Rare earth elements and neodymium isotopes in world river sediments revisited

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Abstract :

Over the past decades, rare earth elements (REE) and their radioactive isotopes have received tremendous attention in sedimentary geochemistry, as tracers for the geological history of the continental crust and provenance studies. In this study, we report on elemental concentrations and neodymium (Nd) isotopic compositions for a large number of sediments collected near the mouth of rivers worldwide, including some of the world's major rivers. Sediments were leached for removal of non-detrital components, and both clay and silt fractions were retained for separate geochemical analyses. Our aim was to re-examine, at the scale of a large systematic survey, whether or not REE and Nd isotopes could be fractionated during Earth surface processes.

Our results confirmed earlier assumptions that river sediments do not generally exhibit any significant grain-size dependent Nd isotopic variability. Most sediments from rivers draining old cratonic areas, sedimentary systems and volcanic provinces displayed similar Nd isotopic signatures in both clay and silt fractions, with $\Delta\epsilon_{Nd}$ (clay-silt) < |1|. A subtle decoupling of Nd isotopes between clays and silts was identified however in a few major river systems (e.g. Nile, Mississippi, Fraser), with clays being systematically shifted towards more radiogenic values. This observation suggests that preferential weathering of volcanic and/or sedimentary rocks relative to more resistant lithologies may occur in river basins, possibly leading locally to Nd isotopic decoupling between different size fractions. Except for volcanogenic sediments, silt fractions generally displayed homogeneous REE concentrations, exhibiting relatively flat shale-normalized patterns. However, clay fractions were almost systematically characterized by a progressive enrichment from the heavy to the light REE and a positive europium (Eu) anomaly. In agreement with results from previous soil investigations, the observed REE fractionation between clays and silts is probably best explained by preferential alteration of feldspars and/or

accessory mineral phases. Importantly, this finding clearly indicates that silicate weathering can lead to decoupling of REE between different grain-size fractions, with implications for sediment provenance studies.

Finally, we propose a set of values for a World River Average Clay (WRAC) and Average Silt (WRAS), which provide new estimates for the average composition of the weathered and eroded upper continental crust, respectively, and could be used for future comparison purposes.

Keywords : World River sediments, Rare earth elements, Neodymium isotopes, Clay minerals, Weathering, Sediment provenance

1. INTRODUCTION

The basic principles behind the application of rare earth elements (REE) and neodymium (Nd) isotopes as tracers for provenance studies and the evolution of the continental crust were set out by the end of the 1980's. At that time, several large-scale investigations had already documented their distribution in natural waters, sediments and other sedimentary rocks (e.g. Haskin et al., 1966; Haskin and Haskin, 1966; Nance and Taylor, 1976; Piepgras et al., 1979; Elderfield and Greaves, 1982; Goldstein et al., 1984; Taylor and McLennan, 1985; Goldstein and Jacobsen, 1987; Goldstein and Jacobsen, 1988a,b; McLennan, 1989; Elderfield et al., 1990). These early works described REE as a group of relatively insoluble elements, exhibiting little fractionation during Earth surface processes (e.g. Taylor and McLennan, 1985; McLennan et al., 1989). The Nd isotopic composition of suspended particles from major rivers was shown to correlate with the mean age and isotopic signature of source rocks from drainage basins, but also with corresponding Nd isotopic values for dissolved river loads (Goldstein et al., 1984; Goldstein and Jacobsen, 1987; Goldstein and Jacobsen, 1988). Taken together, all the above reference works led to the consensus that Nd isotopes were not significantly fractionated during continental weathering and sedimentary processes. This paved the way for their widespread application to sediment provenance studies (e.g. Goldstein and Hemming, 2003).

Since then, REE and Nd isotopes have been routinely applied to the investigation of sedimentary records and river suspended loads worldwide. In particular, geochemical surveys conducted in large river systems such as the Congo River (Négrel et al., 1993; Gaillardet et al., 1995; Dupré et al., 1996; Allègre et al., 1996), Amazon River (Allègre et al., 1996; Gaillardet et al., 1997; Viers et al., 2008; Bouchez et al., 2011; Roddaz et al., 2014), and Ganges-Bhramaputra River (Singh et al., 2002; Stummeyer et al., 2002; Garzanti et al., 2011) have provided a wealth of information on the processes related to the erosion of the upper continental crust. Over the years, however, a number of case studies showed that the general assumption that REE and Nd isotopes were not fractionated during Earth surface processes was possibly largely overstated, and that both sedimentary and weathering processes could lead under specific conditions to decoupling of REE and Nd isotopes. As an example,

Goldstein et al. (1984) had initially suggested that Nd isotopes did not show any grain-size dependency in sediments. However, a few years later, an investigation of several sand-mud pairs from modern turbiditic deposits at ocean margins worldwide showed instead that different grain-size fractions could display distinct Nd isotopic compositions (McLennan et al., 1989). To some extent, the observed differences between fine- and coarse-grained fractions were attributed to preferential breakdown of young volcanic material. In parallel, numerous investigations of soil sequences also suggested that high REE mobility could occur during weathering under all types of climate, leading occasionally to significant decoupling of Nd isotopes between parent rocks, soils and river waters (e.g. Nesbitt, 1979; Banfield and Eggleton, 1989; Braun et al., 1993; Price et al., 1991; Nesbitt and Markovics, 1997; Ohlander et al., 1996; Ohlander et al., 2000; Ohlander et al., 2014; Aubert et al., 2001; Viers and Wasserburg, 2004; Négrel, 2006). This apparent REE fractionation and Nd isotope decoupling in soil systems has been generally attributed to incongruent dissolution of silicate rocks (e.g. Aubert et al., 2001; Viers and Wasseburg, 2004). Finally, more recently, several studies have shown that non-terrigenous sediment phases such as Fe-Mn oxyhydroxides and/or organic compounds could also host substantial amounts of REE (e.g. Bayon et al., 2002; Freslon et al., 2014), and that their presence in sediments could sometimes bias bulk REE and Nd isotope distributions towards non-detrital signatures (Bayon et al., 2002).

All the above findings have placed some potential limitations on the use of REE and Nd isotopes in sediments and other sedimentary rocks for provenance studies. They have also highlighted the need for reassessing whether the „old“ consensus that both REE and Nd isotopes remains largely unfractionated at the Earth's surface still hold today at a global scale. To this purpose, we have re-examined the geochemical composition of world river sediments, by analysing separate size-fractions of clays (<2µm) and silts (2-63µm) previously cleaned of any non-terrigenous components (e.g. Fe-Mn oxyhydroxides, organic matter). In this study, we report new major/trace element concentrations, clay mineral and Nd isotopic data for river-borne sediments collected worldwide. In addition to providing new information about the degree of decoupling of REE and Nd isotopes during weathering and sedimentary processes, these data are also compared to existing sediment reference values and used to propose a new set of consistent values for the average composition of the weathered/eroded upper continental crust (UCC).

2. MATERIALS AND METHODS

2.1. Sample collection

Overall, a total of 53 modern sediment samples was analysed during the course of this study, corresponding to both marine and riverbank sediments deposited near the mouth of rivers (Fig. 1; Table 1). The rivers selected for this study included some of the World's major rivers (e.g. Amazon, Congo, Mississippi, Nile, Niger, Yangtze, MacKenzie, Volga, Murray, Orinoco rivers), plus rivers draining watersheds characterized by various geological and climatic contexts. Studied samples were classified into four categories depending on corresponding basin characteristics: 1) *„Large rivers“*, for those major rivers draining large continental areas (i.e. by convention $> 100,000 \text{ km}^2$); 2) Rivers draining *‘mixed/sedimentary’* formations, such as the Seine (France), Fly (Papua New Guinea) and Chubut (Argentina) rivers, with watersheds smaller than $100,000 \text{ km}^2$; 3) Rivers draining *‘igneous/metamorphic’* terranes, which include rivers from the Precambrian shields of Fennoscandia, North West Ireland, and Northern South America (Guiana Shield), and a small river from the Hercynian Armorican Massif (Elorn River, France); 4) Rivers draining *‘volcanic’* rocks, from both modern (Kamtchatka peninsula, New Zealand, Reunion Island) and ancient (British Tertiary, Northern Ireland) volcanic provinces.

2.2. Sample preparation

Most bulk sediments were freeze-dried by lyophilization for 48 h. Dry sediments were gently crushed in an agate mortar, prior to sieving through a $63\mu\text{m}$ mesh to collect the fine-grained fraction. A sequential leaching procedure was used for removal of the main non-terrigenous sedimentary components (i.e. carbonates, Fe-Mn oxyhydroxides and organic components), based on a method previously developed by Bayon et al. (2002). To this purpose, about 3 g of dry fine-grained sediments were placed into 50-ml centrifuge tubes, and treated successively with 5% (v/v) acetic acid (AA), mixed 15% (v/v) AA and 0.05M hydroxylamine hydrochloride (HH), and 5% hydrogen peroxide (H_2O_2) solutions, respectively. After completion of the leaching process, detrital residues were rinsed twice with ultrapure ($18.2 \text{ M}\Omega$) water ($\text{MQ-H}_2\text{O}$). Clay ($<2\mu\text{m}$) and silt ($2\text{--}63 \mu\text{m}$) fractions were separated using a two-step centrifugation method. The time and angular velocity required for achieving clay separation were calculated using a formula derived from Stokes's law

(Hathaway, 1956). First, 25 ml MQ-H₂O were added to detrital residues within the tubes, shaken vigorously, and centrifuged for 2 min at 1000 rpm. The clay-rich supernatants were immediately transferred into new 50 ml centrifuge tubes. Another 25 ml MQ-H₂O was added to silt-rich detrital residues, mixed thoroughly again, centrifuged for 2.5 min at 800 rpm, and transferred into corresponding centrifuge tubes. Finally, clay-size fractions were collected after decantation (48 h) and centrifugation at 3500 rpm.

2.3. Analytical procedures

2.3.1. Clay mineralogy

Clay-size fraction samples were oriented on glass slides (oriented mounts) and submitted to X-ray diffraction analysis (XRD). The analyses were run between 2.49 and 32.5° 2 θ on either a D2 PHASER or a D8 ADVANCE Brük er X-ray diffractometer at IFREMER (Brest). Three tests were performed on the oriented mounts: (1) untreated sample, (2) glycolated sample (after saturation for 12h in ethylene glycol), and (3) sample heated at 490°C for 2 hours (Holtzapffel, 1985). Each clay mineral was characterized by its layer plus interlayer interval revealed by XRD analysis. Semi-quantitative estimation of clay minerals abundances ($\pm$ 10%) was done according to the method detailed in Holtzapffel (1985), and performed using the MacDiff software developed by R. Petschick.

2.3.2. Major elements

The major element and minor (Sr) composition of both clay- and silt-size fractions was determined at IFREMER by wavelength dispersive X-ray fluorescence (WD-XRF; Brük er S8 Tiger) analysis of fusion beads. The precision of XRF measurements inferred from replicate analyses of one sediment sample during the course of this study gave uncertainties better than 0.4% for Al₂O₃ and SiO₂ wt%, and 0.2% for all other reported major element concentrations.

