganga-Brahmaputra system (Galy et al., 2008b).

The highest OC_{petro} content, 0.26% (±0.11%, 2 sigma uncertainty), is obtained for the Beni at Rurrenabaque. There, OC_{petro} makes up to 50% of the POC, and likely originates from the large outcrops of black shales drained by this river. Lowland sampling locations (Solimões, Madeira and Amazon) all display lower OC_{petro} content, between 0.02% and 0.06%, (or even lower, regarding the uncertainties reported in Tab. 1). Thus, there is a large apparent decrease in OC_{petro} concentration between the entry and the outlet of the Madeira floodplain.

Since the Beni contributes to ca. 40% of the Madeira sedimentary budget (Guyot et al., 1996), potential addition of supposedly OC_{petro}-free sedimentary material by other tributaries of the Madeira River could only lead to an OC_{petro} content decrease by a factor of slightly more than

two. Hence, the apparent 10-fold decrease in OC_{petro} content could mainly be due either to a preferential burial of OC_{petro}-rich material in the floodplain, or to a loss by oxidation.

Burial of sedimentary material occurs in the Amazon basin between the Andean source of sediments and the Amazon mouth, in particular between Rurrenabaque and the mouth of the Madeira (Guyot et al., 1996). If sediment storage is the cause of the observed decrease of OC_{petro} concentration reported here, it would imply the preferential sedimentation of an OC_{petro} enriched component. As stated above, sampling along depth-profiles allows to take into account the whole range of riverine particulate matter in size distribution and mineralogy. Our results (Fig. 2) show that absolute OC_{petro} content is the same along all depth-profiles, despite expected variations in particle size distribution with depth (Curtis et al., 1979). Selective burial of a given size fraction should therefore not affect OC_{petro} concentration of suspended sediments. This observation strongly suggests that the decrease of OC_{petro} concentration along the course of the Madeira is due to OC_{petro} oxidation.

ESTIMATE OF THE MAGNITUDE OF THE CO_2 SOURCE

Given the important amount of sediments transported in the Madeira floodplain (Guyot et al., 1996), the oxidation flux resulting from the large decrease in OC_{petro} content during the transfer of sediments in the floodplain should be significant. A first-order oxidation flux of OC_{petro} can be estimated using previous works on sedimentary budgets in the Madeira River Basin. Among the 212 Mt/yr of sediments delivered by the Beni River to the plain, ca. one half is buried in the foreland basin (Guyot et al., 1996). The amount of Beni sediments actually transiting through the plain is thus on the order of 100 Mt/yr. Hence, given the OC_{petro} concentration reported in this study, 100 Mt/yr of sediments represent a OC_{petro} flux of 0.26 MtC/yr supplied to the plain and not buried. At the outlet, 100 Mt/yr of sediments represent a

OC_{petro} flux of 0.02 MtC/yr that exits the plain. The difference of ca. 0.25 MtC/yr is thus the oxidation flux of OC_{petro} in the Madeira floodplain. This is a first order estimate but also a lower bound of the OC_{petro} oxidation flux of the Madeira basin as we assumed that no OC_{petro} is delivered to the Madeira floodplain by its two other main tributaries. In addition, this estimate does not take into account the oxidation of OC_{petro} upstream Rurrenabaque and in Andean soils which we are not able to address here. Moreover, we assume that no oxidation affects the sediments buried in the foreland basin. The flux of 0.25 MtC/y is thus a minimum bound of the OC_{petro}-derived CO_2 outgassing flux . This number is in the same order of magnitude as the net CO_2 sequestration flux in this basin associated to silicate weathering (0.8 MtC/yr; Gaillardet et al., 1997).

