

The relationship between riverine U-series disequilibria and erosion rates in a basaltic terrain

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Abstract

U-series isotopes have been measured in the dissolved phase, suspended load and bedload of the main rivers draining basaltic catchments in Iceland. For the dissolved phase, ($^{234}\text{U}/^{238}\text{U}$) and ($^{238}\text{U}/^{230}\text{Th}$) range between 1.08 and 2.2, and 7.4 and 516, respectively. For the suspended load and bedload, ($^{234}\text{U}/^{238}\text{U}$) and ($^{238}\text{U}/^{230}\text{Th}$) range from 0.97 to 1.09 and from 0.93 to 1.05, respectively. Chemical erosion rates, calculated from dissolved major elements, range between 13 and 333 $\text{t km}^{-2} \text{ yr}^{-1}$. Physical erosion rates have also been estimated, from existing data, and range between 21 and 4864 $\text{t km}^{-2} \text{ yr}^{-1}$, with an average of 519 $\text{t km}^{-2} \text{ yr}^{-1}$. U-series disequilibria indicate that weathering in Iceland operates at close to steady-state conditions. A model of continuous weathering indicates a maximum weathering timescale of 10 kyr, with an average rate of uranium release into water of $1.6 \cdot 10^{-4} \text{ yr}^{-1}$, which is significant when compared to granitic terrains located at similar latitudes and to tropical basaltic terrains. All river waters display ($^{234}\text{U}/^{238}\text{U}$) greater than secular equilibrium, consistent with the effects of alpha-recoil. The same dissolved phase ($^{234}\text{U}/^{238}\text{U}$) exhibit a negative trend with physical erosion rates, explained by the dominant effect of close-to-congruent chemical weathering of hyaloclastites in the younger basaltic terrains. Therefore, chemical erosion rate and mineral weathering susceptibility play a major role in determining ^{234}U – ^{238}U disequilibria in basaltic river waters. Comparison of global data for river basins in which weathering was recently strongly limited indicates a negative correlation between silicate weathering rates estimated with major elements and the age of weathering estimated with U-series disequilibria. This strongly suggests a key role of time and soil thickness on the chemical erosion of silicates.

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1. Introduction

Weathering of Ca–Mg silicates is the primary sink of atmospheric CO_2 on a geological timescale and is

also implicated in the transient fixation of atmospheric CO₂. The relative importance of basalt weathering has been highlighted in several recent studies [1–4]. About 30–35% of atmospheric CO₂ consumption due to silicate weathering on land can be attributed to basalts [5,6]. Recent comparison of dissolution rates measured far from equilibrium shows that basalts release cations two orders of magnitude faster than granites [7]. More surprisingly, about 25% of CO₂ consumption by basalt weathering comes from the weathering of small volcanic islands [6,8–10]. By comparison, weathering of large basaltic provinces, such as the Deccan Traps, is responsible for less than 10% of the CO₂ consumption at the present-day [5,6]. Runoff and the age of the basalt appear to be two key controls on weathering [9]. In addition, glass may play a major role because it can dissolve up to 6 times faster than crystalline basalt [7,11,12]. However, while extensive work has been carried out on experimental dissolution of synthetic and natural glass (e.g. [13–17]), comparison with field data remains difficult [18–20]. Estimates of silicate weathering and erosion rates on a large scale are fraught with uncertainty, particularly for unmonitored rivers and/or those draining mixed lithologies. Smaller catchments or monolithological basins are simpler to study, with fewer variables, and provide a means to deconvolve the primary controls on silicate weathering rates. The volcanic island of Iceland is one of the few regions where river water and sediment fluxes have been extensively studied and monitored for more than 30 years. Geology and rock composition are also well-constrained and anthropogenic inputs are minimal. In addition, the presence of glaciers has favoured volcanic glass (hyaloclastite) production and provides a unique means to investigate the role of glass during basalt weathering.

Recent studies have shown that U-series nuclides in river waters provide constraints on silicate weathering at the scale of an individual watershed, in particular for basaltic terrains [21,22]. By combining pairs of radioactive nuclides such as ²³⁴U–²³⁸U and ²³⁰Th–²³⁸U, it is possible to estimate the kinetics of uranium release into water and the timescales of weathering at the scale of an individual catchment [23,24]. However, thus, far few data are available and the relationship between physical and chemical erosion rates and weathering timescales recorded by U-series disequilibria remains poorly understood. The weathering timescale reflects the time during which sediments have been leached by waters before being carried out of the watershed by rivers. Weathering timescales therefore depend on the residence times of sediments within a given watershed and

potentially on soil thickness. U-series combined with major elements measured in Icelandic rivers provide a unique insight into the relationship between silicate weathering rates, radioactive disequilibria in rivers and weathering timescales at large scale.

2. Sampling area

Iceland constitutes a series of monolithological basins with basaltic rocks of various ages. Iceland is located on the mid-Atlantic ridge, and there is a symmetrical SW–NE zonation in the age of the basalts, from the centre of the island towards the east and northwest coasts, respectively. The older basalts (>3 Ma) are located in the north and in the east of the island, while the most recent basalts are mainly located in the central and volcanically active zone.

