



Transport and exchange of U-series nuclides between suspended material, dissolved load and colloids in rivers draining basaltic terrains

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ABSTRACT

This study presents uranium and thorium concentrations and activity ratios for all riverine phases (bedload, suspended load, dissolved load and colloids) from basaltic terrains in Iceland and the Azores. Small basaltic islands, such as these, are thought to account for ~25% of CO₂ consumed by global silicate weathering, and for ~45% of the flux of suspended material to the oceans. These data indicate that [U] and [Th] in the dissolved and colloidal fractions are strongly controlled by pH, and to a much lesser extent by levels of dissolved organic carbon (which are low in these environments). At high pH, basalt glass dissolution is enhanced, and secondary mineral formation (e.g. Fe-oxyhydroxides and allophane) is suppressed, resulting in high dissolved [U], and low colloidal [U] and [Th], indicating a direct chemical weathering control on elemental abundances. When the dissolved (²³⁴U/²³⁸U) activity ratio is >1.3 (i.e. when physical weathering, groundwater contribution or soil formation are high), there is little isotope exchange between dissolved and colloidal fractions. At lower activity ratios, the dissolved load and colloids have indistinguishable activity ratios, suggesting that when chemical weathering rates are high, secondary clay formation is also high, and colloids rapidly adsorb dissolved U. Many of the suspended sediment samples have (²³⁴U/²³⁸U) activity ratios of >1, which suggests that uptake of U onto the suspended load is important. Identical (²³⁰Th/²³²Th) in suspended, dissolved and colloidal samples suggests that Th, like U, is exchanged or sorbed rapidly between all riverine phases. This particle-reactivity, combined with poorly constrained contributions from groundwater and hydrothermal water, and short-term variations in input to soils (volcanic and glacial), suggests that U-series nuclides in riverine material from such basaltic terrains are unlikely to reflect steady state erosion processes.

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1. Introduction

The destruction of the continental crust by erosion and chemical weathering, and its subsequent transfer to the oceans not only affects the evolution of the continents over time, but it also plays a pivotal role in removing CO₂ from the atmosphere. In particular, the chemical weathering of continental Ca-Mg silicates results in the net sequestration of atmospheric CO₂ in the oceans and is thus Earth's dominant climate moderating process (Berner, 2003, 2004; Berner et al., 1983; Kump et al., 2000; Walker et al., 1981). Of the silicate lithologies, basalt weathering exerts a disproportionate effect on atmospheric CO₂, as it accounts for ~35% of CO₂ consumption despite only making up <5% of the continental area (Dessert et al., 2003). Weathering of

small basaltic islands (e.g. Iceland, the Azores, Reunion, Hawaii and volcanic arc islands) is thought to account for the majority of basaltic CO₂ consumption, due to very high weathering rates (Gaillardet et al., 1999b) – thus chemical weathering of these islands probably accounts for ~25% of CO₂ consumed by global silicate weathering (Dessert et al., 2003; Louvat and Allegre, 1997, 1998; Louvat et al., 2008). These small basaltic islands are also typical of the high-relief, volcanic and tectonically active islands thought to contribute >45% of the river suspended material to the oceans (Gislason et al., 2006; Milliman and Syvitski, 1992). These islands dominate the suspended material flux to the oceans due to the combined effect of high runoff, the presence of rapidly weathering rocks, and an absence of sedimentary traps. This suspended material undergoes continued weathering during transport to the marine environment, thus acting as a further sink of atmospheric CO₂ (Gislason et al., 2006; Pogge von Strandmann et al., 2008b; Wallmann et al., 2008). The delivery of suspended material to the oceans appears to be far more climate dependent (i.e. sensitive to changes in river discharge/runoff) than

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the riverine dissolved load (Gislason et al., 2006, 2009). Furthermore, there is an inverse relationship between the degree of weathering of the riverine suspended load and the suspended sediment concentration (Gaillardet et al., 1999a). Thus, during warmer and wetter climate intervals, the delivery of suspended material to the oceans will increase and the material itself will be less weathered, resulting in greater weathering in the estuarine environment, providing a strong negative feedback acting to stabilise Earth's climate (Gislason et al., 2006; Pogge von Strandmann et al., 2008b).

Understanding the relationship between continental weathering and climate change demands precise information on the timing and rate of response of weathering to climatic or tectonic forcing, or human activity. In principle, uranium series isotopes can provide key chronological constraints, because their fractionation is time-dependent. The time interval between leaching of U-series nuclides from the rock, and discharge of river water into the ocean, is recorded by radioactive decay of the nuclides. This time interval, in turn, provides information on the kinetics of U release from the rock, as well as the timescale of weathering, which depends on the residence times of sediments within a given watershed and thus on the extent and nature of soil formation (Dosseto et al., 2006a,b,c, 2008a,b; Granet et al., 2007, 2010; Moreira-Nordemann, 1980; Plater et al., 1992; Vigier et al., 2001, 2005, 2006).

The energetic α -decay of ^{238}U to ^{234}U often causes the ($^{234}\text{U}/^{238}\text{U}$) (where parentheses denote activity ratio) of surface waters to be greater than secular equilibrium (= 1). The highest ($^{234}\text{U}/^{238}\text{U}$) are found in waters draining terrains with high physical weathering rates. In contrast, when chemical weathering rates are high, or soil residence times short, riverine activity ratios are usually close to those of the basement lithology (i.e. secular equilibrium) (Andersen et al., 2009; Chabaux et al., 2003; Dosseto et al., 2006a,b,c, 2008a,b; Kigoshi, 1971; Kronfeld and Vogel, 1991; Pogge von Strandmann et al., 2006, 2010; Robinson et al., 2004; Vigier et al., 2001, 2005, 2006). The same process can also cause isotope variations between U and ^{230}Th . Further decoupling of the behaviour of U and Th arises from a difference in valence and complexation behaviour: in oxidising natural waters U exists as soluble uranyl, whereas tetravalent Th is insoluble (although the solubility of U and Th changes when complexing with inorganic or organic ligands) (Chabaux et al., 2003; Faure, 1986), as a result of which U is usually more mobile than Th in the weathering environment.

A further complication arises because both U and Th bind strongly to organic, and to a lesser extent inorganic, colloids (Andersson et al., 1998, 2001; Dosseto et al., 2006; Porcelli et al., 1997; Riotte et al., 2003). Colloids can therefore exert a strong control on U-series nuclide mobility, and thus on the distribution of radioactive disequilibrium amongst different phases in river systems.

This study presents major and trace element compositions, and U and Th activity ratios for suspended, dissolved and colloidal fractions of rivers from two well-characterised, dominantly basaltic, watersheds in Iceland and Sao Miguel (Azores Archipelago) (Pogge von Strandmann et al., 2006, 2008a, 2010). These results illustrate that even inorganic colloids can strongly affect U-series mobility, and that rapid exchange of both U and Th between the different riverine phases is common. Taken together, with poorly quantified inputs from hydrothermal waters and groundwaters, these observations suggest that steady state erosion models may not be applicable in the basaltic terrains in Iceland.

2. Field areas

The dominantly basaltic terrains studied here have been described in detail elsewhere (Pogge von Strandmann et al., 2006, 2010). Briefly, samples from Iceland were collected from a catchment between the Langjökull icecap and the Borgarfjörður estuary in the west of the island (Fig. 1). Some of the rivers here receive water directly from glaciers. While other, direct-runoff, rivers mostly drain the older basaltic areas (given that Icelandic glaciers are generally present on recently erupted volcanic rocks), due to a decrease in rock permeability with rock age.

This is because in the older rocks compaction and sealing by secondary minerals reduces the permeability by up to five orders of magnitude (Sigurdsson and Ingimarsson, 1990). Some samples were also taken from rivers just off the Vatnajökull icecap in the south-east of Iceland.

Samples were collected in September 2003 and August 2005. Element concentrations and Li, U, Mo and Mg isotope data for the dissolved ($<0.2\ \mu\text{m}$) phase have been previously reported and discussed (Pearce et al., 2010; Pogge von Strandmann et al., 2006, 2008a).

In the Azores archipelago samples were taken from Sao Miguel island. Here the only permanent rivers are in the oldest eastern part of the island and around the calderas, which have often formed lakes (Fig. 1). The recent volcanic soils in the west and centre of the island drain too rapidly to carry permanent streams.

Samples were collected in October 2004, and concentrations and Li and U isotope data for the dissolved ($<0.2\ \mu\text{m}$) phase are reported and discussed by Pogge von Strandmann et al. (2010). The primary basalt and secondary weathering mineralogy is similar in both areas: the primary rock type is basaltic, and secondary minerals comprise ubiquitous Fe oxides and oxyhydroxides, as well as clays. The stability of many of these clays is pH-dependent: for example, smectites and allophane are unstable at high pH, while chlorite and talc (which form iddingsite) are only stable at high pH (Arnalds, 2005; Arnorsson et al., 2002; Gislason and Arnorsson, 1990; Gislason et al., 1996; Pogge von Strandmann et al., 2006, 2008a, 2010; Stefansson and Gislason, 2001; Stefansson et al., 2001).