2.3.3. Rare earth and other trace elements (Y, Zr, Ba, Hf, Th)

For trace element and Nd isotopic analyses, about 100 mg of dry sediment powder were digested by alkaline fusion (Bayon et al., 2009). Alkaline fusion of iron-bearing geological samples leads to co-precipitation and pre-concentration of REE and a few other trace elements onto Fe-oxyhydroxide phases. This method ensures complete dissolution of very resistant

refractory minerals such as zircons, and allows quantitative determination of REE, Y, Th, Hf, Zr and Ba concentrations (Bayon et al., 2009). Trace element concentrations in clay- and silt-size fractions were determined by ICP-MS (Quad X-Series 2; Thermo Scientific) at both the Pôle Spectrométrie Océan (Brest, France) and the Royal Museum for Central Africa (Tervuren, Belgium). Polyatomic oxide and hydroxide interferences for the REE were corrected using oxide formation rates determined from the analysis of MQ-H₂O₂, Ba+Ce, Pr+Nd and Sm+Eu+Gd+Tb solutions at the beginning of each measurement cycle. Elemental abundances were calculated using the Tm addition method (Barrat et al., 1996; Barrat et al., 2012; Bayon et al., 2009). The precision on all measurements was better than 5%. The accuracy of our data was assessed by analysing BCR-2, JA-2 and BHVO-2 rock standards. The results obtained for these three reference materials are in good agreement with reference values from the literature (Table 2), although exhibiting on average slightly higher concentrations (~ + 4.2%, + 1.2% and + 1.4% for BCR-2, JA-2 and BHVO-2, respectively).

2.3.4. Neodymium isotopes

Neodymium was purified by conventional ion chromatography (see Bayon et al., 2012 for details). Isotopic measurements were performed at the Pôle Spectrométrie Océan using a Thermo Scientific Neptune multi-collector ICPMS. Mass bias corrections on Nd were made with the exponential law, using $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Nd isotopic compositions were determined using sample-standard bracketing, by analysing JNdi-1 standard solutions every two samples. Mass-bias corrected values for $^{143}\text{Nd}/^{144}\text{Nd}$ were normalized to a JNdi-1 value of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$ (Tanaka et al., 2000). Analyses of a La Jolla standard solution during the course of this study gave $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.511860 ± 0.000009 (2 SD, n=4), agreeing well with the certified value (0.511858 ± 0.000007 ; Lugmair et al., 1983) and corresponding to an external reproducibility of $\sim \pm 0.17\epsilon$ (2 SD). Epsilon Nd values (ϵ_{Nd}) were calculated using $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630$ (Bouvier et al., 2008).

3. RESULTS

3.1. Clay mineralogy

The mineralogical composition of forty one clay fractions is reported in Table 1. Both 'large rivers' and 'mixed/sedimentary' basin sediments display a wide range of clay mineral abundances for smectite, kaolinite, illite, chlorite, gibbsite and vermiculite, which reflects the geological and climatic diversity of corresponding drainage basins. For example, clay mineral assemblages associated with tropical rivers from the Guiana Shield (Rio Caroni, Rio Caura) are dominated by kaolinite, while illite/chlorite preferentially occur in high-latitude Fennoscandian rivers. Finally, associated with rivers draining 'volcanic' provinces are mainly composed of smectite.

3.2. Major elements

The major element composition of silt- and clay-size fractions is listed in Table 3 and 4, respectively. Silts and clays from 'large river' basins exhibit a wide range of major element concentrations. For example, silts display SiO_2 and Al_2O_3 concentrations varying between ~ 45-83 wt% (mean: 66.4 ± 10.4 %) and ~ 8-22 wt% (mean: 13.8 ± 4.0 %), respectively. As expected, corresponding clays are characterized by lower SiO_2 (mean: 52.4 ± 4.1 wt%) and higher Al_2O_3 contents (mean: 21.8 ± 3.7 wt%). In 'large river' sediments, MgO and K_2O are also preferentially associated with clays compared to silt fractions (mean values for MgO: 2.6 ± 0.9 wt% and 1.7 ± 0.7 wt%; K_2O : 2.9 ± 0.9 wt% and 2.2 ± 0.6 wt%, respectively). In contrast, average CaO and Na_2O concentrations in major river sediments are slightly depleted in clay-size fractions relative to silts (mean values for CaO: ~ 0.5 ± 0.3 wt% and 0.9 ± 0.8 wt%; Na_2O : ~ 0.6 ± 0.5 wt% and 1.0 ± 0.7 wt%, respectively). To a large extent, sediments from 'mixed/sedimentary' and 'igneous/metamorphic' river basins display the same major-element characteristics described above for 'large river' basins. For example, SiO_2 and Al_2O_3 contents are systematically higher and lower in silt- relative to clay-size fractions, respectively (Tables 3 and 4). In contrast, river sediments draining 'volcanic' provinces are characterized by distinctive major element compositions. Most elements exhibit similar ranges of concentrations in both clays and silts, for example between ~ 36-70 % and 40-69 % for SiO_2 , and between ~ 10-21 % and 11-18 % for Al_2O_3 , respectively. A notable exception is CaO which is significantly enriched in volcanogenic silts (between ~ 1.4-8.6 wt%) compared to clays (between ~ 0.2-2.2 wt%). Finally, the chemical index of alteration (CIA) is also reported in Tables 3 and 4, which corresponds to $\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$, expressed in molar proportions (Nesbitt and Young, 1982). This index provides a quantitative measure of the depletion of mobile (Ca, Na, K) versus immobile (Al) elements

during chemical weathering, which mainly reflects the degree of feldspar alteration. In sedimentary rocks, CIA may vary from about 35-55 (values for fresh igneous rocks) to 100 for kaolinite, which represents the highest degree of weathering (e.g. Nesbitt and Young, 1982). In this study, clays from *large river* basins display higher CIA values (between 68-92; mean 81 ± 6) than corresponding silts (between 54-92; mean 70 ± 10), which reflects their higher degree of alteration. In sediments from *igneous/metamorphic* terranes, CIA exhibits much higher values in tropical river sediments (between 78-96) than in those from cold environments (e.g. Fenno-Scandinavia; CIA between 48-76).

3.3. Rare earth and other trace elements

The distributions of REE and other trace elements in studied river sediments are reported in Table 5 (silts) and Table 6 (clays). As reported earlier (e.g. Taylor and McLennan, 1985), REE display relatively homogeneous concentrations in *large river* sediments. As an example, Nd abundances range from 18-46 ppm (mean: 32.7 ± 6.9 ppm) in silts, and 20-52 ppm (mean: 35.6 ± 8.8 ppm) in clays. Among the other trace elements measured during the course of this study, only Zr and Ba concentrations show significant grain-size dependency. In *large river* basins, Zr concentrations exhibit much higher concentrations in silts (between 139-706 ppm; mean: 445 ± 154 ppm) than in corresponding clays (between 87-228 ppm; mean: 148 ± 31 ppm). Clearly, this indicates preferential sorting of zircons in coarse-grained fractions (Patchett et al., 1984). Note that the average Zr values given above exclude one sample (Orinoco River) characterized by particularly high Zr contents in the two size-fractions. Similarly, preferential Ba enrichment in silts relative to clays can be ascribed to the presence of barite (Schenau et al., 2001; Tables 5 and 6).

3.4. Shale-normalized REE patterns

The REE abundances were normalized to Post-Archean average Australian Shale (PAAS; Taylor and McLennan, 1985). Shale-normalized patterns for World river silts and clays are presented in Fig. 2 and Fig. 3, respectively. Most silt fractions for *large rivers*, *mixed/sedimentary* and *igneous/metamorphic* basins display relatively homogeneous and flat PAAS-normalized patterns (Fig. 2). An exception is the silt fraction from the Orinoco River, characterized by pronounced heavy REE (HREE) enrichment. Considering its high Zr

content (~ 3500 ppm; Table 5), we are confident that this particular shale-normalized REE pattern is related to a zircon-effect. Interestingly, shale-normalized patterns for clay fractions display subtle differences compared to those for corresponding silts. Apart from one sample (Var River), most clay fractions are characterized by slight mid-REE enrichment over LREE and a progressive HREE depletion (Fig. 3). In contrast, both silt and clay fractions from „volcanic’ provinces typically exhibit marked light REE (LREE) depletion, a positive Eu anomaly and, with the exception of a few samples from Reunion Island and Kamchatka, homogeneous and flat HREE patterns (Fig. 2). The strong LREE depletion observed in shale-normalized REE patterns from „volcanic’’ river sediments compared to other studied samples is a geochemical characteristic inherited from the depleted nature of their source rocks.

3.5. Nd isotopes

Results for $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and corresponding ϵ_{Nd} values are given in Table 7. The river sediments analysed in this study encompass a large range of Nd isotopic compositions from $\epsilon_{\text{Nd}} \sim -29$ to $+7$. The less radiogenic values are obtained on sediments from rivers draining the Proterozoic cratonic areas of Guiana [$\epsilon_{\text{Nd}} = -25.2$ (clay) and -28.5 (silt) for Rio Aro] and Fennoscandia [e.g. $\epsilon_{\text{Nd}} = -22.9$ (clay) and -23.1 (silt) for Kiiminkijoki]. The most radiogenic values are determined on clay-size volcanogenic sediments from Kamchatka ($\epsilon_{\text{Nd}} = +7.2$) and Reunion Island ($\epsilon_{\text{Nd}} = +3.8$). Sediments from ‘large river’ basins exhibit a more restricted range of Nd isotopic compositions (Table 8), with clays being characterized by slightly more radiogenic ϵ_{Nd} values (mean: -10.4 ± 3.2) than corresponding silt fractions (mean: -11.3 ± 2.5). In contrast, the Nd isotopic composition of river sediments from ‘mixed/sedimentary’, ‘igneous/metamorphic’ and ‘volcanic’ provinces do not show any significant grain-size dependency, with average $\epsilon_{\text{Nd}} = -9.9 \pm 4.4$ (silts) and -9.5 ± 4.4 (clays), $\epsilon_{\text{Nd}} = -18.9 \pm 4.6$ (silts) and -19.0 ± 4.2 (clays), and $\epsilon_{\text{Nd}} = -1.5 \pm 4.8$ (silts) and -1.5 ± 5.3 (clays), respectively.

4. DISCUSSION

4.1. Evidence for possible grain-size decoupling of Nd isotopes in large river basins

Globally, most studied sediments display similar Nd isotopic signatures in both clay and silt fractions, with $\Delta\epsilon_{\text{Nd}} (\text{clay-silt})$ ranging between -1 and 1 , thereby confirming the general assumption that river sediments do not exhibit any significant grain-size dependent Nd isotopic variability. However, an interesting feature of our results is the small but significant

decoupling of Nd isotopes between clay and silt fractions observed for a few „large river“ sediments. Seven major river sediments (i.e. Mississippi, Nile, Volga, Mekong, Don, Fraser and Chao Phraya rivers) are indeed characterized by $\Delta\epsilon_{\text{Nd}}(\text{clay-silt}) > 1$, hence systematically shifted towards more radiogenic signatures. The other fourteen sediments do not show any particular grain-size dependent Nd isotopic variability (Fig. 4). Among all the remaining clay-silt pairs analysed during the course of this study (n=28), only five displayed $\Delta\epsilon_{\text{Nd}}(\text{clay-silt})$ higher than unity: two from ‘mixed/sedimentary’ basins (Fly and Chubut rivers), and three from ‘igneous/metamorphic’ cratonic areas (Rio Aro, Tana and Lule rivers). In these latter settings, weathering processes are known to cause high REE mobility within soils, and subsequent redeposition into secondary clay or phosphate minerals (e.g. Aubert et al., 2001). Previous studies have shown that both major rock-forming minerals (mainly feldspars) and accessory phases, such as apatite, allanite, monazite or zircon, can control the REE budget in granitic/granodioritic soil environments, occasionally leading to marked heterogeneous distribution of Nd isotopes along vertical soil profiles (e.g. Aubert et al., 2001; Viers and Wasserburg, 2004; Négrel, 2006; Ohlander et al., 2014). Without going into specific details about each sediment sample, the observed differences in Nd isotopic compositions between clay- and silt- fractions from the Rio Aro, Tana and Lule rivers are most likely related to the incongruent processes listed above. These samples were also collected from river banks, and one cannot exclude the influence of local factors (e.g. mixing between different „local“ sources) that could possibly have caused grain-size geochemical heterogeneity and, perhaps to some extent, the observed ϵ_{Nd} variations. Nevertheless, in absence of any systematic Nd isotopic variability between clays and silts from rivers draining both ‘igneous/metamorphic’ and ‘volcanic’ watersheds, we conclude that no major decoupling of Nd isotopes occurs during silicate weathering, at least at the scale of our large survey of World river sediments.