The climate in Iceland is oceanic boreal, less than 25% of the island is vegetated and about 12% is covered by glaciers. Three types of rivers have been recognized in Iceland: spring-fed rivers, mainly located in the central volcanic part where the high rock permeability precludes significant surface runoff, glacier-fed rivers and direct runoff rivers draining mainly the older basalts, where compaction and sealing by secondary minerals reduces the permeability. Soils are generally thin and the main secondary minerals in soils are allophane and ferrihydrite [25].

Quaternary volcanic rocks formed under ice during the last 3 Myr are glassy (hyaloclastites) but those formed when the island was ice free are mostly in the form of lava flows. Thus, the most recent basalts are characterized by a glassy texture, in contrast with the older northern lava flows which are mainly crystalline.

Twenty rivers were sampled across Iceland in June 2001 (Fig. 1). The sampled rivers are mainly located where the age of the source basalt is old enough to assume initial secular equilibrium for ²³⁸U–²³⁰Th (>300 ka). Also, no ²³⁴U–²³⁸U disequilibria have been observed in young and fresh basalts (e.g. [26,27]). We avoided central catchments where the hydrothermal contribution to rivers can be significant in the volcanically active zone. However, the Hvita-S River (#2), Hvita W River (#4) and Jokulsa a Fjollum River (#15) drain a few thermal springs. Glacier-fed rivers have also been sampled, in particular the Skaftafellsa River (#23) that is sourced directly by the large Vatnajokull glacier. Raudilaekur (#28) is a small ‘tea river’, whose red colour is attributed to abundant Fe–Mn particles. An extensive part (about 18%) of the Jokulsa i Fljotsdal River basin is characterized by wetlands where reducing conditions prevail [28] (Table 1).

3. Analytical procedure

River waters were sampled from a bridge when possible, from the main channel, filtered and acidified the same day at $\text{pH}=2$, with nitric acid. Suspended sediments were separated from the dissolved phases of rivers on the day of sampling, with $0.2\ \mu\text{m}$ cellulose acetate filters using a Sartorius frontal filtration unit. Where possible sands were collected in or close to the river bed with a small spade. In the laboratory, sediments were dried and ground in an agate mortar, attacked in a concentrated $\text{HF-HClO}_4\text{-HNO}_3\text{-HCl}$ mixture (in proportion 1:2:3:4, respectively) and dissolved completely in the appropriate acid for analyses or chromatographic columns.

3.1. Major and trace elements

The anion concentrations in the dissolved load were measured by ion chromatography, with an uncertainty of $\pm 1\text{--}3\%$. Cation concentrations were measured by ICP-MS. Major elements were calibrated against a set of synthetic multi-elemental standards prepared gravimetrically from high purity single element standard solutions. The trace element composition (including U and thorium contents) of an internal standard (Scottish

river water, SCO 2/15) and the river water samples were then calibrated against this standard. The accuracy of the analysis was assessed by running the natural water certified reference material SLRS4. The following certified reference materials were used for external calibration during sediment analyses: BHVO-1, BIR-1, JB-2 and UBN. BHVO-1 was used as a monitoring standard for each batch of measurements.

3.2. U-series nuclides

For Th and U isotope analysis of the dissolved fractions, iron hydroxide co-precipitations were performed in the field using about 15 l of filtered river water [29]. U–Th separation for isotopic measurements was undertaken using an anion exchange resin, following the procedure described in [30]. During the period of study, U and Th total procedural blanks ranged between 5 pg and 10 pg, which represents a negligible maximum contribution of 0.2–0.4%, respectively.

U isotope analyses have been performed using the Open University Nu-Instruments MC-ICP-MS, in a dynamic multi-collection mode where the $^{235}\text{U}/^{238}\text{U}$ ratio is measured twice: first using two faraday cups and then again in a Faraday/ion counting (IC1) mode. During the first cycle, ^{234}U is also counted with IC1. This