3. Methods

3.1. Sample collection and filtration

On the day of collection, water samples were initially filtered through $0.2\ \mu\text{m}$ cellulose acetate filters contained in a teflon unit. Where possible, $>0.2\ \mu\text{m}$ material was recovered from the filters. Subsequently (also on the day of collection), aliquots of the filtered water were passed through a Sartorius tangential ultrafiltration system at 10 kD, using Sartocon polyethersulphone (PESU) slice cassettes to separate retentate (colloidal) fractions from truly dissolved ($<10\ \text{kD}$) fractions. The nature of tangential filtration (cross-flow filtration) is that flow is directed tangentially along the surface of the membrane, with most of the solution circulated back to the feed tank. This circulation of the water means that the retentate volume gradually decreases, while the retained particle concentration remains constant, effectively concentrating the colloids in a small (known) amount of solution. This solution has the same concentrations as the dissolved load, so colloidal concentrations are further corrected for this. Total organic carbon (TOC) was measured commercially by Severn Trent. Thorium was co-precipitated with Fe-oxyhydroxide (using Fe powder purified by column chemistry) from 15 L of filtered water (Edwards et al., 1987). For the purposes of this study, and to allow direct comparison with studies that have not conducted ultrafiltration, material $>0.2\ \mu\text{m}$ is classified as suspended, $<0.2\ \mu\text{m}$ as dissolved, $10\ \text{kD} < x < 0.2\ \mu\text{m}$ as colloidal (i.e. ultrafiltration retentate), and $<10\ \text{kD}$ as ultrafiltered.

3.2. Cation analyses

Water and colloidal samples were calibrated against a set of synthetic multi-element standards prepared gravimetrically from high purity single element standard solutions. Some colloidal material was pre-treated with dilute H_2O_2 in order to ensure dissolution. However, there was no difference in the composition of H_2O_2 -treated vs. non-treated samples. The accuracy of the analyses was assessed by running the natural water certified reference material SLRS-4, as well as in-house standards. The 2σ external uncertainty of these measurements is better than $\pm 3.2\%$ for major elements and $\pm 5\%$ for trace elements.

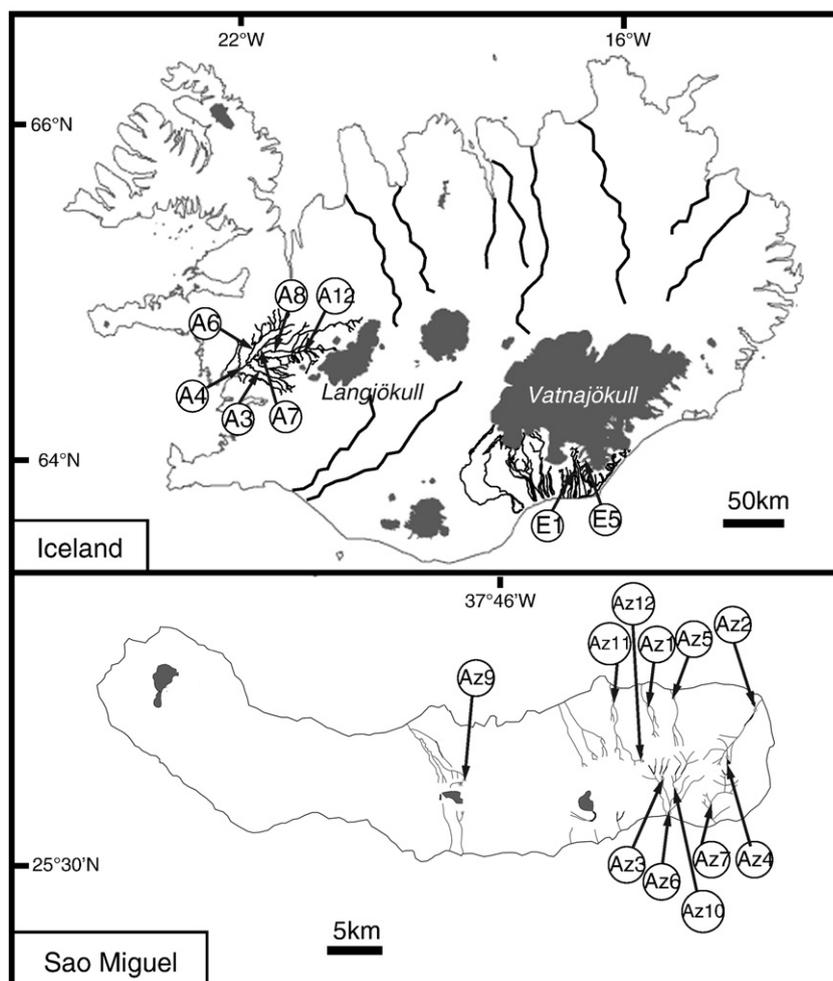


Fig. 1. Maps detailing sample locations. Grey areas represent icecaps in Iceland and lakes in Sao Miguel. (For more detail, see Pogge von Strandmann et al., 2006, 2010.)

3.3. Isotope analyses

Uranium isotope analyses were performed as described in Pogge von Strandmann et al. (2006, 2010). The $2\sigma_{SD}$ external uncertainty on ($^{234}\text{U}/^{238}\text{U}$) activity ratios, determined both by repeated measurements of a diluted (25 pg/g), spiked U112a standard and by repeated analyses of diluted (25 pg/g) seawater (average = 1.146, $n = 8$), is ± 0.056 .

For Th isotope analysis on basaltic and colloidal samples, Th was collected during the U chemistry in the 6 M HCl column step outlined elsewhere (Pogge von Strandmann et al., 2010; Turner et al., 2001). For water samples, in order to cope with the high Fe concentration induced by coprecipitation, 4 ml of AG-1 resin was used, and elution volumes were adjusted accordingly. Th analyses were performed on a Nu Instruments multi-collector ICP-MS, using a sample-standard bracketing technique, relative to the in-house Th “U” standard. ^{232}Th was measured on a Faraday cup, whereas ^{230}Th was measured on an ion counter fitted with a deceleration lens. A 20 ppb solution resulted in a ^{232}Th intensity of ~ 4 V, compared to a background of ~ 3 mV. The total procedural blank, including the co-precipitation step, is < 1 pg Th.

The $2\sigma_{SD}$ external uncertainty on ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio was assessed by analysing diluted Th “U” standard (Turner et al., 2001; van Calsteren and Schwieters, 1995), and diluted TML rock standards ($^{230}\text{Th}/^{232}\text{Th} = 5.77 \times 10^{-6}$ (Turner et al., 2001)), and is $\pm 5.2\%$ (2σ) for a 0.1 ppb solution, which compares well with the 2σ internal error of $\pm 18\%$ reported for samples of similar concentration (Vigier et al., 2006).

4. Results

4.1. Ultrafiltration mass balance

A critical check to ascertain that elemental concentrations are not being affected by the ultrafiltration processes (either by irreversibly binding to the filtration cassette, or by a blank contribution from the cassette) is to calculate a mass balance where the 10 kD retentate (colloids) and 10 kD permeate (ultrafiltered water) should balance to equal the concentrations measured in the 0.2 μm permeate filtered water (Dupre et al., 1999). The results show that most elements are unaffected by ultrafiltration; however particle-reactive elements show evidence of having been affected by the ultrafiltration slice cassette. Specifically, Fe and Th are depleted by up to 80%, which suggests that they are retained within the 10kD membranes. Aluminium is also retained, but to a lesser extent ($\sim 20\%$), while Mn and U can be either depleted or enhanced. For U, an experiment was conducted where Milli-Q H_2O was filtered through the ultrafiltration system. The input water and the retentate (water which had not passed through the 10 kD cassette after a fixed filtration time) had U concentrations of 0.04–0.06 pmol/l, compared to the 10 kD permeate which had > 3 pmol/l U. This strongly suggests that a blank contribution from the cassette contaminates the < 10 kD fraction; it is not clear whether this has affected the ultrafiltrate isotope ratio. Therefore the ultrafiltered water data has not been further utilised. However, the > 10 kD material appears to be unaffected, allowing determination of the U abundance and isotope composition of the true colloidal fraction.

A similar experiment for Th, using Milli-Q water doped with a known concentration of Th, showed that the volume adjusted retentate had the same concentration as the initial solution, whereas the <10 kD fraction had ~40–60% less Th. Again, this suggests that the <10 kD fraction is affected by ultrafiltration, but that the >10 kD colloidal fraction can be quantitatively utilised.

4.2. Elemental concentrations

A full discussion of the elemental composition of the dissolved phase, and suspended and bed sediments, is reported elsewhere

(Pogge von Strandmann et al., 2006, 2010). Here, we report the results of new analyses, as well as a summary of relevant aspects of the previously published data.

4.2.1. Organic carbon

The TOC concentrations in the dissolved fraction range from 0.4–1.7 mg/l (Table 1) and are highest close to the glacial source and tend to decrease downstream, which may be due to a dilution effect. In contrast, colloidal organic carbon increases from a minimum of 0.02 mg/l in the glacial source river to 0.37 mg/l close to the river mouth. This results in a trend of an increasing percentage of the total carbon in colloids from ~1%

Table 1
Concentrations and isotope ratios of the dissolved (<0.2 μm), ultrafiltered (<10 kD) and colloidal (10 kD<x<0.2 μm) fractions (note that particle-reactive elements in the ultrafiltered fraction may be compromised by the filtration process – see text for details). Colloidal data have been adjusted to account for retentate and filtrate volumes. Previously published data are the (²³⁴U/²³⁸U) activity ratios and cation concentrations for the dissolved (<0.2 μm) fraction (Pogge von Strandmann et al., 2006, 2010).