Based on the above, it seems therefore unlikely that the grain-size Nd isotopic decoupling observed between clay and silt fractions in the aforementioned ‘large river’ basins is related to incongruent weathering processes. Possible explanations accounting for the observed decoupling would also involve sorption of Nd onto clays from the dissolved load of rivers, which tend to have slightly more radiogenic Nd isotopic compositions than corresponding suspended loads in major rivers draining primarily sedimentary rocks (Goldstein and Jacobsen, 1987). In addition, anthropogenic pollution is known to affect the modern

distribution of REE in rivers (e.g. Kulaksiz and Bau, 2013), and hence could also perhaps account for the small shift observed between clays and silts. In this study, however, our sequential leaching procedure has certainly led to quantitative removal of any adsorbed fraction and/or authigenic/organic phases that would host any dissolved or anthropogenic REE signal, respectively. We are confident therefore that these hypotheses cannot explain the Nd isotopic differences observed between clay and silt fractions.

In contrast with the other categories of rivers investigated during the course of this study, *'large river'* basins host a wide diversity of lithologies. The observed ϵ_{Nd} grain-size systematic decoupling could be hence best explained by preferential weathering of particular rock types on land. In fact, this hypothesis would be directly supported by evidence that the river sediments exhibiting $\Delta\epsilon_{Nd} \text{ (clay-silt)} > 1$ are generally also characterized by high proportions of smectite and vermiculite, i.e. two groups of clay minerals typically related to alteration of volcanic rocks (Fig. 5). Indeed, many of the clay-silt pairs displaying high $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ in this study [i.e. Fraser (+4.3), Nile (+2.5) and Chubut (+1.2) rivers] correspond to basins with large occurrences of basaltic outcrops. For example, volcanic rocks represent about 40% and 25% of the entire Fraser and Chubut river basin areas, respectively (Peucker-Ehrenbrink et al., 2010; Pasquini et al., 2005). Most likely, in such river basins, preferential alteration of volcanic rocks could lead to overrepresentation of volcanogenic clays in the fine-grained suspended load transported to the ocean, thereby explaining the observed ϵ_{Nd} decoupling between clays and silts. A recent investigation of river sediments from the Ganges basin also led to similar conclusions, clearly showing that suspended particulates in surface waters displayed a basalt-like Nd isotopic signature, while ϵ_{Nd} values of corresponding bedloads were shifted significantly (to about 6 epsilon units) towards geochemical compositions of regional crystalline and sedimentary rocks (Garçon and Chauvel, 2014). Interestingly, similar ϵ_{Nd} variations between sand and mud fractions have also been reported in recent marine turbidites (McLennan et al., 1989). In that study, McLennan and co-authors proposed that the observed grain-size ϵ_{Nd} variability (up to 7 epsilon units) was controlled by mechanical separation during sedimentary transport and sorting. While this hypothesis could also equally apply to our major river sediments, the presence of high proportions of smectites associated with high $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ values suggests instead that preferential weathering of basalts relative to other rock types may be a more appropriate explanation. In Fig. 5, the rivers draining volcanic watersheds do not display any particular grain-size isotopic variability. However, in these river basins, volcanic rocks

represent the dominant lithology, and their erosion/weathering hence leads to products of erosion having similar Nd isotopic compositions. An exception however is the case of the clay-silt pair for the Mississippi River sediment, also characterized by $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ higher than unity (+1.5). In contrast to the aforementioned river basins, the Mississippi watershed is mainly composed of marine sedimentary formations, with only minor outcrops of extrusive rocks (Peucker and Ehrenbrink, 2010). Presumably, in this particular context, one possible explanation would be that both the presence of smectites and observed ϵ_{Nd} grain-size dependent decoupling have been inherited from ancient episodes of basalt weathering, during former sedimentary cycles. This would suggest that grain-size decoupling of Nd isotopes can also take place in sedimentary basins.

4.2. Fractionation of REE between clay and silt fractions during silicate weathering

Another interesting feature of our results is the apparent REE fractionation between clay and silt fractions. Average shale-normalized REE patterns for the four distinct groups of sediments investigated in this study are presented in Fig. 6. With the exception of sediments from 'volcanic' areas, average silt fractions display shale-normalized REE distributions similar to PAAS, hence characterized by homogeneous and flat patterns (Fig. 6A). This general uniformity of REE patterns in fine-grained sediments and other sedimentary rocks is well documented in the literature, being generally considered as representative of the average UCC composition (Taylor and McLennan, 1985). However, as shown here, the REE distribution in river clays clearly departs from a typical UCC-like shale-normalized pattern (Fig. 6B). This is nicely illustrated when normalizing average REE concentrations for clays to corresponding silt values (Fig. 6C). In Fig. 6C, all four sediment groups exhibit progressive enrichments from HREE to LREE, starting from relatively homogeneous Lu_{clay}/Lu_{silt} values close to unity. In addition, except for 'volcanic' sediments, average clays from all three other groups are also characterized by positive Eu anomalies relative to corresponding silt fractions.

Most likely, preferential basalt weathering in watersheds cannot possibly explain the observed fractionation between clays and silts. Indeed, if this was the case, one would expect clay fractions to exhibit depleted LREE concentrations relative to coarse-grained sediments. Instead, in contrast to what was proposed above to account for the observed ϵ_{Nd} decoupling between clays and silts, the apparent grain-size fractionation for REE is probably related to

selective alteration of LREE and Eu enriched mineral phases during silicate weathering. Investigations of soil profiles have often documented the preferential loss of LREE over HREE in upper soil horizons (e.g. Tyler, 2004). Both experimental and soil studies have shown that the early stages of weathering in granitic/granitoid settings involve alteration of accessory minerals, such as apatite, allanite and sphene (e.g. Braun et al., 1993; Harlavan and Erel, 2002; Aubert et al., 2004; Erel et al., 2004; Bayon et al., 2006). All these minerals are characterized by significant LREE enrichments over other REE (Taylor and McLennan, 1985), and have been shown to play an important role in REE cycling in soils (e.g. Banfield and Eggleton, 1989; Braun et al., 1993; Condie et al., 1995). Despite displaying much lower REE concentrations than the abovementioned accessory minerals, alteration of K-feldspars and plagioclase can also influence the distribution of REE in soils (e.g. Aubert et al., 2001; Viers and Wasserburg, 2004). Both minerals display pronounced LREE enrichments and marked Eu positive anomalies (e.g. Taylor and McLennan, 1985). In soils, secondary clay minerals act as a net sink for these elements released incongruently during silicate weathering, hence leading to preferential incorporation of both LREE and Eu (e.g. Aubert et al., 2001; Viers and Wasserburg, 2004). Taken together, all the above consideration identifies a possible mechanism for fractionating REE in clay and silt fractions from river sediments. While these processes have been mainly described locally so far, our results suggest that the same observation could also equally apply at a global scale. Using major and trace element data, we have further investigated whether preferential alteration of feldspars could indeed possibly explain the observed grain-size dependent REE fractionation in studied samples. No relationship was found however between parameters related, at least to some extent, to feldspar alteration (e.g. CIA, Sr) and the degree of Eu-anomaly and LREE enrichment (e.g. La/Yb ratios) between clays and silts. To a first approximation, the absence of any particular relationship between major/trace element data and the observed grain-size REE decoupling could hence suggest that this latter is mainly controlled by alteration of secondary accessory minerals, rather than by feldspar weathering. Of course, different lithologies have a different susceptibility to erosion processes, and one would certainly expect that this can also affect the degree of REE fractionation in soils. In our study, this is suggested by the fact that the magnitude of LREE enrichments between clays and silts vary from one group to another, from La_{clay}/La_{silt} ratios ~ 1.5 for sediments from 'igneous/metamorphic' river basins, to ~ 1.3 in 'mixed/sedimentary' basins, ~ 1.2 in 'large rivers', and ~ 1.1 in 'volcanic' areas (Fig. 6C). Compared to granitic/granitoid settings, basalt weathering leads most probably to more

congruent release of REE. This would hence explain the smaller degree of fractionation observed between clay and silt fractions from 'volcanic' river sediments.

4.3. Geochemical significance of the World River average clay (WRAC) and silt (WRAS)

All the results discussed above have allowed us to place further constraints on the weathering and erosion processes that ultimately control the distribution of REE and Nd isotopes in clay- and silt-size fractions of river sediments. Collectively, in this study, the cumulative area of the twenty two major rivers with watersheds larger than $> 100,000 \text{ km}^2$ accounts for $30.5 \times 10^6 \text{ km}^2$. This represents about 30% of the entire continental area that drains into the global ocean ($105 \times 10^6 \text{ km}^2$; Milliman and Farnsworth, 2011). This relatively large coverage area suggests that the mean values reported in Tables 3-7 for 'large rivers' can provide reliable estimates for the geochemical composition of a World River average clay and World River average silt, hereafter referred to as WRAC and WRAS, respectively.

This assumption is first supported by Nd isotope evidence. The mean ϵ_{Nd} values determined in this study for 'large river' clays ($\epsilon_{\text{Nd}} = -10.4 \pm 3.2$) and silts ($\epsilon_{\text{Nd}} = -11.3 \pm 2.5$) agree well with previous estimates for the upper continental crust, inferred from investigations of river particulates (-11.4 ± 2.5 ; Goldstein et al., 1984) and aeolian loess deposits (-10.3 ± 1.2 ; Chauvel et al., 2014). In addition, major and trace element chemistry also provides further constraints on the geochemical significance of WRAC and WRAS. In Table 8, the major element compositions for WRAS and WRAC are compared to other global reference data for the upper continental crust (UCC; Rudnick and Gao, 2003), the average suspended sediment in World rivers (Viers et al., 2009; which we refer to as SSWR herein), and continental-scale reference data for loess (Gallet et al., 1998; Jahn et al., 2001) and soil (Shacklette and Boerngen, 1984; de Caritat et al., 2012; Reimann et al., 2012; Négrel et al., 2015). Average loess data are generally considered as good estimates of the composition of the eroded upper continental crust (e.g. Taylor et al., 1983; Gallet et al., 1998). The average geochemical composition of soils on continents sometimes differ from average crustal values (e.g. de Caritat et al., 2012), but their comparison in the context of this study to our average river clay and silt compositions still provides useful constraints on the significance of WRAC and WRAS. Overall, both major element compositions (Table 8) and UCC-normalized spider diagrams (Fig. 7) show similarity between our river sediment estimates and other global reference values. For SiO_2 , World River Average Silt ($66.4 \pm 10.3 \text{ wt\%}$) agrees relatively well

with reference values for UCC and average loess/soil worldwide (between 65 and 78 wt%; Table 8). In contrast, the SiO_2 value for WRAC is significantly lower (52.1 ± 4.1 wt%), but very similar to the average SiO_2 concentration of suspended sediments in world rivers (SSWR; 51.9 wt%). Similarly, major-element compositions for WRAC and SSWR indicate preferential enrichment for Al_2O_3 , TiO_2 and Fe_2O_3 in river clays and suspended sediments relative to WRAS, UCC and continental loesses and soils. These elements are immobile during alteration processes, and hence particularly enriched in the products of chemical weathering exported from soils (e.g. Young and Nesbitt, 1998). One of the most striking differences between our river sediment estimates and average loess and soil compositions is the strongly negative Ca anomaly relative to UCC (Fig. 7). Clearly, this reflects the absence of carbonates in our leached detrital fractions and could explain, by simple dilution effect, the observed differences in REE abundances between WRAS, WRAC and average loess compositions (Fig. 7). Similar to loess and soils, both WRAC and WRAS also display negative UCC-anomalies for Ba, Sr, and/or Na in UCC-normalized diagrams, which indicate preferential losses of mobile elements during continental weathering (Fig. 7). In contrast, however, two other mobile elements (MgO and K_2O) appear to display substantially higher concentrations in river clays and silts (but also in UCC and SSWR) compared to average soil values worldwide (Table 8). Previous studies have already pointed out the discrepancy for some elements between the average soil composition on continents and UCC estimates (e.g. de Caritat et al., 2012; Négrel et al., 2015). Continental-scale surveys for soil geochemistry typically integrate analyses for the upper soil layers (e.g. the first tens of centimetres of soils; de Caritat et al., 2012; Reimann et al., 2012). Because weathering processes redistribute elements within soil profiles, the upper soil horizon is generally characterized by strong depletion in mobile elements and its composition may therefore not be representative of the fine-grained sediment load exported by rivers. This would explain why our estimates for WRAC and WRAS differ from average soil compositions on continents. Therefore, based on the above consideration, we propose that the average values determined for our so-called World River average clay (WRAC) and average silt (WRAS) most likely represent reliable estimates for the average composition of the silicate portion of both the *weathered* and *eroded* upper continental crust, respectively.