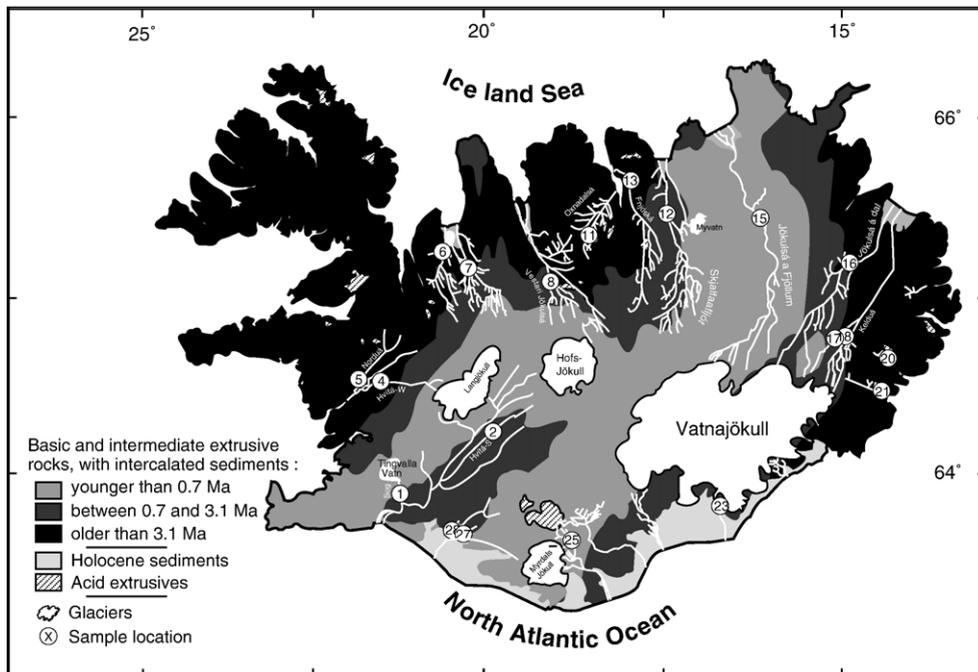


Fig. 1. Map of the Icelandic rivers sampled during June 2001 for U-series nuclide analyses. Sample numbers refer to sample designation as given in Tables 1, 2 and 3.

Table 1

Major and trace elements, total dissolved solids (TDS_w) and total suspended solids (TSS), for the Icelandic rivers

Sample	River name	pH	Na (ppm)	Mg (ppm)	Ca (ppm)	K (ppm)	Si (ppm)	Al ($\mu\text{g/l}$)	Mn ($\mu\text{g/l}$)	Rb ($\mu\text{g/l}$)	Sr ($\mu\text{g/l}$)	Cl (ppm)	SO ₄ (ppm)	TSS (mg/l)	TDS _w ^a (mg/l)	Mean age (Ma)	Glaciated area (%)	Runoff (mm/an)	Mech. er. rate (t/km ² /yr)	Chem. er. rate (t/km ² /yr)	
#1	Sog	7.8	8.09	1.33	4.27	0.61	3.97	12.01	2.23	0.73	5.36			7.7 \pm 2, $n=6^b$		0.27	0%	7234	56.0		
#2	Hvita-S at Bruarhlöd	8.0	6.67	1.27	4.10	0.56	5.59	39.48	2.24	0.49	5.09	3.30	4.55	92.2 \pm 15, $n=106$	26.4	0.67	21%	1735	160	45.8	
#4	Hvita-W at Kljafoss	7.6	6.26	0.94	2.90	0.40	5.56	47.98	1.54	0.52	4.00	4.18	1.85	90.9 \pm 14, $n=103$	20.8	1.22	9%	2596	236	54.0	
#5	Nordura at Stekkur	7.9	5.60	1.39	3.45	0.31	4.21	5.89	2.43	0.31	6.12	7.86	1.95	34.3 \pm 30, $n=7$	15.3	5.90	0%	1628	55.8	25.0	
#6	Vididalsa	8.0	7.12	3.55	6.32	0.77	6.53	3.39	11.84	1.01	17.2			29.5 \pm 10, $n=16$		4.13	0%	528	16		
#7	Vatnsdalsa	8.1	8.67	2.51	5.13	1.09	7.71	9.28	1.80	1.05	10.8	6.32	1.62	40.6 \pm 28, $n=8$	30.3	1.88	0%	432	18	13.1	
#8	Vestari Jökulsa, Goddölum	7.6	7.99	4.13	4.99	1.14	7.96	19.78	0.66	1.11	6.98	2.81	2.04	304.1 \pm 49, $n=112$	35	2.43	12%	804	245	28.1	
#11	Öxnadalsa	7.5	2.16	0.70	2.14	0.31	4.17	6.99	0.44	0.36	5.16	2.10	0.58		13.1	5.90	0%				
#12	Skjalfaafjot, at Godafoss	7.7	6.99	1.72	4.49	0.48	6.05	26.24	1.72	0.50	5.24	2.23	3.41	207.8 \pm 143, $n=5$	28.2	1.29	5%	965	201	27.2	
#13	Fnjóska ofan Arbugsar	7.4	3.00	0.81	2.79	0.25	4.84	8.41	1.41	0.26	2.08			25 \pm 11, $n=3$	14.1	4.76	0%	1304	32.6	18.4	
#15	Jökulsa a Fjöllum at Grímsstadir	7.9	11.01	1.64	4.22	0.59	5.61	28.16	0.83	0.47	4.67			1017 \pm 117, $n=60$		0.30	20%	997	1014		
#16	Jökulsa a Dal at Hjardarhagi	7.2	3.27	0.79	3.87	0.21	3.57	35.50	2.54	0.16	1.79			325		1.71	43%	1334	433		
#17	Jökulsa i Fljotsdal at Holl	7.5	2.73	0.84	6.46	0.19	2.67	21.35	5.64	0.12	4.89	1.35	2.51	266		17.3	2.14	26%	1832	487	31.7
#18	Keldua after Fellsa confluence	7.7	1.55	0.74	1.83	0.14	2.98	8.86	0.83	0.15	3.19	1.96	0.55	35.4 \pm 17, $n=4$	9.6	4.89	6%	1793	63.4	17.2	
#20	Fossa	7.6	2.47	0.65	1.59	0.10	2.81	2.37	0.51	0.08	2.81			10.0 \pm 2, $n=7$		5.90	0%	3407	34.1		
#21	Geithellnadalur	7.6	2.40	0.67	1.98	0.14	2.55	7.28	0.53	0.12	3.02	3.00	0.91	45.3 \pm 36, $n=14$	9.1	5.90	11%	5677 ⁺	257	51.7	
#23	Skaftafellsa	9.2	5.51	0.32	10.27	0.33	2.69	299.73	8.57	0.29	4.28	3.26	1.72	797.8 \pm 114, $n=21$	21.3	1.66	100%	6096 ⁺	4864	130	
#25	Holmsarvatn	7.6	5.64	1.10	3.21	0.48	4.82	11.18	2.93	0.56	8.3	2.77	2.80	523.2 \pm 43, $n=203$	21.2	0.21	41%				
#27	Ytri Ranga at Arbaejarfoss	8.4	22.48	5.28	10.38	1.33	5.71	6.81	4.70	0.95	34.3	10.8	15.8	114.5 \pm 18, $n=59$	58.8	0.86	0%	5665	649	333	
#28	Raudilaeukur	7.0	16.31	12.00	19.96	1.45	12.80	5.59	406.1	1.95	79.9	14.3	4.47	28, $n=1$	69.9	3.17	0%				