	Colloid conc factor	pH	TOC (mg/l)	Li (ng/l)	Na (mg/l)	Mg (mg/l)	Al (μg/l)	Si (mg/l)	K (mg/l)	Ca (mg/l)	Mn (μg/l)	Fe (mg/l)	U (ng/l)	Th (ng/l)	(²³⁴ U/ ²³⁸ U)	(²³⁰ Th/ ²³² Th)	(²³⁰ Th/ ²³⁸ U)
<i>Iceland</i>																	
A3#2	Dissolved	8.08	1.20	163	10.1	1.66	6.21	6.49	0.49	3.92	1.86	3.30	1.67	0.016	1.69 ± 1	1.73 ± 4	0.00428 ± 12
	Ultrafiltered												1.81		1.59 ± 2		
	Colloid	10.0	0.29	17.2	0.94	0.16	1.07	0.74	0.05	0.39	0.23	17.3	0.40	0.012	1.33 ± 2	1.48 ± 3	0.672 ± 0.3
A4#2	Dissolved	8.15	0.40	332	6.87	1.16	42.9	6.79	0.39	3.16	1.59	15.7	3.25	0.074	1.57 ± 2	1.35 ± 3	0.0108 ± 2
	Ultrafiltered			365	6.39	1.07	29.4	11.0	0.39	3.04	2.39	3.65	5.51	2.14	1.67 ± 4		
	Colloid	14.3	0.37	25.8	0.46	0.08	8.44	0.55	0.031	0.240	0.21	7.33	0.55	0.066	1.19 ± 1	1.17 ± 8	0.470 ± 3
A6#2	Dissolved	8.27	0.60	84.9	7.44	1.88	5.76	6.42	0.40	4.73	0.35	21.2	1.27	3.55	1.27 ± 2	0.99 ± 2	0.00192 ± 18
	Ultrafiltered			89.3	7.28	1.81	4.38	7.11	0.41	4.48	0.50	4.77	2.16	0.85	1.54 ± 1		
	Colloid	1.79	0.21	5.55	0.43	0.11	1.34	0.39	0.026	0.29	0.057	10.8	0.28	0.82	2.41 ± 2	1.10 ± 2	1.08 ± 2
A7#2	Dissolved	8.15	1.40	372	11.2	3.40	3.91	7.30	0.90	5.72	3.40	59.7	3.42	1.44	1.64 ± 1	1.82 ± 14	0.255 ± 19
	Ultrafiltered												3.71		1.52 ± 1		
	Colloid	17.8	0.25	21.5	0.64	0.20	1.37	0.43	0.053	0.35	0.09	24.2	0.56	0.42	2.09 ± 2	2.01 ± 7	0.495 ± 5
A8#2	Dissolved	8.87	0.40	293	6.25	0.87	74.3	6.69	0.36	2.88	0.44	24.4	4.17	1.81	1.53 ± 2	2.36 ± 17	0.340 ± 20
	Ultrafiltered			293	6.14	0.85	8.04	7.57	0.39	2.74	0.56	4.44	3.71	1.97	1.47 ± 1		
	Colloid	48.0	0.04	7.09	0.15	0.023	5.08	0.184	0.01	0.08	0.05	4.24	0.28		1.13 ± 1		
A12	Dissolved	9.30	1.70	258	6.15	0.83	72.7	6.58	0.35	2.79	0.54	24.3	4.52	1.66	1.39 ± 2	1.45 ± 5	0.176 ± 6
	Ultrafiltered												2.84		1.49 ± 2		
	Colloid	28.6	0.02	9.10	0.22	0.03	2.50	0.25	0.01	0.10	0.03	0.83	0.13	0.36	3.13 ± 6	1.44 ± 13	1.34 ± 8
E1	Dissolved	9.11		0.39	4.70	0.66	95.5	1.97	0.19	4.22	2.43	89.6	8.09	2.13	1.70 ± 4	0.86 ± 2	0.0743 ± 17
E5	Dissolved	9.69		0.11	3.03	0.32	97.5	1.28	0.14	3.69	0.88	25.3	12.9	0.75	1.60 ± 1	0.91 ± 2	0.0175 ± 4
<i>Azores</i>																	
Az1	Dissolved	7.98	1.00	318	10.4	1.53	18.2	11.6	2.45	2.37	0.52	8.89	7.31	6.94	1.47 ± 3		
	Ultrafiltered			318	10.3	1.53	2.96	11.5	2.35	2.36	0.11	5.67	13.2		1.93 ± 2		
	Colloid	58.0	0.10	0.07	0.003	15.2	0.09	0.10	0.01	0.01	0.40	3.22	1.57		1.10 ± 1		
Az2	Dissolved	7.78	1.00	91.5	7.40	1.62	15.6	8.73	1.28	2.96	0.22	9.13	6.18	4.75	1.75 ± 3		
	Ultrafiltered			89.3	7.26	1.53	14.0	8.64	1.21	2.71	0.03	7.3	7.3		1.49 ± 1		
	Colloid	58.0	0.29	2.16	0.13	0.087	1.64	0.09	0.07	0.25	0.19	9.13	1.61	1.38	1.13 ± 1		
Az3	Dissolved	8.32	1.00	497	12.0	2.75	16.6	16.3	3.31	5.27	1.41	13.6	40.7	5.41	1.06 ± 1		
	Ultrafiltered			489	11.8	2.56	15.2	16.3	3.25	4.24	1.22	0.44	22.0		1.23 ± 2		
	Colloid	58.0	0.12	7.94	0.15	0.19	1.39	0.016	0.06	1.03	0.20	13.2	2.96	1.35	1.06 ± 1		
Az4	Dissolved	7.96	0.60	137	7.48	1.21	23.0	7.23	1.06	1.59	0.11		2.99	3.15	1.50 ± 2		
	Ultrafiltered			131	7.39	1.10	22.1	6.82	1.03	1.53	0.10	6.70	14.9		1.42 ± 1		
	Colloid	58.0	0.10	5.38	0.09	0.12	0.88	0.41	0.03	0.06	0.02		0.43	0.40	1.14 ± 1		
Az5	Dissolved	7.65	0.80	138	8.43	1.51	8.71	8.72	1.76	1.77	0.10	0.44	4.63	2.74	1.86 ± 5		
	Ultrafiltered			140	8.38	1.36	8.49	8.62	1.58	1.53	0.02		2.5		1.09 ± 2		
	Colloid	58.0	0.08		0.05	0.15	0.22	0.10	0.18	0.24	0.09	0.44	0.72	0.42	1.35 ± 2		
Az6	Dissolved	8.24	0.80	1380	17.5	7.02	10.2	21.8	5.46	10.80	3.62	18.0	77.1	1.99	1.27 ± 1		
	Ultrafiltered			1370	17.1	6.54	9.40	21.1	4.95	10.08	1.09	3.65	153		1.44 ± 3		
	Colloid	20.0	0.14	13.8	0.42	0.49	0.81	0.76	0.51	0.72	2.52	14.4	3.38		1.26 ± 1		
Az7	Dissolved	8.22	0.90	269	14.7	4.39	13.1	16.4	3.43	7.39	0.48	8.61	40.8	2.06	1.24 ± 1		
	Ultrafiltered			253	14.5	4.27	12.7	17.1	3.55	7.33	0.11		46.7		1.29 ± 1		
	Colloid	58.0	0.09	15	0.24	0.12	0.40			0.06	0.37	8.61	2.26		1.42 ± 4		
Az9	Dissolved	6.14	1.10	2180	10.1	0.86	46.4	11.9	3.75	1.00	56.0	63.9	107	14.55	1.03 ± 1		
	Ultrafiltered			2090	9.83	0.82	8.94	11.6	3.38	0.98	46.8	6.91	14.7		1.06 ± 2		
	Colloid	58.0	0.15	95.0	0.23	0.04	37.5	0.30	0.37	0.02	9.22	57.0			1.05 ± 2		
Az10	Dissolved	7.86	0.90	250	7.89	2.31	32.1	11.1	1.77	3.94	0.92	17.5	31.7	7.29	1.18 ± 1		
	Ultrafiltered			266	7.77	2.14	20.2	11.0	2.06	3.85	0.26		111		1.03 ± 1		
	Colloid	58.0	0.20		0.12	0.17	12.0	0.05		0.09	0.66	17.5	5.83		1.17 ± 1		
Az11	Dissolved	7.99	1.00	400	12.8	1.69	29.4	14.7	4.00	2.38	1.18	14.7	20.9	8.27	1.02 ± 2		
	Ultrafiltered			384	12.6	1.61	14.7	14.6	3.81	2.21	1.03		11.0		1.04 ± 2		
	Colloid	58.0	0.12	15.3	0.16	0.07	14.8	0.10	0.18	0.17	0.16	14.7	2.35		1.08 ± 1		
Az12	Dissolved	7.60	1.00	238	7.35	0.79	18.5	8.26	2.01	1.07	0.22	1.03	1.45	9.81	0.89 ± 2		
	Ultrafiltered			229	7.30	0.75	13.6	8.25	1.91	0.97	0.06		1.68		0.89 ± 2		
	Colloid	58.0	0.14	9.27	0.06	0.04	4.89	0.01	0.10	0.10	0.16	1.03	0.17		1.03 ± 2		

to ~93% downstream. This may be due to changing pH (Baalousha et al., 2008; Gundersen and Steinnes, 2003): glacial sample A12 has a pH of 9.3 (due to isolation from atmospheric CO₂), whereas pH then decreases downstream (~8.15), due to atmospheric contact, increasing vegetative cover and organic carbon concentration in downstream soils. Sample A8 has a low amount of TOC in colloids, which may be because local hydrothermal input is changing the water chemistry, resulting in colloids being precipitated from solution (Pogge von Strandmann et al., 2006; Porcelli et al., 1997, 2001).

In contrast, dissolved load TOC in Sao Miguel shows a much narrower range (0.6–1.1 mg/l). Colloidal TOC ranges from 0.08–0.29 mg/l, with 10–29% of total organic carbon present in colloidal form. These levels of TOC are slightly lower, but of the same order of magnitude, as samples taken from the basaltic Mount Cameroon (Riotte et al., 2003).

