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# High rates of rock organic carbon oxidation sustained as Andean sediment transits the Amazon foreland-floodplain

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## 24 Author Contributions:

- 25 MD, RGH and AJW designed the research and obtained funding. All authors contributed to
- fieldwork and sample collection. MD undertook the geochemical analysis of materials for this
  work. MD analyzed and interpreted the data with RGH. MD and RGH wrote the manuscript
  with input from all authors.
- 29

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- 31 The authors declare no competing interests.
- 32

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- 38
- 39
- 40

### 41 Abstract

- 42 The oxidation of organic carbon contained within sedimentary rocks ("petrogenic" carbon, or 43 hereafter OC<sub>petro</sub>) emits nearly as much CO<sub>2</sub> as is released by volcanism, thereby playing a key 44 role in the long-term global C budget. High erosion rates in mountains have been shown to 45 increase OC<sub>petro</sub> oxidation. However, these settings also export un-weathered material that may 46 continue to react in downstream floodplains. The relative importance of OC<sub>petro</sub> oxidation in 47 mountains versus floodplains remains difficult to assess as disparate methods have been used 48 in the different environments. Here, we investigate the sources and fluxes of rhenium (Re) in 49 the Rio Madre de Dios to quantify OC<sub>petro</sub> oxidation from the Andes to the Amazon floodplains 50 using a common approach. Dissolved rhenium concentrations (n=131) range from 0.01 to 63 51 pmol.L<sup>-1</sup> and vary depending on lithology and geomorphic setting. We find that >75% of the 52 dissolved Re derives from OC<sub>petro</sub> oxidation and that this proportion increases downstream. We 53 estimate that in the Andes, OC<sub>petro</sub> oxidation releases 11.2<sup>+4.5</sup>/-2.8 tC km<sup>-2</sup> yr<sup>-1</sup> of CO<sub>2</sub>, which 54 corresponds to ~41% of the total OC<sub>petro</sub> denudation (sum of oxidized and solid OC<sub>petro</sub>). A Re
- mass balance across the Rio Madre de Dios shows that 46% of  $OC_{petro}$  oxidation takes place in the Andes, 14% in the foreland-lowlands, and 40% in the Andean-fed floodplains. This doubling of  $OC_{petro}$  oxidation flux downstream of the Andes demonstrates that, when present, floodplains can greatly increase  $OC_{petro}$  oxidation and  $CO_2$  release.
- 59

## 60 Significance Statement:

Erosion and weathering play key roles in Earth's carbon cycle, controlling climate over millions of years by transferring CO<sub>2</sub> to and from the atmosphere. Weathering of sedimentary rocks in mountains can release CO<sub>2</sub> when ancient organic carbon in rocks is chemically broken down. However, mountain erosion also moves rock organic carbon that has not been broken down and is transported by rivers to lowland floodplains to an unknown fate. Here we use rhenium in

- <sup>66</sup> rivers to quantify rock organic carbon weathering in the Andes and adjacent floodplain. Erosion
- 67 in the Andes leads to high rates of  $CO_2$  release. However,  $CO_2$  release doubles when including
- the floodplains. The presence or absence of floodplains next to mountains governs CO<sub>2</sub> releaseby weathering.
- 70

## 71 Main text:

72

## 73 Introduction

74 Substantial climatic changes have occurred throughout geologic time, with the evolution of the 75 carbon cycle and the planet's habitability modulated by the interplay between tectonic, climatic,

- records and biological processes. Over long timescales (>10<sup>5</sup> years), the abundance of  $CO_2$  in
- 77 the atmosphere is determined by the balance of the major carbon sources and sinks (1). It has
- 78 been widely debated how the Earth system responds to transient imbalances in the long-term
- 79 carbon (C) cycle, with much focus of prior research on the  $CO_2$  sink associated with the
- 80 chemical weathering of silicate minerals (1, 2). However, recent studies have highlighted the
- potential importance of changes in  $CO_2$  fluxes linked to oxidative weathering (OW) reactions of sedimentary rocks on the continents (3–5). Although receiving less attention to date, OW of
- reduced phases in sedimentary rocks is central to both the C and O cycles (6, 7). Carbon dioxide
- release and  $O_2$  consumption can result from both (i) oxidation of fossil (i.e. "rock-derived" or
- 85 "petrogenic") organic matter (OC<sub>petro</sub>) and (ii) the OW of sulfides that produces sulfuric acid,
- 86 which can be neutralized by carbonate minerals, or by the carbonate buffer of continental waters

87 leading to net  $CO_2$  release to the atmosphere (8, 9).

88 The export of particulate  $OC_{petro}$  by rivers in their sediment load has been documented 89 in many places (10–16), but only a few field-based studies have estimated the rate of OW of 90  $OC_{petro}$  (3). The highest fluxes of OW of  $OC_{petro}$  (reported as a yield per catchment area, of 5 to 91 30 tC.km<sup>-2</sup>.yr<sup>-1</sup>) have been measured in small high standing islands composed of sedimentary 92 rocks such as in Taiwan (17) and New Zealand (4), as well as in catchments from major mountain ranges (0.5 to 5 tC.km<sup>-2</sup>.yr<sup>-1</sup>) like the Yamuna (18), Swiss Alps (19) and in the 93 Mackenzie River basin (20). This reflects the role of physical erosion rate in mountains that can 94 95 continuously supply OC<sub>petro</sub> to oxygenated surface waters and the atmosphere (17, 21). A 96 consequence is that, in combination with carbonate weathering by sulfuric acid, CO<sub>2</sub> release by 97 OC<sub>petro</sub> oxidation can be larger than CO<sub>2</sub> consumption by silicate weathering in many erosive settings (3), challenging the idea that chemical weathering in mountain belts is a long-term 98 99 carbon sink (22–24).

100 While physical erosion can enhance the supply of reduced phases to OW reactions and 101 increase the weathering flux (8, 17, 25), the overall intensity of weathering can also decline (26), meaning that erosive catchments can also export very large amounts of 'unweathered' 102 103 particulate OC<sub>petro</sub> (7). These particulate fluxes can be very high, for instance reaching 250 104 tC.km<sup>-2</sup>.yr<sup>-1</sup> (13, 26). The subsequent fate of this material is critical to governing how physical 105 erosion and weathering impact the carbon cycle. It has been proposed (10, 14) that this OC<sub>petro</sub> 106 can be largely oxidized in floodplains when present (e.g. in the Amazon and Ganges floodplain), because of the long residence time of sediments and the warm and oxidative 107 108 conditions that prevail in the floodplains relative to upstream mountainous area. Hence, the 109 mountain catchments underlain by sedimentary rocks with river floodplains could have greater 110 net  $CO_2$  release from OW than mountain catchments without floodplains. Over  $10^5$ - $10^6$  year timescales, the configuration of continental drainages can shift dramatically (27) and young, 111 112 high standing mountain ranges potentially operate differently in terms of OW and CO<sub>2</sub> release 113 relative to mountain ranges with floodplain drapes.

114 Despite the recognition of these geomorphological controls on OW (3), the relative 115 contributions of mountain versus floodplain weathering to OC<sub>petro</sub> oxidation and CO<sub>2</sub> release 116 remains unknown. This knowledge gap arises in part because different methods have been used 117 to assess OW of OC<sub>petro</sub> in mountain catchments (4, 17) versus floodplains (10, 14). In mountain 118 catchments, dissolved rhenium (Re) fluxes have been used for quantifying OC<sub>petro</sub> oxidation 119 fluxes (17), whereas studies on floodplains have used sediment fluxes and radiocarbon content 120 of river sediments (Bouchez et al., 2010). Both methods have benefits and drawbacks. 121 Dissolved Re fluxes are easier to measure because water discharge is usually known with more 122 precision than sediment flux. On the other hand, there are large uncertainties on the source of 123 dissolved Re and on the estimation of the Re/OC<sub>petro</sub> ratio of the bedrock (20). Because water 124 and sediments integrate over different spatial and temporal scales, their direct comparison can 125 also be problematic. Overall, the influence of floodplains on the global OC<sub>petro</sub> budget remains 126 an open question (3, 28).