OC_{petro} STRUCTURAL CHARACTERIZATION

OC_{petro} is derived from organic carbon initially trapped in sediments and has been structurally and chemically transformed during diagenesis and metamorphism. Structural characterization of OC_{petro} by Raman microspectroscopy has been performed both in riverine sediments and bedrock samples. Because volcanic rocks of the high cordillera may not contain any significant amount of solid OC, the main sources of OC_{petro} are most likely the sediments, mainly black shales, drained by the Rio Beni. Three samples representative of the main bedrock lithologies from the Tipuani, Mapiri and Coroico basin have been investigated (Fig. 1). They contain two main OC_{petro} fractions (Fig. 3): one is rather disordered, exhibiting Raman spectra typical of greenschist facies (Beyssac et al., 2002), in agreement with the thermal history of these rocks. The second is highly graphitic and supposedly represents a detrital pool. Both fractions are found in all riverine sediments either as isolated particles or as inclusions or aggregates within minerals (mostly quartz, phyllosilicates or plagioclases, Fig. 3). As shown in Fig. 3, the graphitic

phases become dominant in samples of downstream sediment (Rio Beni and then Rio Madeira), while the disordered fraction progressively disappears. Graphite thus appears to be the most stable phase with respect to the oxidation process.

DISCUSSION AND CONCLUSION

This study thus shows that the oxidation of OC_{petro} during fluvial transport is a significant flux for the long-term atmospheric CO_2 budget. Fluvial oxidation of OC_{petro} may counteract the consumption flux of CO_2 by silicate weathering, which is conventionally thought to be the only significant process, with organic carbon sequestration, to control atmospheric CO_2 at geological timescales (Berner, 2004; Wallmann, 2001). The degradation of physically mobilized ancient organic matter in large fluvial systems is most probably dependent on a number of factors such as residence time of particles in floodplains (Blair et al., 2003), or on climatic conditions. This important oxidation flux found here is probably favored by the warm and oxidative conditions that prevail in the soils of Amazonian floodplains. Whether this oxidation of OC_{petro} occurs via biotic (Petsch et al., 2001) or abiotic (Chang and Berner, 1999) pathways, is beyond the scope of the paper but would need further investigations.

Galy et al. (2008b) showed that 30%–50% of the OC_{petro} present in the Himalayan source rocks were preserved and are still present in the marine sediments of the Bengal Fan. Our estimate of the OC_{petro} preservation in the Madeira floodplain, 15%, is an upper bound of the extent of OC_{petro} preservation in the Madeira basin, as it does not take into account the oxidation taking place in Andean soils, downstream the sampling locations, or even in the ocean, before or after deposition. The Amazon basin is hence a better incinerator of OC_{petro} than the Himalayan system. This is likely due to differences in the sources of OC_{petro}. Low-grade metamorphic rocks with disordered OC are common in the Andes, while high-grade metamorphic rocks generating

highly graphitic OC are widespread in the Himalaya (Beyssac et al., 2004). Disordered OC is more prone to oxidation than graphite because of its chemistry (aromatic skeleton with radicalization) and structure, as micro- and nano-porosity enhance oxidation rates.

Over geological timescale, geodynamic (metamorphic grade, erosion intensity…) settings probably control the extent of preservation of OC_{petro} during the erosion-transport-sedimentation cycle. Over shorter timescale (tens to hundreds kyrs), and for a given geodynamic context, climate is likely to control the oxidation or preservation of OC_{petro}, through erosion, temperature, and probably the nature of microbial communities (and their metabolic activity) present in the floodplain.

We speculate that, in response to an atmospheric CO_2 rise, increased global temperature would probably enhance oxidation of petrogenic OC in large river floodplains and associated CO_2 outgassing. This mechanism possibly constitutes a new positive feedback in the long-term carbon cycle.

ACKNOWLEDGMENTS

This study was funded by CNRS-INSU program Reliefs de la Terre, and realized in the frame of the HyBAm project (cooperation agreement with CNPq n° 492685/2004-5). We sincerely ackowledge the following Brazilian Institutions and Universities: ANA, UnB, UFF, CPRM. We thank C. Guilmette for technical assistance in the stable isotopes laboratory and R. Hilton for improving the quality of the text. This is IPGP contribution N°2564.