4.2.2. Elemental ratios

Of the major elements in the Icelandic dissolved load (Na, K, Ca, Mg, Si), on average only 5.9–6.7% of the <0.2 μm fraction is in colloids. This figure is much higher for the particle-reactive elements (Dupre et al., 1999; Merkel and Planer-Friedrich, 2005; Pokrovsky et al., 2005; Sholkovitz, 1992); for example, colloids account for, on average, 18%, 10% and 36% of Al, Mn and Fe, respectively, in the dissolved fraction. In the Azores, the percentage of the major elements in colloids ranges from 1.0 to 6.7% of the total <0.2 μm fraction. On the other hand, on average 29% Al, 54% Mn and 75% Fe of the <0.2 μm fraction are associated with colloids.

The Ca/Na ratio of the dissolved phase in Icelandic rivers varies between 0.32 and 0.64; Mg/Na ratios range from 0.13 to 0.30 (respective averages are 0.46 and 0.19). Corresponding colloid Ca/Na ratios range from 0.41 to 0.68, with an average of 0.52. Colloidal Mg/Na ratios range from 0.14 to 0.31, with an average of 0.20. In comparison, the Ca/Na ratio of the bedload is 10.6 ± 4.9 (2sd), and Mg/Na is 5.7 ± 4.7, and suspended load Ca/Na = 10.0 ± 6.4 and Mg/Na = 5.6 ± 3.0 (Pogge von Strandmann et al., 2006). Icelandic colloidal elemental ratios are thus effectively indistinguishable from those of the dissolved load, but very different from those of the bedload or suspended load.

In the Azores, the average Ca/Na and Mg/Na ratios of the dissolved load are 0.32 (0.10–0.62) and 0.20 (0.09–0.40) respectively. Colloidal Ca/Na ranges from 0.10 to 6.70, with an average of 1.78. Colloidal Mg/Na ranges from 0.05 to 2.85, with an average of 0.96. Bedload Ca/Na = 3.52 ± 4.2 (2sd) and Mg/Na = 2.62 ± 3.3, and suspended load Ca/Na = 5.82 ± 8.86, and Mg/Na = 1.06 ± 2.0 (Pogge von Strandmann et al., 2010). Thus colloids on the Azores show much greater ranges in elemental ratios compared to Iceland, and have ratios either similar to the dissolved load or to host basalt.

4.2.3. U-series

The Icelandic dissolved samples have U concentrations ranging between 1.7 and 4.5 ng/l (Table 1), generally with high concentrations associated with hydrothermal input (A8). Colloidal U concentrations range from 0.13 to 0.56 ng/l, and increase with distance from the source. Thorium concentrations in the dissolved load range from 0.016 to 3.6 ng/l; low concentrations of Th in the dissolved load are not surprising because Th is rapidly scavenged from solution (Andersson et al., 1995; Chabaux et al., 2003). Colloidal Th concentrations vary between 0.012 and 0.82 ng/l. Bedload U and Th concentrations average at 0.44 and 1.53 ppm, respectively. Published data from the nearby Snaefellsjökull and Langjökull basaltic volcanic rocks indicates [U] that ranges from 0.05–4.1 ppm, and [Th] from 0.15–13.7 ppm (Kokfelt et al., 2003, 2009). The U/Th ratios vary between 0.36 and 106 in the dissolved load, and from 0.34 to 33 in the colloidal fraction, compared to an average ratio of 0.28–0.29 for river sediments, and 0.30 ± 0.08 for published bedrock. The three orders of magnitude fractionation in the dissolved load compared to source material is consistent with the preferential release of U relative to Th into waters, due to the greater mobility of U relative to Th during chemical weathering (Fig. 2). This is

because in oxic environments, U is oxidised to U⁶⁺, which is soluble, whereas Th remains as Th⁴⁺, which is insoluble.

The (²³⁴U/²³⁸U) activity ratios in the dissolved fraction range from 1.27 to 1.70, whereas colloidal (²³⁴U/²³⁸U) varies between 1.13 and 3.13. Bedload (²³⁴U/²³⁸U) is within analytical uncertainty of secular equilibrium, and the suspended load ranges from 1.00 to 1.47 (Pogge von Strandmann et al., 2006). The (²³⁰Th/²³²Th) activity ratios in the Icelandic bedload are 0.79–1.02 (Table 2). Suspended load Th activity ratios vary between 0.95 and 2.11. (²³⁰Th/²³²Th) activity ratios in the dissolved fraction range from 0.86 to 2.36, with high values associated with hydrothermal input. Higher activity ratios would be predicted in waters, due to recoil effects and preferential release of ²³⁰Th (daughter of ²³⁴U) over ²³²Th (Vigier et al., 2006). Colloidal (²³⁰Th/²³²Th) varies between 1.10 and 2.00. The (²³⁰Th/²³⁸U) activity ratios in the bedload from Iceland are at secular equilibrium. Suspended load activity ratios range from 1.27 to 2.72. In the dissolved load (²³⁰Th/²³⁸U) range from 0.0019 to 0.340 (where the highest ratio is affected by hydrothermal input), and colloidal activity ratios vary between 0.495 and 1.34.

In the dissolved fraction from Sao Miguel, uranium concentrations range from 1.45 to 77.1 ng/l (Table 1); the sample with the highest concentration is probably affected by mixing with seawater. Corresponding colloidal concentrations vary between 0.17 and 5.83 ng/l. The Th concentrations range from 2.0 to 14.6 ng/l, where the highest concentrations are associated with hydrothermal input. Colloidal [Th] varies between 0.4 and 1.4 ng/l. Bedload average [U] and [Th] are 1.79–3.95 and 8.6–16.6 ppm, respectively (where highest concentrations are associated with trachytes). In comparison, published data for basalt from Sao Miguel has a [U] range of 1.25–1.89 and [Th] range of 4.54–7.27 ppm (Turner et al., 1997), whereas trachyte has [U] of 4.27–13.0 ppm and [Th] of 16.7–48.5 ppm (Widom et al.,

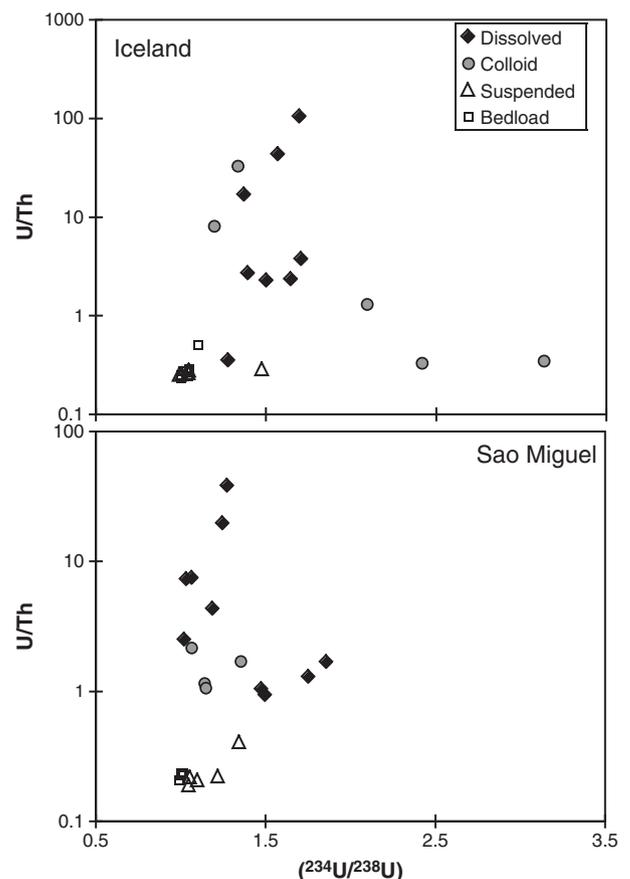


Fig. 2. Elemental Th/U ratios as a function of U activity ratio for both areas. This demonstrates the ~3 orders of magnitude U/Th fractionation occurring at the weathering interface.

Table 2
U and Th concentrations and activity ratios of the bedload and suspended load. U and Th concentration data, and ($^{234}\text{U}/^{238}\text{U}$) activity ratios are from Pogge von Strandmann et al. (2006, 2010). TSS, area and discharge data are from Pogge von Strandmann et al. (2006).

