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### ► To cite this version:

Germain Bayon, Thibault Lambert, Nathalie Vigier, Patrick de Deckker, Nicolas Freslon, et al.. Rare earth element and neodymium isotope tracing of sedimentary rock weathering. *Chemical Geology*, Elsevier, 2020, 553, pp.1-15. 10.1016/j.chemgeo.2020.119794 . hal-03045577

**HAL Id: hal-03045577**

**<https://hal.inrae.fr/hal-03045577>**

Submitted on 5 Jan 2021

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# Rare earth element and neodymium isotope tracing of sedimentary rock weathering

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Word count: 7,321

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## Abstract

1 Chemical weathering plays an important role in sequestering atmospheric CO<sub>2</sub>, but its  
2 potential influence on global climate over geological timescales remains debated. To some  
3 extent, this uncertainty arises from the difficulty in separating the respective contribution of  
4 sedimentary and crystalline silicate rocks to past weathering rates in the geological record;  
5 two types of rocks having presumably different impact on the long-term carbon cycle. In this  
6 study, we investigate the use of rare earth element (REE) and neodymium isotopes ( $\epsilon_{\text{Nd}}$ ) in  
7 leached iron oxide fractions of river sediments for tracing the origin of weathered rocks on  
8 continents. A new index, called ‘concavity index’ (CI), is defined for measuring the degree of  
9 mid-REE enrichment in geological samples, which enables the determination of the source of  
10 iron oxides in sediments, such as seawater-derived Fe-oxyhydroxide phases, ancient marine  
11 Fe oxides derived from the erosion of sedimentary rocks, and recent secondary oxides formed  
12 in soils via alteration of crystalline silicate rocks or pyrite oxidation. Using this index, we  
13 demonstrate that the  $\epsilon_{\text{Nd}}$  difference between paired Fe-oxide and detrital fractions in river  
14 sediments (defined here as  $\Delta\epsilon_{\text{Nd Feox-Det}}$ ) directly reflects the relative contribution of  
15 sedimentary *versus* crystalline silicate rocks during weathering. While rivers draining old  
16 cratons and volcanic provinces display near-zero  $\Delta\epsilon_{\text{Nd Feox-Det}}$  values indicative of dominant  
17 silicate weathering ( $0.5 \pm 1.1$ ; n=30), multi-lithological catchments hosting sedimentary  
18 formations yield systematically higher values ( $2.7 \pm 1.2$ ; n=44), showing that sedimentary  
19 rock weathering can be traced by the occurrence of riverine Fe oxides having more radiogenic  
20 Nd isotope signatures compared to detrital fractions. This assumption is reinforced by the  
21 evidence that calculated  $\Delta\epsilon_{\text{Nd Feox-Det}}$  values agree well with previous estimates for carbonate  
22 and silicate weathering rates in large river basins.

23 Examining the influence of climate and tectonics on measured Nd isotopic compositions,  
24 we find that  $\Delta\epsilon_{\text{Nd Feox-Det}}$  is strongly dependent on temperature in lowlands, following an  
25 Arrhenius-like relationship that reflects enhanced alteration of silicate rocks and formation of  
26 secondary Fe oxides in warmer climates. In contrast, in high-elevation catchments,  $\Delta\epsilon_{\text{Nd Feox-}}$   
27  $\text{Det}$  defines striking correlation with maximum basin elevation, which we also interpret as  
28 reflecting the intensification of silicate weathering and associated Fe oxide formation as  
29 elevation decreases, due to the combined effects of thicker soils and warmer temperature.

30 Overall, our new findings are consistent with previous assertions that the alteration of  
31 sedimentary rocks prevails in high-elevation environments, while silicate weathering  
32 dominates in floodplains. This novel approach combining REE and Nd isotopes opens new  
33 perspectives for disentangling the weathering signals of sedimentary and crystalline silicate  
34 rocks in the geologic record, which could be used in future studies to reassess the causal  
35 relationships between mountain uplift, erosion and climate throughout Earth's history.

36

37 **Keywords:** World rivers; iron oxides; neodymium isotopes; Mid-REE enrichment; concavity  
38 index; silicate weathering; carbonate weathering; sulphide weathering

39

## 40 **1. Introduction**

41 On the continents, rocks are dissolved through chemical weathering, a process that  
42 consumes substantial amounts of carbon dioxide and plays a major role in regulating Earth's  
43 climate through time (Walker et al., 1981; Berner et al., 1983; Kump et al., 2000). A  
44 contentious view is that mountain building events during Earth's history were followed by  
45 enhanced physical erosion and accelerated dissolution of crystalline silicate rocks, resulting in  
46 a net drawdown of atmospheric CO<sub>2</sub> and global climate cooling (e.g. Raymo and Ruddiman,  
47 1992; Li and Elderfield, 2013). A first difficulty with this hypothesis has been the relatively  
48 small size of the atmospheric CO<sub>2</sub> reservoir, meaning that over millions of years, any  
49 significant increase in CO<sub>2</sub> removal via silicate weathering would have led to an unrealistic  
50 near complete depletion of carbon in the atmosphere (Berner and Caldeira, 1997).  
51 Additionally, several studies have also argued for relatively invariant silicate weathering rates  
52 at times when erosion of mountains was intensifying, suggesting that the evolution of  
53 atmospheric CO<sub>2</sub> in response to mountain uplift could reflect progressive changes in the  
54 susceptibility of crystalline rocks to weathering, rather than being simply proportional to  
55 silicate weathering fluxes on continents (Willenbring and von Blanckenburg, 2010; Caves et  
56 al., 2016; Caves Rugestein et al., 2019).

57

58 When examining the nature of the relationships between mountain uplift, chemical  
59 weathering and global climate, much complexity is brought by the fact that regions of high  
60 elevation are frequently composed of continental margin sequences of old sediments rather  
61 than crystalline basement (e.g. Hartmann and Moosdorf, 2012). These sequences invariably  
62 contain marine carbonates and other marine authigenic phases, which weather more rapidly  
63 than crystalline rocks. While mountainous regions with high denudation rates display the  
64 highest silicate weathering rates on continents (e.g. West et al., 2005), field observations

65 indicate that chemical weathering fluxes from tectonically active mountain ranges are mostly  
66 dominated by dissolved inputs from carbonate weathering, even in watersheds hosting  
67 primarily igneous or metamorphic rocks (e.g. Stallard and Edmond, 1983; Jacobson and  
68 Blum, 2003; Jacobson et al., 2003; Moore et al., 2013). Carbonate weathering is generally  
69 considered to have no impact on the long-term carbon cycle. This is because the amount of  
70 carbon initially consumed during the dissolution of carbonate minerals by carbonic acid is  
71 quantitatively returned to the atmosphere upon subsequent carbonate precipitation in the  
72 ocean. However, carbonate dissolution on continents can also proceed in presence of  
73 sulphuric acid released by the oxidation of pyrite and other sulphide minerals (e.g. Spence and  
74 Telmer, 2005; Calmels et al., 2007; Torres et al., 2016; Torres et al., 2017). This coupled  
75 sulphide-carbonate weathering process can be particularly active in catchments hosting shales  
76 and other sulphide-bearing sedimentary formations, resulting, in terms of global impact on the  
77 carbon cycle, in a net release of CO<sub>2</sub> to the atmosphere (e.g. Stallard and Edmond, 1983;  
78 Calmels et al., 2007; Torres et al., 2016; Blattmann et al., 2019). Similarly, the oxidation of  
79 petrogenic organic carbon stored in sedimentary rocks also returns CO<sub>2</sub> to the atmosphere  
80 (Bouchez et al., 2010), especially in high mountains and glacial environments (Torres et al.,  
81 2016; Horan et al., 2017). On top of the current debate about the presumed importance of  
82 silicate weathering to the long-term carbon cycle, the above-mentioned evidence that  
83 alteration of carbonates and other sedimentary rocks dominate in high mountain environments  
84 have re-emphasized the need to characterize the separate evolution of sedimentary and  
85 crystalline silicate rock weathering through geologic time. To date, however, there is no  
86 reliable proxy that can decipher different rock weathering signatures from the geological  
87 record.  
88