APPENDIX: OC_{petro} AND ^{14}C AGE OF OC_{recent} CALCULATION

We use a method described in Galy et al., 2008b. Briefly, we describe the OC pool as a binary mixture of OC_{petro}, derived from the rocks, and OC_{recent} derived from the biosphere (vegetation, soils and autotrophic production in the river). These two component have distinct ^{14}C activity,

206 OC_{petro} being ^{14}C-free ($pMC_{petro} = 0$). For each sample, the absolute content of Modern C (POC x
207 pMC – "Modern" refering here to a present ^{14}C standard) can thus be written as:
208 $$\%\text{Modern C} = \text{POC} \times pMC_{recent} - \%OC_{petro} \times pMC_{recent},$$
209 where pMC_{recent} is the ^{14}C activity of OC_{recent} and $\%OC_{petro}$ is the absolute content of OC_{petro}. In a
210 %Modern C vs. POC plot, samples having the same pMC_{recent} and the same $\%OC_{petro}$ define a
211 single straight line. The pMC_{recent} is given by the slope of the line and allows the calculation of
212 the age of the recent component. Moreover, the absolute content of OC_{petro} is given by the
213 opposite of the intercept/slope ratio.
214 Despite the auto-correlated nature of the two plotted variables, and as shown in Tab. 1, the
215 relationships we obtain are more significantly correlated than in the case of randomly distributed
216 POC and pMC (either assuming an uniform or normal distribution, within boundaries defined by
217 the ranges covered by the values measured in our samples).
218 Uncertainties on the determined slope and intercept (and thus on $\%OC_{petro}$ and pMC_{recent}) are
219 yielded by a full inversion method (Tarantola and Valette, 1982). Relatively low uncertainties on
220 pMC_{recent} (i.e. on the slope) stem from the good alignment of data points.

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FIGURE CAPTIONS

Figure 1. Map of the Amazon basin and sampling sites.

Figure 2. Modern C content (POC*pMC, expressed in weight % of the whole sample) *vs*. POC for sediments collected along a depth profile in different rivers of the Amazon basin. The linear regression solution for each sampling location is also shown. Open symbols stand for bedload sediments, closed symbols for suspended load sediments. Samples are plotted regardless of their position in the hydrological cycle.

Figure 3. Representative Raman spectra of riverine and bedrock material, with the location of the main graphite G band, and the D1, D2 and D3 defect bands. Minerals associated with C are also indicated. Fossil organic matter was found as free particles, inclusions in minerals such as quartz or rutiles, or aggregates with phyllosilicates. Free particles were as large as 20 μm in diameter.

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TABLE 1. SAMPLE LIST AND RESULTS:
ANALYTICAL ABSOLUTE UNCERTAINTIES (2σ) ARE 0.5 M
FOR SAMPLING DEPTH, 0.3% FOR PMC AND 0.02% FOR POC

Sample	River	Water stage	Depth (m)	pMC (%)	POC (%)	pMC_{recent} (%)	OC_{petro} (%)
AM-05-35	Amazon	Falling	58	78.6	0.65	84	0.06
AM-05-37		Falling	30	78.4	0.92	± 0.04	± 0.05
AM-05-39		Falling	2	81.4	1.22	(r^2=0.995)	
AM-06-64		Rising	20	76.9	0.93		
AM-06-66		Rising	Bedload	77.3	0.65		
AM-05-04	Solimões	High	28	86.2	0.79	87	0.03
AM-05-08		High	2	83.3	1.13	± 0.03	± 0.02
AM-05-10		High	Bedload	37.5	0.06	(r^2=0.998)	
AM-06-10		Rising	22	82.7	0.95		
AM-06-36	Madeira	High	15	70.6	0.62	71	0.02
AM-06-38		High	0	68.3	0.65	± 0.04	± 0.03
AM-06-44		High	Bedload	45.5	0.05	(r^2=0.999)	
AM-01-14-a	Beni	High	1	44.1	0.51	96	0.26
AM-01-14-b		High	3	55.1	0.61	± 0.13	± 0.11
AM-01-14-c		High	5	42.0	0.45	(r^2=0.986)	
AM-01-14-d		High	7	41.0	0.47		

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