		TSS (mg/l)	Area (km ²)	Discharge (m ³ /sec)	U (ppm)	Th (ppm)	($^{234}\text{U}/^{238}\text{U}$)	($^{230}\text{Th}/^{232}\text{Th}$)	($^{230}\text{Th}/^{238}\text{U}$)
<i>Iceland</i>									
A3	Bedload	522			0.48	0.94	1.10 ± 1		
	Susp. load				0.26		1.00 ± 1		
A4	Bedload	612	3560	189	0.14	0.55	1.04 ± 1	0.81 ± 1	1.02 ± 1
	Susp. load				0.20	0.70	1.04 ± 2	1.25 ± 2	1.48 ± 2
A6	Bedload	525	500	35.2	0.73	2.88	1.00 ± 2		
	Susp. load				0.05		1.26 ± 2		
A7	Bedload	558	480	25.3	0.42	1.77	1.00 ± 1	0.79 ± 0.5	1.07 ± 1
	Susp. load				0.05	0.18	1.47 ± 2	2.10 ± 1	2.41 ± 1
A8	Bedload	635	1690	94.5	0.33	1.17	1.03 ± 1		
	Susp. load				0.17	0.65	1.04 ± 1	2.15 ± 2	2.72 ± 2
E1	Bedload	1890	200	200	0.33	1.15	1.04 ± 2	1.02 ± 1	1.07 ± 1
	Susp. load				0.78	3.08	0.99 ± 1	0.98 ± 0.4	1.29 ± 0.5
E5	Bedload	2790	25	50	0.63	2.25	1.01 ± 1	0.89 ± 1	1.03 ± 1
	Susp. load				0.89	3.41	1.00 ± 1	0.95 ± 0.3	1.27 ± 0.4
<i>Azores</i>									
Az1	Bedload				3.04	13.2	1.00 ± 1		
	Susp. load				3.70	17.7	1.10 ± 2		
Az2	Bedload				1.79	8.6	0.99 ± 1		
	Susp. load				0.31	1.4	1.22 ± 1		
Az3	Bedload				3.95	16.6	1.01 ± 1		
	Susp. load				2.59	13.6	1.04 ± 1		
Az4	Bedload				3.09	13.1	1.00 ± 1		
Az5	Bedload				2.83	12.4	1.00 ± 1		
	Susp. load				1.12	2.7	1.34 ± 2		
Az6	Bedload				3.75	15.7	1.01 ± 1		
	Susp. load				1.71	7.8	1.05 ± 2		
Az7	Bedload				3.18	13.4			
	Susp. load				4.75	15.9	1.02 ± 1		

1992). The ($^{234}\text{U}/^{238}\text{U}$) activity ratios in the dissolved load vary from 0.89 to 1.86. Colloidal ($^{234}\text{U}/^{238}\text{U}$) activity ratios range from 1.04 to 1.42. There are no obvious correlations in U concentrations or activity ratios between the dissolved and colloidal fractions. Bedload ($^{234}\text{U}/^{238}\text{U}$) activity ratios are also within uncertainty of secular equilibrium, whereas suspended load activity ratios range from 1.04–1.34.

U and Th speciation were calculated using the PHREEQC programme (Merkel and Planer-Friedrich, 2005; Parkhurst and Appelo, 1999). In Iceland uranyl hydroxides dominate at pH < 8.5 (up to 90% of total U at pH 8), whereas at higher pH uranyl-carbonato complexes dominate (Chabaux et al., 2003; Langmuir, 1978), which may be of importance because the uranyl-carbonato complexes are thought to sorb more weakly than uranyl (Bargar et al., 1999; Catalano and Brown, 2005). In the Azores the pH range is smaller, and neither uranyl species is dominant.

5. Discussion

5.1. Colloid composition

Organic matter (such as humic or fulvic acids) is generally considered to act as a ligand for many elements, including U-series nuclides (Chabaux et al., 2003; Dupre et al., 1999; Porcelli et al., 1997; Viers et al., 1997). The TOC levels in organic-dominated rivers (such as the Kalix (Porcelli et al., 1997)) can be as high as ~9 mg/l, although colloidal material contains ≤ 1.2 mg/l. In contrast, rivers with low concentrations of organic matter, such as those that drain basaltic terrains (this study and Mount Cameroon (Riotte et al., 2003)) have approximately an order of magnitude lower TOC in all phases. It is thought that colloids form in one of four ways: 1) direct precipitation from the dissolved phase of surface waters; 2) precipitation from dissolved elements in soil solutions (neofomed particles); 3) assimilation to small particles of the suspended load (residual particles); 4) formation from organic material (Bolt et al., 1991;

Chabaux et al., 2003; Eberl, 1984; Riotte et al., 2003). Figure 3 compares Ca/Na ratios of the dissolved phase and colloidal fractions, where on average <7% of total Ca or Na are on colloids. All Icelandic samples plot along a 1:1 line, which strongly suggests that Icelandic colloids have precipitated directly from solution or are neofomed in soil solutions, with little accompanying Ca/Na fractionation. In contrast, only a few samples from Sao Miguel plot along an equiline – colloidal Ca/Na tends to be higher than the dissolved fraction (Fig. 3). Ultrafiltered (<10kD) Ca/Na ratios are identical to those in the dissolved fraction. This suggests either that colloids from Sao Miguel are not dominantly precipitated from the dissolved load, or there is a significant fractionation of Ca/Na during incorporation into the colloids. The colloidal Ca/Na ratios for Sao Miguel are within the

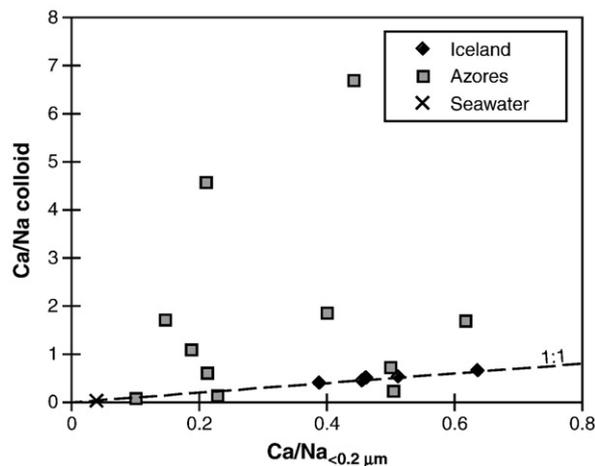


Fig. 3. Ca/Na mass ratios for the dissolved phase and colloids. Icelandic data plot along the 1:1 line, suggesting direct precipitation of the colloidal phase from the dissolved load. Azores colloids have additional input.

range seen in the suspended load, which raises the possibility that these colloids consist of directly precipitated material and/or residual particles in the suspended load.

5.2. Uranium and Thorium behaviour – secondary mineral control

Because organic matter acts as a ligand for U and Th, colloidal U-series nuclides in rivers with high organic carbon content are dominantly bound with organics (Chabaux et al., 2003; Porcelli et al., 1997; Viers et al., 1997). Basaltic, low organic carbon rivers (<2.2 mg/l in <0.2 μm fraction) from Mount Cameroon (Riotte et al., 2003) and this study also show a general trend of increasing colloidal U transport with higher colloidal organic carbon (Fig. 4). While this suggests that organic carbon, even at very low concentrations, acts to bind U to colloidal material, the data also suggest that organic carbon is not the dominant control on U transport in these rivers.

The U concentrations in the dissolved fraction show a positive relationship with riverine pH (Iceland: $r^2 = 0.73$; Azores: $r^2 = 0.59$). In basaltic terrains, pH is controlled by 1) dissolution of Ca–Mg silicates, which drives pH higher; 2) uptake of atmospheric CO_2 (directly or via organic matter decay) drives pH lower; 3) precipitation of secondary minerals, which also drives pH lower (Gislason et al., 1996; Pogge von Strandmann et al., 2010). This pH–U relationship also holds for the larger compilation of (non-hydrothermal) Icelandic rivers for which colloids were not collected ($r^2 = 0.44$; significant >99%, $n = 18$; Pogge von Strandmann et al., 2006). Conversely the Icelandic colloidal [U] shows a negative covariation with pH ($r^2 = 0.66$) (Fig. 5). In other words, as pH increases in Iceland, the relative amount of total riverine U located in the colloidal fraction decreases from ~24% at pH ~8 to ~3% at pH 9.3. There are three possible explanations for this dissolved and colloidal behaviour: 1) during basalt weathering, secondary minerals such as Fe-oxyhydroxides,

smectites and allophane become unstable at higher pH (≤ 10) (Arnorsson et al., 2002; Gislason and Arnorsson, 1990; Gislason et al., 1996; Pogge von Strandmann et al., 2006, 2008a, 2010; Sigfusson et al., 2008; Stefansson and Gislason, 2001; Stefansson et al., 2001). Fe-oxyhydroxides coprecipitate U and Th, and clays such as montmorillonite are known to adsorb uranyl (Catalano and Brown, 2005), therefore if such minerals are either destabilised or not forming in the first place, then relatively more U is likely to be present in solution. If the colloids are clay-rich, then at high pH less colloids would form, decreasing the U content in that phase; 2) Although olivine and pyroxene approach saturation at high pH, slowing their dissolution, the dissolution rate of basaltic glass, the dominant U host in basalts, and plagioclase increases with pH (Oelkers and Gislason, 2001), thus leading to greater U input into river waters. In Iceland this is compounded by the combination of enhanced formation of glass during sub-glacial eruptions, and the high pH of the same glacial waters due to isolation from atmospheric CO_2 . Both of these processes may also result in reduced clay mineral and thus soil formation at higher pH, which would, in turn, have an effect on colloid formation. 3) As pH increases, the dominant uranyl complex becomes uranyl-carbonato species, which are thought to be more weakly sorbing than uranyl itself (Bargar et al., 1999; Catalano and Brown, 2005). Thus as pH increases, less U is adsorbed by colloids, leading to higher dissolved load concentrations, and lower colloidal concentrations. It seems likely that all these processes are affecting U concentrations in the rivers, however the effect of uranyl-carbonato sorption on the dissolved and colloidal fractions is relatively minor in this pH range (Catalano and Brown, 2005), and so the effects of weathering and secondary mineral formation are expected to be relatively greater.

In the Azores the relationship between pH and [U] is less clear, partly because the pH range in the Azores is far smaller (7.6–8.3). However the positive covariation between [U] in the dissolved load and pH does suggest that similar processes are controlling U in the stream waters. Colloidal [U] in the Azores, on the other hand, also covaries positively with pH. However, the percentage of total riverine U on colloids shows no trend with pH, and this suggests relatively constant adsorption of U from the dissolved load to colloids.