89 Continental detrital sediments may contain various authigenic mineral phases depending on  
90 the original source rock, including iron (Fe) oxides. Authigenic Fe oxide phases precipitate  
91 from water and pore fluids in the oceans, lakes and river estuaries, concentrating trace  
92 elements such as neodymium and beryllium (e.g. Boyle et al., 1977), which can be used to  
93 help identify the origin of weathered rocks on continents (e.g. von Blanckenburg et al., 2015;  
94 Hindshaw et al., 2018; Sufke et al., 2019; Jang et al., 2020). Iron oxides are also ubiquitous  
95 weathering products in soils, which can be transported as particulates in rivers prior to  
96 deposition as sediments (Bayon et al., 2004; Kraft et al., 2013). Recently, a study conducted  
97 in the Svalbard archipelago showed that the Fe oxide fractions leached from fjord sediments  
98 surrounding glaciated catchments composed of sedimentary rocks typically displayed Nd  
99 isotope signatures ( $^{143}\text{Nd}/^{144}\text{Nd}$ ; or  $\epsilon_{\text{Nd}}$  in epsilon notation) more radiogenic than  
100 corresponding detrital fractions (Jang et al., 2020). In agreement, Hindshaw et al. (2018)  
101 reported similar differences in  $\epsilon_{\text{Nd}}$  between both the easily dissolvable component of  
102 catchment rocks and their silicate residues, and dissolved and particulate riverine loads in  
103 Svalbard. These data were interpreted as reflecting the preferential dissolution of marine  
104 precipitates hosted by sedimentary rocks. In fact, the same suggestion had been already  
105 presented more than two decades ago (Goldstein and Jacobsen, 1987), in order to account for  
106 the observation that the Nd isotopic composition of filtered river waters was also more  
107 radiogenic than corresponding suspended sediment loads in certain rivers. In the above  
108 mentioned examples, the evidence that significant Nd isotope decoupling can occur in  
109 sedimentary watersheds due to preferential alteration of marine precipitates is consistent with  
110 the fact that the global Nd isotopic composition of seawater ( $\epsilon_{\text{Nd}} -8.8$ ; Lacan et al., 2012) is on  
111 average more radiogenic than the mean continental detrital input to the ocean ( $-11.3 \pm 2.5$ ;  
112 Bayon et al., 2015). Sedimentary carbonate rocks dissolve indeed at a much faster rate than  
113 crystalline silicate rocks, and therefore largely control the chemistry of river waters

114 worldwide and associated dissolved inputs to the ocean (Gaillardet et al., 1999; Jacobson et  
115 al., 2002).

116

117 In this study, we define a novel approach based on the combined use of rare earth elements  
118 (REE) and Nd isotopes in the Fe oxide fraction associated with river sediments. Our  
119 approach exploits a systematic difference in Nd isotopic ratios between the Fe oxide and  
120 silicate fractions of the sediment (defined here as  $\Delta\epsilon_{Nd_{FeOx-Det}}$ ), similar to that observed  
121 between filtered waters and suspended particulate matter (Goldstein and Jacobsen, 1987;  
122 Hindshaw et al., 2018). This traces the relative contribution of sedimentary rock inputs with  
123 an inherited old authigenic Nd isotopic signature *versus* silicate rock inputs with a  
124 composition set by their silicate source. Our data set has a global reach, spanning samples  
125 from different lithologies, topographies and weathering regimes. The relative amounts of  
126 sedimentary- *versus* crystalline silicate- derived sources remaining in the riverine Fe oxide  
127 fraction are found to display systematic trends with basin parameters, such as temperature and  
128 relief that we link to different regimes of weathering, with fundamental implications for the  
129 silicate weathering feedback.

130

## 131 **2. Materials and methods**

### 132 **2.1. World river sediments: Climatic, physical and lithological characteristics of** 133 **watersheds**

134 We analysed a total of 74 sediment samples from either rivers (n=43), deltas (n=7),  
135 estuaries (tide-dominated environments; n=15), or submarine deltas (wave-dominated  
136 environments; n=4). Additionally, five marine sediment samples (Congo, Niger, Nile, Sepik,  
137 Gaoping) collected from more distal locations near the mouth of rivers, in deep-sea fan  
138 environments (Fig 1; Table S1). The geographical coordinates of studied samples are listed in



139 Table S1. Selected samples include some of the world's largest rivers (e.g. Amazon, Congo,  
140 Mississippi, Nile, Yangtze, Mackenzie, Ganges-Brahmaputra), in addition to other smaller  
141 rivers associated with particular geological settings (Fig. 1). All river sediments were scooped  
142 from recent river banks or correspond to suspended particulates for the case of the Congo  
143 River tributaries. Other sediment samples were collected using various coring devices,  
144 corresponding typically to centimetre-thick layers of core-tops or sub-surface sediment  
145 horizons. All studied samples correspond either to modern or relatively recent sediments that  
146 have been presumably deposited during the last few centuries.

147  
148 Mean annual air temperature (MAT) for each river system were derived from the literature  
149 (e.g. Pinet and Souriau, 1988; Bayon et al., 2016, 2018). Corresponding information for  
150 maximum elevation in river basins was either derived from Milliman and Farnsworth (2011),  
151 or determined in the geographical information system (GIS) software ArcGis (ESRI 2001,  
152 ArcGis Desktop 10.3.1) using the hydrological data and maps based on shuttle elevation  
153 derivatives HydroBASINS (Lehner and Grill, 2013). Finally, information on the lithological  
154 composition of each river basin was extracted from the GLiM global lithological map  
155 database (Table S1; Hartmann and Moosdorf, 2012).

156  
157 Studied samples were classified into distinct categories depending on the lithological  
158 composition of corresponding basins. A series of samples (n=24) came from rivers draining  
159 igneous/metamorphic terranes, in particular from the Precambrian cratons of Africa (West  
160 African and Congo Shields), North America (Canadian Shield), northern South America  
161 (Guiana Shield), Fennoscandia, West Australia and Northwest Ireland. Six samples were  
162 derived from rivers draining both modern (New Zealand, Reunion Island, Indonesia) and  
163 ancient (Northern Ireland) volcanic provinces. The rest of studied samples (n=44)

164 corresponded to rivers draining mixed and/or sedimentary rock formations. This latter  
165 category of samples was sub-classified into 2 groups: rivers draining mountains (with  
166 maximum elevation > 1000 m), including most of the world's largest rivers (n=30); and rivers  
167 draining lowlands, such as large Russian rivers (Volga, Don, Northern Dvina) and other small  
168 rivers from e.g. France and the British Isles (n=14).

169

## 170 **2.2. Chemical preparation and sequential leaching procedure**

171 Sieved (<63  $\mu\text{m}$ ) bulk sediment samples were first treated with 5% (v/v) acetic acid (AA)  
172 for removal of carbonate minerals. Easily reducible Fe-oxide fractions were then extracted  
173 using a mixed solution of 15% (v/v) AA and 0.05M hydroxylamine hydrochloride (HH),  
174 following a procedure adapted from Bayon et al. (2002) and Gutjahr et al. (2007). With this  
175 latter leaching step, we specifically targeted the extraction of easily reducible and poorly  
176 crystalline Fe-oxide phases, such as ferrihydrite and lepidocrocite (Poulton and Canfield,  
177 2005). The mineral fractions dissolved during this AA-HH leaching step are referred to as  
178 'HH leachates' in the discussion below. Finally, after subsequent removal of organic  
179 compounds using 5% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solutions, silt-size (~4-63  $\mu\text{m}$ ) detrital  
180 fractions were separated from the residual detritus by centrifugation, prior to digestion by  
181 alkaline fusion (Bayon et al., 2015).

182

## 183 **2.3. Geochemical analyses**

184 Major (Mg, Al, Ca, Mn and Fe) and trace element (REE, Y, Sr) concentrations in the HH  
185 leachates were determined with a Thermo Scientific Element XR sector field ICP-MS, using  
186 the Tm addition method (Barrat et al., 1996). Isobaric interferences on measured REE signals  
187 were corrected using oxide formation rates determined by analysing mono-elemental  
188 solutions of Ba-Ce, Nd-Pr and Sm-Eu-Gd-Tb. The in-run uncertainties on all measurements

189 were generally better than 5%. The accuracy of our data was assessed by analysing seven  
190 different geological certified reference materials (AGV-1; AN-G; BCR-1; DR-N; UB-N; WS-  
191 E; and IF-G, i.e. an iron-ore deposit). All results were in full agreement with reference values  
192 from the literature (<13%; Table S2). Neodymium isotopic measurements were performed at  
193 the Pôle Spectrométrie Océan (Brest) using a Thermo Scientific Neptune multi-collector  
194 ICPMS, after Nd purification by conventional ion chromatography. Mass bias corrections on  
195 Nd were made with the exponential law, using  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ , and  $^{143}\text{Nd}/^{144}\text{Nd}$   
196 corrected values were normalized to a JNdi-1 value of  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$ . Repeated  
197 analyses of a JNdi-1 standard solution during this study gave  $^{143}\text{Nd}/^{144}\text{Nd}$  of  $0.512121 \pm$   
198  $0.000009$  (2 SD, n=33), hence corresponding to an external reproducibility of  $\sim \pm 0.17\epsilon$  (2  
199 SD). Epsilon Nd values ( $\epsilon_{\text{Nd}}$ ) were calculated using  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630$  (Bouvier et al.,  
200 2008).