To resolve these issues, here we investigate the source and fluxes of dissolved and 127 128 particulate rhenium (Re) in the Madre de Dios watershed, part of the larger Amazon Basin. We 129 focus on an elevation transect ranging from the high Andes to the low-elevation floodplains and use Re to quantify the flux of CO<sub>2</sub> released by OC<sub>petro</sub> oxidation. These catchments have 130 been well-characterized by previous studies in terms of erosion rates and their major dissolved 131 132 load (11, 23, 29), and benefit from time-series samples over a range of river discharges. Most 133 importantly, this setting provides an opportunity to determine the rate of OC<sub>petro</sub> oxidation in 134 each of the different geomorphological settings (mountain, foreland, floodplain) within a single 135 river basin. 136

#### 137 Study site

- 138 The Madre de Dios watershed (124,231 km<sup>2</sup> at the confluence with the Rio Beni in Bolivia) is
- 139 one of the main headwaters of the Amazon basin (30), the largest river basin in the world. The
- 140 precipitation in the Madre de Dios region is between <1000 and >6000 mm.yr<sup>-1</sup> and the mean

141 annual temperature varies with elevation from 4 to 25°C (30-32). The Rio Madre de Dios 142 drains: i) the eastern flank of the Andes in Peru with elevations from 1300 m to 6300 m, ii) the 143 mountain front with elevations from 500 m to 1300 m, iii) the foreland corresponding to 144 elevations of less than 500 m, in which river basins are not Andean-fed but had undergone some 145 recent uplift associated with the Fitzcarrald Arch, and iv) the Andean-fed floodplains, which 146 are the low-relief environments adjacent to active river channels from rivers originating from 147 the Andes and where sediments are deposited and exchanged with the main channel. The 148 bedrock in the headwaters is primarily composed of Paleozoic and Mesozoic sedimentary and 149 metasedimentary rocks (with  $[OC_{petro}] \sim 0.4$  to 0.6%) and some minor granitic intrusions in the 150 Andes (23). Observations from the neighboring Beni catchment with similar lithologies to the 151 Madre de Dios show that this OC<sub>petro</sub> is a mixture of disordered and graphitic carbon (10).

152 To characterize the spatial variability of dissolved Re concentrations ([Re]<sub>diss</sub>) across 153 the Madre de Dios River basin (Fig. 1A), we studied a large number of small tributaries draining 154 each geomorphological setting that have been subject to prior work on water, sediment and 155 carbonate and silicate weathering fluxes (11, 23, 29, 33–35). To characterize the dissolved Re 156 sources, we sampled stream, spring and lysimeter waters from small first-order catchments in 157 each geomorphological setting (referred as Wayqecha Small Catchment "WAY-SC", Villa 158 Carmen Small Catchment "VC-SC" and CICRA Small Catchment "CICRA-SC"; Burt et al., 159 2022). To examine the downstream evolution of OC<sub>petro</sub> weathering processes across these 160 geomorphic settings, we studied in detail four main nested sub-catchments that define a geomorphic gradient from the Andes to the Foreland-floodplain: the Rio Kosñipata at 161 162 Waygecha in the Andes (referred as "WAY", altitude 2250 m); the Rio Kosñipata at San Pedro 163 in the Andes ("SP", altitude 1360 m); the Alto Madre de Dios at Manu Learning Center ("MLC", altitude 479 m) at the transition between the Andes and the Foreland; and the Madre 164 165 de Dios at CICRA-Los Amigos research station ("CICRA", altitude 217 m). Time series [Re]diss and discharge data from the years 2010-2011 are used to characterize changes in Re 166 167 concentration during the hydrological cycle. The measured annual runoff for the year 2010-168 2011 was 3065 mm.yr<sup>-1</sup> at the "WAY" site (Upper Andes) to 2796 mm.yr<sup>-1</sup> at SP. The 169 suspended sediment flux (a proxy for erosion rate) at San Pedro (SP) measured during the same period is 3500 t.km<sup>-2</sup>.yr<sup>-1</sup> (11), similar to the estimated suspended sediment load from the 170 171 Andean area of the entire Madre de Dios watershed (3208 t.km<sup>-2</sup>.yr<sup>-1</sup>; 35). Finally, to integrate weathering processes over large areas and establish a Re mass-budget, we studied several large 172 173 tributaries with Andean-fed floodplains that drain all geomorphic settings (Rios Manù, 174 Colorado, Chiribi, Inambari and Tambopata).

#### 175 **Results**

176 Rhenium concentrations were measured on water samples collected from several field 177 campaigns, including (i) from the Madre de Dios mainstem and major tributaries sampled 178 unders different flow conditions in 2012 and 2013 (23, 34, 38), and again at high and low flow 179 in March and May 2019 (35), (ii) from time-series samples collected at four nested catchment 180 sites (areas 50 to 27 830 km<sup>2</sup>) in 2010 and 2011 at various hydrological conditions (29, 33), and 181 (iii) from another time series of samples collected from smaller first-order catchments (<1 km<sup>2</sup> 182 area) across the elevation gradient (36). The time-series dataset is used to characterize the 183 relationship between Re concentration and instantaneous runoff.

184

#### 185 Spatial variability of dissolved Re concentrations

186 Rhenium concentrations in dissolved samples (n=133) range from 0.01 to 63 pmol.L<sup>-1</sup>, with

- 187 spatial variability depending on the sample type, bedrock lithology and geomorphic setting
- 188 (Fig. 1B; Dataset S1). Rivers have [Re]<sub>diss</sub> ranging from 0.1 to 9.5 pmol.L<sup>-1</sup>. The rainwater
- 189 sample collected in the Andes has  $[Re]_{diss}$  below detection limit ( $[Re]_{diss} < 0.05 \text{ pmol}.L^{-1}$ ) while 190 [Re] in the through fall sample from the same leastion is 0.26 rmal L<sup>-1</sup>. Ly important samples
- 190  $[Re]_{diss}$  in the throughfall sample from the same location is 0.36 pmol.L<sup>-1</sup>. Lysimeter samples

191 from first-order small catchments in the Andes and in the Foreland have also very low [Re]<sub>diss</sub>, 192 ranging from 0.09 to 0.12 pmol.L<sup>-1</sup> (n=4). In contrast, the two hot springs samples from Aguas 193 Caliente have very high [Re]<sub>diss</sub> (39 pmol.L<sup>-1</sup> and 63 pmol.L<sup>-1</sup>). However, the [Re]<sub>diss</sub> of the Alto 194 Madre de Dios downstream of the hot springs is unchanged compared to [Re]<sub>diss</sub> upstream of 195 the hot springs, suggesting that their contribution to the Re budget is negligible.

196 In terms of lithology, small rivers draining mostly granitic rocks in the High Andes have 197 lower Re concentrations ( $0.56\pm0.44$  pmol.L<sup>-1</sup>,  $1\sigma$ , n=6) than rivers draining sedimentary rocks 198 ( $2.90\pm2.06$  pmol.L<sup>-1</sup>,  $1\sigma$ , n=25). Rivers draining the mountain front composed of mostly 199 granites also have lower [Re]<sub>diss</sub> (1.32 pmol.L<sup>-1</sup>, n=2) than those draining sedimentary rocks 200 ( $3.88\pm1.12$  pmol.L<sup>-1</sup>,  $1\sigma$ , n=10).