Between 22 and 89% of riverine Th in Iceland is carried on colloids, with an increase downstream away from the glacial source, and therefore also an increase with colloidal TOC content (Fig. 4) and with decreasing pH. There is little variation in colloidal [Th] in the rivers of Sao Miguel (Fig. 4) although the data are few. Thorium speciation is dominantly $\text{Th}(\text{OH})_4$ in these waters, consequently changes in sorption due to speciation are unlikely to be significant. Thus, as for U, Th behaviour in these waters appears to be controlled by glass dissolution (also the dominant Th host) and secondary mineral formation (both pH-controlled), and to some extent by the organic carbon contents of the colloids (Santschi et al., 2006). However the latter may also simply be a function of the quantity of colloidal material that is able to form in high pH glacial rivers.

Therefore it seems likely that dissolved and, to a certain extent, colloidal U and Th concentrations in these terrains are controlled by dissolution of glass (which is enhanced at high pH) and formation of secondary minerals such as Fe-oxyhydroxides (which is favoured at low pH).

5.3. Colloid transport of U-series nuclides

The ($^{234}\text{U}/^{238}\text{U}$) ratios of the colloids give some insight into their origin, and into nuclide transport. Figure 6 compares the ($^{234}\text{U}/^{238}\text{U}$) of the suspended, dissolved and colloidal fractions for the data presented here, and for all other available basaltic catchments. Colloids from Mount Cameroon (<5 kD) have activity ratios that are similar to their corresponding dissolved loads, as do a majority of the Azores samples, suggesting rapid adsorption by colloids (Porcelli et al., 1997, 2001). The Azores colloids that do not have similar ($^{234}\text{U}/^{238}\text{U}$) to the corresponding dissolved waters tend to possess seawater-like activity

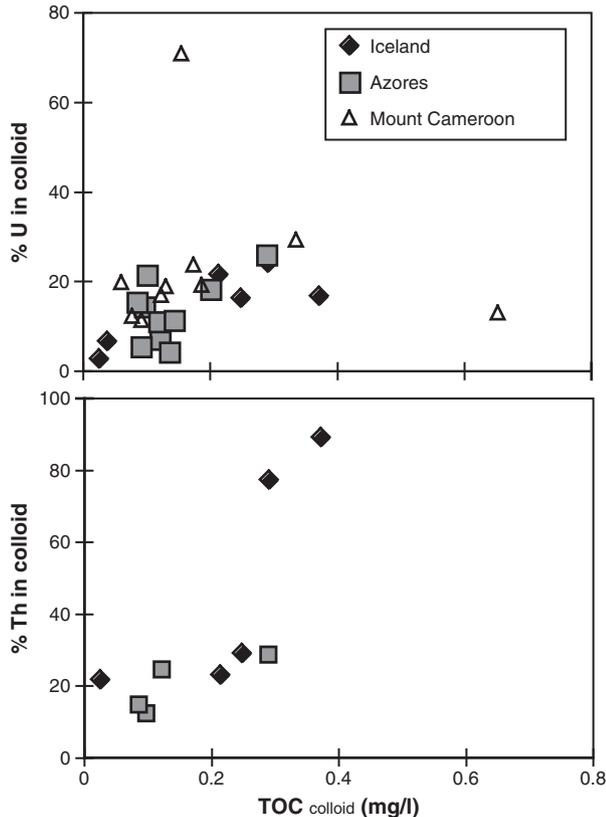


Fig. 4. Percentage of dissolved (<0.2 μm) U and Th that is bound to colloids as a function of the concentration of colloidal organic carbon for basaltic terrains. Data for Mount Cameroon are from Riotte et al. (2003). These data suggest only a minimal dependence of U and Th on organic matter in these relatively inorganic terrains.

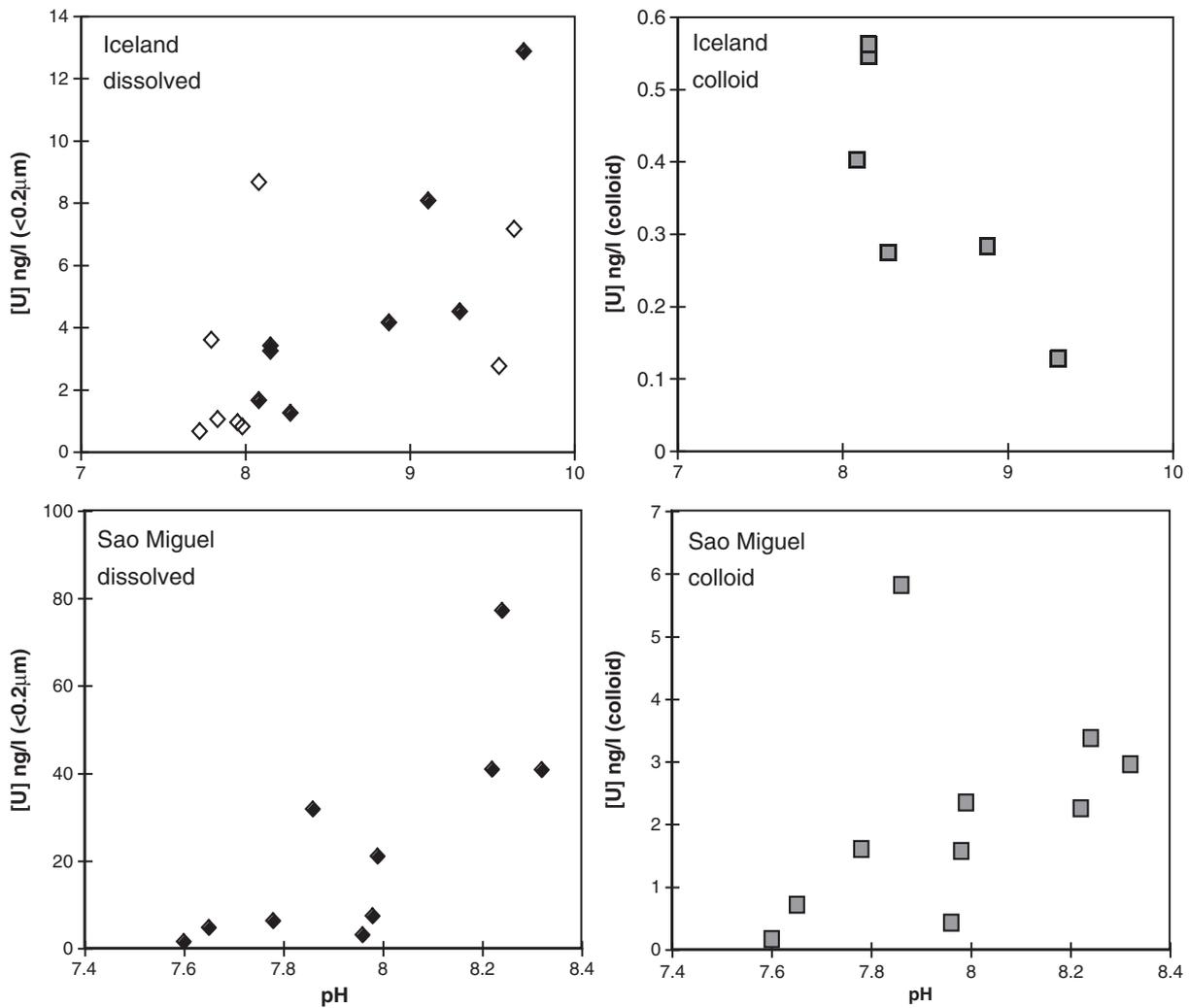


Fig. 5. U concentrations in the <0.2 μm and colloidal fractions as a function of riverine pH for Iceland and Sao Miguel. Open symbols are rivers for which no colloids were collected (Pogge von Strandmann et al., 2006). Icelandic trends are significant >99% (Spearman-Rank correlation). These trends suggest a strong pH control on U, via the formation and precipitation of secondary minerals.

ratios, reflecting the dominant source of precipitation in the Azores (Pogge von Strandmann et al., 2010). However these colloids have major element ratios that are very different from seawater, suggesting that they originated from another source, but possibly gained their U from marine aerosols or areas close to the stream source where waters are dominantly sourced by precipitation.

Generally, rivers with $(^{234}\text{U}/^{238}\text{U}) < 1.27$ in the dissolved fraction tend to have identical colloidal $(^{234}\text{U}/^{238}\text{U})$, whereas those with dissolved $(^{234}\text{U}/^{238}\text{U}) > 1.27$ have widely varying colloidal $(^{234}\text{U}/^{238}\text{U})$. It is generally thought that in basaltic terrains, where glass is the major U-bearing phase, high physical weathering rates, groundwater contribution or soil formation, combined with low chemical weathering rates, raise the activity ratio of the dissolved load. Conversely, high chemical weathering or glass dissolution will lower the dissolved activity ratio towards secular equilibrium (Andersen et al., 2009; Pogge von Strandmann et al., 2010; Porcelli, 2008; Robinson et al., 2004). Thus it appears that when chemical weathering rates are relatively low, there is little or no U exchange between the dissolved and colloidal fractions. This may be because the amount of clay mineral formation in such rivers is low and consequently there are fewer mineral surfaces or colloids for U adsorption. In some Icelandic streams this effect may be enhanced by glaciation, which raises pH and thus lowers Fe-oxyhydroxide and allophane content. By contrast, the colloids that are present may have formed in areas of high soil or glacial till (neof ormation), raising their

activity ratio. Thus, for example, sample A12 from close to the Langjökull icecap, has high pH (9.3), relatively low dissolved $(^{234}\text{U}/^{238}\text{U}) = 1.39$, suggesting an element of glass dissolution, but very high colloidal $(^{234}\text{U}/^{238}\text{U})$ (3.13), suggesting a source with high grain surface area, such as glacial till. This further suggests that colloids with very high activity ratios have U sources decoupled from the dissolved load, as also suggested by their U/Th (Fig. 2). In samples further downstream, pH is lower, clay mineral saturation is higher, and colloidal activity ratios are much lower. Because Icelandic colloids have similar major element ratios to the dissolved load (Fig. 3), this implies that soil solutions must also have similar element ratios. Soil solution data from an area close to the studied Icelandic catchment (Sigfusson et al., 2008) show similar averages and ranges in Ca/Na and Mg/Na ratios to dissolved and colloidal fractions measured by this study.