⁺ Runoff is for 2001 except for these two rivers [45].^a TDS_w have been calculated with Ca, Mg, Na, K, Si and SO₄, corrected from atmospheric input, assuming all Cl to be derived from the atmosphere with X/Cl seawater ratios.^b n is the number of measurements used for calculating the average TSS and associated uncertainty (standard error).

Table 2
U-series disequilibria for Icelandic river filtered waters, sands and suspended particles

River name	Sample	River phase	U	Th	(²³⁴ U/ ²³⁸ U)	(²³⁰ Th/ ²³² Th)	(²³⁸ U/ ²³⁰ Th)	(²³⁸ U/ ²³² Th)
Sog	#1	Water	4.84		1.23	6.00±2.2		
		Sands	0.197	0.612	1.04	1.01	0.96	0.96
Hvita-S	#2	Water	7.24	0.385	1.20	5.23±3.6	10.8±6.5	56.3
		Susp. part.	0.92 ^a	3.04 ^a	1.05	0.95	0.957	0.907
Hvita-W	#4	Sands	1.082	3.654	1.01	0.92	0.962	0.887
		Water	4.87	0.255	1.42			57.3
Nordura	#5	Sands	0.222	0.717	1.02	0.96	0.96	0.93
		Water	0.68	0.24	1.22	0.82±0.3	10.3±3.5	8.5
Vididalsa	#6	Sands	0.375	1.408	0.98	0.87	0.918	0.798
		Water	4.12	0.77	1.64			16.03
Vatnsdalsa	#7	Susp. part.				1.14		
Vestari Jökulsa	#8	Water	12.77	0.415	1.65	1.61±0.2	57.3±6.5	92.2
		Sands	30.2	0.545	1.48			166.0
Öxnadalsa	#11	Sands	0.366	1.244	1.01	0.91	0.96	0.88
		Water	0.66	0.19	1.35	1.38±0.2	7.6±1	10.4
Skjalfaaflljot	#12	Sands	0.485	1.688	1.00	0.85	0.991	0.86
		Water	7.89	0.28	1.27	2.51±0.2	33.7±2.5	84.4
Fnjoska ofan Arbugsar	#13	Sands	0.241	0.792	1.01	0.99	0.917	0.912
		Water	1.57	0.495	1.50	1.07±0.2	8.9±1.5	9.5
Jökulsa a Fjöllum	#15	Susp. part.			1.02	0.97		
		Water	16.7	0.225	1.24	1.06±0.2	209±39	222
Jökulsa a Dal	#16	Susp. part.	0.35 ^a	1.04 ^a	0.99	0.96	1.045	1.01
		Sands	0.422	1.39	1.0	0.973	0.935	0.909
Jökulsa i Fljotsdal	#17	Water	2.78	0.165	1.18			50.47
		Susp. part.	0.33 ^a	0.94 ^a	0.99	0.96	1.098	1.05
Keldua	#18	Water	4.00	0.708	2.20			16.93
		Susp. part.	0.52 ^a	1.72 ^a	1.09	1.0	0.904	0.906
Fossa	#20	Sands	0.783	2.57	1.03	0.98	0.935	0.913
		Water	0.55	0.225	1.21	0.99±0.2	7.4±1.5	7.4
Geithellnadalur	#21	Sands	0.364	1.335	0.97			0.817
		Water	0.43	0.315	1.68			4.09
Skaftafellsa	#23	Sands	0.52	1.81	0.98	0.92	0.94	0.861
		Water	17.19	17.45	1.31			2.95
Holmsarvatn	#25	Susp. part.			0.99	0.89		
		Water	4.31	0.325	1.07			39.7
Ytri Ranga	#27	Sands	0.625	1.945	1.00	0.99	0.97	0.96
		Water	72.72	0.461	1.08			472.5
Raudilækur	#28	Water	31.7	0.175	1.11	1.05±0.2	516±98	542
		Susp. part.			1.09			

Parentheses indicate activity ratios.