4.4. Comparison of REE abundances in WRAC and WRAS to other sediment reference values

The PAAS reference sediment was defined as the average of 23 Australian shales ranging in age from Proterozoic to Triassic (Nance and Taylor, 1976). Over the years, PAAS has been widely used as a standard for comparison in various geochemical studies. The geochemical values for PAAS are generally derived from Taylor and McLennan (1985), but its REE abundances have been recently revised by Pourmand et al. (2012). Other well-known sets of reference values for REE in sediments also include two composite materials for North American Palaeozoic shales (NASC; Haskin and Haskin, 1966; Gromet et al., 1984) and European shales (ES; Haskin et al., 1966b), and MUQ (Mud from Queensland), an average of fine-grained alluvial sediments from NE Australia (Kamber et al., 2005). In addition, an average chemical composition for suspended sediments in World Rivers (referred to as SSWR in this study) has been recently compiled (Viers et al., 2009), which can also serve for comparison purposes. Similarly, an earlier estimate for the average REE distribution in river suspended load had also been proposed as a reference for the normalization of modern erosion products (Goldstein and Jacobsen, 1988b). In Fig. 8, our estimated REE concentrations for World River average clay (WRAC) and silt (WRAS) are normalized to PAAS values, together with MUQ, SSWR and the average river suspended load proposed by Goldstein and Jacobsen (1988b; referred to as ARSL in this study). For comparison, both the „old“ (Taylor and McLennan, 1985) and „recent“ (Pourmand et al., 2012) PAAS values have been considered for normalization. Clearly, the five distinct reference sediments (WRAC, WRAS, MUQ, SSWR, ARSL) exhibit marked MREE enrichments over both LREE and HREE (i.e. MREE „bulge“) when normalized to the „old“ PAAS values. While it is clear that the use of the most „recent“ set of PAAS data leads to overall flattening of REE patterns, all five reference sediments still show prominent positive Eu anomalies and, to a lesser extent, minor Gd and Ce anomalies. Without going into details, these observations clearly suggest that Eu concentration in PAAS differs from the average upper continental crust abundance, and that caution should be taken with PAAS-normalization as it can lead to anomalous apparent Eu enrichments. Nevertheless, apart from Eu, our average REE data for WRAS display a remarkably flat pattern when normalized to „recent“ PAAS values, while exhibiting slightly lower concentrations (about 10%). As discussed previously, the shale-normalized pattern for MUQ is clearly shifted towards basaltic signatures, exhibiting strong LREE depletion (Kamber et al., 2005). However, the strong HREE depletion of estimates for river suspended sediments (i.e. SSWR and ARSL) relative to WRAS is quite unexpected, as these sediment references represent estimates for the fine-grained material transported by World rivers (Fig. 7). The cause for this difference is unclear, but could be due, at least partly, to the fact that

the compiled data for SSWR are derived from a large number of sources, with possible analytical bias between different laboratories (e.g. incomplete dissolution of heavy minerals such as zircons during sample preparation). Another possible explanation would be that sediment sorting during river transport associated with preferential settling of heavy minerals within the river water column leads to natural depletion of zircons and other dense accessory minerals in river suspended loads worldwide (e.g. Bouchez et al., 2011; Garçon and Chauvel, 2014). In any case, both explanations would result in the apparent HREE depletion observed in SSWR and ASRL relative to our average estimates for world river clays and silts.

5. CONCLUDING REMARKS

The data presented in this study show that incongruent dissolution of silicate rocks during continental weathering clearly leads to grain-size decoupling of REE in river sediments. Selective alteration of feldspars and/or accessory mineral phases in soils causes progressive enrichment of LREE and Eu in the clay-size fraction transported by rivers compared to corresponding silts. At a global scale, these processes do not appear to significantly decouple Nd isotopes. In most river sediments, the Nd isotopic composition of clay-size fractions is indeed very similar to corresponding silt signatures. An exception is the case of a few major river systems, in which clays typically display more radiogenic signatures than associated silts. We attribute this apparent grain-size Nd isotopic variability to preferential weathering of volcanic and/or sedimentary rocks relative to other lithologies during continental weathering. This result has implications for sediment provenance studies, suggesting that the radiogenic isotopic signature of fine-grained river sediments may not be necessarily representative of the average composition of corresponding drainage basins. Finally, our results for major river sediments are used to define a World River Average Clay (WRAC) and World River Average Silt (WRAS), whose geochemical compositions could serve as new estimates for the average composition of the weathered and eroded upper continental crust, respectively. In particular, the proposed set of REE values for river silts (WRAS) could represent a more appropriate alternative than PAAS for future shale-normalization purposes.

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FIGURE CAPTIONS

Figure 1. World map and location of studied river-borne sediments. The rivers selected for this study include some of the World's major rivers and rivers draining watersheds characterized by various geological contexts. The green-colored drainage basins correspond to the 22 studied river systems with areas > 100,000 km².

Figure 2. Shale-normalized (PAAS; Taylor and McLennan, 1985) REE patterns for World river silt fractions. Symbols: large river basins (black circles); rivers draining sedimentary formations (white diamonds); rivers draining igneous/metamorphic terranes (light grey squares); rivers draining volcanic rocks (dark grey triangles).

Figure 3. Shale-normalized (PAAS; Taylor and McLennan, 1985) REE patterns for World river clay fractions.

Figure 4. Relationship between $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ and $\epsilon_{Nd} \text{ clay}$. $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ represents the difference between the Nd isotopic compositions of clay and silt fractions in World river sediments. Arbitrarily, we assume that the samples characterized by $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ between -1 and +1 do not display any significant grain-size dependent Nd isotopic variability (i.e. those falling within the yellow shaded area). Symbols: large river basins (black circles); rivers draining sedimentary formations (white diamonds); rivers draining igneous/metamorphic terranes (light grey squares); rivers draining volcanic rocks (dark grey triangles).

Figure 5. Relationship between $\Delta\epsilon_{Nd} \text{ (clay-silt)}$ and clay mineralogical composition of World river sediments. The river sediments with $\Delta\epsilon_{Nd} \text{ (clay-silt)} > 1$ are generally characterized by high proportions of smectite and vermiculite, i.e. two clay-mineral groups typically related to alteration of volcanic rocks. Symbols: large river basins (black circles); rivers draining sedimentary formations (white diamonds); rivers draining igneous/metamorphic terranes (light grey squares); rivers draining volcanic rocks (dark grey triangles).

Figure 6. Average shale-normalized (PAAS; Taylor and McLennan, 1985) REE patterns for silt-fractions (A) and clay-fractions (B) of World river sediments. (C) Distribution patterns of average clay versus corresponding silt fractions, illustrating the fractionation of REE during silicate weathering.

Figure 7. UCC-normalized spider diagrams for World River Average Clay (WRAC) and World River Average Silt (WRAS). The patterns for European (Gallet et al., 1998) and Chinese (Jahn et al., 2001) average loess compositions, and for the average suspended sediment of World Rivers (SSWR; Viers et al., 2009) are shown for comparison. Major and trace element concentrations for UCC composition are from Rudnick and Gao (2003).

Figure 8. Shale-normalized REE patterns for World River Average Clay (WRAC) and World River Average Silt (WRAS), using PAAS values of both Taylor and McLennan (1985) and Pourmand et al. (2012). The patterns for three other reference sediments: Mud of Queensland (MUQ; Kamber et al., 2005), Suspended sediment in World Rivers (SSWR; Viers et al., 2009) and the average river suspended load (ARSL; Goldstein and Jacobsen, 1988b) are shown for comparison.

Table 1

Geographical location of studied river sediments and corresponding clay-mineral compositions.

Sample #	River	Area (10 ³ km ²)	Country	Sampling Environment	Lat.	Long.	Smec (%)	Illi (%)	Kaol (%)	Chlo (%)	Gibb (%)	Verm (%)
Large rivers												
1	Amazon	6300	Brazil	Sub Delta	3.10	43.39	59	15	20	6	-	-
2	Congo	3800	DRC	Margin	-5.70	11.23	16	5	79	-	-	-
3	Mississippi	3300	USA	Sub Delta	28.93	89.49	75	13	12	-	-	-
4	Nile	2900	Egypt	Margin	32.51	30.38	73	6	19	<5	-	-
5	Niger	2200	Nigeria	Sub Delta	3.20	6.68	37	9	54	-	-	-
6	Yangtze	1800	China	Estuary	31.62	121.01	21	49	11	19	-	-
7	MacKenzie	1800	Canada	Sub Delta	69.26	-137.29	5	53	21	21	-	-
8	Volga	1400	Russia	Estuary	45.71	47.92	61	11	6	5	-	17
9	Murray	1100	Australia	River	-35.41	139.23	24	41	32	-	-	-
10	Orinoco	1100	Venezuela	River	7.65	-66.18	-	-	not analysed			
11	Danube	820	Romania	River	45.06	29.62	52	38	10	-	-	-
12	Mekong	800	Cambodia	Delta	10.96	105.06	<5	20	38	18	-	23
13	Yellow River	750	China	Delta	37.80	118.91	49	33	7	12	-	-
14	Amu Darya	535	Uzbekistan	River	42.22	60.12	-	-	not analysed			
15	Don	420	Russia	River	47.29	39.10	73	14	7	5	-	-
16	Northern Dvina	357	Russia	Estuary	65.09	39.00	41	28	16	15	-	-
17	Fraser	230	Canada	Sub Delta	49.16	-123.37	51	19	5	25	-	-
18	Rhine	220	Netherlands	Estuary	51.91	4.48	52	27	7	14	-	-
19	Vistula	200	Poland	Gulf	54.65	19.28	<5	60	14	26	-	-
20	Red River	160	Vietnam	Delta	20.26	106.52	<5	64	14	20	-	-
21	Chao Phraya	160	Thailand	Delta	13.57	100.58	55	13	22	10	-	-
22	Loire	120	France	Estuary	47.28	-1.90	46	27	19	9	-	-
Rivers draining mixed/sedimentary formations												
23	Seine	79	France	Estuary	49.47	0.42	63	17	20	-	-	-
24	Fly	76	PNG	Sub Delta	-8.67	144.00	24	35	6	35	-	-
25	Guadiana	67	Portugal	Estuary	37.21	-7.42	-	-	not analysed			
26	Chubut	45	Argentina	River	-43.25	-65.20	-	-	not analysed			
27	Mae Klong	31	Thailand	River	13.43	99.95	47	32	21	-	-	-
28	Shannon	23	Eire	Estuary	52.69	-8.91	13	58	5	23	-	-
29	Adour	16	France	River	43.49	-1.47	5	55	20	21	-	-
30	Sefid Rud	13	Iran	River	37.47	49.94	61	20	7	11	-	-
31	Mayenne	4.4	France	River	47.50	-0.55	<5	29	29	13	-	30
32	Var	2.8	France	River	43.67	7.20	9	69	<5	19	-	-
33	Blackwater	1.1	Ireland	River	54.51	-6.58	19	16	19	46	-	-
34	Moyola	0.3	Ireland	River	54.75	-6.52	9	54	18	19	-	-
Rivers draining igneous/metamorphic terranes												
35	Rio Caroni	95	Venezuela	River	8.33	-62.71	<5	5	66	15	13	-
36	Narva	56	Estonia	Estuary	59.54	27.58	<5	75	12	12	-	-
37	Rio Caura	48	Venezuela	River	7.58	-64.94	-	5	95	-	-	-
38	Kymijoki	37	Finland	Estuary	60.46	26.91	-	72	19	9	-	-
39	Rio Aro	30	Venezuela	River	7.39	-64.01	-	-	not analysed			
40	Ume	26	Sweden	Estuary	63.72	20.27	-	-	not analysed			
41	Lule	25	Norway	River	65.68	21.82	-	-	not analysed			
42	Tana	16	Norway	River	70.20	28.19	-	-	not analysed			
43	Kiiminkijoki	3.8	Finland	River	65.13	25.73	<5	57	-	40	-	-
44	Foyle	2.9	Ireland	River	54.76	-7.45	-	-	not analysed			
45	Elorn	0.3	France	Estuary	48.40	-4.38	-	59	-	41	-	-
46	Swilly	0.1	Ireland	River	54.93	-7.81	14	37	25	24	-	-
Rivers draining volcanic rocks												
47	Kamchatka	56	Russia	River	-	-	-	-	not analysed			
48	Waikato	14	New Zealand	River	-38.49	176.29	93	<5	<5	<5	-	-
49	Lower Bann	5.8	Ireland	River	54.86	-6.48	73	6	20	-	-	-
50	Maine	0.29	Ireland	River	54.75	-6.32	64	10	16	10	-	-
51	Six Mile	0.3	Ireland	River	54.70	-6.15	98	-	-	<5	-	-
52	Glenariff	<0.1	Ireland	River	55.02	-6.11	82	<5	<5	-	-	13
53	Galets	<0.1	Reunion Island	River	-20.95	55.30	92	-	5	<5	-	-