201 We observe a notable geomorphic control on [Re]<sub>diss</sub> for the tributaries and first-order 202 catchments draining specific settings, but not for the nested catchments (Fig. 1B). Tributaries 203 draining sedimentary rocks in the High Andes and Mountain front have significantly higher 204  $[\text{Re}]_{\text{diss}}$  (3.22±1.82 pmol.L<sup>-1</sup>, 1 $\sigma$ , n=38) than those draining the foreland (0.70±0.53 pmol.L<sup>-1</sup>, 205  $1\sigma$ , n=9). For first-order catchments, [Re]<sub>diss</sub> is the highest in the High Andes (0.12 to 0.48) pmol.L<sup>-1</sup>), as compared to <0.15 pmol.L<sup>-1</sup> in the Mountain front and Foreland. In contrast, no 206 207 significant change in [Re]<sub>diss</sub> downstream is observed for nested catchments, although the 208 average concentration at WAY (3.76 $\pm$ 0.76 pmol.L<sup>-1</sup>, 1 $\sigma$ , n=6) is slightly higher than at the SP 209 site (2.59±0.44 pmol.L<sup>-1</sup>, 1 $\sigma$ , n=7). We note that in March 2019, [Re]<sub>diss</sub> was higher (4.22) 210 pmol.L<sup>-1</sup>) at SP than the average [Re]<sub>diss</sub> of time-series measurements from the 2010-2011 period, perhaps related to a large landslide in this catchment in the intervening period. At the 211 212 foreland-floodplain site (CICRA),  $[Re]_{diss} = 3.69 \pm 0.98 \text{ pmol}.L^{-1}$  (1 $\sigma$ , n=9). For the main tributaries of the Madre de Dios, we observe the highest [Re]<sub>diss</sub> in the Manù (1.5 to 9.5 pmol.L<sup>-</sup> 213 214 <sup>1</sup>), lowest [Re]<sub>diss</sub> in the Chiribi and Colorado rivers (0.5 to 2.2 pmol.L<sup>-1</sup>), and intermediate 215 [Re]<sub>diss</sub> in the Alto Madre de Dios (3.4 to 4.7 pmol.L<sup>-1</sup>), Inambari (3.3 pmol.L<sup>-1</sup>) and the 216 Tambopata (2.3 pmol.L<sup>-1</sup>).

217

#### 218 Temporal variability of dissolved Re concentrations

In the four nested-catchments, [Re]diss generally decreases with increasing instantaneous runoff, 219 220 Q, except for the high-altitude Andean site (WAY) where [Re]<sub>diss</sub> shows no clear relationship 221 with runoff (Fig. 1C). The relationship can be modeled using a power law  $[Re]_{diss} = a \times Q^b$ , with a and b as the two fitted constants. For our samples, we observe a decrease of the b value 222 223 from the Andes ( $-0.09\pm0.12$  in WAY,  $-0.15\pm0.08$  in SP;  $1\sigma$ ) to the mountain front ( $-0.40\pm0.06$ 224 in MLC) and the foreland-floodplain (-0.46±0.08 in CICRA), indicating a more chemostatic 225 behavior of Re in the Andes, and more dilutional behavior in the Foreland-floodplain. This 226 decrease of the b value with elevation is similar to that observed for most major elements (29). 227

#### 228 **Re concentrations in solids**

229 The Re concentration in bedloads ([Re]<sub>BM</sub>) from Andean rivers draining shales ranges from 230 0.12 to 0.50 ppb with an average of  $0.28\pm0.06$  ppb ( $\pm2SE$ , n=14; Fig. 2). These are higher than the Re concentration in Andean soil samples (39) collected close the SP site 0.07±0.07 ppb 231 232  $(\pm 2SE, n=3)$  and in the Foreland-floodplain 0.04 $\pm 0.01$  ppb  $(\pm 2SE, n=4)$ . The [Re]<sub>BM</sub> is slightly 233 higher in WAY (0.31 to 0.36 ppb) compared to SP (0.23 to 0.26 ppb). Two rock samples were 234 analyzed: [Re] of the OC<sub>petro</sub> and sulfur-rich sedimentary rock sample is almost 100 times higher 235 (4.61 ppb) than the igneous rock (0.06 ppb). The [Re]/[OC] ratio in bedloads and rocks vary from  $0.27 \times 10^{-7}$  to  $2.65 \times 10^{-7}$  g.g<sup>-1</sup> with an average of  $0.93 \pm 0.38 \times 10^{-7}$  g.g<sup>-1</sup> (±2SE, n=16; Fig. 2). 236 The average [Re]/[OC] for the Kosñipata stream (WAY and SP sites) is  $0.80\pm0.12\times10^{-7}$  g.g<sup>-1</sup> 237 238 (±2SE, n=5). This [Re]/[OC] ratio value is similar to bedload from New Zealand Southern Alps 239 (4) but lower than bedloads from Taiwan (17), the Yamuna River (18) and the Mackenzie River

240 (20).

241

#### 242 **Discussion**

Our aim is to determine the rates and controls of OW of  $OC_{petro}$  across the transition from the Andes Mountains to Amazon floodplain in the Madre de Dios basin. To do so, we need to characterize the source, behavior, and fluxes of dissolved Re. Following previous studies (4, 17, 19, 20, 40), the  $OC_{petro}$  oxidation yield ( $J_{OCpetro-ox}$ , tC km<sup>-2</sup> yr<sup>-1</sup>) can be estimated from:

- 247
- 248 249

$$J_{\text{OCpetro-ox}} = J_{\text{Re}} \times f_{\text{C}} \times ([\text{OC}]/[\text{Re}])_{\text{solids}} \times (1 - f_{\text{graphite}})$$
<sup>[1]</sup>

250 Where "J<sub>Re</sub>" is the dissolved Re yield (in g km<sup>-2</sup>yr<sup>-1</sup>), the product of the Re concentration 251 and runoff (J<sub>Re</sub> = [Re]<sub>diss</sub> × Q), while "([OC]/[Re])<sub>solids</sub>" is the OC/Re ratio in sedimentary rocks 252 being weathered (in g.g<sup>-1</sup>), " $f_C$ " is the fraction of dissolved Re deriving from the oxidation of 253 OC<sub>petro</sub> and " $f_{graphite}$ " is the proportion of graphite in the rocks that may be resilient to OW (14). 254

#### 255 Dissolved Re source and yield

256 To determine the OC<sub>petro</sub> oxidation flux using the Re proxy, we must first quantify the 257 proportion of dissolved rhenium derived from OC<sub>petro</sub> oxidation relative to other potential Re 258 sources (rainwater, carbonates, sulfides, silicates, carbonates; ref.18). Following the approach 259 developed in ref. (20), we use the [Re]/[SO<sub>4</sub><sup>\*</sup>] and [Re]/[Na<sup>\*</sup>] ratios to do so ([Na<sup>\*</sup>] and [SO<sub>4</sub><sup>\*</sup>] 260 are concentrations corrected for atmospheric-derived contributions). In general sulfides have 261 low Re/SO<sub>4</sub> (41) and silicates low Re/Na relative to OC<sub>petro</sub> (20), and both Na and SO<sub>4</sub> are conservative soluble species in the Madre de Dios catchment (34, 35, 38). In analogy with 262 263 studies on silicate and carbonate weathering, here we use local constraints on the end member 264 compositions, using the combination of water samples from first-order catchments and 265 tributaries (e.g. refs. 39, 40), combined with river sediments and rocks (23, 44) (Materials and 266 Methods).

267 We find that small Upper Andes tributaries draining shales have a large range of 268 [Re]/[SO<sub>4</sub><sup>\*</sup>] and [Re]/[Na<sup>\*</sup>] ratios that can be interpreted as a mixing trend between sulfides and 269 OC<sub>petro</sub> weathering, with limited Re contribution from silicate weathering (Fig. 3). In contrast, 270 Andean tributaries draining granites, and rivers draining the foreland, have ratios that can be 271 mostly explained by a mixture between silicates and OC<sub>petro</sub> (Fig. 3). A mixing analysis 272 (Materials and Methods) shows that the fraction of dissolved Re derived from OC<sub>petro</sub> oxidation, 273  $f_c$  (Equation 1), is >0.75 in the Andes (sites WAY and SP) and increases downstream to >0.90. 274 Seasonal variability of the Re source is small but significant (less than 20% variability), with 275 higher proportion of Re derived from OC<sub>petro</sub> oxidation in the Andes at higher runoff. This could 276 reflect the larger contribution of shallow groundwaters from the unsaturated zone above the 277 sulfide OW front (19). The fraction of Re derived from sulfide OW decreases from ~0.15-0.25 278 in the Andes (WAY and SP) to <0.05 in the Foreland-floodplain (CICRA). The fraction of Re 279 derived from silicate weathering is generally <0.05 but reaches ~0.2 for rivers draining only the 280 foreland (e.g. Los Amigos River). Altogether, this shows that in the Madre de Dios basin, the 281 majority of dissolved Re is derived from OC<sub>petro</sub> oxidation, confirming observations in other 282 catchments where sedimentary rocks dominate the geology (19, 20, 45).