U and Th contents are given in ng l^{-1} for dissolved phases (waters) and in ppm for bedload (sands) and suspended sediments. Except for (²³⁰Th/²³²Th) ratios measured for river dissolved fractions (specified in column 7), 2 σ errors for (²³⁴U/²³⁸U), (²³⁰Th/²³²Th), and U and Th contents are ~1%.

^a Taken from [35].

technique allows internal corrections for each measurement both of the Faraday-IC1 yield and the instrumental mass fractionation. The abundance sensitivity was also checked regularly at mass 238 and found to be ~0.1 ppm. Several reference materials and U standards have been run. U112a standard ($n=75$) gave a mean value for $^{234}\text{U}/^{238}\text{U}=5.30(\pm 0.06) \cdot 10^{-5}$, and five replicates of AthO basalt lead to a mean $^{234}\text{U}/^{238}\text{U}$ ratio of 5.49 (± 0.05) $\cdot 10^{-5}$, which compares well with published data for secular equilibrium material (e.g. [31]) (given uncertainties represent the external reproducibility, at

the 2 σ level). Also, single measurements of (²³⁴U/²³⁸U) (where parentheses denote activity ratios) were performed for UB-N (peridotite) and BHVO-1 (basalt) and yield 1.01 and 1.00, respectively ($\pm 1\%$ at the 2 σ level).

Th isotope compositions for the low level dissolved fractions have been measured with a high sensitivity Neptune MC-ICP-MS at Bristol University. Measurements of the TML rock standard, run for the same amount of Th (relative to river waters) and passed through the same analytical procedure, give a ²³⁰Th/²³²Th ratio of $5.75 \cdot 10^{-6}$ with 2 σ internal error of 18%. Th isotopes for

the sediments (bedload sands and suspended particles) have been measured using the Open University Nu-Instrument MC-ICP-MS, following a method modified from [32]. $^{230}\text{Th}/^{232}\text{Th}$ ratio measurements gave a mean value of $5.40(\pm 0.04) \cdot 10^{-6}$ for the ThS1 standard ($n=13$) using a standard bracketing technique (given external error is at the 2σ level). Nine measurements of the TML rock standard give a mean value for $^{230}\text{Th}/^{232}\text{Th}$ of $5.72 \cdot 10^{-6}$ (with a 2σ external error of 0.8%) that compares well with published data (e.g. [33,34]).

4. Results

4.1. Major and trace elements

The sampled river waters display a temperature range of 2°C – 11°C and a pH range between 7.0 and 8.4, typical of waters exposed to atmospheric CO_2 during or just after rock interaction (pH and T were measured on the field at the sampling time). An exception to this is sample #23 (Skaftafellsa), which has a more basic pH (9.2). This water was sampled at the base of the Skaftafell glacier tongue, which is part of the Vatnajökull glacier. Basic pH values (>10) are typically measured for waters originating from the base of glaciers and are caused by the isolation of groundwaters from atmospheric CO_2 (e.g. [9,18,19]). The onset of water–rock interaction consumes protons and in exchange releases cations like Ca^{2+} , Mg^{2+} , Na^+ and K^+ into the aqueous phase [16].

The main dissolved elements are Na, Si and Ca, confirming that basalt weathering is significant and dominates river chemistry. The average TDS_w (total dissolved solids corrected from atmospheric inputs) is 26 mg l^{-1} , which is very close to previously published values for Iceland (21 mg l^{-1} [35], 24.3 mg l^{-1} [9]). Mean TDS_w for rivers draining young rocks ($<1 \text{ Ma}$) is 35.5 mg l^{-1} , whereas for rivers draining 1–3 Ma rocks and $>3 \text{ Ma}$ rocks, TDS_w are 26.1 mg l^{-1} and 21.9 mg l^{-1} , respectively. This decrease of TDS_w with rock age indicates that, in Iceland, young basalts are more susceptible to weathering processes relative to the older rocks [9].

Mean molar Ca/Na and Mg/Na ratios for the sampled rivers are 1.03 ± 0.6 and 0.48 ± 0.4 , respectively, which compares well with published data for Iceland ([19], 0.96 ± 1.2 and 0.9 ± 0.9 , respectively). The low Ca/Na and Mg/Na values also suggest little input from secondary carbonate minerals (for comparison, the mean Ca/Na and Mg/Na are 1.3 and 1.0, respectively, for worldwide monolithological basaltic rivers [6]).

Cl and SO_4 contents are relatively low and homogeneous for the analyzed rivers with an average of 4.0 ppm ($113 \mu\text{mol/l}$) and 3.1 ppm ($32 \mu\text{mol/l}$), respectively, indi-

cating that there is little contribution from anthropogenic or hydrothermal sources to the sampled rivers. River catchments in which hydrothermal springs are located (samples #2, #4, #5 and #12) do not display a different composition, with no significant enrichment in Cl, Si and Na. This suggests an hydrothermal contribution that is negligible relative to direct runoff water.