201

## 202 **3. Results**

### 203 **3.1. Major and trace elements in the leachates**

204 For clarity, measured concentrations ( $\mu\text{g/g}$ ) are reported relative to the initial mass of bulk  
205  $<63\mu\text{m}$  sample prior to leaching (Table S3). The HH leachates are dominated by Fe and Ca,  
206 except for two intensively weathered sediments from the Orinoco River Basin (i.e. Rio Caroni  
207 and Caura), both characterized by comparatively slightly higher Al abundances reflecting  
208 presumably the presence of gibbsite ( $\text{Al}(\text{OH})_3$ ) in these samples. Measured Fe/Ca ratios vary  
209 largely amongst studied leachates, from about 0.04 to 20 ( $\mu\text{g}/\mu\text{g}$ ) (mean value of  $\sim 3$ ). Note  
210 that three sediment samples (Nile, Danube, Var) display even lower Fe/Ca ratios ( $< 0.02$ )  
211 together with very high Ca concentrations (up to 20wt% of initial sample mass), which  
212 indicate that they are largely dominated by carbonate material. Measured Fe/Mn ratios range  
213 from  $\sim 1$  to 230 (mean value of  $\sim 25$ ), mostly reflecting the predominance of Fe- over Mn-

214 oxide phases in most samples. Rare earth elements in sediment leachates also display a large  
215 range of concentrations (with Nd varying from ~ 0.2 to 28  $\mu\text{g/g}$ ; mean ~2.5  $\mu\text{g/g}$ ; Table S3)  
216 and distribution patterns (Fig. 2), as normalized to the world river average silt values (WRAS;  
217 Bayon et al., 2015). The average REE patterns for each river category differ significantly  
218 from one group to another (Fig. 2). Note that shale-normalized REE patterns are also reported  
219 as normalized to Gd in Fig. 2, using the WRAS value for Gd (5.188  $\mu\text{g/g}$ ), in order to remove  
220 any dilution effect. The HH leachates from catchments dominated by igneous/metamorphic  
221 rocks are relatively enriched in light- (LREE) relative to heavy-REE (HREE) (Fig. 2a), while  
222 those from volcanic regions are characterized by marked LREE depletion (Fig 2b), both  
223 displaying shale-normalized patterns that closely resemble those for corresponding detrital  
224 clays (see Fig. 3 of Bayon et al., 2015). In contrast, the sediment leachates from multi-  
225 lithological catchments hosting sedimentary rocks are characterized by more pronounced mid-  
226 REE (MREE) enrichments relative to LREE and HREE (Fig. 2c,d).

227

### 228 **3.2. Neodymium isotopes**

229 Measured Nd isotopic compositions for the HH leachates are given in Table 1, together  
230 with  $\epsilon_{\text{Nd}}$  values for corresponding detrital silt-size fractions. Note that a total of 49 data for  
231 silt-size fractions were already reported in Bayon et al. (2015). Detrital and Fe-oxide fractions  
232 from studied river sediments encompass a large range of  $\epsilon_{\text{Nd}}$  values from -28.7/-30.9  
233 (Churchill) to +4.1/+4.4 (Brantas), respectively (Table 1; Fig. 3a). The Nd isotopic  
234 composition of Fe-oxide phases is almost systematically more radiogenic than associated  
235 detrital sediments, hence resulting in positive  $\Delta\epsilon_{\text{Nd FeOx-Det}}$  values, except for 7 samples (i.e.  
236 Kasai, Niger, Orinoco, Churchill, Kymijoki, Ume, Swilly) all derived from rivers draining old  
237 crystalline basement. River sediments from these ancient igneous/metamorphic provinces and  
238 volcanic regions display  $\Delta\epsilon_{\text{Nd FeOx-Det}}$  close to 0 epsilon units ( $0.5 \pm 1.1$ ;  $n=30$ ; Fig. 3b). In

239 contrast, for the majority of samples where the basin lithology contains sedimentary rocks, the  
240 Nd isotopic composition ( $\epsilon_{\text{Nd}}$ ) of Fe oxide phases is systematically more radiogenic than  
241 associated silicate residues, resulting in positive  $\Delta\epsilon_{\text{Nd Feox-Det}}$  in both lowlands ( $2.1 \pm 0.3$ ;  
242  $n=14$ ) and mountainous ( $2.4 \pm 0.7$ ;  $n=30$ ) catchments. The observed differences in  $\Delta\epsilon_{\text{Nd Feox-Det}}$   
243 values are substantial and significant in magnitude; up to 6 epsilon units.

244

## 245 **4. Discussion**

### 246 **4.1. Significance of Nd isotope and REE compositions in leached sediment fractions**

#### 247 *4.1.1 Identification of leached mineral phases*

248 An important prerequisite for interpreting measured REE and Nd isotopic compositions as  
249 potential weathering signatures in riverine Fe-oxides is to identify the different mineral phases  
250 dissolved during the chemical leaching. As mentioned above, the presence of relatively high  
251 Ca contents in the HH leachates indicates that substantial dissolution of residual carbonates  
252 (i.e. left behind the first AA extraction step) may have occurred. Using an endmember mixing  
253 model based on Sr/Ca and Mg/Ca ratios (Bayon et al., 2007), the relative proportions of  
254 aragonite, low-Mg calcite, high-Mg carbonates and silicate detritus in leached sediment  
255 fractions can be quantitatively estimated (Fig. 4). Most samples from catchments hosting  
256 igneous/metamorphic and volcanic rocks plot on a diffuse mixing trend between the silicate  
257 and low-Mg calcite endmembers, indicating that the Ca budget in these leachates is mostly  
258 controlled by detrital inputs (> 80%). In contrast, the HH leachates from multi-lithological  
259 catchments generally extends towards the field of high-Mg carbonates characterized by low  
260 Sr/Ca ratios (e.g. high-Mg calcite, dolomite, siderite). In leached sediment fractions from the  
261 Ganges and the rivers draining the eastern Canadian shield (Nelson, Churchill), more than  
262 60% of extracted Ca appear to be derived from dolomite (Fig. 4). By analogy, the presence of  
263 high-Mg carbonates and partial dissolution of the silicate detritus could also account for some

264 of the Fe signal in the HH leachates. However, except for a few samples (e.g. Nile, Danube,  
265 Mekong, Nelson, Churchill), most leachates display Fe/Mg and Fe/Al ratios that fall into the  
266 general range of values for various iron oxide formations and marine ferromanganese  
267 deposits, departing significantly from the high-Mg carbonate and silicate detritus endmember  
268 compositions (Fig. 5). This demonstrates that a substantial Fe fraction in the HH leachates is  
269 derived from the dissolution of Fe oxide phases. Importantly, the REE exhibit strong linear  
270 relationships with Fe in sediment leachates (e.g.  $R^2 = 0.84$  for Gd), but no correlation with Mg  
271 or Al ( $R^2 \sim 0$ ; graphs not shown). Therefore, although the chemical leaching may have  
272 resulted in the dissolution of detrital and carbonate phases, the above relationships between  
273 major elements implicitly suggest that the REE signal extracted with our HH solution is  
274 mostly associated with Fe-oxide phases.

275

#### 276 *4.1.2 Potential issues related to the influence of particle-seawater interactions*

277 The fundamental premise behind the use of REE and Nd isotopes in both the silicate  
278 residue and Fe oxides is that they are tracers of source. Whilst the  $\epsilon_{Nd}$  value and REE  
279 distribution patterns of the silicate residue can be relatively unambiguously interpreted as  
280 being controlled primarily by the provenance of the silicate material, REE and  $\epsilon_{Nd}$  signatures  
281 of the Fe-oxide fractions of river sediments may be inherited from multiple sources and hence  
282 be more complicated to interpret. One particular concern is the fact that a number of samples  
283 in this study (n=24) were collected in the marine environment (i.e. estuaries, submarine  
284 deltas, deep-sea fans), raising the possibility that their REE and Nd isotopic compositions  
285 partially reflect the influence of particle-seawater interactions and/or the presence of marine  
286 Fe-oxyhydroxide phases. In estuaries, while intense REE scavenging typically takes place in  
287 the low salinity regions, due to Fe-oxyhydroxide coprecipitation and coagulation of organic  
288 colloids, significant REE release can also occur when salinity increases, through dissolution