283 Calculation of dissolved Re yield  $(J_{Re})$  can be done in several ways, i.e. using average 284 [Re]<sub>diss</sub> (4, 17, 18, 46), discharge-weighted average [Re]<sub>diss</sub> (41) or rating curve-derived [Re]<sub>diss</sub> 285 (19) and annual or instantaneous water discharge estimates. Here, these methods return similar 286 results (Materials and Methods; Dataset S3). Therefore, we take advantage of paired [Re]<sub>diss</sub> 287 and discharge measurements (at the four nested catchment sites and at the main tributaries) and 288 use discharge-weighted average [Re]<sub>diss</sub> and annual water discharge to derive dissolved Re 289 yield. For the main tributaries, the highest  $J_{Re}$  is in the Manu River catchment (2.0<sup>+0.9</sup>/<sub>-0.7</sub> g km<sup>-</sup>  $^{2}$  yr<sup>-1</sup>) and the lowest for the Las Piedras river (0.3±0.1 g km<sup>-2</sup> yr<sup>-1</sup>). For the nested catchments, 290

291 the Re yield is  $2.1\pm1.0$  g km<sup>-2</sup> yr<sup>-1</sup> and  $1.3\pm0.2$  g km<sup>-2</sup> yr<sup>-1</sup> for WAY and SP sites respectively, 292 and  $1.6\pm0.4$  g km<sup>-2</sup> yr<sup>-1</sup> for the Foreland-floodplain (CICRA) site. Although there is slight 293 decrease with elevation, the main result is that the specific Re yield of the Rio Alto Madre de 294 Dios does not change, within uncertainty, when the Rio Alto Madre de Dios (Andes) reaches 295 the Foreland-Floodplains.

296

#### 297 Rates and control of OC<sub>petro</sub> oxidative weathering in the Andes

298 We compute the OC<sub>petro</sub> oxidative weathering rate (Equation 1) using the parameter 299 values defined above (Dataset S3). As we have no constraint on  $f_{\text{graphite}}$  in this setting, we do 300 not account for this term here. To estimate the uncertainties, we use Monte Carlo 301 simulations with 10 000 resolutions of the equation with distribution sampling of values within the errors of each parameter (4). The estimated OC<sub>petro</sub> oxidative weathering fluxes based on 302 dissolved Re yield are  $16.7^{+11.9}/_{-8.8}$  tC km<sup>-2</sup> yr<sup>-1</sup> for the WAY site and  $11.2^{+4.5}/_{-2.8}$  tC km<sup>-2</sup> yr<sup>-1</sup> 303 for the SP site. The lower uncertainty on the J<sub>OCpetro-ox</sub> for SP is due to a higher precision on the 304 305 water flux at this site (33).

306 It has been proposed that physical erosion rate is a major control on the rate of OW (3, 307 8), with a potential role for landslide erosion supplying fresh mineral surfaces (24). The present-308 day erosion rate of the Rio Kosñipata is high, with values between 1200 and 3500 t.km<sup>-2</sup>.yr<sup>-1</sup> 309 (11) and frequent landslides (47). The J<sub>OCpetro-ox</sub> for the Kosñipata are much higher than in the Mackenzie (0.45 to 1.01 tC km<sup>-2</sup> yr<sup>-1</sup>) and the Swiss Alps (3.6 to 5.7 tC km<sup>-2</sup> yr<sup>-1</sup>) characterized 310 by lower erosion rates, and more similar to rivers in New Zealand and Taiwan (4 to 30 tC km<sup>-</sup> 311 312  $^{2}$  yr<sup>-1</sup>) which have higher erosion rates (3). Results from this study thus confirm the general control of erosion rate on the rate of OC<sub>petro</sub> oxidation (3), though other factors can also play an 313 important role (3, 48). The un-weathered solid OC<sub>petro</sub> export at the SP site has been determined 314 315 previously to be 16.1±1.4 tC.km<sup>-2</sup>.yr<sup>-1</sup> using sediment samples collected across the same time period (11). These fluxes imply that 41±10% of the total bedrock OC<sub>petro</sub> is oxidized in the 316 Andes, and the remainder is exported downstream. This OC<sub>petro</sub> weathering intensity value is 317 318 slightly lower than in the Mackenzie River basin (50%), similar to the Swiss Alps (19) and 319 higher than in Taiwanese rivers (<20%) (17).

320 Our estimate of the flux of OC<sub>petro</sub> oxidation in the Rio Kosñipata is the first attempt to 321 quantify the CO<sub>2</sub> emission from weathering of OC<sub>petro</sub> in the Andes. This estimate can also be 322 compared with other carbon fluxes relevant to the long-term carbon cycle in the Andes in the 323 Kosñipata catchment. In the SP catchment, the rate of biospheric organic carbon (OCbio) export in river suspended sediments is 12.6±0.4 tC km<sup>-2</sup> yr<sup>-1</sup> (11), which is slightly higher than the 324 OC<sub>petro</sub> oxidative weathering yield. At the same site, the yield of carbon release associated with 325 carbonate weathering by sulfuric acid is ~ 6 tC km<sup>-2</sup> yr<sup>-1</sup> (23), 45% lower than the rate of CO<sub>2</sub> 326 release by OC<sub>petro</sub> oxidation. Together, the OW of reduced phases (OC<sub>petro</sub> and sulfides) in 327 Andean sedimentary rocks release about 17 tC km<sup>-2</sup> yr<sup>-1</sup> to the atmosphere, confirming that OW 328 329 of sedimentary rocks in mountain belts is a large source of CO<sub>2</sub> to the atmosphere.

330

#### 331 Oxidative weathering in the foreland and in the Andean-fed floodplains

332 Once the OC<sub>petro</sub> that survived OW in the Andes has reached the foreland and the floodplains, 333 it can undergo further OW during transport and deposition in the floodplains (10). It has been 334 suggested that this process can be a large source of CO<sub>2</sub> to the atmosphere in the neighbouring 335 Beni catchment (10) and in the Ganges floodplain (14). Here we take several approaches to 336 isolate the weathering signal from the foreland (here defined as <500 m) versus the Andean-337 fed floodplain (<500 m and low relief adjacent to active river channels where Andean-derived 338 sediments are exchanged). First, we assess the OC<sub>petro</sub> weathering flux in the foreland by using 339 data from the Las Piedras river catchment, since it drains the foreland exclusively with no 340 Andean contribution. The [Re]<sub>diss</sub> concentration at Las Piedras ( $1.24\pm0.35$  pmol.L<sup>-1</sup>, 2SE) is low like the two other medium-size foreland rivers, the Blanco  $(0.36\pm0.06 \text{ pmol.L}^{-1})$  and the Los Amigos  $(0.50\pm0.16 \text{ pmol.L}^{-1})$ . The [Re]/[OC] ratio of bedrock in Las Piedras can be reasonably assumed to be equivalent to the Andean-derived bedload from the Rio Kosñipata, given that the foreland-floodplain region is predominantly underlain by Andean-derived sediments (23). Using this, we calculate a J<sub>OCpetro-ox</sub> of  $1.9^{+1.2}/_{-0.8}$  tC.km<sup>-2</sup>.yr<sup>-1</sup> which is about 6 times lower than in the Andes and similar to the rate measured in the Mackenzie River basin (20).