Suspended and bedload sediments have very similar Na/Th and K/Th and U/Th ratios. The mean K/Th ratios for suspended sediments [35] is $3664 (\pm 1000, 1\sigma)$, while for sands (bedload sediments) measured in this study, the mean K/Th is $2966 (\pm 1000, 1\sigma)$; not shown here). For comparison, K/Th for typical Icelandic tholeiites is 2500 [35]. In addition, U/Th ratios are not significantly lower in suspended sediments and bedload sands when compared to fresh rocks. The mean U/Th ratio is 3.2 ± 0.2 for young and fresh Iceland basalts [36–38] and is 3.2 ± 0.2 for suspended sediments and 3.5 ± 0.2 for sands (Table 2). This strongly suggests that sands and suspended material are not significantly depleted in mobile elements compared with unweathered source rocks, which highlights a close-to-congruent weathering process (e.g. [39]). Additionally, suspended sediments do not represent material that is significantly more weathered than sands. There is therefore no mineralogical sorting during sediment transport.

4.2. U-series nuclides

($^{234}\text{U}/^{238}\text{U}$), ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{238}\text{U}/^{230}\text{Th}$) (where parentheses denote activity ratios) and the U/Th concentration ratios have been measured for river water and

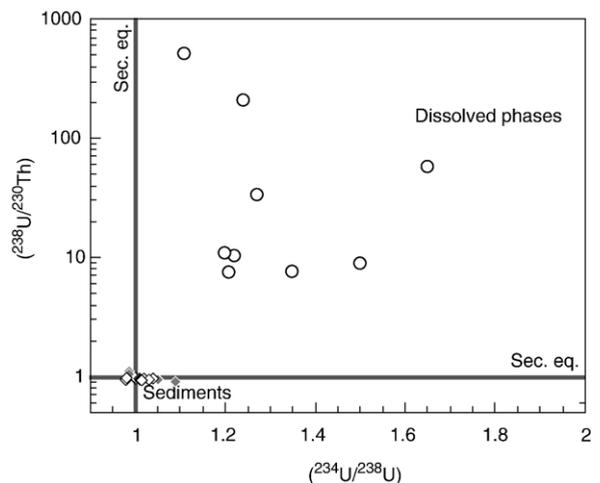


Fig. 2. ($^{238}\text{U}/^{230}\text{Th}$) versus ($^{234}\text{U}/^{238}\text{U}$) for suspended sediments (grey diamonds), bedload sands (open diamonds) and dissolved phases (open circles) of the Icelandic rivers.

river sediment samples (Table 2 and Fig. 2). U and Th contents have also been measured in a filtered and melted ice sample coming from the surface of Langjökull glacier and are found to be similar to the U and Th contents measured by ICP-MS in the nitric acid blank measured the same day (not shown here). We therefore consider negligible atmospheric contribution for U and Th.

Icelandic river waters display low and variable U and Th contents, ranging between 0.43 to 72.7 ng l⁻¹ and 0.17 to 17.4 ng l⁻¹, respectively. All river waters display (²³⁴U/²³⁸U) greater than secular equilibrium (between 1.07 and 2.2), indicating the preferential release of ²³⁴U relative to ²³⁸U, in accord with the predicted effects of alpha-recoil [40] during leaching of silicate material in secular equilibrium. Also (²³⁸U/²³⁰Th) in the river waters are systematically higher than one (between 7.4 and 516) and higher than in sediments, reflecting the preferential release

of U relative to Th into waters. These two features are commonly observed in natural surface waters draining rocks in secular equilibrium (see e.g. review in [41,42]). The high (²³⁴U/²³⁸U) for Jökulsa í Fjötsdal (#17, Table 2) is consistent with water draining a reducing medium in wetlands (e.g. [43]) and therefore will not be directly compared with the other waters studied here. (²³⁰Th/²³²Th) in waters range between 0.99 and 6 and are systematically greater than (²³⁰Th/²³²Th) measured in corresponding sediments, again as would be predicted from recoil effects and preferential release of ²³⁰Th (²³⁴U-daughter) relative to ²³²Th.

(²³⁴U/²³⁸U) for suspended sediments range between 0.99 and 1.09 and for bedload sands between 0.97 and 1.04, indicating a material that is close in composition to fresh rocks in secular equilibrium. Some samples display ²³⁴U enrichment both in sediments and in waters, suggesting either significant ²³⁴Th adsorption (²³⁴Th further