289 of lithogenic suspended sediments (e.g. Sholkovitz et al., 2000; Rousseau et al., 2015). Taken  
290 together with other mechanisms, such as groundwater discharge and benthic fluxes (e.g.  
291 Johannesson and Burdige, 2007; Haley et al., 2017), these processes play an important role in  
292 controlling the oceanic distribution of REE and can certainly influence the REE distribution  
293 of labile sedimentary Fe-oxide phases at ocean margins, but also, to some extent, their Nd  
294 isotope composition (e.g. Adebayo et al., 2018). Despite this potential concern, several  
295 investigations have previously suggested that the sedimentary Fe-oxide fractions extracted  
296 from marine depositional settings receiving high inputs of river-borne material could still  
297 preserve a riverine  $\epsilon_{Nd}$  signature (e.g. Bayon et al., 2004; Kraft et al., 2013; Jang et al., 2020).  
298 In this study, this latter hypothesis is supported by the fact that sedimentary Fe-oxides at the  
299 Niger deep-sea fan and those extracted from riverbank sediments collected along the Niger  
300 mainstem, both display similar  $\epsilon_{Nd}$  and  $\Delta\epsilon_{Nd\ Feox-Det}$  values (Table 1). Additionally, we do not  
301 observe any particular relationships between the degree of Nd isotope decoupling between  
302 detrital and Fe-oxide fractions and the types of depositional environments, as inferred from  
303 the similar range of  $\Delta\epsilon_{Nd\ Feox-Det}$  values displayed by samples from both terrestrial (rivers,  
304 deltas) and marine (estuaries, submarine deltas, deep-sea fans) environments (Fig. S1).  
305 Nevertheless, the  $\epsilon_{Nd\ Feox}$  value of the Congo deep-sea fan sediment ( $-15.6 \pm 0.1$ ) appears to be  
306 slightly more radiogenic than those for the suspended particulate loads of the Kasai ( $-15.8 \pm$   
307  $0.1$ ) and Oubangui ( $-16.9 \pm 0.1$ ) rivers; i.e. the two main sediment contributors to the Congo  
308 River. In this particular case, this small Nd isotope discrepancy could possibly arise from the  
309 occurrence of seasonal  $\epsilon_{Nd}$  variability within the Congo watershed (Allègre et al., 1996;  
310 Bayon et al., 2019), complicating the comparison between  $\epsilon_{Nd}$  signatures of suspended loads,  
311 which represent an instantaneous snapshot of the chemical composition of river particulates,  
312 and of fine-grained sediments deposited near the mouth of rivers, which integrate spatially-  
313 integrated source signatures over a much longer period of time. Another exception is the case

314 of the Nile River, for which our leachate  $\epsilon_{Nd}$  value ( $-5.4 \pm 0.1$ ) strongly differs from the  
315 available dissolved  $\epsilon_{Nd}$  estimate ( $-1.5$ ; Scriviner et al., 2004). As discussed in the above  
316 section 4.1.1, this sample is clearly contaminated by the presence of biogenic carbonate  
317 material and, as a consequence, it probably hosts a substantial proportion of seawater-derived  
318 Nd scavenged from overlying water masses having distinctive  $\epsilon_{Nd}$  composition ( $\sim -6.5$ ;  
319 Tachikawa et al., 2004).

320  
321 Based on the above discussion, our working hypothesis in the sections below is that the  
322 observed differences in both the degree of Nd isotope decoupling between detrital and Fe  
323 oxide fractions and the REE distribution patterns in riverine Fe oxides can carry useful  
324 information on weathering patterns in watersheds. This excludes those samples that are  
325 clearly dominated by carbonate phases (i.e. Nile, Danube, Var, Nelson, Churchill; see section  
326 4.1.1). Finally, note that any of the conclusions that will be yielded below regarding the  
327 parameters controlling  $\Delta\epsilon_{Nd, FeOx-Det}$  and other REE indices would still be valid if only  
328 considering the ‘terrestrial’ samples (i.e. excluding those deposited in marine-influenced  
329 environments).

330

#### 331 **4.2 Tracing the sedimentary origin of river Fe-oxides with REE patterns**

332 In addition to seawater-derived Fe-oxyhydroxide phases, another potential source of Fe-  
333 oxides in river sediments includes secondary oxide phases formed in soils during weathering  
334 processes. This type of Fe oxides is expected to dominate in floodplains and other transport-  
335 limited regions characterized by thick soil sequences, low denudation rates and intense silicate  
336 weathering processes (e.g. West et al., 2005). Secondary Fe oxides may also form in response  
337 to the alteration of sulphide minerals; a reaction that can further promote sulphuric acid-  
338 mediated rock weathering in river catchments (e.g. Spence and Telmer, 2005; Calmels et al.,



339 2007; Blattmann et al., 2019). Finally, the alteration and/or erosion of sedimentary rocks  
340 containing ancient marine Fe oxides is likely to influence the REE and Nd isotopic  
341 compositions of leached oxide fractions in sediments issued from glaciated catchments (Jang  
342 et al., 2020), but also in high mountainous and weathering-limited environments with high  
343 denudation rates, where reduced soil cover should be accompanied with limited formation of  
344 recent secondary Fe-oxides. Such preformed oxides correspond to ‘old’ authigenic phases  
345 formed presumably diagenetically at the time of sediment deposition in marine basins, hence  
346 inheriting the  $\epsilon_{Nd}$  of seawater from that basin at that point in time and acquiring the REE  
347 signature of corresponding reduced pore waters (e.g. Haley et al., 2017).

348

349 As reported above, the HH leachates extracted from sedimentary catchments and multi-  
350 lithological river systems typically display MREE-enriched shale-normalized REE patterns,  
351 while those issued from rivers draining crystalline silicate rocks exhibit REE signatures  
352 mostly inherited from corresponding source rocks (Fig. 2). This can be quantified using  
353 indices, such as MREE/MREE\*, that are generally calculated on a linear scale (e.g. Haley et  
354 al., 2004; Martin et al., 2010; Tostavin et al., 2016). In this study, the shape of the REE  
355 patterns was quantified differently, assuming that the behaviour of REE is linear on a log-  
356 linear plot (Lawrence and Kamber, 2005), and using shale-normalized ( $_N$ ) Gd and the  
357 geometric means of  $La_N$  and  $Yb_N$  (as illustrated in Fig. 2). This new index, referred to as  
358 *concavity index* (CI), is defined as follows:

359

$$360 \quad CI = Gd_N / (La_N^6 \times Yb_N^7)^{1/13} \quad (1)$$

361

362 The concavity index can be visually represented in a  $(Gd/Yb)_N$  vs  $(La/Gd)_N$  plot using (Eq. 2),  
363 where  $x$  represents theoretical values for CI (Fig. 6):

364

$$365 \quad (La/Gd)_N = [(Gd/Yb)_N \times 1/x]^{7/6} / x \quad (2)$$

366

367 A CI value of  $\sim 1$  indicates a quasi-linear shale-normalized REE pattern, such as those  
368 displayed by most detrital fractions of river sediments in Fig. 6 (see the CI=1 line), except for  
369 those sediments derived from volcanic provinces. In contrast, a concavity index  $> 1$   
370 corresponds to shale-normalized REE patterns displaying downward-concave shapes,  
371 increasing as the degree of MREE enrichment relative to the other REE increases. Compared  
372 to the commonly used HREE/LREE vs MREE/MREE\* plot (e.g. Haley et al., 2004; Martin et  
373 al., 2010; Du et al., 2016), the concavity index - and its representation within the  $(Gd/Yb)_N$  vs  
374  $(La/Gd)_N$  plot - appears to be particularly well-suited for distinguishing the potential influence  
375 of seawater, pore water and detrital signals in authigenic mineral phases (Fig. 6). While  
376 seawater typically displays  $(Gd/Yb)_N$  values  $< 1$ , sub-seafloor pore waters define a vertical  
377 array in Fig. 6, with  $(Gd/Yb)_N$  values up to  $\sim 2.5$ . This array corresponds to the observed  
378 range of pore water REE signatures encountered in both oxic and reduced environments,  
379 extending from seawater-like distribution patterns (with CI  $\sim 1$ ) to pronounced MREE  
380 enrichments (with CI up to  $\sim 2.5$ ), respectively (e.g. Haley et al., 2004; Abbott et al., 2015).  
381 Most hydrogenous Fe-Mn crusts, diagenetic nodules and Fe-oxyhydroxide phases extracted  
382 from marine sediments overlap well with the field defined by pore waters (Fig. 6b), hence  
383 indicating that this array is probably also representative of marine Fe oxide precipitates.

384

385 In comparison, Fe oxide fractions from river sediments draining crystalline silicate rocks  
386 generally depart from the field of pore waters and marine Fe oxide precipitates (Fig. 7a), with  
387 volcanogenic Fe oxide fractions being clustered in the bottom-left part of the  $(Gd/Yb)_N$  vs.  
388  $(La/Gd)_N$  plot (mean CI value:  $2.1 \pm 0.4$ ; Fig. 2b), and Fe oxides derived from igneous and

389 metamorphic provinces displaying comparatively higher  $(La/Gd)_N$  values and CI values  
390 ranging between  $\sim 2$  and 1.2 (mean CI value:  $1.6 \pm 0.3$ ; Fig. 2a). Instead, many riverine Fe  
391 oxides from both lowland and mountainous catchments draining sedimentary rocks are  
392 located within the field of marine authigenic Fe oxides (Fig. 7a), typically exhibiting CI  
393 values  $> 2$  (mean CI values of  $2.3 \pm 0.3$  and  $2.4 \pm 0.7$ , respectively; Fig. 2c,d). Based on the  
394 above discussion, this observation suggests that such MREE enrichments in riverine Fe oxide  
395 fractions probably trace the source signature of ancient marine Fe oxides associated with the  
396 erosion and/or alteration (followed by subsequent precipitation of Fe-oxyhydroxides in soils  
397 or river systems) of sedimentary rocks. Upon formation, sedimentary rocks are likely to  
398 experience various diagenetic and post-depositional processes, which most probably result in  
399 the preferential dissolution of easily dissolvable hydrogenous Fe oxyhydroxide phases and  
400 possibly explaining why riverine oxides derived from multi-lithological catchments plot in the  
401 upper part of the field defined by pore waters (Fig. 7a). An exception is the case of those HH  
402 leachates extracted from the Rhine, Var and Nile sediment samples, which display markedly  
403 lower CI values ( $\sim 1.6$ ). However, as discussed above, these HH leachates are dominated by  
404 biogenic carbonates and presumably also contain a fraction of marine hydrogenous Fe-  
405 oxyhydroxides, which could hence explain their particular REE distribution patterns.