Thus suspended load U activity ratios appear to be altered by U adsorption, and the $(^{234}\text{U}/^{238}\text{U})$ of colloids is probably dependent on the pH-controlled formation of secondary minerals, and thus the degree to which these clays or Fe-oxyhydroxides scavenge U from the river waters.

5.4. Thorium activity ratios – rapid exchange between all phases

Thorium is insoluble in its natural state in oxidising waters (ThO_2), but its solubility is dramatically increased by association with organic and inorganic complexes (the most common of the latter in this pH

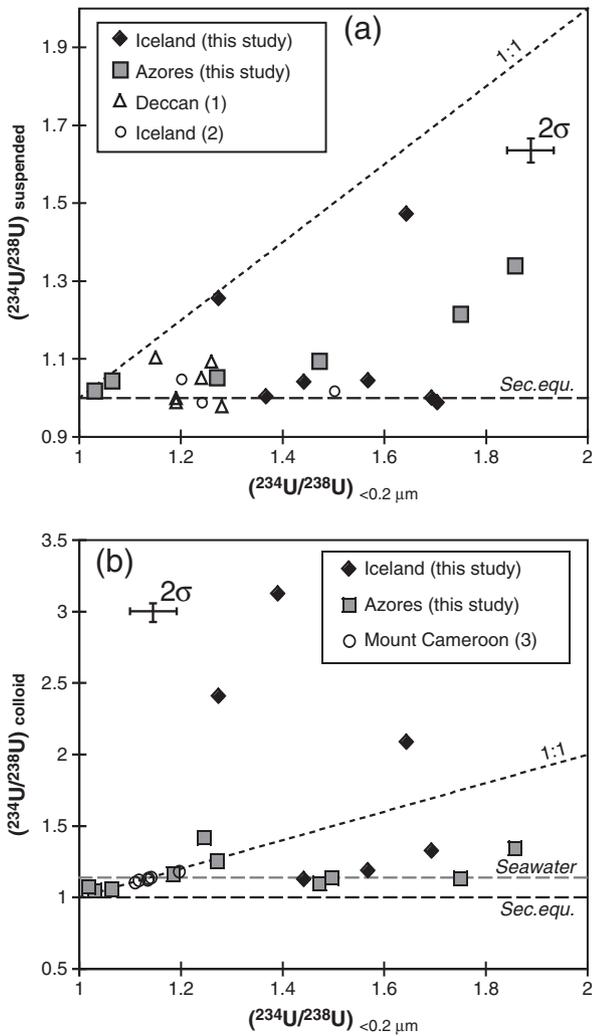


Fig. 6. U activity ratios compared for the suspended, <0.2 μm and colloidal fractions for rivers draining basaltic terrains. (1) Vigier et al., 2005; (2) Vigier et al., 2006; (3) Riotte et al., 2003. The error bars represent the 2sd external error of the analyses. High suspended load activity ratios suggest U adsorption.

range is Th(OH)₄ (Langmuir and Herman, 1980). Thorium is also strongly adsorbed onto neoformed minerals, such as clay particles, and/or Fe-oxyhydroxides (Andersson et al., 1995; Middleburg et al., 1988). As a consequence Th may be extremely immobile, and in a number of rivers up to 99% of Th is carried by suspended or colloidal particles (Andersson et al., 1995, 1998; Porcelli et al., 1997, 2001; Swarzenski et al., 2004; Vigier et al., 2001). Similarly, in the rivers studied here >99% of Th is carried by the suspended particles, primarily because they are basaltic in nature, and the [Th] in the dissolved and colloidal fractions is very low.

Rapid adsorption of dissolved Th onto colloids or isotopic exchange is therefore most likely to be the cause of approximately equivalent (²³⁰Th/²³²Th) activity ratios in the corresponding dissolved and colloidal fractions (and therefore also in the truly dissolved load) in Iceland and the Deccan (Fig. 7b) (Plater et al., 1992; Porcelli et al., 2001; Vigier et al., 2005). That the dissolved and suspended loads from this study also have similar (²³⁰Th/²³²Th) activity ratios is even more surprising. Data from other basaltic catchments are also plotted, and it is evident that most Icelandic data lie close to the 1:1 line. It is unlikely that the suspended particles originally had (²³⁰Th/²³²Th) activity ratios >1.5, given that studies of pristine Icelandic and Sao Miguel lavas report (²³⁰Th/²³²Th) = 0.89–1.19 (Kokfelt et al., 2003, 2009; Turner et al., 1997). Instead it appears that these sediments have adsorbed Th from high concentration soil solutions, which

dominate both the measured particulate and dissolved load (²³⁰Th/²³²Th) activity ratio (as evidenced by lower average U/Th than the bedload). This could be due to high secondary mineral formation on the suspended sediment surfaces, evidence for which is seen in both Li and Mg isotopes in the same suspended particles (Pogge von Strandmann et al., 2006, 2008a). The two samples from Vigier et al. (2005, 2006) with very high dissolved (²³⁰Th/²³²Th) are waters which were taken from close to the source of the stream, which may simply suggest that there was insufficient time for the suspended load to adsorb a significant amount of Th. In the Icelandic data the suspended loads from closest to the riverine source have lower Th activity ratios than those further downstream, suggesting more uptake with time. However the trend is not significant (*r*² = 0.3), and in any case would not necessarily be expected, given variations in pH, and thus secondary minerals, as well as groundwater and hydrothermal water input across the catchments.

High Th particle-reactivity and exchange between riverine phases has been previously reported (Chabaux et al., 2003; Plater et al., 1992; Porcelli et al., 2001), although not for basaltic terrains. This process can create a problem for the calculations of weathering timescales, since these generally assume that there is no exchange between particles and the dissolved or colloidal phases subsequent to weathering in soils (Dosseto et al., 2006b, 2008a; Vigier et al., 2001, 2005, 2006). Thus differences in timescales calculated using suspended vs. bedload (assuming the bedload is unaffected by Th

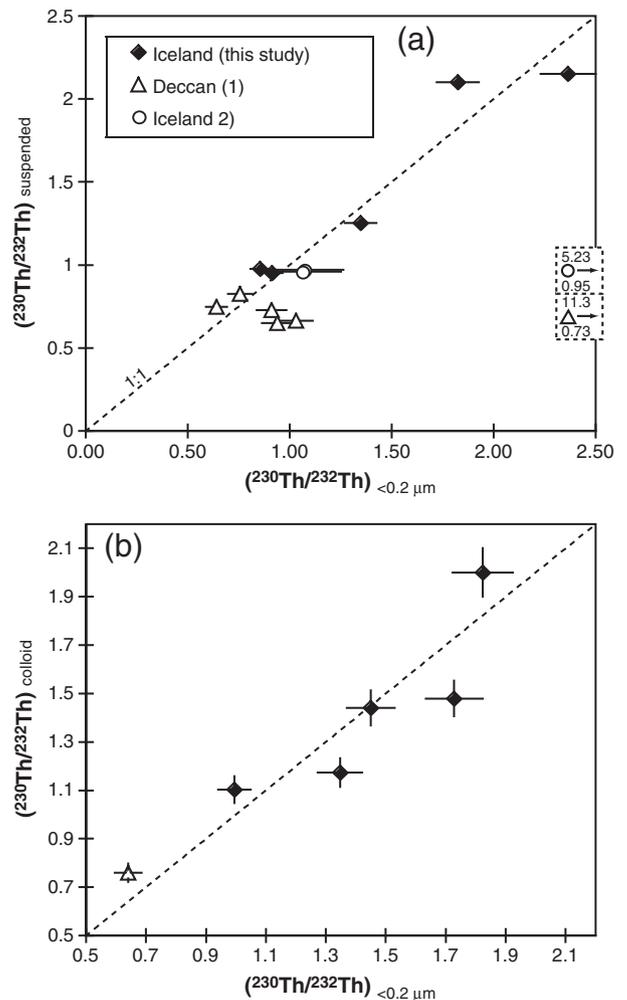


Fig. 7. Th activity ratios compared for the suspended, <0.2 μm and colloidal fractions, for rivers draining basaltic terrains. References are the same as for Figure 6. Error bars represent the external uncertainty reported for each study. The trends suggest rapid Th exchange and adsorption between all the phases.

adsorption) are up to 22% (Vigier et al., 2006), which may be due to modification of suspended load ratios.

5.5. The ^{238}U decay chain and erosion rates

As with other basaltic watersheds (Vigier et al., 2005, 2006), dissolved ($^{230}\text{Th}/^{238}\text{U}$) $\ll 1$, and suspended activity ratios are >1 (Fig. 8), because U is much more mobile than Th during weathering. Colloids have ($^{230}\text{Th}/^{238}\text{U}$) much closer to secular equilibrium than the dissolved load, suggesting that Th is strongly adsorbed or scavenged from the dissolved load or soil solutions, and demonstrates that even relatively inorganic colloids and particles have a high affinity for Th and U. It may also be that the higher chemical weathering rates in the Deccan (Vigier et al., 2005) have lowered the dissolved ($^{230}\text{Th}/^{238}\text{U}$) compared to Iceland, because more U is mobilised relative to Th during mineral and rock dissolution.