348 To estimate the OC<sub>petro</sub> weathering flux in the floodplains, we attempt a mass-balance 349 at the scale of the whole Madre de Dios catchment (118 459 km<sup>2</sup> at El Sena station near 350 Riberalta, Ref. 36). Assuming the J<sub>OCpetro-ox</sub> from SP (Upper Andes) is representative of the Andean area (40 868 km<sup>2</sup>; defined as <500 m) of the Madre de Dios, we calculate a total Andean 351 Jocpetro-ox of 0.46<sup>+0.18</sup>/-0.11 MtC.yr<sup>-1</sup>. This assumption is justified as the SP catchment has similar 352 erosion rates as the inferred Andean erosion rate for the whole Madre de Dios River (37). The 353 354 contribution from foreland weathering (< 500m; 77 591 km<sup>2</sup>) can be estimated using the J<sub>OC petro-</sub> 355 ox from the Las Piedras River (19 630 km<sup>2</sup>) as  $0.15^{+0.09}/_{-0.06}$  MtC.yr<sup>-1</sup>. The total J<sub>OCpetro-ox</sub> at the mouth of the Madre de Dios is 1.00<sup>+0.43</sup>/-0.28 MtC.yr<sup>-1</sup>. Hence, the contribution of Andes + 356 Foreland is lower than the total  $J_{OCpetro-ox}$  of the Madre de Dios at its mouth by  $0.39^{+0.16}/_{-0.11}$ 357 358 MtC.yr<sup>-1</sup>, which we attribute to weathering in the floodplain. This mass-balance indicates that 359 ~46% of the total OC<sub>petro</sub> oxidation takes place in the Andes, ~40% in the floodplains, and ~14% 360 in the foreland-lowlands (Fig. 4A).

The deposition and weathering of sediments in the floodplain constitutes a different 361 362 mechanism compared to upland weathering (29, 49). Sediment and water exchange and storage during floodplain transit by rivers can result in long sediment residence times (50), and 363 influence water flux, and redox state, which could all facilitate OW (7). In addition, the warmer 364 365 climatic conditions in the floodplain relative to the Andes could be important in setting reaction 366 rates (21), while the length of floodplains and their channel migration rates (51) could also be 367 important controlling variables. Scaled laboratory experiments have been used to suggest that in-situ oxidation during within river transport is small (52) meaning reactions in sediment stores 368 369 of floodplains are likely to be of most importance (53).

370 Our paired instantaneous [Re]<sub>diss</sub> and discharge measurements from the same sampling 371 trips (in 2013 and 2019, both wet and dry seasons) covering both upstream and downstream 372 floodplain sections constrain the location of OC<sub>petro</sub> oxidation reactions in the floodplains 373 between MLC and CICRA (Fig. 4B). The ~85 km long section of the river along the course of 374 the Alto Madre de Dios floodplain, between the Mountain Front (MLC) and the confluence 375 with the Rio Manu, is mostly braided and multi-channel, with mobile channel bars comprised 376 of sand and fine gravel. Measurements show a significant increase of J<sub>Re</sub> (Re flux). Water isotopes indicate lack of significant water, and therefore likely Re, contribution from tributaries 377 in this river reach (see Materials and Methods). Hence, we attribute this J<sub>Re</sub> increase (from 4 to 378 379 30%, Fig. 4B) to weathering of OC<sub>petro</sub> from Andean sediments transiting in the floodplains (SI 380 Appendix). The same calculation can be done using mean annual Re flux, but with a larger 381 uncertainty. We calculate that the mean annual J<sub>Re</sub> increases by 31±20% which corresponds to 382 a flux of CO<sub>2</sub> release through OC<sub>petro</sub> oxidation in the floodplain reach between MLC (Mountain 383 front) and AMdD of 0.03±0.01 MtC.yr<sup>-1</sup>. In comparison, the CO<sub>2</sub> release through OC<sub>petro</sub> 384 oxidation in the Andean part of the Alto Madre De Dios catchment is 0.08±0.02 MtC.yr<sup>-1</sup>. As 385 the solid OC<sub>petro</sub> load at MLC is 0.12±0.01 MtC.yr<sup>-1</sup> (Ref. 32, assuming similar solid OC<sub>petro</sub> yield as at SP), this would suggest that ~25% of Andean-derived solid OC<sub>petro</sub> is oxidized before 386 387 reaching the confluence with the Rio Manu over a floodplain length of 85 km.

In contrast, in the section between AMdD and CICRA (~180 km long), where a larger, single channel meanders through the floodplain, we observe no significant Re flux increase in wet seasons (2013 and 2019) and dry season 2019. For the dry season in 2013, we even observe 391 a small decrease of Re yield along the section (Fig. 4B). Similarly, using mean annual  $J_{Re}$ , we calculate no significant increase in OC<sub>petro</sub> oxidation, within uncertainties (Fig. 4B, SI 392 393 Appendix), in this section nor in the CICRA-PM section (~170 km long). Over the transit from 394 MLC to CICRA, the isotopic composition of sulfate suggests minimal sulfate reduction (36), 395 suggesting that oxygen is available for OW weathering along this river reach. In addition, the 396 warm tropical climate could drive higher reaction rates and OC<sub>petro</sub> oxidation (21). Therefore, 397 the apparent limited floodplain weathering could reflect an exhaustion of reactive OC<sub>petro</sub> 398 supplied from Andean erosion upstream. Regardless of the mechanisms at play, the Rio Madre 399 de Dios example shows that high rates of OC<sub>petro</sub> oxidation in the mountain headwaters can be 400 matched by OW in the foreland (Fig. 4). A large proportion of floodplain weathering appears 401 to happen over a relatively short-length scale (~<85 km) after exiting the Andes.

402 Finally, for the section furthest downstream, PM-Ribe (~560 km long), calculation using 403 mean annual  $J_{Re}$  show a 10% increase in Re flux. This may reflect OW of reactive  $OC_{petro}$ 404 supplied by the Inambari and/or the Tambopata, in combination with a longer time sediments 405 spend in this long floodplain section (e.g. see ref. 50). Yet, this observation should be 406 interpreted with caution due to the large uncertainty (±13%) associated with our calculation. 407 Additional work on this part of the catchment is necessary to refine these calculations.

408

#### 409 Implications for the long-term carbon cycle

Previous studies on the Amazon River found significant CO2 release from OCpetro 410 oxidation during the transit of fluvial sediments in the Madeira floodplain (10, 11). They found 411 412 that the solid OC<sub>petro</sub> flux from the Madeira at the confluence with the Amazon is much lower 413 than the solid OC<sub>petro</sub> supplied by the Beni at the mountain front and transported through the 414 plain. They estimated a CO<sub>2</sub> emission of 0.50 MtC.yr<sup>-1</sup> across the Rio Beni floodplain. Our Re-415 based estimate of OC<sub>petro</sub> oxidation during the transit of Madre de Dios sediments in the floodplain (0.39<sup>+0.16</sup>/-0.11 MtC.yr<sup>-1</sup>) is of similar magnitude. The total CO<sub>2</sub> emission from OC<sub>petro</sub> 416 oxidation in the whole Madre de Dios catchment  $(1.00^{+0.43}/_{-0.28} \text{ MtC.yr}^{-1})$  is more than twice the 417 silicate weathering CO<sub>2</sub> drawdown (0.43<sup>+0.22</sup>/<sub>-0.09</sub> MtC.yr<sup>-1</sup>; ref. 53). Considering that sulfide 418 oxidation also contributes to the carbonate weathering flux (23), the net  $CO_2$  balance during 419 420 weathering in the Madre de Dios catchment appears to be tipped firmly toward being a CO<sub>2</sub> 421 source (3).