406

407 Interestingly, in Fig. 7a, a number of samples from multi-lithological catchments depart from  
408 the fields for pore waters and marine Fe-oxyhydroxide phases. This includes the samples from  
409 the Narva and Vistula rivers, which both drain extensive sedimentary rock formations from  
410 the East European platform (Table S1) that could be possibly tagged with distinctive REE  
411 signatures, but also the samples from the Ganges-Brahmaputra river system and the Lower  
412 River Bann in Northern Ireland, which plot in the field of volcanogenic Fe-oxides (Fig. 7a). A  
413 large part of the Lower River Bann catchment is composed of Tertiary basalts (34%; Table

414 S1), meaning that partial dissolution of volcanogenic Fe-oxide and/or detrital particles is  
415 likely to have occurred in this particular sample during the HH leaching step. In contrast, the  
416 Ganges-Brahmaputra river basin only host minor amounts of volcanic rocks (~ 6%), hence  
417 making a contamination by volcanogenic particles unlikely in these samples. Instead, we  
418 speculate that the distinctive REE signatures observed in these leachates could point towards a  
419 particular source composition, perhaps related to the presence of extensive metamorphosed  
420 carbonate deposits within the G.-B. watershed (e.g. Jacobson et al., 2002; Bickle et al., 2005).  
421 This latter hypothesis would be in agreement with the presumed evidence for the presence of  
422 dolomite in the same HH leachates, as inferred from major element data (see section 4.1.1).

423

424 Another striking feature of our results is the fact that a few Fe oxide fractions display REE  
425 concavity indices distinctively higher than previously investigated marine Fe-Mn  
426 oxyhydroxide phases and reduced pore waters (Fig. 7a). This corresponds in particular to the  
427 following samples: Fly (CI = 4.5), Mackenzie (4.1), Gaoping (3.5) and Paraná (3.2) rivers  
428 (Fig. 7a). For these latter samples, we do not have any clear explanation for the occurrence of  
429 such pronounced MREE enrichments. One hypothesis would be that these REE characteristics  
430 relate to the oxidation of sulphide minerals in corresponding watersheds. Previous  
431 investigations have indeed shown that intense sulphide weathering proceeds in at least two of  
432 these river catchments (i.e. Mackenzie and Gaoping), strongly influencing the chemistry of  
433 their dissolved river loads (Calmels et al., 2007; Blattmann et al., 2019). The oxidative  
434 weathering of pyrite and other sulphide minerals commonly leads to the formation of  
435 secondary Fe oxides, but can also result in siderite ( $\text{FeCO}_3$ ) precipitation in environments  
436 dominated by carbonate weathering (e.g. Lara et al., 2015). Siderite is also a common  
437 diagenetic mineral in marine sediments and shales, typically characterized by strong depletion  
438 of LREE (e.g. Bau and Möller, 1992; Franchi et al., 2017) and pronounced MREE

439 enrichments (with CI up to ~50; Rongemaille et al., 2011). In the Sr/Ca vs Mg/Ca plot (Fig.  
440 4), the above mentioned rivers (i.e. Fly, Mackenzie, Gaoping and Paraná) do not appear to  
441 cluster in the immediate proximity of the siderite endmember, hence suggesting that the  
442 occurrence of high CI values in these particular samples may more directly reflect the  
443 presence of secondary Fe oxides derived from sulphide-oxidation processes. While further  
444 investigation would be clearly needed to more precisely identify the various mechanisms  
445 controlling the distribution of REE in river Fe oxide fractions, the main message from the  
446 above discussion is that the shape of shale-normalized REE patterns and corresponding  
447 concavity index can be used to identify the source of leached Fe oxide phases in sediments:  
448 i.e. marine Fe-Mn oxyhydroxide phases, volcanogenic Fe oxides, secondary Fe oxides related  
449 to the alteration of silicate rocks, secondary Fe oxides (or other mineral phases) related to the  
450 oxidation of sedimentary sulphide minerals, and ancient marine oxides associated with  
451 sedimentary rocks (Fig. 7a). Importantly, a remarkable feature of our results is that the  
452 occurrence of pronounced MREE enrichments (with CI > 2) represents an ubiquitous  
453 characteristics of riverine Fe oxides derived from sedimentary catchments.

454

### 455 **4.3. Causes of non zero $\Delta\epsilon_{\text{Nd Feox-Det}}$**

456 For samples draining crystalline rocks (granitic, metamorphic and basaltic rocks), the Fe-  
457 oxide fraction has a  $\epsilon_{\text{Nd}}$  that is similar to the silicate residue (Fig. 3). This indicates that these  
458 Fe-oxides have sourced their Nd, and by inference Fe, from silicate weathering of the source  
459 rocks. Except maybe for the Churchill River sample, which was shown to contain substantial  
460 amounts of sedimentary dolomite (see section 4.1), the observed  $\Delta\epsilon_{\text{Nd Feox-Det}}$  variability in all  
461 other rivers draining crystalline silicate basement most likely reflect subtle Nd isotopic  
462 decoupling during incongruent silicate weathering (e.g. Dausmann et al., 2019). In contrast,  
463 in sedimentary and multi-lithological catchments, the appreciable and systematic difference in

464  $\epsilon_{Nd}$  between the Fe oxide fraction and silicate residue demonstrates that the REE and Fe in the  
465 oxides must have a distinct origin from the silicate detrital material. This observation is  
466 supported by the evidence that  $\Delta\epsilon_{Nd\ Feox-Det}$  display a broad correlation with the concavity  
467 index in leached sediment fractions (Fig. 7b). Based on the above discussion (section 4.2),  
468 this general relationship indicates that the degree of Nd isotope decoupling between paired  
469 Fe-oxide and detrital fractions in river sediments is mostly controlled by the relative  
470 contribution of secondary Fe oxides derived from the alteration of crystalline silicate rocks  
471 (typically characterized by  $\Delta\epsilon_{Nd\ Feox-Det} < 1.6$  and CI values  $< 2$ ) and ancient marine Fe oxides  
472 derived from the erosion and/or alteration of sedimentary rocks in watersheds (with  $\Delta\epsilon_{Nd\ Feox-}$   
473  $_{Det} > 1.6$  and CI values  $> 2$ ). Interestingly, the observed REE differences reported above  
474 between sedimentary watersheds possibly influenced by sulphide weathering (with CI  $> 2.5$ )  
475 and the other high-elevation catchments (with CI  $< 2.5$ ) are not accompanied by any  
476 particular differences in  $\Delta\epsilon_{Nd\ Feox-Det}$  values. This indicates that the difference in the Nd  
477 isotopic composition of paired Fe oxide and detrital fractions probably represents a more  
478 effective tracer than REE distribution patterns for identifying the respective contribution of  
479 sedimentary *versus* crystalline silicate rocks to weathering, whilst REE can provide additional  
480 complementary constraints on the type of Fe oxides and associated weathered rocks.

481

#### 482 **4.4. Links between $\Delta\epsilon_{Nd\ Feox-Det}$ and carbonate weathering indices based on river** 483 **chemistry**

484 In order to further investigate whether riverine Fe-oxide phases can be used for tracing the  
485 origin of weathered rocks in watersheds, we can also compare our  $\Delta\epsilon_{Nd\ Feox-Det}$  values to  
486 previous estimates of carbonate and silicate weathering rates in large river basins, as inferred  
487 from inverse modelling of river chemistry data (Gaillardet et al., 1999). Apart from a few  
488 particular exceptions, most rivers display a general correlation between  $\Delta\epsilon_{Nd\ Feox-Det}$  and the

489 relative contribution of carbonate *versus* silicate rock weathering in corresponding watersheds  
490 (Fig. 8). Amongst the rivers that depart significantly from these relationships, the Yangtze,  
491 Seine and Rhine rivers correspond to highly industrialized and polluted river systems. As  
492 previously suggested for the Seine River using Fe isotopes, it is possible that a fraction of Fe-  
493 oxides hosted in these samples derives from anthropogenic activities (Chen et al., 2014).  
494 Following the discussion in section 4.2, another potential contamination issue comes from the  
495 preferential alteration of easily dissolvable volcanic rocks in watersheds (and also potentially  
496 during the leaching process; Elmore et al., 2011), presumably accompanied by highly  
497 radiogenic signatures. This effect could possibly account for the high  $\Delta\epsilon_{\text{Nd Feox-Det}}$  values  
498 determined in the leached sediment fractions from the Paraná and Fraser river basins, which  
499 both depart from the observed relationships in Fig. 8. Although the influence of any  
500 contamination by volcanogenic material in these particular samples was not suspected from  
501 REE data (i.e. these two samples plotting away from the volcanogenic Fe oxide endmember  
502 in Fig. 6), both catchments do indeed cover extensive areas of flood basalts and other volcanic  
503 formations (~14% and 40%, respectively; Table S1), so that it is possible that their Nd  
504 isotopic composition and corresponding  $\Delta\epsilon_{\text{Nd Feox-Det}}$  signatures are biased towards more  
505 radiogenic composition. Taken together with the findings from sections 4.2 and 4.3, the  
506 general agreement observed between  $\Delta\epsilon_{\text{Nd Feox-Det}}$  and rock weathering indices inferred from  
507 river chemistry data provides additional evidence that leached Fe-oxide fractions from river-  
508 borne sediments can be used to characterize the relative contribution of sedimentary *versus*  
509 crystalline silicate rock weathering in watersheds.