Generally, two approaches have been adopted to constrain watershed erosion rates. Physical data (such as discharge rates) can be used to derive average watershed erosion rates (Gaillardet et al., 1999a; Louvat et al., 2008). These require information that enables the calculation of suspended matter fluxes, which however only give a snapshot at the time of sampling. Average sediment fluxes may be considerably different, because the concentration of suspended matter varies across any river cross section, sediment is additionally transported in the bedload, and temporal variations make it unlikely that such punctual sampling will reflect long-term fluxes. Erosion rates can, theoretically, also be calculated using constraints from U-series (Dosseto et al., 2006a; Vigier et al., 2001, 2005, 2006). This approach assumes that the isotope composition of river water represents the average of water draining a watershed, and the sediments found in the river represent the average surface sediments across the watershed. This model (see Vigier et al., 2001 for equations) requires knowledge of the total activity ratio of the system (combined bulk sediment and water). Vigier et al. (2001) obtain the total activity ratios by assuming weathering to be in steady state. Thus, material removed from the weathering profile is balanced by new material added by the weathering of bedrock. Because the bedrock is in secular equilibrium, steady state requires that bulk material being removed also be in secular equilibrium.

In these Icelandic waters, the high dissolved ($^{234}\text{U}/^{238}\text{U}$) is generally accompanied by suspended sediment ($^{234}\text{U}/^{238}\text{U}$) that is close to secular equilibrium. Mass balance considerations suggest that enrichment of ^{234}U in the dissolved load should be accompanied by ^{234}U depletion in sediment. However, dissolved [U] is very low, and

the complementary depletion in suspended ^{234}U may therefore not be resolvable. Two samples, however, have suspended ($^{234}\text{U}/^{238}\text{U}$) >1 , together with bedloads at secular equilibrium. This suggests that the suspended sediment, which may have a greater concentration of clays and smaller grain size and so greater adsorptive capacity, have incorporated a significant fraction of dissolved U. Overall, the U isotopes do not appear to be useful for constraining erosion rates.

The suspended sediment ($^{230}\text{Th}/^{238}\text{U}$) are >1 , and appear to be complementary to dissolved activity ratios, which are <1 (Fig. 8). Using these ($^{230}\text{Th}/^{238}\text{U}$) ratios, the model gives suspended sediment values of 9–53 mg/L and erosion rates of 0.005 to 1.1 m/kyr (compared to 0.34 to 58.4 m/kyr obtained from using the measured total suspended sediment (TSS) (530–2790 mg/L) for the total sediment flux). Clearly these estimates are very different, and a concern here relates to the redistribution of ^{230}Th between the dissolved species and the suspended load (Section 5.4). If Th is adsorbed onto the sediments during riverine transport, then the ($^{230}\text{Th}/^{238}\text{U}$) ratio of both the dissolved species and the sediments can be changed, so altering the calculated average concentration of transported sediment. If the suspended ($^{230}\text{Th}/^{238}\text{U}$) increases due to adsorption, the calculated suspended sediment value is lowered. The extent to which this can occur is however low. For example, in sample A4, with a TSS of 0.612 g/L and 0.7 ppm Th, there is 420 ng Th/L. Since only 0.074 ng/L is dissolved, adsorption of dissolved riverine Th onto particles is unlikely to have a large effect on sediment Th (adsorption of all dissolved Th would decrease the calculated erosion rate from 0.0192 to 0.0188 m/kyr).

Other explanations must therefore be sought for the two orders of magnitude difference between erosion rates from ($^{230}\text{Th}/^{238}\text{U}$) and from physical data. Positive values for erosion rates can always be obtained wherever ($^{230}\text{Th}/^{238}\text{U}$)_p >1 and ($^{230}\text{Th}/^{238}\text{U}$)_D <1 . These values are to be expected because U is soluble, and therefore mobile, and Th is very insoluble. This means that other criteria must be applied before the obtained rates can be considered reasonable. There are a number of reasons why bulk material entering a weathering system may not be in steady state, meaning that the model may not apply to regions such as this: 1) the near-surface weathering profile is not in steady state, due to changes in Arctic climatic conditions (e.g. temperature, precipitation, permafrost distribution, glaciation). Variations in these parameters occur over different timescales, but in many cases more recently than the time for steady state conditions to be reached. 2) Addition of new volcanic rock and ash, or glacial debris (including fine suspended matter), to the near-surface weathering profile will also perturb the system from steady state. New volcanic material may not have reached steady state weathering conditions, and will, together with glacial material, do so at a different rate than material added to the base of the weathering profile. 3) Significant amounts of groundwater may travel below the shallow weathering regions (see Vigier et al., 2001), due to the porosity of basalt, enhanced permeability between different basaltic flows, and substantial topographical relief, or simply be added directly to the rivers. The ($^{234}\text{U}/^{238}\text{U}$) in groundwaters can be much higher than surface waters, because of lower weathering rates (for example, values of 1.6 to 3.0 have been found in a basaltic aquifer in Idaho (Luo et al., 2000)). 4) Depleted surface sediments may not be the only source of material. In all basaltic terrains studied to date (Fig. 6), many suspended load samples have activity ratios ≥ 1 , which suggests that U from another source has been incorporated into the suspended, and eventually into dissolved, material (Andersson et al., 1998; Dosseto et al., 2006a; Pogge von Strandmann et al., 2006, 2008b, 2010; Porcelli et al., 2001; Vigier et al., 2005, 2006). This is clearly shown by the suspended particles from the Azores, which exhibit a positive covariation with dissolved load activity ratios (Fig. 6). Since it is difficult to predict, without further data, the effects of these factors on the ($^{230}\text{Th}/^{238}\text{U}$) and ($^{234}\text{U}/^{238}\text{U}$) ratios of the bulk material entering the rivers, it is not possible to take them into account in calculating weathering rates.

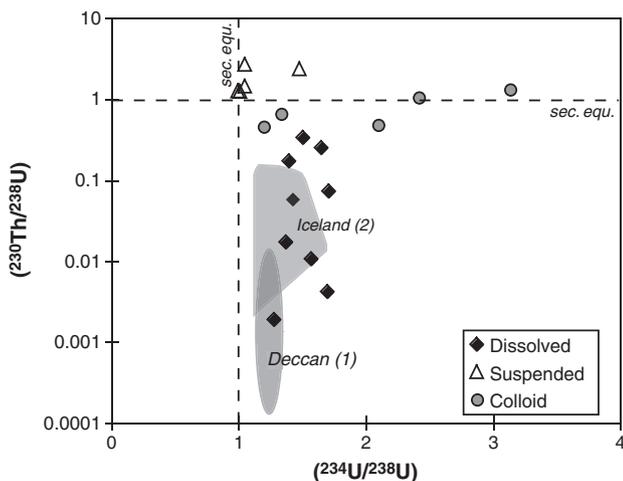


Fig. 8. Activity ratios of the ^{238}U decay chain. Shaded areas represent dissolved load values from (1) Vigier et al., 2005 and (2) Vigier et al., 2006. The analytical error on the samples is smaller than the symbols. High colloidal ($^{230}\text{Th}/^{238}\text{U}$) suggests Th adsorption.

6. Conclusions

This study presents major and trace element and uranium and thorium activity ratios from bedload, suspended load, dissolved load and colloidal fractions from organic-poor rivers on basaltic terrains in Iceland and the Azores. The principal conclusions are:

- 1) There is a strong pH control (and lesser influence by organic carbon) on U in the dissolved load and colloids: at high pH dissolved [U] is high, and colloidal [U] is low. This suggests that at high pH, when glass dissolution is maximised and many secondary minerals that incorporate/adsorb U (mainly Fe-oxyhydroxides and allophane) are unstable, the proportion of U entering the dissolved phase is high, but inorganic colloid formation is low. Colloidal thorium appears to be similarly affected, although to a lesser extent, suggesting that both nuclides are strongly controlled by chemical weathering and secondary mineral formation processes occurring in the catchments.
- 2) The U activity ratios in many of the suspended load samples are greater than secular equilibrium, suggesting adsorption from the riverine dissolved load or soil solutions. Uranium activity ratios in the dissolved load and corresponding colloids are similar when ($^{234}\text{U}/^{238}\text{U}$) < 1.3, but very different at higher activity ratios. This suggests that when chemical weathering rates are low (in glacial rivers, or when soil formation is extensive), there is little or no U exchange between colloids and the dissolved load. This may be because many basaltic secondary minerals are unstable at high pH, and therefore are not present to adsorb U.
- 3) The ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios in colloids and the corresponding dissolved load are similar, as are the activity ratios in the corresponding suspended load. This suggests rapid Th exchange and adsorption (by secondary minerals or onto mineral surfaces) between all riverine phases in these terrains. The possibility of U and Th exchange between particles and the dissolved phase (and to a lesser extent colloidal phases if these flocculate out during a pH change) suggests that riverine phases, at least in basaltic terrains, will rarely preserve evidence of steady state weathering for U-series nuclides.
- 4) It is unlikely that steady state weathering processes are maintained in this arctic basaltic terrain. Addition of material with different weathering histories (glacial or volcanic material), groundwater contributions, weathering changes to the near-surface environment, and U or Th addition from other sources (such as hydrothermal input) are likely to perturb the system. It is not possible for these processes to be quantified in weathering timescale calculations, rendering them inapplicable in such settings.

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