422 Our findings from the Rio Madre de Dios catchment allow us to postulate a broader role for floodplain weathering in enhancing the CO2 release by OCpetro oxidation. Uplift and 423 424 exhumation of sedimentary rocks in a mountain range can increase the supply of OC<sub>petro</sub> to an 425 oxygenated weathering zone (17, 21) and increase the rates of OC<sub>petro</sub> oxidation and CO<sub>2</sub> 426 release, as we observe in the Andes (Fig. 4). However, the overall weathering intensity can be 427 low, with only  $\sim 20\%$  to 50% of OC<sub>petro</sub> oxidized, meaning there is further potential for CO<sub>2</sub> 428 release. On high standing mountain islands, floodplains are short. For instance, in Taiwan rivers 429 have floodplains <40 km long, and many are shorter than 5 km, and there un-weathered OC<sub>petro</sub> 430 is re-buried offshore (16). However, if the tectonic setting permits the growth of a larger 431 continental floodplain, additional OC<sub>petro</sub> oxidation is very likely to occur even if just ~100 km 432 in length based on our findings (Fig. 4). In this case, only extremely refractory OC<sub>petro</sub> escapes oxidation (10). While future work will need to establish how temperature and O2-supply impact 433 434 OC<sub>petro</sub> oxidation rates in floodplains (7, 21), our results suggest that the formation of floodplain adjacent to a mountain range allows more complete OC<sub>petro</sub> oxidation during sediment transit. 435 Over multi-million year timescales, the growth and waning of riverine floodplains and 436 437 continental sediment storage (27) could thus act as a powerful carbon cycle modifier throughout 438 Earth's history.

439

#### 440 Materials and methods

441 The materials and methods are summarized here; further details are provided in SI Appendix. All data 442 used in this study are reported in Datasets S1–S5.

443

444 Sample collection and discharge measurements. Major cation and anion concentration data of 445 samples from 2010 to 2013 are from Torres et al., (2015, 2016). Detailed information on the sampling 446 protocol can be found in those studies. In summary here, for the four main nested catchment sites (WAY, 447 SP, MLC and CICRA, Fig. 1), time-series samples were collected between 2010 and 2011 using a clean 448 PP bottle and filtered on site with 0.2 µm porosity nylon filter (29). At these sites, water discharge was 449 measured at the same time as sampling by monitoring water levels manually and converting to discharge 450 using a rating curve. At the SP site, river level was monitored with a water level logger that recorded 451 river level measurements every 15 min (33). At other localities, samples were collected on fieldtrips in 452 2012, 2013, 2016 and 2019 (Dataset S1). Water samples were collected from the river surface using 453 clean bucket and transferred to 10 or 20 L plastic bags before filtration. Samples were filtered within 24 454 to 48h of collection with 0.2µm porosity polyethersulfone (PES) filters. The discharge ("Q") at CICRA 455 was measured during each sampling trip using an Acoustic Doppler Current Profiler (ADCP, RD1 456 Sentinel GED154 in March 2013 and SonTek M9 in August 2013 and in March and May 2019). In 457 2019, the discharge of the Alto Madre de Dios, Rio Manù, Chiribi and Colorado were also measured by 458 ADCP. All discharge measurements are from Torres et al., (2017) and Burt et al., (2021)

459

460 Re concentration measurements in water and sediments. The dissolved Re concentrations were 461 measured following the same protocol as described in ref. (19). Briefly, dissolved Re concentrations 462 ([Re]<sub>diss</sub>) were measured by direct calibration against a set of seven standards with varying Re 463 abundances and similar matrixes to river water, by quadrupole inductively coupled plasma mass 464 spectrometry (O-ICP-MS, Agilent Technologies 7900). Calibration standards and samples were doped 465 with 0.025 mg/L concentration of internal standard Tb and Bi to correct for instrumental drift and matrix 466 drift. Accuracy and precision of the measurements was assessed by repeated measurements of various 467 riverine standard reference materials, in particular reference materials SLRS-5 and SLRS-6 at various 468 dilutions. The standards confirmed better than 10% accuracy and precision. For sediment samples, the 469 rhenium concentrations were determined using the method in ref. (55). A mass of 0.2 to 0.5g was 470 digested using a mixture of 3 mL 27M HF and 3 mL 16M HNO<sub>3</sub> for 24 to 48h at 120°C on a hot plate. 471 Digested solutions were processed through AG1-X8 resin to separate Re from the rest of the matrix. 472 Rhenium concentrations were then measured with a Neptune MC ICP-MS at Durham University.

473

474 Dissolved Re vield calculations. Several methods can be used to determine dissolved ion vields 475 depending on the number of paired water discharge (Q) and concentration measurements, their 476 frequency and the behavior of the element of interest in relation with discharge (56). Previous studies 477 with large datasets of Re concentration and discharge (19, 20) have used a rating curve approach to 478 quantify dissolved yields, by fitting power law functions to the trends in the data and using this 479 relationship to predict predicted for each daily discharge value and annual fluxes. Other studies have 480 used discharge-weighted average concentration (41) or average concentration of several measurements 481 (4, 17, 18, 46) combined with annual water discharge estimates.

482 The four nested catchments in our dataset have between five and nine Q and [Re]<sub>diss</sub> data pairs 483 for each catchment (Fig. 1C). For the large tributaries (Manu, Colorado, Chiribi, Alto Madre de Dios), 484 our dataset includes 4 paired Q and [Re]diss measurements each. For all the sites, we use three different 485 methods to calculate the Re yield and uncertainties: i) mean [Re]<sub>diss</sub>±SE multiplied by annual discharge; 486 ii) discharge-weighted mean [Re]<sub>diss</sub>±SE multiplied by annual discharge; and iii) average of measured instantaneous Re fluxes,  $J_{Re} \pm SE$ . The advantage of the first method is that it includes more [Re]<sub>disc</sub> 487 488 measurements (since the instantaneous discharge was not measured for all samples). The disadvantage 489 is that there is a potential bias toward high concentration by not weighting to discharge. The third method 490 is useful if annual discharge is not known, however it has the disadvantage of being less accurate because 491 instantaneous fluxes vary more than instantaneous concentrations (56). Discharge values and 492 uncertainties are reported in Dataset (S3). For the WAY and SP catchments, we use annual discharge 493 values from Clark et al., (2014), determined over the year 2010. In addition, we use average annual 494 discharge values dataset for the main tributaries of the Madre de Dios that were determined by water 495 balance over the period 1968-1982 (57). They calculate a total discharge at the mouth of the Madre de 496 Dios (Riberalta) of 6369 m<sup>3</sup>.s<sup>-1</sup> which are very close (only 12% higher) to the discharge measured during 497 the 2002–2011 period (5661 m<sup>3</sup>.s<sup>-1</sup>; Vauchel et al., 2017). For CICRA, the discharge can be estimated 498 by adding the annual discharge values of the Manu, Alto Madre de Dios, Colorado from Abastos Lara, 499 (1987) and considering that the Rio Chiribi contributes 7.5% of the total discharge in CICRA (see 500 Dataset S5). This gives a value of 2165 m<sup>3</sup>.s<sup>-1</sup>. For instantaneous discharge of the main tributaries (Alto 501 Madre de Dios, Manù, Chiribi and Colorado) that were measured or calculated during the 2013 and 502 2019 sampling trip, we use values from previous studies (34, 35).

503 Calculation of uncertainty is done by a Monte Carlo simulation (run 10 000 times for each 504 watershed). As the calculated distributions follow skewed rather than normal distributions, we report 505 the median value (50th percentile) with the uncertainty range defined by the 16th and 84th percentiles 506 (equivalent to 68% of the entire population; SI Appendix). Comparison between the various methods 507 shows good agreement between the different methods for the different sites within uncertainties (Dataset 508 S3). The third method gives larger uncertainty compared to methods 1 and 2. This could reflect the 509 lower number of samples used, the uncertainty on the discharge measurement or an imbalance between 510 the discharge during the 1968-1982 period and the 2010-2020 period. When quantifying OC<sub>petro</sub> 511 oxidation fluxes from the dissolved Re flux for all sites, we use the second method (discharge-weighted 512 [Re]<sub>diss</sub>) when possible and the first method (mean [Re]<sub>diss</sub>) otherwise.