Table 2

Trace element composition (ppm) of certified reference materials.

	BCR-2			JA-2			BHVO-2		
	This study	Reference values ^a	Deviation %	This study	Reference values ^b	Deviation %	This study	Reference values ^c	Deviation%
Y	40.1	37	8	19.12	18.1	5	28.5	27.6	3
Zr	190	184	3	111.0	112	-1	166.8	164.9	1
Ba	682	677	1	310	315	-2	131	131	0
La	25.89	24.9	4	16.04	16.10	0	15.3	15.2	1
Ce	55.22	52.9	4	33.49	33.70	-1	37.7	37.5	0
Pr	7.14	6.7	6	3.80	3.70	3	5.41	5.31	2
Nd	29.93	28.7	4	14.65	14.20	3	24.8	24.5	1
Sm	6.88	6.58	4	3.18	3.10	3	6.16	6.07	2
Eu	2.02	1.96	3	0.908	0.91	0	2.12	2.07	2
Gd	7.15	6.75	6	3.16	3.00	5	6.43	6.24	3
Tb	1.10	1.07	3	0.493	0.48	3	0.95	0.94	1
Dy	6.61	6.41	3	2.99	2.90	3	5.34	5.31	1
Ho	1.376	1.28	7	0.633	0.61	4	1.02	1.00	2
Er	3.85	3.66	5	1.79	1.70	5	2.58	2.54	2
Yb	3.47	3.38	3	1.69	1.68	1	2.00	2.00	0
Lu	0.521	0.503	4	0.246	0.25	-2	0.27	0.27	2
Hf	5.13	4.9	5	2.89	2.93	-1	4.49	4.28	5
Th	6.0	5.7	5	4.74	5.00	-6	1.19	1.21	-2

Table 3

Major element composition of World river silts.

#	Sample River	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	CaO (%)	MgO (%)	K ₂ O (%)	Na ₂ O (%)	TiO ₂ (%)	P ₂ O ₅ (%)	LOI (%)	Total (%)	CIA
Large rivers														
1	Amazon	63.75	17.78	5.88	0.06	0.46	1.58	3.03	0.84	1.07	0.13	5.114	99.694	76
2	Congo	48.51	22.13	13.34	0.02	0.19	1.23	1.42	0.03	0.23	1.04	12.40	100.5	92
3	Mississippi	71.46	13.03	4.21	0.02	0.54	1.20	2.56	0.90	0.15	0.82	4.74	99.6	71
4	Nile	63.16	12.27	5.74	0.05	3.21	3.55	2.26	0.88	0.19	1.10	7.68	100.1	56
5	Niger	52.69	22.56	8.18	0.03	0.56	1.71	1.61	0.13	0.09	1.09	10.98	99.6	88
6	Yangtze	66.29	15.69	5.20	0.04	0.84	2.24	3.11	1.41	0.13	0.95	3.97	99.9	69
7	MacKenzie	68.85	14.23	4.99	0.01	0.44	1.55	2.71	0.63	0.21	0.89	5.41	99.9	75
8	Volga	73.49	10.95	4.43	0.04	0.93	1.47	2.16	1.43	0.12	0.86	4.22	100.1	63
9	Murray	57.01	19.35	8.66	0.02	0.23	1.46	2.26	0.28	0.10	0.88	9.79	100.0	85
10	Orinoco	82.91	7.68	3.31	0.02	0.40	0.53	1.32	0.65	0.08	1.02	1.85	99.8	70
11	Danube	44.70	10.97	5.53	0.03	0.97	1.49	1.89	0.53	0.23	0.58	32.85	99.7	70
12	Mekong	79.76	10.00	3.25	0.00	0.31	0.52	1.50	0.70	0.05	0.93	3.11	100.1	75
13	Yellow River	74.39	11.27	3.28	0.03	1.29	1.52	2.19	2.18	0.15	0.69	2.38	99.4	58
14	Amu Darya	71.55	12.17	4.44	0.05	2.33	2.08	1.82	2.43	0.21	0.89	2.06	100.0	54
15	Don	81.82	8.06	2.33	0.00	0.58	0.71	1.81	1.28	0.16	0.58	3.10	100.4	61
16	Northern Dvina	54.03	14.43	13.07	0.15	1.06	2.75	2.79	1.29	1.85	0.77	7.72	99.9	67
17	Fraser	65.79	14.56	5.61	0.05	2.41	2.44	1.95	2.33	0.21	0.90	3.43	99.7	59
18	Rhine	73.79	9.83	3.17	0.02	1.96	2.04	2.15	1.13	0.18	0.66	5.04	100.0	56
19	Vistula	65.29	13.15	4.53	0.02	0.48	1.84	3.34	0.67	0.12	0.77	9.23	99.4	70
20	Red River	69.52	14.61	5.12	0.01	0.34	1.65	2.84	0.68	0.13	0.94	3.83	99.7	75
21	Chao Phraya	72.87	12.46	4.99	0.05	0.34	1.12	1.96	0.56	0.10	0.90	5.15	100.5	77
22	Loire	59.99	17.37	6.45	0.05	0.86	1.73	2.96	0.76	0.25	1.06	8.33	99.8	74
	WRAS	66.4	13.8	5.7	0.03	0.9	1.7	2.3	1.0	0.3	0.8			70
	(± 1s)	10.3	4.0	2.9	0.03	0.8	0.7	0.6	0.7	0.4	0.2			10
Rivers draining mixed/sedimentary formations														
23	Seine	85.88	6.20	1.87	0.02	0.61	0.49	1.71	1.06	0.13	0.69	1.88	100.5	57
24	Fly	64.23	16.55	6.22	0.04	0.56	1.51	2.06	1.38	0.14	0.96	5.45	99.1	75
25	Guadiana	not analysed												
26	Chubut	63.93	15.79	5.24	0.08	4.16	1.73	1.72	2.89	0.14	1.20	3.39	100.3	53
27	Mae Klong	67.93	15.34	4.83	0.07	0.24	1.34	2.47	0.14	0.17	0.82	6.52	99.9	82
28	Shannon	79.57	8.77	3.32	0.03	0.44	1.03	1.52	1.07	0.18	1.04	2.54	99.5	68
29	Adour	80.50	8.93	2.83	0.02	0.80	0.95	1.59	0.57	0.12	0.93	2.59	99.8	68
30	Sefid Rud	66.09	14.16	6.08	0.05	1.61	2.17	2.30	1.92	0.20	1.11	4.30	100.0	62
31	Mayenne	71.14	13.47	4.85	0.03	0.35	0.98	2.34	0.88	0.30	1.01	5.10	100.5	74
32	Var	67.80	14.17	5.69	0.01	0.88	2.31	2.84	1.06	0.21	0.76	4.16	99.9	69
33	Blackwater	73.14	12.14	3.66	0.02	0.54	1.40	2.09	1.84	0.11	1.12	4.20	100.3	66
34	Moyola	65.54	14.05	5.61	0.06	1.04	2.07	2.92	1.37	0.21	1.22	5.87	100.0	66
Rivers draining igneous/metamorphic terranes														
35	Rio Caroni	59.51	22.44	3.69	0.04	0.38	0.55	2.42	0.17	0.10	1.27	8.58	99.2	86
36	Narva	69.49	12.60	4.55	0.02	0.82	1.35	4.23	0.81	0.27	0.76	4.62	99.5	63
37	Rio Caura	59.05	23.11	3.36	0.03	0.35	0.58	2.47	0.20	0.10	1.17	9.01	99.4	86
38	Kymijoki	60.75	13.95	6.28	0.04	1.21	1.76	3.55	1.61	0.22	0.63	9.71	99.7	62
39	Rio Aro	63.61	15.49	7.25	0.06	0.53	0.40	2.31	0.57	0.12	1.49	7.37	99.2	78
40	Ume	68.13	13.97	4.38	0.05	2.23	1.82	2.96	2.74	0.22	0.78	2.35	99.6	54
41	Lule	66.21	13.50	5.67	0.08	3.28	1.82	3.16	3.31	0.27	0.93	1.52	99.8	48
42	Tana	59.25	13.71	7.06	0.08	3.33	3.26	1.58	2.97	0.82	0.08			52
43	Kiiminkijoki	66.76	13.81	4.53	0.07	2.62	2.30	2.60	3.20	0.10	0.79	3.16	99.9	52
44	Foyle	66.26	13.76	5.10	0.06	0.75	1.65	2.88	1.83	0.31	1.14	6.10	99.8	65
45	Elorn	68.50	14.39	4.63	0.03	0.45	1.15	2.59	0.91	0.24	0.99	6.39	100.3	74
46	Swilly	65.89	14.69	6.87	0.07	2.45	1.46	2.36	3.22	0.32	1.86	1.88	101.1	54
Rivers draining volcanic rocks														
47	Kamchatka	not analysed												
48	Waikato	69.11	12.78	3.39	0.06	1.40	0.39	2.28	2.96	0.36	0.32	6.75	99.8	56
49	Lower Bann	58.94	14.80	9.77	0.08	2.08	2.98	1.74	1.02	0.11	1.86	5.94	99.3	67
50	Maine	48.59	18.30	12.43	0.10	4.12	5.03	0.41	1.53	0.16	1.78	7.68	100.1	64
51	Six Mile	52.61	15.49	10.50	0.10	4.87	5.06	0.68	1.45	0.31	1.92	7.15	100.1	56
52	Glenariff	40.35	16.17	19.14	0.22	5.31	5.75	0.23	1.05	0.16	3.69	8.18	100.2	58
53	Galets	46.69	10.99	13.34	0.17	8.59	12.49	0.71	1.53	0.17	2.45	3.34	100.5	37

WRAS: World River Average Silt. The precision (RSD) on measurements is 0.4% for Al₂O₃ and SiO₂ wt%, and 0.2% for all other element concentrations.