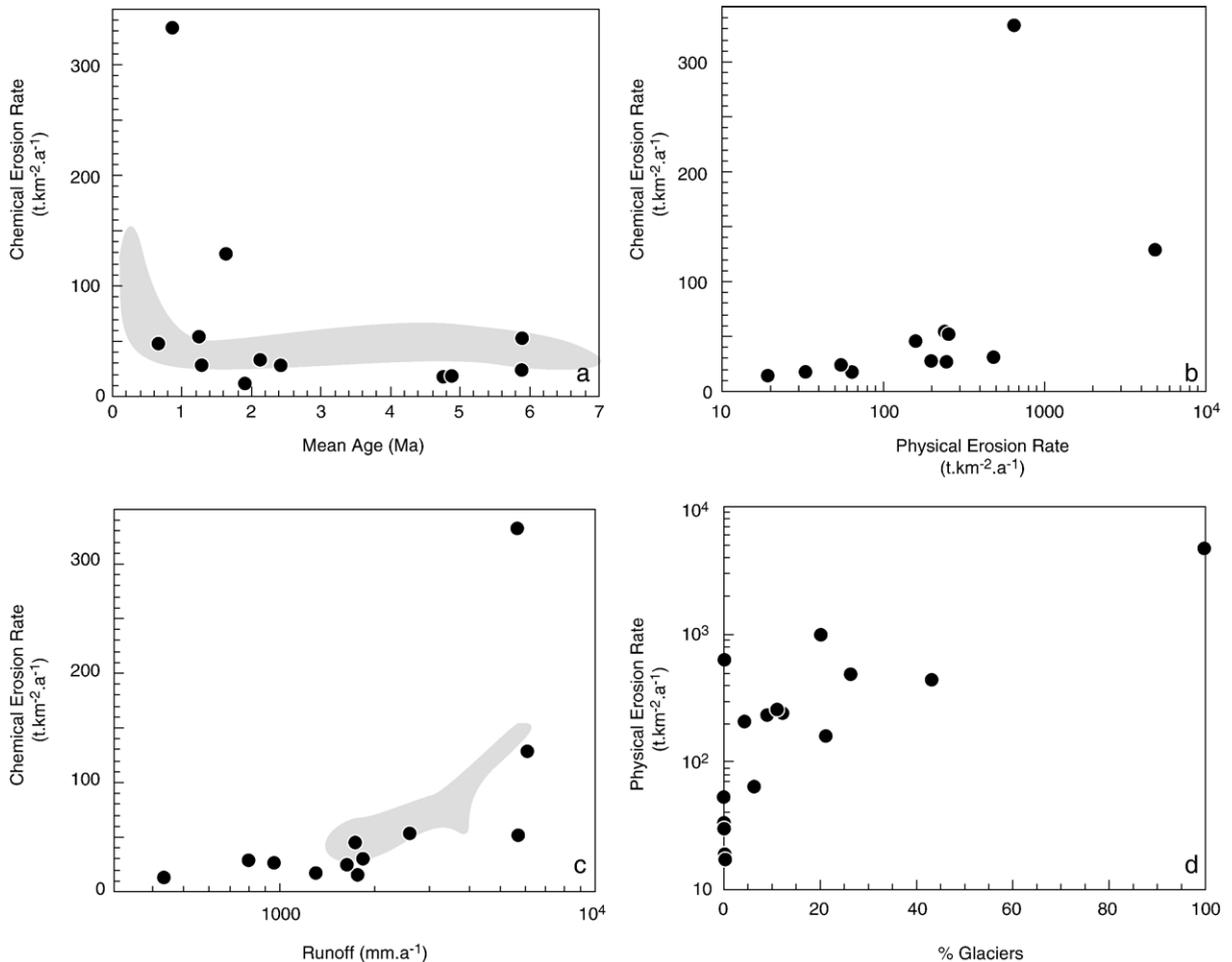


Fig. 3. (a) Chemical erosion rates versus mean rock age. (b) Chemical erosion rates versus physical erosion rate. (c) Chemical erosion rates versus runoff. (d) Physical erosion rates versus the percent of glacier cover of the river catchments. Results from [9] are also shown for comparison (shaded areas).

decays into ^{234}U), or U enrichment of sediments. The range in U/Th for sediments (Fig. 5) is very close to or slightly lower than the range observed for freshly erupted Icelandic basalts [36–38], indicating that the observed particulate ^{234}U enrichments are not associated with significant U enrichment, when compared to the fresh rock. Also, for all rivers, $^{230}\text{Th}/^{232}\text{Th}$ for suspended and bedload sediments are systematically lower than for corresponding dissolved phases (Table 2), suggesting little exchange of Th between both phases. The Raudilaekur River, ‘tea’ river characterized by abundant Fe–Mn oxides, displays almost identical ($^{234}\text{U}/^{238}\text{U}$) both for water and suspended sediments, showing a complete isotopic reequilibration of both phases [44].

4.3. Erosion rates

River monitoring by the University of Iceland and the Hydrological Division of the National Energy Authority provides precise estimates of discharge and corresponding runoff for each watershed studied here. Also, the TSS (total suspended sediments) has been regularly measured for a number of Icelandic rivers for the last four decades [45,46]. Both records provide valuable information that can be used to estimate physical and chemical erosion rates for most of the rivers sampled in this study.

The 2001 mean discharge combined with the mean annual TSS estimates (see Table 1) gives a wide range of physical erosion rates in Iceland, between 21 and 4864 t km⁻² yr⁻¹, with an average of 519 t km⁻² yr⁻¹ which compares well with previous estimates [47] and is about twice the world average estimated by Milliman and Meade [48]. The chemical erosion rates, which can be estimated by the flux of dissolved elements exported by rivers, are lower than physical erosion rates, ranging from 13 to 333 t km⁻² yr⁻¹.