513

514 Source partitioning of dissolved rhenium. To quantify the OC<sub>petro</sub> oxidation flux using dissolved Re, 515 we need to: i) correct for Re inputs from precipitation and/or atmospheric deposition; ii) quantify the Re 516 input from non-OC<sub>petro</sub> sources (i.e. sulfide, carbonate and silicate minerals). Solutes in precipitation can 517 come from dissolution of sea salts, dust or biogenic particles. The [Re]/[Cl] ratio (~7.5×10<sup>-5</sup> pmol.µmol<sup>-</sup> 518 <sup>1</sup>) of the ocean is very low (58) compared to the [Re]/[Cl] of rivers from the Madre de Dios. The [Cl]<sub>diss</sub> 519 in rivers from this study are also low, indicating that the proportion of Re derived from sea salts is very 520 small. While we have only one rainwater sample from the upper Andes, its [Re]diss was below detection limit of the measurement session ( $< 0.05 \text{ pmol}.L^{-1}$ ), supporting this conclusion. Among all the samples, 521 522 the lowest measured [Re]<sub>diss</sub> and [Re]/[Cl] ratio correspond to a lysimeter sample in the Foreland (PER19-38) with values of 0.009 pmol.L<sup>-1</sup> and 1.4×10<sup>-3</sup> pmol.µmol<sup>-1</sup> respectively. The [Re]/[Cl] ratio 523 524 of this sample is ~20 times higher than the [Re]/[Cl] ratio of the ocean. The major element concentration 525 for this sample is in the range of the average composition of rainwater from the Andes from Torres et 526 al., (2015). Hence, we use this sample as representative of the maximum Re/Cl ratio of rainwater. For 527 calculating the proportion of Re derived from each source we used the following mass-balance. For the 528 contribution of the rain:

529 530

531

$$[\text{Re}]_{\text{rain}} = \left(\frac{\text{Re}}{\text{Cl}}\right)_{\text{rain}} \times [\text{Cl}]_{\text{cycl}}$$
[1]

Where (Re/Cl)<sub>rain</sub> is the proposed elemental ratio between Re and the Cl in the rain (1.4×10<sup>-3</sup> pmol.µmol<sup>-</sup> 532 533 <sup>1</sup>) and [Cl]<sub>cycl</sub> is the cyclic chlorine concentration. Since the marine evaporite contribution is small or 534 negligible in the Madre de Dios catchment (23, 29), we consider that [Cl]<sub>cycl</sub> = [Cl]<sub>riv</sub>. The concentration 535 of any element X corrected for rainwater and evaporite inputs is referred as " $[X^*]$ ". We find that the 536 proportion of riverine Re deriving from rainfall is negligible, being generally less than 0.5%, with a 537 maximum of 6%. For SO<sub>4</sub> rain concentration we use a (SO<sub>4</sub>/Cl) value of 0.53 corresponding to the 538 median value of precipitation data from Torres et al., (2015). This value is only slightly lower than the 539 lowest (SO<sub>4</sub>/Cl) measured in our dataset (sample PER19-38, value of 0.60).

540 We then move to quantify the proportion of dissolved rhenium derived from OC<sub>petro</sub> oxidation 541 relative to other potential Re sources (sulfides, silicates, carbonates). Previous work has suggested carbonates are not a major source of dissolved Re (18). If the Re/Ca of carbonates is  $\sim 5 \times 10^{-5}$  pmol.mol<sup>-</sup> 542 543  $^{1}$  (18), <1% of total dissolved Re in the studied rivers here can be accounted for by carbonate weathering 544 (a maximum proportion using this Re/Ca ratio and assuming all dissolved Ca in the Madre de Dios 545 catchments is derived from carbonates). We therefore follow the approach developed in Horan et al., 546 (2019), that uses the (Re/SO<sub>4</sub>)\* and (Re/Na)\* ratio to characterized Re input from sulfides, silicates and 547 OC<sub>petro</sub>.

548 Sulfides have low Re/S (Miller et al., 2011) and silicates low Re/Na relative to OC<sub>petro</sub> (Horan 549 et al., 2019) and both Na and SO<sub>4</sub> are conservative soluble species in the Madre de Dios catchment 550 (Baronas et al., 2017; Torres et al., 2017; Burt et al., 2021). Assuming that all the  $[SO_4^{2-*}]$  is derived 551 from pyrite oxidation (i.e. no evaporite contribution, Torres et al., 2016), we estimate the Re 552 concentration derived from sulfide oxidation:

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555

$$[\text{Re}]_{\text{diss.sulfides}} = \left(\frac{\text{Re}}{\text{SO}_4^{2-}}\right)_{\text{sulfides}} \times [\text{SO}_4^{2-} *]$$
[2]

556 Where (Re/SO<sub>4</sub><sup>2-</sup>)<sub>sulfides</sub> is the sulfide composition. Then we can determine the concentration of 557 Re deriving from silicate weathering ([Re]<sub>diss-sil</sub>) using sodium and assuming that all the [Na\*] is derived 558 from silicate weathering:

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565 566

$$[\text{Re}]_{\text{diss.sil}} = \left(\frac{\text{Re}}{\text{Na}}\right)_{\text{silicates}} \times [\text{Na}*]$$
[3]

Where (Re/Na)<sub>sil</sub> is the silicate signature. Then we attribute the excess Re to the oxidation of
 OC<sub>petro</sub>, calculated as:

$$[Re]_{diss.OC} = [Re*] - [Re]_{diss.sulfides} - [Re]_{diss.sil}$$
[4]

567 In analogy with studies on silicate and carbonate weathering, we use small tributaries (e.g. 568 Gaillardet et al., 1997; Galy and France-Lanord, 1999) and/or sediment composition (23, 44) to 569 constrain local weathering end-members [Re]/[SO4] and [Re]/[Na] ratio values (20). Small Andean 570 tributaries draining sulfur-rich metasedimentary rocks display two orders of magnitude variability in 571 [Re]/[SO4<sup>\*</sup>] and [Re]/[Na<sup>\*</sup>] ratios and are positively correlated. Several Andean rivers with low 572  $[Re]/[SO_4^*]$  values (Fig. 3) have similar composition to the median Re/S values of pyrite from the literature  $(1.8^{+4.2}/_{-1.7} \times 10^{-3} \text{ pmol}.\mu\text{mol}^{-1}$ , Miller et al., 2011) with the lowest  $[\text{Re}]/[\text{SO}_4^{2-}]$  ratio 573 corresponding to a lysimeter sample (PER19-97) in the riparian area of a small catchment ([Re]\*/[SO4<sup>2-</sup> 574 575  $]^* = 2.2 \times 10^{-4}$  pmol.µmol<sup>-1</sup>) and a river sample (r2400) from another small catchment in the Andes  $([\text{Re}]^*/[\text{SO}_4^2^-]^* = 4.8 \times 10^{-4} \text{ pmol}.\mu\text{mol}^{-1})$ . They both have high SO<sub>4</sub> concentration indicating a high rate 576 577 of sulfide oxidation. The  $[Re]/[SO_4^*]$  ratio of these samples is similar to the sulfide-oxidation rich 578 sample in the Mackenzie basin (Horan et al., 2019). Hence, this suggests that the Re and  $SO_4$ 579 composition of these rivers is dominated by sulfide oxidation of pyrite and that they can be used as end-580 member values for  $(\text{Re/SO}_4)_{\text{sulfides}}$ . The lowest  $(\text{Re/SO}_4)^*$  value  $(2.2 \times 10^{-4} \text{ pmol}.\mu\text{mol}^{-1})$  measured here 581 could represent the most "pure" sulfide oxidation end-member and higher [Re]/[SO4\*] for other rivers 582 would be explained by a small contribution of Re from rock organic carbon oxidation. Alternatively, it 583 is possible that the Re/S from the local bedrock is variable and explains the range of  $[Re]/[SO_4^*]$ 584 observed in rivers dominated by sulfide oxidation. A third possibility is that the very low [Re]/[SO<sub>4</sub><sup>\*</sup>] 585 and [Re]/[Na<sup>\*</sup>] of some samples is due to non-conservative behavior and removal of dissolved Re 586 because some of these rivers have low pH values (as low as 3.5) and ReO<sub>4</sub><sup>-</sup> is less stable under acidic 587 conditions (60). However, this cannot explain the low  $[Re]/[SO_4^*]$  value of sample PER19-3 (3.5×10<sup>-3</sup>) 588 pmol.µmol<sup>-1</sup>) which has pH value of 8. Considering the above discussion we consider (Re/SO<sub>4</sub>)<sub>sulfides</sub> ranging from  $2 \times 10^{-4}$  to  $4 \times 10^{-3}$  pmol.µmol<sup>-1</sup> that encompass the range of [Re]/[SO<sub>4</sub><sup>\*</sup>] of Andean rivers 589 590 that we identified as typical of sulfide oxidation.