Table 4

Major element composition of World river clays.

#	Sample River	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	CaO (%)	MgO (%)	K ₂ O (%)	Na ₂ O (%)	TiO ₂ (%)	P ₂ O ₅ (%)	LOI (%)	Total (%)	CIA
Large rivers														
1	Amazon	48.14	25.38	10.01	0.05	0.06	1.89	2.88	<0.2	0.80	0.28	9.80	99.3	88
2	Congo	46.18	26.10	11.00	0.01	0.18	1.17	1.33	0.34	1.02	0.26	13.26	100.9	92
3	Mississippi	52.78	20.94	9.02	0.05	0.40	2.19	2.62	0.20	0.73	0.30	11.32	100.6	84
4	Nile	50.28	20.96	10.13	0.04	1.25	4.09	2.31	0.23	1.09	0.27	10.43	101.1	80
5	Niger	57.22	27.48	10.25	0.03	0.54	2.04	1.70	1.06	1.08	0.10	12.50	101.4	86
6	Yangtze	50.69	23.31	9.46	0.05	0.51	3.14	3.92	0.92	0.88	0.16	8.61	101.6	78
7	MacKenzie	57.15	24.00	9.92	0.03	0.48	2.49	4.42	0.40	0.86	0.37	9.10	99.8	79
8	Volga	57.89	20.95	12.68	0.05	0.67	3.85	2.87	0.70	0.94	0.28	12.10	100.6	79
9	Murray	56.96	20.24	7.27	0.04	0.22	1.73	2.34	<0.2	1.04	0.12	9.48	99.4	86
10	Orinoco	not analysed												
11	Danube	not analysed												
12	Mekong	45.58	27.76	9.60	0.01	0.25	1.58	2.82	0.47	0.82	0.06	10.98	99.9	87
13	Yellow River	56.61	18.62	8.63	0.06	0.87	3.84	3.48	2.01	0.79	0.11	7.13	102.1	68
14	Amu Darya	not analysed												
15	Don	52.11	17.57	9.66	0.05	0.45	2.37	2.37	0.21	0.73	0.71			82
16	Northern Dvina	49.48	16.01	15.11	0.16	0.82	3.37	2.97	1.39	0.76	1.79	9.34	101.2	70
17	Fraser	55.75	16.51	9.28	0.07	1.01	3.38	2.18	0.93	0.80	0.34	10.25	100.5	74
18	Rhine	52.90	19.41	7.19	0.03	1.15	3.08	3.43	0.30	0.74	0.35	11.46	100.0	76
19	Vistula	55.05	17.40	6.75	0.03	0.35	2.71	3.89	0.77	0.74	0.17	12.69	100.6	74
20	Red River	47.80	25.86	9.92	0.04	0.24	2.36	4.42	0.59	1.01	0.24	8.50	101.0	81
21	Chao Phraya	46.75	24.43	10.89	0.09	0.24	1.89	2.62	0.34	0.81	0.22	12.85	101.1	86
22	Loire	50.30	22.07	9.49	0.05	0.46	2.00	2.68	0.23	0.86	0.36	11.62	100.1	84
	WRAC	52.1	21.8	9.8	0.05	0.5	2.6	2.9	0.7	0.9	0.3			81
	(±1s)	4.1	3.7	1.9	0.03	0.3	0.8	0.8	0.5	0.1	0.4			6
Rivers draining mixed/sedimentary formations														
23	Seine	51.91	18.82	10.13	0.02	0.87	2.21	2.83	0.25	0.86	0.47	12.35	100.7	79
24	Fly	55.29	27.40	10.29	0.04	0.34	2.30	3.19	0.96	1.21	0.29	9.70	101.0	83
25	Guadiana	45.86	26.00	8.10	0.04	0.18	1.96	3.69	0.41	0.85	0.20	11.97	99.3	84
26	Chubut	61.21	16.32	7.46	0.05	1.36	2.55	1.74	0.96	0.90	0.14	8.46	101.2	73
27	Mae Klong	56.48	28.12	8.95	0.11	0.30	2.19	3.18	0.32	0.90	0.28	11.70	100.6	86
28	Shannon	47.22	23.26	9.47	0.05	0.32	2.23	4.15	0.40	0.82	0.50			80
29	Adour	48.16	25.36	8.35	0.03	0.39	1.87	3.36	0.44	0.91	0.36	11.15	100.4	83
30	Sefid Rud	49.95	20.73	10.25	0.06	0.66	3.34	2.70	0.42	0.95	0.28	11.45	100.8	81
31	Mayenne	53.40	27.86	11.18	0.05	0.27	1.74	3.38	0.69	0.91	0.82	12.20	99.5	84
32	Var	not analysed												
33	Blackwater	50.03	24.26	7.05	0.04	0.29	3.06	2.60	0.23	0.81	0.18	12.21	100.7	87
34	Moyola	44.59	20.05	9.95	0.06	0.34	3.16	3.14	0.27	0.80	0.51	17.81	100.7	82
Rivers draining igneous/metamorphic terranes														
35	Rio Caroni	39.33	35.42	5.63	0.02	0.15	0.67	1.19	0.03	1.23	0.18	15.88	99.7	96
36	Narva	53.14	18.17	9.22	0.05	0.67	2.78	4.76	0.61	0.90	0.59	9.26	100.2	71
37	Rio Caura	39.27	35.01	5.17	0.02	0.14	0.68	1.21	0.02	1.22	0.16	16.81	99.7	96
38	Kymijoki	53.98	15.13	8.58	0.05	0.81	2.36	3.55	1.28	0.69	0.26	13.41	100.1	67
39	Rio Aro	not analysed												
40	Ume	not analysed												
41	Lule	not analysed												
42	Tana	40.71	17.19	13.07	0.07	0.67	3.32	2.72	0.78	0.78	0.72			76
43	Kiiminkijoki	not analysed												
44	Foyle	46.36	16.20	9.20	0.07	0.25	2.75	3.09	0.32	0.70	0.93	20.40	100.3	79
45	Elorn	55.86	27.22	9.84	0.02	0.37	2.10	3.66	0.55	0.96	0.74	14.10	100.6	83
46	Swilly	not analysed												
Rivers draining volcanic rocks														
47	Kamchatka	60.64	9.82	9.32	0.10	2.26	1.79	1.04	2.22	0.38	1.92	10.08	99.6	52
48	Waikato	70.00	15.51	9.78	0.03	0.71	0.47	1.29	1.27	0.43	1.82	14.8	99.5	76
49	Lower Bann	44.36	21.21	13.15	0.08	0.25	2.84	1.89	0.20	0.94	0.17			88
50	Maine	44.25	20.79	13.53	0.08	0.66	4.61	0.19	0.13	0.98	0.29	15.01	100.5	93
51	Six Mile	46.08	19.43	10.65	0.07	0.55	4.25	0.46	0.24	0.73	0.75	17.33	100.5	91
52	Glenariff	36.37	20.06	15.23	0.15	0.48	3.72	0.04	0.15	1.01	0.34			95
53	Galets	not analysed												

WRAC: World River Average Clay. The precision (RSD) on measurements is 0.4% for Al₂O₃ and SiO₂ wt%, and 0.2% for all other element concentrations.

Table 5

Trace element composition (ppm) of World river silts.