510

#### 511 **4.5. Temperature-dependency of $\Delta\epsilon_{\text{Nd Feox-Det}}$ in lowlands**

512 There is plentiful evidence for the dependence of mineral dissolution rates on climate and  
513 tectonics (e.g. Velbel, 1993; White et al., 1999; West et al., 2005; West, 2012; Gaillardet et

514 al., 2019). As a consequence, the climatic and geomorphic characteristics of studied  
515 catchments can also be used to provide information on the factors controlling the distribution  
516 of Nd isotopes in riverine Fe oxides, and to further investigate their potential utility as  
517 weathering proxies. Below, we examine the relationships between  $\Delta\epsilon_{\text{Nd Feox-Det}}$  and: i) the  
518 mean annual temperature (MAT); ii) the maximum basin elevation; and iii) the percentage  
519 area of carbonaceous sedimentary rocks in studied catchments, which, to a first  
520 approximation, can be used as proxies for the climate, geomorphic and lithological parameters  
521 in catchments. In rivers draining lowlands, measured  $\epsilon_{\text{Nd}}$  differences between paired Fe-oxide  
522 and detrital sediment fractions define a strong exponential anti-correlation ( $R^2 = 0.62$ ;  $n=11$ ;  
523 Fig. 9a) with temperature, but no particular relationships with maximum elevation (Fig. 9b)  
524 and lithology (Fig. 9c). An exponential dependency of  $\Delta\epsilon_{\text{Nd Feox-Det}}$  on temperature is strongly  
525 suggestive of a relationship similar to the Arrhenius dependency of silicate mineral  
526 dissolution rates ( $\varpi$ ) of the form:  $\varpi = A e^{-E_a/RT}$ , where  $A$  is a pre-exponential factor,  $E_a$  the  
527 activation energy and  $R$  the gas constant. Silicate weathering rates increase exponentially  
528 with temperature as demonstrated in previous experimental and field-based investigations  
529 (White et al., 1999; Li et al., 2016). This visible Arrhenius dependency is what would be  
530 predicted for transport-limited weathering regimes, where the temperature dependency of  
531 silicate mineral dissolution occurs at a faster rate than the supply of detrital material through  
532 denudation and erosion. In low-elevation regions and other transport-limited weathering  
533 environments, the above relationship between  $\Delta\epsilon_{\text{Nd Feox-Det}}$  and MAT hence probably reflects  
534 the combination of two factors: 1) the increased rate of secondary Fe oxide formation as both  
535 temperature and silicate weathering intensity increases; and 2) the dissolution of carbonaceous  
536 rocks and associated ancient marine Fe oxides, which occur preferentially between 10 and  
537 15°C in river catchments (Gaillardet et al., 2019).

538



#### 539 **4.6. Elevation-dependency of $\Delta\epsilon_{\text{Nd Feox-Det}}$ in mountainous catchments**

540 For mixed lithology mountainous basins, measured  $\Delta\epsilon_{\text{Nd Feox-Det}}$  values do not display any  
541 correlation with temperature (Fig. 10a), but define instead a striking positive relationship with  
542 maximum basin elevation ( $R^2 = 0.75$ ;  $n=21$ ; Fig. 10b), where the catchments with the highest  
543 elevations display the most positive  $\Delta\epsilon_{\text{Nd Feox-Det}}$  values. Note that those samples potentially  
544 influenced by: i) anthropogenic contamination (Yangtze, Rhine; see section 4.4); ii) the  
545 dissolution of silicate detritus (Mekong; Fig. 5); iii) the dissolution of volcanogenic material  
546 in catchments draining large areas of volcanic rocks (Fraser: 40%; Chubut: 31%; Sefid Rud:  
547 29%; Paraná: 14%; Table S1); or iiiii) the presence of high amounts of carbonates in  
548 corresponding leachates (Nile, Danube, Nelson; section 4.1.1), were excluded from the  
549 regression analysis.

550  
551 One hypothesis is that the observed relationship between  $\Delta\epsilon_{\text{Nd Feox-Det}}$  and maximum elevation  
552 in corresponding watersheds simply reflects the overabundance of sedimentary rocks in  
553 mountainous regions relative to crystalline silicate rocks. Assuming that limestones and  
554 dolostones preferentially outcrop in high-elevation regions rather than in lowlands, it would  
555 make sense that the proportion of ancient marine Fe oxides in river sediments increases as  
556 elevation increases in watersheds. However, neither  $\Delta\epsilon_{\text{Nd Feox-Det}}$  (Fig. 10c), maximum  
557 elevation (Fig. S2a), nor carbonate weathering indices (Fig. S2b) appear to correlate with the  
558 percentage areal coverage of carbonaceous sedimentary rocks in studied watersheds, hence  
559 making this assumption unlikely. This apparent lack of lithological control on  $\Delta\epsilon_{\text{Nd Feox-Det}}$  and  
560 other weathering indices in studied watersheds is coherent with the fact that mineral  
561 dissolution rates in high-mountain environments are primarily controlled by climate and  
562 geomorphic parameters (Riebe et al., 2001; Jacobson et al., 2003; West et al., 2005; West,  
563 2012). To some extent, it could also indicate that a substantial proportion of carbonate

564 weathering in high-elevation watersheds is not derived from carbonaceous sedimentary rocks,  
565 but from various trace carbonate phases associated for example with siliciclastic sediments  
566 (e.g. Hartmann et al., 2014).

567

568 Instead, we hypothesise that in mountainous catchments the observed difference in  $\epsilon_{Nd}$  is large  
569 when a significant fraction of the ancient marine Fe-oxides remains in the sediment, but  
570 becomes gradually reduced as the degree of weathering of the detrital fraction increases, when  
571 'young' secondary oxides derived from modern silicate weathering progressively replace or  
572 overprint the ancient marine Nd signal preserved in riverine Fe oxide fractions. Areas of high  
573 topography typically have high denudation rates and are commonly weathering-limited as  
574 defined by water chemistry (e.g. West et al., 2005; West et al., 2012). This means that the  
575 rate of supply of particulate material in these high-elevation environments is more rapid than  
576 silicate mineral dissolution. Because the rate of silicate mineral dissolution is low relative to  
577 the supply of particulate matter, there is little scope to reset the  $\epsilon_{Nd}$  of Fe oxides through  
578 recrystallization and addition of Nd through silicate mineral dissolution. As elevation  
579 decreases, denudation rates also decrease, making the proportion of silicate mineral  
580 dissolution higher relative the supply of particulate matter. In this case, the  $\epsilon_{Nd}$  of Fe-oxides  
581 becomes progressively reset by supply of Nd from silicate dissolution and, as a consequence,  
582  $\Delta\epsilon_{Nd\ Feox-Det}$  decreases. This hypothesis would be in full agreement with results obtained  
583 earlier for various river basins in Switzerland and New Zealand, which have clearly shown  
584 that silicate weathering rates significantly decrease with increasing elevation (Drever and  
585 Zobrist, 1992; Jacobson and Blum, 2003; Jacobson et al., 2003; Moore et al., 2013).