591 Rivers draining mostly granites (sulfide-poor and no OC<sub>petro</sub>) have low Re/Na but an order of 592 magnitude higher [Re]/[SO<sub>4</sub>] ratios relative to Andean tributaries draining shales (Fig. 3). Interestingly, 593 rivers and lysimeter samples from the foreland have similar composition as rivers draining granites. For 594 Foreland rivers, especially at low elevations, deeply weathered soils and high weathering intensity 595 probably leads to almost complete oxidation of pyrite due to its fast kinetics, and therefore we expect 596 the chemical composition of those samples to be less influenced by OW of pyrite than Andean rivers. 597 Altogether, rivers draining granite and the foreland have ratios that are inferred to reflect mostly mixing 598 between weathering of silicates and weathering of OC<sub>rock</sub>. These observations are supported by river bed 599 sediment samples. For Andean rivers, the [Re]/[Na] ratio of river bed sediments is similar to the low [Re]/[Na<sup>\*</sup>] of small tributaries draining granites (lowest value is 2.2×10<sup>-3</sup> pmol.µmol<sup>-1</sup> for sample 600 PER19-26) and of samples from small first-order catchments draining the foreland (lowest value is 601 602  $1.5 \times 10^{-3}$  pmol.µmol<sup>-1</sup> for sample PER19-35). In addition, one rock sample, corresponding to an igneous

for rock (a granophyre), has a very low [Re]/[Na] ratio of  $4.3 \times 10^{-4}$  pmol.µmol<sup>-1</sup>, similar to the crystalline rock endmember [Re]/[Na] ratio value in the Himalaya ( $2 \times 10^{-4}$  pmol.µmol<sup>-1</sup>, Ref. 18). Hence, we consider here a [Re]/[Na] ratio between  $4 \times 10^{-4}$  and  $2 \times 10^{-3}$  pmol.µmol<sup>-1</sup> for silicates, which spans the range of lowest [Re]/[Na] values from local solid and river samples.

607 Using Eq. (1-4) and the range of above defined  $(\text{Re/SO}_4)_{\text{sulfides}}$  and  $(\text{Re/Na})_{\text{silicates}}$  values for our 608 study area, we can calculate  $[\text{Re}]_{\text{diss.OC}}$  for each sample. The calculation of  $[\text{Re}]_{\text{diss.OC}}$  is done by a Monte 609 Carlo simulation (run 10 000 times for each river) assuming random distribution of  $(\text{Re/SO}_4)_{\text{sulfides}}$  values 610 between  $2 \times 10^{-4}$  and  $4 \times 10^{-3}$  pmol.mol<sup>-1</sup> and  $(\text{Re/Na})_{\text{silicates}}$  values between  $4 \times 10^{-4}$  and  $2 \times 10^{-3}$  pmol.µmol<sup>-</sup> 611 <sup>1</sup> (SI Appendix; Dataset S4). Fractions of dissolved Re derived from OC<sub>petro</sub> OW ( $f_c = [\text{Re}]_{\text{diss.OC}}/[\text{Re}]_{\text{diss}}$ ) 612 are reported in Dataset S3.

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614 Floodplain mass-balance of dissolved Re. The section of the Alto Madre de Dios river between MLC 615 (mountain front) and AMdD (confluence with Manu River) has relatively minimal tributary input. Over 616 three sampling trips, we observe an increase in the Re concentration between MLC and AMdD by 3% 617 (March 2013), 26% (March 2019) and 12% (May 2019). There is also a systematic increase in Re/Na 618 and Re/SO<sub>4</sub> ratio. The Re concentration of sub-Andean tributaries is about 0.8 ppt, which is higher than 619 the Re concentration at MLC and could explain part of the observed increase. The contribution of water 620 and weathering inputs from sub-Andean-foreland tributaries can be assessed using  $\delta D$  and  $\delta^{18}O$  since tributaries (PER19-53, Rio Carbon, Rio Pini Pini) have higher  $\delta D$  (-54.9 to -70.2‰) and  $\delta^{18}O$  values (-621 8.2 to -10.4 ‰) compared to the Alto Madre de Dios at MLC ( $\delta D \sim -72.5\%$  and  $\delta^{18}O \sim -10.6\%$ ). The 622 623  $\delta D$  and  $\delta^{18}O$  of the Alto Madre de Dios does not change significantly which indicates that any Re 624 contribution from these tributaries is too small to explain the observed 26% increase in Re concentration 625 in 2019. Therefore, we conclude that this increase is due to ongoing OC<sub>petro</sub> oxidation of sediment during 626 transit and/or within the floodplain between MLC and AMdD.

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#### **Figures**





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Figure 1. (A) Map of the Madre de Dios River basin with the location of the samples from this study. (B) Inset showing the location of the samples in the High Andes. (C) Re concentration (in pmol.L<sup>-1</sup>) in the various geomorphic settings for all river samples from this study. The [Re]diss from the two hot springs samples are not shown. (D) [Re]<sub>diss</sub> versus instantaneous runoff W (water discharge normalized by catchment area, mm day<sup>-1</sup>) at the time of sampling for the main nested catchments of this study (WAY, SP, MLC and CICRA).



822 **Figure 2.** (A) Rhenium concentration in solids ([Re]<sub>solids</sub>): rock samples (red stars), bedloads (red box) and soils 823 (yellow box). The middle line in boxes is the average value, upper and lower box limits correspond to the  $\pm 2SE$ 824 values, the upper and higher bars represent extreme data points. (B) Average  $\pm 2SE$  and extreme values of the 825 [Re]/[OC] ratio in bedloads and rocks.

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850 851 852 853 854 855 Figure 3. Rhenium to sodium, [Re]/[Na\*], and rhenium to sulfate, [Re]/[SO4\*], ratios (pmol µmol<sup>-1</sup>) for river waters from this study (High Andes = triangles; Andean Mountain front = square; Foreland = diamond; circles = Foreland-Floodplains). For the four nested-catchments, only the average values are represented. The red crosses correspond to the river sediments (bedloads) and bedrocks from the Kosnipata River basin. The shaded ovals show the ranges of elemental ratios associated with the rock weathering end-members (sulfides, silicates and OC<sub>petro</sub>). 856 The lines correspond to the mixing proportions between the rock weathering end-members, with the average 857 proportion of Re derived from OC<sub>petro</sub> weathering shown (in %).

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865Figure 4. (A) Estimated net contribution (vertical arrows) of each geomorphic zones to the total flux of  $OC_{petro}$ 866oxidation and associated  $CO_2$  release at the scale of the whole Madre de Dios River basin. MLC=Mountain Front,867AMdD=Alto Madre de Dios, PM=Madre de Dios at Puerto Maldonado, Ribe=Madre de Dios at Riberalta. The red868squiggly line corresponds to the 500m elevation. (B) Ratio between the measured dissolved rhenium flux derived869from  $OC_{petro}$  oxidation (J<sub>Re-OC</sub><sup>meas</sup>) and the predicted flux (J<sub>Re-OC</sub><sup>calc</sup>) using the tributary mixing model (SI Appendix)870as a function of the channel distance from MLC. A value >1 can be interpreted as  $OC_{petro}$  oxidation in the871floodplain. Vertical bars represent the uncertainties. This studied floodplain transect correspond to the channel872highlighted in light blue on panel A.