Sample	Sr	Y	Zr	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Hf	Th
Large rivers																			
1	149	37.2	203	597	42.4	92	10.35	40.3	7.52	1.53	6.21		6.08	1.21	3.62	3.54	0.54	5.30	12.9
2	79	24.5	141	446	53.3	117	12.58	46.0	8.35	1.79	6.44	0.96	5.22	1.00	2.67	2.44	0.36	4.21	17.5
3	131	27.6	320	553	34.9	70	8.10	30.3	5.65	1.06	4.89	0.79	4.64	0.96	2.79	2.85	0.43	8.42	10.2
4	149	31.6	518	370	36.1	74	8.39	31.6	6.13	1.23	5.33	0.86	5.19	1.08	3.11	3.19	0.48	13.1	11.6
5	145	23.6	139	864	54.8	114	12.06	43.2	7.61	1.48	5.70	0.85	4.67	0.89	2.39	2.22	0.32	3.95	15.4
6	121	28.5	210	523	40.4	82	9.27	34.0	6.36	1.24	5.35	0.85	4.95	1.02	2.89	2.79	0.41	5.97	12.5
7	117	26.2	174	1041*	37.8	74	8.60	31.1	5.58	1.02	4.56	0.72	4.33	0.91	2.65	2.62	0.39	4.80	10.2
8	165	27.7	706	406	30.4	65	7.51	27.9	5.45	1.00	4.80	0.76	4.52	0.97	2.91	3.01	0.47	17.6	8.3
9	70	23.5	158	255	28.7	55	6.73	25.6	5.13	1.11	4.42	0.68	4.01	0.83	2.39	2.41	0.35	4.61	11.7
10*	68	69.5	3476	230	47.8	102	11.48	42.4	8.15	1.46	8.27	1.57	10.39	2.31	7.50	9.05	1.48	82.4	16.6
11	79	not analyzed																	
12	83	28.4	363	274	34.8	71	7.80	28.7	5.26	0.97	4.36	0.74	4.54	0.96	2.87	2.86	0.43	9.20	11.3
13	179	26.8	398	456	32.8	68	7.74	29.0	5.59	1.01	4.66	0.75	4.49	0.92	2.71	2.72	0.41	10.2	10.0
14	188	33.3	484	396	40.1	82	9.11	34.4	6.66	1.21	5.68	0.91	5.48	1.15	3.33	3.37	0.52	12.6	12.3
15	114	16.4	371	361	20.0	42	4.77	18.0	3.45	0.64	2.83	0.46	2.76	0.57	1.71	1.85	0.28	8.81	6.0
16	142	27.0	158	440	42.2	85	9.90	37.5	7.09	1.49	5.80	0.86	4.94	0.97	2.67	2.48	0.37	4.37	10.9
17	255	22.9	171	605	26.5	53	6.31	24.3	4.84	1.12	4.29	0.67	3.92	0.80	2.24	2.10	0.32	4.59	6.3
18	95	25.1	443	346	30.1	62	7.17	27.2	5.37	0.83	4.50	0.70	4.13	0.85	2.50	2.55	0.39	11.5	10.7
19	87	24.1	235	466	33.4	66	7.53	27.8	4.98	0.90	4.07	0.66	4.00	0.84	2.43	2.50	0.37	6.28	10.5
20	81	32.1	234	419	45.5	92	10.12	37.1	6.76	1.27	5.64	0.87	5.33	1.09	3.09	3.05	0.44	6.20	14.3
21	87	30.0	223	275	34.8	72	8.07	30.3	5.74	1.09	5.08	0.80	4.95	1.01	2.88	2.87	0.42	6.07	14.2
22	144	31.3	214	480	46.8	93	10.60	39.7	7.477	1.49	6.08	0.94	5.42	1.06	2.99	2.85	0.41	5.77	14.6
WRAS	127	29.4	445	449	37.8	78	8.77	32.7	6.15	1.19	5.19	0.82	4.95	1.02	2.97	3.01	0.46	11.2	11.8
($\pm 1s$)	46	5	154	142	9	19	1.9	6.9	1.2	0.3	0.9	0.1	0.7	0.1	0.4	0.4	0.1	3.7	2.9
Rivers draining mixed/sedimentary formations																			
23	83	26.6	606	292	29.2	60	6.91	25.7	4.94	0.81	4.19	0.70	4.27	0.90	2.64	2.84	0.44	14.2	8.6
24	161	27.2	281	335	34.6	75	8.47	32.4	6.31	1.32	5.12	0.81	4.82	0.98	2.79	2.72	0.41	7.34	10.8
25																			
26	358	25.9	613	460	29.6	61	7.13	26.8	5.25	1.23	4.65	0.72	4.24	0.90	2.67	2.95	0.48	14.8	8.1
27	47	31.7	210	340	46.6	94	10.23	37.4	7.11	1.16	5.77	0.91	5.31	1.07	3.08	3.03	0.45	5.90	22.1
28	94	40.7	841	312	37.3	76	8.71	33.0	6.47	1.28	6.17	1.05	6.46	1.37	4.02	4.11	0.64	20.0	9.2
29	145	32.0	599	255	39.3	80	9.00	33.6	6.36	1.09	5.10	0.83	5.06	1.08	3.18	3.21	0.48	15.9	9.9
30	254	24.6	229	479	30.4	59	6.87	26.2	5.15	1.20	4.50	0.70	4.15	0.86	2.42	2.37	0.35	6.00	7.7
31	77	32.5	354	404	35.6	74	8.65	32.6	6.42	1.22	5.64	0.90	5.43	1.11	3.19	3.15	0.46	9.12	9.8
32	106	21.7	233	400	33.5	65	7.43	27.1	4.83	0.75	3.93	0.61	3.63	0.76	2.11	2.09	0.31	6.44	10.2
33	96	23.9	479	430	28.8	61	6.97	26.0	4.97	1.07	4.24	0.68	4.04	0.85	2.42	2.45	0.37	12.0	7.9
34	114	24.5	566	594	33.6	68	7.72	28.6	5.22	1.16	4.59	0.71	4.20	0.87	2.49	2.51	0.39	14.5	8.1
Rivers draining igneous/metamorphic terranes																			
35	75	29.3	1476	727	44.8	75	9.10	31.1	5.42	0.93	4.19	0.72	4.59	1.03	3.25	4.16	0.69	34.9	21.1
36	128	33.3	302	549	40.9	86	9.87	36.9	7.13	1.29	6.04	0.96	5.67	1.15	3.28	3.32	0.48	8.03	11.5
37	86	24.2	811	731	43.1	72	8.69	29.8	4.98	0.89	3.93	0.64	4.06	0.87	2.72	3.25	0.52	20.2	18.8
38	162	33.2	192	555	51.2	108	12.13	44.5	8.19	1.20	6.48	1.02	5.85	1.17	3.34	3.21	0.46	5.57	17.1
39	78	28.3	920	644	61.5	124	12.15	42.6	7.27	1.14	5.57	0.85	4.97	1.01	2.92	3.12	0.46	23.7	32.5
40	219	35.1	394	587	45.5	93	11.00	41.8	7.91	1.23	6.61	1.03	6.05	1.22	3.40	3.33	0.47	10.6	10.4
41	259	43.2	623	738	39.2	85	10.35	41.0	8.30	1.56	7.37	1.18	7.27	1.53	4.33	4.51	0.65	15.6	8.5
42	258	22.4	231	487	32.5	64	7.98	30.8	5.88	1.34	4.79	0.72	4.05	0.80	2.29	2.18	0.33	6.16	6.8
43	244	22.2	350	657	29.7	61	7.08	26.8	5.12	1.10	4.25	0.65	3.80	0.79	2.12	2.16	0.32	9.10	7.4
44	126	32.7	715	665	44.4	91	10.32	38.6	7.23	1.43	6.08	0.93	5.46	1.16	3.22	3.38	0.52	18.3	10.3
45	103	35.4	452	462	44.6	91	10.45	39.3	7.66	1.39	6.38	1.00	5.96	1.24	3.45	3.52	0.51	12.0	13.7
46	227	53.3	1024	565	52.1	112	13.19	49.7	9.86	1.79	8.73	1.43	8.68	1.88	5.54	5.54	0.84	25.8	15.0
Rivers draining volcanic rocks																			
47	not analyzed																		
48	127	31.4	217	570	24.8	53.7	6.12	23.6	5.10	1.03	5.12	0.84	5.28	1.11	3.19	3.10	0.48	5.89	9.9
49	111	29.4	286	321	20.1	42.6	5.08	20.6	4.58	1.29	4.83	0.79	4.92	1.04	2.96	2.90	0.44	7.49	5.00
50	137	30.1	154	172	9.8	26.2	3.19	14.8	4.04	1.46	4.80	0.81	5.05	1.05	2.96	2.76	0.41	4.09	1.30
51	133	29.5	188	198	12.5	28.4	3.62	15.9	4.11	1.34	4.76	0.79	4.85	1.03	2.86	2.67	0.39	4.99	2.30
52	110	34.1	193	105	7.0	18.1	3.02	15.8	4.95	1.84	5.95	0.99	6.09	1.25	3.48	3.18	0.46	5.19	0.92
53	244	20.5	190	159	15.3	33.7	4.36	18.8	4.53	1.62	4.59	0.70	3.94	0.76	1.99	1.59	0.22	4.94	1.83

* not included in the calculation of WRAS (World River Average Silt)

The precision on reported trace element concentrations is better than 5% (RSD).

Table 6

Trace element composition (ppm) of World river clays.

Sample	Sr	Y	Zr	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu	Hf	Th
Large rivers																			
1	90	35.0	124	370	53.1	114	12.46	48.2	9.43	1.90	7.50		6.27	1.21	3.44	3.18	0.50	3.35	22.3
2	61	25.8	129	264	56.7	123	12.70	45.4	8.28	1.77	5.87	0.91	4.93	0.93	2.52	2.34	0.34	3.47	17.6
3	81	34.5	135	380	47.1	95	10.63	39.8	7.61	1.58	6.25	0.99	5.65	1.13	3.14	2.98	0.44	3.65	15.9
4	129	29.2	228	186	47.1	104	9.97	35.8	6.49	1.33	5.07	0.80	4.61	0.93	2.63	2.59	0.38	5.33	12.3
5	121	25.1	118	456	58.2	121	12.34	43.6	7.64	1.57	5.43	0.83	4.49	0.84	2.25	2.10	0.30	2.92	15.0
6	94	31.8	145	494	44.7	88	9.74	35.8	6.77	1.41	5.59	0.90	5.28	1.06	3.03	3.04	0.45	3.90	21.2
7	168	31.9	150	1287*	52.2	99	11.06	39.8	6.92	1.43	5.39	0.83	4.87	1.02	3.03	3.12	0.47	3.88	16.4
8	109	30.4	151	308	35.9	75	8.28	31.1	6.08	1.35	5.33	0.83	4.84	0.99	2.78	2.71	0.40	3.77	12.1
9	84	24.2	139	247	29.7	54	6.60	25.1	5.02	1.08	4.13	0.66	3.84	0.80	2.28	2.32	0.35	3.68	12.0
10*		44.7	377	468	63.5	127	14.26	52.1	9.61	1.75	7.82	1.20	7.19	1.48	4.27	4.36	0.66	9.25	15.9
11		17.9	87	391	35.8	54	6.07	21.8	3.95	0.80	3.08	0.48	2.78	0.56	1.63	1.67	0.25	2.09	10.6
12	72	38.9	137	422	45.3	98	10.24	39.0	7.96	1.75	7.02	1.11	6.41	1.28	3.61	3.50	0.52	3.73	19.5
13	113	25.4	125	577	35.2	69	7.58	27.4	5.03	1.02	4.01	0.66	3.95	0.81	2.36	2.37	0.35	3.16	14.5
14		24.8	186	456	27.5	56	6.24	23.3	4.59	0.95	3.89	0.65	3.97	0.84	2.46	2.47	0.38	5.01	13.0
15	84	25.1	139	319	34.3	75	7.86	29.2	5.59	1.20	4.54	0.73	4.22	0.84	2.39	2.36	0.35	3.61	12.3
16	138	30.6	125	379	47.7	96	10.74	39.6	7.27	1.53	5.72	0.87	4.86	0.97	2.67	2.45	0.37	3.20	12.4
17	113	22.3	124	570	21.1	44	5.14	20.1	4.22	1.01	3.87	0.61	3.60	0.73	2.10	2.07	0.32	3.04	8.3
18	93	22.9	96	322	35.3	70	7.41	26.1	4.65	0.92	3.47	0.58	3.51	0.71	2.10	2.11	0.31	2.36	15.1
19	79	24.4	119	383	41.8	82	9.07	32.9	5.77	1.06	4.35	0.67	3.85	0.80	2.29	2.30	0.35	3.31	13.8
20	115	41.8	183	476	64.7	128	14.02	51.1	9.41	1.87	7.30	1.16	6.68	1.35	3.90	3.89	0.59	4.74	19.3
21	168	39.1	127	284	56.1	97	10.11	37.7	7.69	1.61	6.67	1.07	6.30	1.27	3.57	3.43	0.50	3.42	15.6
22	175	30.6	114	307	48.5	94	10.58	39.0	7.43	1.57	5.78	0.92	5.06	0.99	2.66	2.43	0.34	3.04	17.4
WRAC	110	29.8	148	380	44.6	89	9.69	35.6	6.70	1.38	5.37	0.83	4.87	0.98	2.78	2.72	0.41	3.81	15.1
($\pm 1s$)	34	6	31	104	11	24	2.4	8.8	1.6	0.3	1.3	0.2	1.1	0.2	0.6	0.6	0.1	0.8	3.6
Rivers draining mixed/sedimentary formations																			
23	88	30.6	135	265	44.6	84	9.26	33.4	6.04	1.22	4.67	0.76	4.44	0.90	2.56	2.48	0.36	3.41	16.5
24	178	28.3	184	369	36.6	78	8.57	32.7	6.40	1.50	5.09	0.82	4.78	0.99	2.90	3.01	0.46	4.88	13.8
25	77	29.5	147	558	39.9	80	9.16	34.1	6.78	1.45	5.70	0.89	4.99	1.01	2.88	2.94	0.45	3.93	15.2
26	225	37.5	192	269	33.3	71	8.38	32.4	6.75	1.32	6.18	0.99	5.83	1.19	3.36	3.28	0.50	4.49	10.3
27	53	38.2	117	337	55.0	111	11.99	43.4	8.38	1.44	6.79	1.10	6.32	1.25	3.46	3.36	0.49	3.24	31.4
28	92	34.2	151	623	47.4	94	10.71	39.7	7.39	1.54	5.60	0.87	5.10	1.06	3.08	3.12	0.47	3.89	15.0
29	155	32.1	113	457	49.7	96	10.52	38.7	7.14	1.48	5.60	0.88	5.01	1.00	2.79	2.65	0.39	2.91	19.0
30	112	33.9	166	422	40.2	74	8.69	32.9	6.53	1.50	5.57	0.89	5.25	1.08	3.08	3.00	0.45	3.97	13.2
31	84	35.1	188	510	43.5	89	10.05	38.3	7.86	1.66	6.66	1.05	5.91	1.16	3.18	3.06	0.45	3.68	14.7
32		21.0	124	515	43.2	77	8.36	29.0	4.37	0.85	3.05	0.53	3.28	0.72	2.16	2.23	0.34	3.72	15.2
33	50	38.9	135	384	45.3	95	11.03	43.0	8.62	2.04	7.44	1.13	6.44	1.26	3.48	3.19	0.47	3.43	12.3
34	89	32.0	97	511	53.2	111	11.76	43.6	7.89	1.81	6.15	0.93	5.14	0.99	2.69	2.32	0.34	2.49	13.9
Rivers draining igneous/metamorphic terranes																			
35	56	27.9	207	409	83.4	127	15.24	50.7	8.24	1.59	5.84	0.92	5.30	1.03	2.89	2.92	0.44	4.94	29.4
36	121	42.4	172	433	64.0	131	14.36	52.6	9.66	1.69	7.74	1.18	6.78	1.35	3.77	3.55	0.53	4.33	19.7
37	55	29.7	202	447	89.2	136	16.25	54.0	8.66	1.67	6.03	0.96	5.62	1.07	3.01	3.09	0.46	4.66	31.1
38	117	35.7	109	517	59.6	126	13.55	48.4	8.55	1.18	6.53	1.02	5.82	1.15	3.21	2.94	0.44	3.05	20.1
39		22.8	108	173	57.2	115	11.05	38.8	6.93	1.54	5.35	0.79	4.38	0.83	2.18	2.00	0.29	2.84	17.3
40		40.2	131	552	80.0	160	18.06	64.1	11.20	1.64	8.82	1.32	7.23	1.36	3.70	3.31	0.49	3.71	27.3
41		35.2	161	718	49.2	102	11.88	43.7	8.23	1.29	6.47	1.04	6.03	1.21	3.43	3.29	0.49	4.38	22.4
42	73	27.2	106	626	56.8	117	14.18	53.3	10.41	2.02	8.04	1.12	5.84	1.10	3.01	2.70	0.41	3.21	25.7
43		26.5	137	597	51.5	100	10.75	38.4	6.58	1.22	4.76	0.75	4.28	0.86	2.36	2.30	0.34	3.56	17.5
44	66	41.6	100	554	70.2	148	15.93	59.6	10.82	2.28	8.46	1.26	6.94	1.33	3.55	3.07	0.45	2.56	18.7
45	130	25.7	107	395	42.4	81	9.48	35.4	6.85	1.41	5.28	0.83	4.57	0.90	2.46	2.40	0.36	3.17	18.1
46		58.7	171	1087	81.7	150	15.17	77.9	14.78	2.64	12.62	1.80	10.1	1.96	5.32	4.81	0.70	4.33	35.0
Rivers draining volcanic rocks																			
47	188	9.1	81	290	6.4	14.4	1.83	7.6	1.75	0.49	1.65	0.26	1.52	0.32	0.92	0.94	0.15	2.04	1.71
48	83	40.9	156	394	26.8	61.0	6.86	26.9	6.15	1.29	6.47	1.16	7.26	1.48	3.98	3.61	0.52	4.01	12.0
49	59	31.8	134	255	29.9	56.0	6.85	26.3	5.40	1.42	5.12	0.82	5.07	1.06	3.04	2.94	0.44	3.33	8.03
50	67	36.3	107	94	10.4	34.4	3.46	16.4	4.81	1.36	5.64	0.96	5.97	1.25	3.55	3.30	0.49	2.68	2.01
51	50	30.6	93	128	12.7	28.4	3.56	15.6	4.06	1.16	4.53	0.77	4.85	1.02	2.90	2.73	0.41	2.54	3.31
52	31	33.1	134	82	7.2	19.5	3.03	15.6	4.97	1.74	5.76	0.97	5.91	1.19	3.33	3.07	0.44	3.13	1.27
53		15.2	193	123	16.4	36.9	3.87	15.4	3.19	1.06	3.08	0.47	2.68	0.53	1.37	1.20	0.16	4.29	3.37