586

587 Given the temperature dependency that is observed in lowlands, it is possible that the  
588 observed relationship between maximum basin elevation and  $\Delta\epsilon_{Nd\ Feox-Det}$  in mountainous

589 regions (Fig. 10b) could be partially driven by temperature in upstream catchment areas (i.e.  
590 differing from the mean annual temperatures listed in Table 1, which correspond to the mean  
591 average T°C at the entire basin scale). It is well known that temperature decreases with  
592 elevation in mountains. Although this relationship may vary significantly, as a function of  
593 moisture for example, the corresponding temperature gradient (i.e. the so-called adiabatic  
594 thermal lapse rate) is generally about 0.6°C per 100 m (Meyer, 1992). In lowlands, the  
595 observed range of temperature (~ 20°C) between sub-Arctic (e.g. Northern Dvina) and sub-  
596 tropical (Fitzroy) catchments corresponds to about 3  $\Delta\epsilon_{\text{Nd Feox-Det}}$  units (Fig. 9). To a first  
597 approximation, the same range of temperature would represent about a 3500 m difference in  
598 elevation in mountainous regions. Interestingly, this would be fully coherent with the  
599 observed evolution of  $\Delta\epsilon_{\text{Nd Feox-Det}}$  with elevation in Fig. 10, ranging from ~1 to 4 between  
600 about 2000 m and 5500 m. By analogy, this observation would suggest that temperature also  
601 plays a role in controlling the evolution of  $\Delta\epsilon_{\text{Nd Feox-Det}}$  in mountainous regions, through direct  
602 effect on the relative contribution of sedimentary *versus* crystalline silicate rock to total  
603 weathering rates. In contrast to high-elevation catchments, where cold temperatures inhibit  
604 the dissolution of silicate minerals, the gradual shift towards warmer temperatures as  
605 elevation decreases would be accompanied by intensifying silicate weathering and, as a  
606 consequence, enhanced precipitation of secondary Fe oxides, resulting in turn in river  
607 sediments having lower  $\Delta\epsilon_{\text{Nd Feox-Det}}$ .

608

#### 609 **4.7. Final implications and future perspectives**

610 One important implication of our results is that high mountains and glacial environments  
611 are dominated by alteration of sedimentary rocks, whereas silicate weathering prevails in low-  
612 elevation environments. This finding is entirely consistent with previous works, which  
613 proposed a similar decoupled weathering pattern between ‘cold’ tectonically active high

614 mountain ranges - where carbonates and other sedimentary rocks are preferentially weathered,  
615 and 'warm' floodplains - characterised by more intense silicate weathering (e.g. Stallard and  
616 Edmond, 1983; Jacobson and Blum, 2003; Jacobson et al., 2003; Moore et al., 2013; Torres et  
617 al., 2016; Yu et al., 2020). In contrast with the above-mentioned studies, mostly based on  
618 water chemistry data, our new approach that combines the use of REE and Nd isotopes in  
619 leached Fe oxide fractions of river-borne sediments could be potentially applicable to  
620 sediment records, thereby providing a novel means for reconstructing the evolution of  
621 sedimentary *versus* crystalline silicate weathering during past mountain building events, and  
622 its links to the global carbon cycle and climate. This would require a careful selection of  
623 well-suited sedimentary records located near the mouth of large river systems (e.g. Amazon  
624 margin, Bay of Bengal) and characterized by high sedimentation rates of terrigenous material.  
625 An important prerequisite for applying this new approach to sediment records will also be to  
626 investigate whether leached Fe oxide phases truly correspond to river-borne oxides and assess  
627 the extent to which early diagenesis and other post-depositional processes may affect the  
628 preservation of pristine REE and Nd isotope signatures.

629

## 630 **5. Concluding remarks**

631 This study reports on a novel approach for disentangling silicate and non-silicate  
632 weathering signals in the sedimentary record based on rare earth elements and neodymium  
633 isotopes. In modern river sediments, the Nd isotopic difference between paired iron oxide and  
634 detrital fractions ( $\Delta\epsilon_{Nd_{Feox-Det}}$ ) can provide qualitative information on the relative contribution  
635 of sedimentary *versus* crystalline silicate rocks during continental weathering, in line with  
636 previous estimates based on river chemistry data. In order to better distinguish between Fe  
637 oxides derived from the erosion and/or alteration of sedimentary rocks in river catchments and  
638 secondary Fe oxides related to silicate weathering or oxidative weathering of sulphide

639 minerals in soils, a new REE index is also proposed: the concavity index (CI), which provides  
640 a quantitative measure of the shape of shale-normalized patterns and corresponding MREE  
641 enrichments. Overall, our global survey for Nd isotopes and REE in river sediments  
642 demonstrates a clear link between  $\Delta\epsilon_{Nd_{Feox-Det}}$ , temperature and maximum elevation in river  
643 basins, which reflects a gradual temperature-dependent shift from silicate- to carbonate-  
644 dominated weathering regimes, from lowlands to high-mountain environments, respectively.

645

646

## 647 **Acknowledgements**

648 We gratefully acknowledge all our friends and colleagues who very kindly provided us with  
649 the studied samples: O. Adeaga, J. Allard, C. Bigler, F. Busschers, G. Calvès, K. Cohen, F.  
650 Darchambeau, B. Dennielou, F.X. Gingele, S. Goodbread, D. Haynes, P.R. Hill, B.  
651 Hoogendoorn, S. Jorry, G. Kowaleska, T. Leipe, S. Leroy, L. Lopez, J.P. Lunkla, I. Mendes,  
652 D. Meunier, J.C. Montero-Serrano, C. Nittrouer, A. Pasquini, V. Ponomareva, D; Repert, G.  
653 Saint-Onge, E. Schefuß, V. Shevchenko, L. Tiron, S. VanLaningham, A. Wheeler; with  
654 special thanks to A. Borges, S. Toucanne, and Y. Saito. We are also grateful to A. De Prunelé  
655 and J.A. Barrat for assistance during MC-ICPMS analyses and fruitful discussions regarding  
656 REE distribution patterns, respectively. Finally, we thank the Editor (K. Johannesson) and the  
657 anonymous reviewers who provided very constructive and insightful comments on the earlier  
658 versions of this manuscript. This work was funded through an IEF Marie Curie fellowship to  
659 G.B. (SI-PALEO; Grant No. FP7-PEOPLE-2012-IEF 327778). ETT was funded by NERC  
660 Grant (NE/P011659/1) for research into sediment compositions of large rivers.

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## 895 **Figure captions**

896 **Figure 1.** The location of studied sediment samples and corresponding river basins. Yellow  
897 and green diamonds correspond to rivers from cratonic areas (associated with  
898 igneous/metamorphic crystalline basement rocks) and volcanic watersheds, respectively.  
899 Black circles indicate rivers draining coastal plains, lowlands and uplands; and white  
900 triangles, those flowing from mountain environments with an elevation higher than 1000  
901 meters above sea-level. Note that the numbers corresponds to the samples listed in Table  
902 1. The digital elevation model is derived from the ETOPO1 Global relief Model  
903 (<https://www.ngdc.noaa.gov/mgg/global/global.html>). Digital hydrographic information  
904 for rivers and watersheds is derived from HydroBASINS  
905 (<http://www.hydrosheds.org/page/overview>; Lehner and Grill, 2013).

906

907 **Figure 2.** Shale-normalized (WRAS; Bayon et al., 2015) REE patterns for riverine Fe oxides  
908 from (a) igneous and metamorphic crystalline basements; (b) volcanic provinces; (c) low-  
909 elevation regions (< 1000m) draining sedimentary and multi-lithological catchments  
910 regions; and (d) mountainous regions (> 1000m) draining sedimentary and multi-  
911 lithological catchments. For clarity, note that the REE data for leached sediment fractions  
912 (reported relative to the initial mass of bulk sediment) were also normalized Gd<sub>WRAS</sub>.  
913 The thin grey lines correspond to individual samples, while the thicker line with symbols  
914 represent the average shale-normalized pattern for each sample category. Also reported  
915 are the concavity indices (CI) for each category of rivers, calculated using the weighted  
916 geometric means of shale-normalized La and Yb (see text for details).

917

918 **Figure 3.** The distribution of Nd isotopes in paired Fe-oxide and silicate detrital fractions of  
919 world river sediments. In (a) the dotted line corresponds to a 1:1 relationship between  
920 Nd isotopes (expressed using the epsilon notation  $\epsilon_{Nd}$ ) in Fe-oxide and detrital fractions.  
921 In (b)  $\Delta\epsilon_{Nd\ Feox-Det}$  represents the Nd isotopic difference measured between paired Fe-  
922 oxide and detrital silicate fractions. River sediments from crystalline basements (yellow  
923 diamonds) and volcanic watersheds (green diamonds) display near zero  $\Delta\epsilon_{Nd\ Feox-}$   
924  $_{Det}$  values (mean  $0.5 \pm 1.1$ ), indicating that Fe-oxides are mostly derived from alteration  
925 of silicate rocks. The other studied sediment samples (black circles: coastal plains and  
926 lowlands; white triangles: mountains) come from watersheds hosting mixed lithologies,  
927 and are systematically shifted towards positive  $\Delta\epsilon_{Nd\ Feox-Det}$  values, which we interpret  
928 here as mainly reflecting the signature of ancient Fe oxides of marine origin derived from  
929 the alteration and/or erosion of sedimentary rocks.