* not included in the calculation of WRAC (World River Average Clay)

The precision on reported trace element concentrations is better than 5% (RSD).

Table 7

Nd isotopic compositions of World river clays and silts.

#	Sample River	Clays		Silts		$\Delta\epsilon_{Nd}$ (clay -silt)
		$^{143}Nd/^{144}Nd$ $\pm 2\text{ se}$	ϵ_{Nd}	$^{143}Nd/^{144}Nd$ $\pm 2\text{ se}$	ϵ_{Nd}	
Large rivers						
1	Amazon	0.512092 $\pm$ 4	-10.5	0.512083 $\pm$ 4	-10.7	0.2
2	Congo	0.511841 $\pm$ 8	-15.5	0.511820 $\pm$ 5	-15.8	0.3
3	Mississippi	0.512087 $\pm$ 8	-10.8	0.512001 $\pm$ 4	-12.3	1.5
4	Nile	0.512274 $\pm$ 12	-7.1	0.512138 $\pm$ 4	-9.6	2.5
5	Niger	0.512030 $\pm$ 8	-11.9	0.512018 $\pm$ 5	-11.9	0.1
6	Yangtze	0.512098 $\pm$ 8	-10.5	0.512047 $\pm$ 6	-11.4	0.9
7	MacKenzie	0.512011 $\pm$ 9	-12.2	0.511965 $\pm$ 4	-13.0	0.7
8	Volga	0.512152 $\pm$ 10	-9.5	0.512027 $\pm$ 5	-11.8	2.3
9	Murray	0.512336 $\pm$ 8	-5.9	0.512275 $\pm$ 4	-6.9	1.0
10	Orinoco	0.511933 $\pm$ 9	-13.8	0.511952 $\pm$ 4	-13.2	-0.5
11	Danube	0.512201 $\pm$ 15	-8.5	not analyzed		
12	Mekong	0.512196 $\pm$ 12	-8.6	0.512094 $\pm$ 5	-10.5	1.8
13	Yellow River	0.512030 $\pm$ 9	-11.9	0.512071 $\pm$ 5	-10.9	-0.9
14	Amu Darya	0.512188 $\pm$ 10	-8.8	0.512168 $\pm$ 3	-9.0	0.2
15	Don	0.512161 $\pm$ 6	-9.3	0.512065 $\pm$ 6	-11.0	1.7
16	Northern Dvina	0.511729 $\pm$ 9	-17.7	0.511753 $\pm$ 6	-17.1	-0.6
17	Fraser	0.512423 $\pm$ 10	-4.2	0.512195 $\pm$ 5	-8.5	4.3
18	Rhine	0.512159 $\pm$ 13	-9.3	0.512166 $\pm$ 4	-9.1	-0.3
19	Vistula	0.511893 $\pm$ 8	-14.5	0.511887 $\pm$ 6	-14.5	0.0
20	Red River	0.512014 $\pm$ 7	-12.2	0.511974 $\pm$ 5	-12.8	0.6
21	Chao Phraya	0.512209 $\pm$ 13	-8.4	0.512128 $\pm$ 7	-9.8	1.4
22	Loire	0.512231 $\pm$ 8	-7.9	0.512203 $\pm$ 5	-8.3	0.4
		WRAC	-10.4	WRAS	-11.3	0.8 $\pm$ 1.2
Rivers draining mixed/sedimentary formations						
23	Seine	0.512051 $\pm$ 8	-11.3	0.512041 $\pm$ 4	-11.5	0.2
24	Fly	0.512433 $\pm$ 10	-3.8	0.512376 $\pm$ 6	-4.9	1.1
25	Guadiana	0.512144 $\pm$ 3	-9.5	not analyzed		
26	Chubut	0.512611 $\pm$ 10	-0.4	0.512549 $\pm$ 7	-1.6	1.2
27	Mae Klong	0.511927 $\pm$ 9	-13.7	0.511897 $\pm$ 5	-14.3	0.6
28	Shannon	0.512055 $\pm$ 5	-11.2	0.512040 $\pm$ 6	-11.5	0.3
29	Adour	0.512064 $\pm$ 9	-11.0	0.512033 $\pm$ 6	-11.6	0.6
30	Sefid Rud	0.512393 $\pm$ 8	-4.6	0.512400 $\pm$ 5	-4.5	-0.1
31	Mayenne	0.512141 $\pm$ 9	-9.5	0.512140 $\pm$ 5	-9.6	0.0
32	Var	0.512081 $\pm$ 9	-10.7	0.512099 $\pm$ 4	-10.4	-0.4
33	Blackwater	0.512037 $\pm$ 8	-11.6	0.511985 $\pm$ 5	-12.6	1.0
34	Moyola	0.511804 $\pm$ 10	-16.1	0.511800 $\pm$ 4	-16.2	0.1
Rivers draining igneous/metamorphic terranes						
35	Rio Caroni	0.511560 $\pm$ 8	-20.9	0.511547 $\pm$ 5	-21.1	0.3
36	Narva	0.511773 $\pm$ 9	-16.7	0.511809 $\pm$ 3	-16.0	-0.7
37	Rio Caura	0.511549 $\pm$ 9	-21.1	0.511551 $\pm$ 5	-21.0	-0.1
38	Kymijoki	0.511617 $\pm$ 14	-19.8	0.511648 $\pm$ 3	-19.2	-0.6
39	Rio Aro	0.511337 $\pm$ 12	-25.2	0.511170 $\pm$ 5	-28.5	3.3
40	Ume	0.511673 $\pm$ 7	-18.7	0.511728 $\pm$ 4	-17.6	-1.1
41	Lule	0.511587 $\pm$ 8	-20.4	0.511709 $\pm$ 6	-18.0	-2.4
42	Tana	0.511453 $\pm$ 4	-23.0	0.511518 $\pm$ 5	-21.7	-1.3
43	Kiminkijoki	0.511455 $\pm$ 8	-22.9	0.511448 $\pm$ 5	-23.1	0.1
44	Foyle	0.511853 $\pm$ 8	-15.2	0.511809 $\pm$ 4	-16.0	0.9
45	Elorn	0.512073 $\pm$ 8	-10.9	0.512054 $\pm$ 5	-11.2	0.4
46	Swilly	0.511915 $\pm$ 8	-13.9	0.511949 $\pm$ 4	-13.3	-0.7
Rivers draining volcanic rocks						
47	Kamchatka	0.513000 $\pm$ 8	7.2	not analyzed		
48	Waikato	0.512649 $\pm$ 11	0.4	0.512655 $\pm$ 5	0.5	-0.1
49	Lower Bann	0.512176 $\pm$ 11	-8.9	0.512172 $\pm$ 5	-8.9	0.1
50	Maine	0.512661 $\pm$ 13	0.6	0.512637 $\pm$ 5	0.1	0.5
51	Six Mile	0.512467 $\pm$ 13	-3.2	0.512485 $\pm$ 5	-2.8	-0.3
52	Glenariff	0.512817 $\pm$ 6	3.7	0.512822 $\pm$ 9	3.7	-0.1
53	Galets	0.512827 $\pm$ 12	3.8	not analyzed		

The precision (external reproducibility) on reported Nd isotopic compositions is 0.17 ϵ_{Nd} .

Table 8

Major element composition (wt%) of World River Average Silt (WRAS) and Clay (WRAC), and other global and continental-scale reference data.

	WRAS	WRAC	UCC	SSWR	Loess / soils China	Loess Europe	Soil Europe	Soil Australia	Soil USA
SiO₂	66.4	52.1	66.6	51.9	65.6	78.2	66.8	77.5	66.3
Al₂O₃	13.8	21.8	15.4	16.5	13.2	8.4	10.5	8.1	13.6
Fe₂O₃	5.7	9.8	5.6	8.3	5.0	3.1	3.6	3.2	3.7
MnO	0.03	0.05	0.1	0.2	0.1	0.1	0.08	0.04	0.07
CaO	0.9	0.5	3.6	3.6	8.6	5.5	1.2	0.5	3.4
MgO	1.7	2.6	2.5	2.1	2.5	0.9	1.0	0.5	1.5
K₂O	2.3	2.9	2.8	2.0	2.6	1.8	1.9	1.2	1.8
Na₂O	1.0	0.7	3.3	1.0	1.7	1.1	0.8	0.3	1.6
TiO₂	0.27	0.87	0.64	0.7	0.7	0.7	0.62	0.58	0.48
P₂O₅	0.84	0.34	0.15	0.5	0.2	0.1	0.18	0.06	0.10

WRAS: World River Average Silt (this study)

WRAC: World River Average Clay (this study)

UCC: Upper Continental Crust (Rudnick and Gao, 2003)

SSWR: Suspended Sediment World River (Viers et al., 2009)

Loess / soils China: Jahn et al. (2001)

Loess Europe: Gallet et al. (1998)

Soil Europe (GEMAS project): de Caritat et al. (2012)

Soil Australia (NGSA project): de Caritat et al. (2012)

Soil USA: Shacklette and Boerngen (1984)

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

Fig 8