930



931 **Figure 4.** Relationship between Sr/Ca and Mg/Ca ratios in leached (Fe-oxide bearing)  
932 sediment fractions. The endmember mixing model is adapted from Bayon et al. (2007),  
933 using the following endmember compositions: aragonite (Sr: 10,500 ppm; Mg: 180 ppm;  
934 Ca: 39%; Bayon et al., 2007), low-Mg calcite (Sr: 1,200 ppm; Mg: 250 ppm; Ca: 42.2%;  
935 Bayon et al., 2007), detrital silicate (Sr: 127 ppm; Mg: 9,980 ppm; Ca: 6,735 ppm;  
936 WRAS values; Bayon et al., 2015) and dolomite (Sr: 100 ppm; Mg: 11.5%; Ca: 22.5%;  
937 compilation of literature data). The blue dots on mixing lines correspond to 20%  
938 contribution increments from each two endmembers. The symbols for leached sediment  
939 fractions correspond to river sediments from igneous/metamorphic terranes (yellow  
940 diamonds), volcanic watersheds (green diamonds), low- (black circles) and high-(red  
941 triangles) elevation sedimentary catchments. The black crosses correspond to  
942 corresponding silt-size silicate fractions.

943

944 **Figure 5.** Relationships between (a) Sr/Ca and Fe/Mg and (b) Sr/Ca and Fe/Al in leached  
945 sediment fractions. For symbols; see the caption of Fig. 6. The blue squares correspond to  
946 potential end-members for detrital sediments (WRAS; Bayon et al., 2015) and dolomite  
947 (compilation of literature data). The departure of leached sediment fractions from the  
948 above endmember Fe/Mg and Fe/Al compositions indicates that Fe in these samples is  
949 mostly associated with Fe-oxide mineral phases. The blue fields correspond to the  
950 observed range of elemental ratios for various certified reference materials corresponding  
951 to terrestrial iron formations (FeR-1, Fe-R2, FeR-4, IF-G) and marine Fe-rich precipitates  
952 (OOPE601, OOPE603, NOD-A-1, GSPN-1, GL-O) [data derived from the GEOREM  
953 web portal; Jochum et al., 2005].

954

955 **Figure 6.** Shale-normalized  $(\text{Gd}/\text{Yb})_{\text{N}}$  versus  $(\text{La}/\text{Gd})_{\text{N}}$  plot in (a) pore waters, seawater and  
956 detrital fractions of river sediments; and (b) marine Fe-oxyhydroxide phases. The dashed  
957 lines correspond to theoretical values of the concavity index (CI) of corresponding shale-  
958 normalized REE patterns, calculated geometrically from La and Yb on a log-linear REE  
959 pattern using the following equation  $(\text{La}/\text{Gd})_{\text{N}} = [(\text{Gd}/\text{Yb})_{\text{N}} \times 1/x]^{7/6} / x$ ; where  $x$   
960 represents theoretical CI values. Data for sub-seafloor pore waters (Elderfield and  
961 Sholkovitz, 1987; Sholkovitz et al., 1989; Sholkovitz et al., 1992; Haley et al., 2004;  
962 Bayon et al., 2011; Himmler et al., 2013; Abbott et al., 2015), detrital river sediments  
963 (Bayon et al., 2015), diagenetic and hydrogenous Fe-Mn deposits (Bau et al., 2014) and  
964 leached Fe-oxyhydroxide phases from marine sediments (Bayon et al., 2004; Martin et  
965 al., 2010; Basak et al., 2011; Wilson et al., 2013; Molina-Kescher et al., 2014; Casse et  
966 al., 2019) are shown for comparison. The references used for seawater values are listed in  
967 Table S4. The coloured field in panel (b) represents the range of sub-seafloor pore water  
968 data. Note that the colour gradient from yellow to blue indicates changing pore water  
969 REE compositions from oxic to suboxic conditions, respectively (e.g. Haley et al., 2004;  
970 Abbott et al., 2015).

971

972 **Figure 7.** Using the concavity index (CI) and Nd isotopes for discriminating the source of Fe-  
973 oxides in sediments. (a) Shale-normalized  $(\text{Gd}/\text{Yb})_{\text{N}}$  versus  $(\text{La}/\text{Gd})_{\text{N}}$  plot in leached Fe-  
974 oxide fractions of river sediments. The dashed lines correspond to theoretical values of  
975 the concavity index (CI) of corresponding shale-normalized REE patterns, which enable  
976 to distinguish between several types of Fe-oxides in sediments: marine Fe-oxyhydroxide  
977 phases, volcanogenic Fe-oxides, secondary Fe-oxides (formed via alteration of silicate  
978 rocks), secondary Fe-oxides (formed presumably via oxidative weathering of sedimentary  
979 sulphide minerals), ancient marine Fe oxides derived from the alteration and/or erosion of

980 sedimentary rocks. The coloured field in represents the range of marine Fe-oxyhydroxide  
981 phases inferred from pore water data. Note that the colour gradient from yellow to blue  
982 indicates changing pore water REE compositions between hydrogenous and diagenetic  
983 Fe-oxides formed under oxic and suboxic conditions, respectively. (b) REE concavity  
984 index (CI) versus  $\Delta\epsilon_{Nd\ Feox-Det}$  in leached Fe oxide fractions. The broad correlation  
985 between CI and  $\Delta\epsilon_{Nd\ Feox-Det}$  indicates that the Nd isotope decoupling in paired Fe-oxide  
986 and detrital fractions in river sediments is mostly controlled by the relative contribution  
987 of secondary Fe oxides derived from the alteration of crystalline silicate rocks (when  
988  $\Delta\epsilon_{Nd\ Feox-Det} < 1.6$  and CI values  $< 2$ ) and ancient marine Fe oxides derived from the  
989 erosion and/or alteration of sedimentary rocks in watersheds (when  $\Delta\epsilon_{Nd\ Feox-Det} > 1.6$  and  
990 CI values  $> 2$ ).

991

992 **Figure 8.** Comparison of  $\Delta\epsilon_{Nd\ Feox-Det}$  with carbonate-silicate weathering indices in major  
993 world river basins. The estimates for carbonate-silicate weathering rates reported here for  
994 comparison were calculated by inverse modelling of river chemistry data (Gaillardet et  
995 al., 1999). (a)  $\Delta\epsilon_{Nd\ Feox-Det}$  versus percentage relative contribution of carbonate  
996 weathering to total weathering rates. (b)  $\Delta\epsilon_{Nd\ Feox-Det}$  versus carbonate-silicate weathering  
997 ratio (logarithmic scale). The observed general relationships suggest that  $\Delta\epsilon_{Nd\ Feox-Det}$  can  
998 be used as a proxy for estimating the relative contribution of sedimentary (carbonate-rich)  
999 versus crystalline silicate rock weathering in modern and past environments. The symbols  
1000 with dotted contours correspond those samples that depart from the observed  
1001 relationships due to preferential alteration of basaltic rocks (Paraná and Fraser) or  
1002 anthropogenic influence (Seine, Rhine, Yangtze).

1003

1004 **Figure 9.** Relationships between  $\Delta\epsilon_{Nd\ Feox-Det}$  and (a) mean annual temperature (MAT), (b)  
1005 maximum basin elevation and (c) percentage contributions of carbonate and mixed  
1006 sedimentary rocks in low-elevation river basins (with maximum elevation < 1000 m). The  
1007 observed exponential correlation between  $\Delta\epsilon_{Nd\ Feox-Det}$  and MAT indicate that temperature  
1008 controls the relative contribution of sedimentary *versus* crystalline silicate rock  
1009 weathering in low-elevation watersheds. The dotted circles in the panel (a) corresponds to  
1010 samples that were excluded in the regression analysis, due to potential anthropogenic  
1011 contamination (Seine) or dissolution of volcanogenic particles in watersheds hosting  
1012 substantial basaltic outcrops (Lower River Bann: 34%; Moyola: 32%).

1013

1014 **Figure 10.** Relationships between  $\Delta\epsilon_{Nd\ Feox-Det}$  and (a) mean annual temperature, (b)  
1015 maximum basin elevation and (c) percentage contributions of carbonaceous sedimentary  
1016 rocks in high-elevation river basins (with maximum elevation > 1000 m). The observed  
1017 correlation between  $\Delta\epsilon_{Nd\ Feox-Det}$  and maximum basin elevation reflects a gradual shift  
1018 from carbonate-dominated to silicate-dominated weathering regimes from high mountain  
1019 environments to lowlands. The dotted triangles in the panel (a) correspond to those  
1020 samples that were excluded from the regression analysis due to potential anthropogenic  
1021 contamination (Yangtze, Rhine), dissolution of volcanogenic particles in catchments  
1022 draining large areas of volcanic rocks (Fraser: 40%; Chubut: 31%; Sefid Rud: 29%;  
1023 Paraná: 14%), dissolution of silicate detritus (Mekong) or due to the inferred presence of  
1024 high amounts of carbonates in corresponding leachates (Nile, Danube, Nelson). Note that  
1025 both exponential and linear best fit lines return similar coefficients of correlation ( $R^2 =$   
1026 0.75 and 0.72, respectively). However, the presumed temperature-dependency of this  
1027 relationship suggests that exponential regression analysis may be more appropriate here.

1028