Chemical erosion rate shows a positive correlation with physical erosion rate and runoff and a negative trend with the mean age of the drained basalts (Fig. 3a, b and c). These covariations are similar to those observed by [9,12], taken to indicate the primary role of weathering of basaltic glass material that is abundant in the hyaloclastites of the young volcanic and recently glaciated areas. The subglacial eruptions occurring during the last 3 Ma in the young volcanic areas favoured glass-rich hyaloclastite formation. This material is visibly very physically friable. In addition, natural and experimental studies of glass dissolution experiments [11,20,49,50] have demonstrated near congruent leaching of elements at the onset of weathering process. The high runoff in young areas further enhances mechanical disaggregation and therefore hyaloclastite dissolution. In contrast, old basalts in the

northern and eastern parts of Iceland are more crystalline and often organized in massive superposed horizontal flows. Most of the glass, if originally present in the groundmass, has now been removed by weathering, and secondary minerals have developed.

5. Discussion

5.1. The steady-state nature of erosion processes

In order to constrain the timescales of weathering, it is important to first estimate if erosion processes in Iceland operate in steady-state. A steady-state model of erosion is characterized by a constant thickness of soils at the scale of the watershed, or that there is no net accumulation or loss of sediments within the basin. In this context, the composition of eroded material leaving the watershed (dissolved+solids) is considered to be equal to the mean composition of the local rocks. This hypothesis is usually assumed for constraining physical erosion rates and can be tested using mass balance constraints on the dissolved and suspended loads of rivers [51–53]. For conventional tracers (e.g. Sr isotopes), the main difficulty lies in constraining the mean composition of the parent rocks at the scale of the basin. By contrast, for U-series nuclides, secular equilibrium can be assumed for all rocks older than 1 Ma or 300 ka when considering the ^{234}U – ^{238}U system and the ^{230}Th – ^{238}U system respectively. It is then possible to compare the steady-state physical erosion rates, calculated from U-series, with the physical erosion rates obtained from field measurements. Previous studies have shown that some tropical basins, that are tectonically (and climatically) stable, are in steady-state (shield basins of the Amazon and the Congo for example [54]), while for other basins weathering processes have been strongly affected by recent climate variations and display far from steady-state conditions (in Canada and the Andes [23,24]).

The steady-state condition of the weathering processes can be tested in Iceland with the approach outlined by [55], and using both ^{234}U – ^{238}U and ^{230}Th – ^{238}U systems: the mean annual TSS can be calculated assuming initial secular equilibrium for the fresh rocks, and mass balance equations for U between rock, river sediments and river dissolved phase (see [23,24] and Appendix A for corresponding equations). These calculations in a first approximation do not consider any radioactive decay, which implies that the weathering timescales is assumed to be small relative to the half-lives of ^{234}U and ^{230}Th . Also, the bedload U flux is considered as negligible relative to suspended particle U flux. Steady-state TSS (Table 3 and Fig. 4) can be compared to the measured TSS (Table 1). Only rivers showing little U enrichment in sediments (with

Table 3

Timescale of weathering and releasing rates for ^{238}U , ^{234}U and ^{230}Th (k_8 , k_4 and k_0), calculated using the continuous weathering model

River name	#—Phase	k_8 (10^{-4} yr $^{-1}$)	k_4 (10^{-4} yr $^{-1}$)	k_0 (10^{-6} yr $^{-1}$)	Weathering timescale (yr)	Predicted TSS (mg/l) using ($^{234}\text{U}/^{238}\text{U}$)	Predicted TSS (mg/l) using ($^{230}\text{Th}/^{238}\text{U}$)
Hvita-S	#2—Susp. part.	1.11±0.05	1.34±0.06	10.1±0.5	2216 ^a ±164		159±53
	#2—Sands	0.94±0.04	1.10±0.05	8.4±0.3	2097±163		154±58
Nordura	#5—Sands	1.56±0.09	1.9±0.1	14.1±0.8	6306±532	20±6	18±5
Öxnadalsa	#11—Sands	0.33±0.01	0.45±0.02	4.3±0.2	3358±984		130±75
Skjalfaafliot	#12—Sands	1.9±0.2	2.4±0.3	5.3±0.5	2075±276		351±44
Jökulsa a Fjöllum	#15—Susp. part.	2.9±0.1	3.7±0.2	0.57±0.03	1979 ^b ±306		683±88
	#15—Sands	3.2±0.2	4.0±0.2	0.57±0.04	979±90		566±81
Keldua	#18—Sands					11±3	

^a ($^{234}\text{U}/^{238}\text{U}$)_{Susp. part.} was taken equal to 1.01 for calculations (ratio obtained for corresponding sands).

^b ($^{230}\text{Th}/^{238}\text{U}$)_{Susp. part.} was taken equal to 0.935 for calculation (ratio obtained for corresponding sands).

($^{234}\text{U}/^{238}\text{U}$) and ($^{238}\text{U}/^{230}\text{Th}$) ≤ 1) have been considered. Results obtained from both ^{234}U – ^{238}U and ^{230}Th – ^{238}U systems for the Nordura River (#5) are very consistent, with TSS equal to 20±6 mg/l and 18±5 mg/l, respectively. This strongly suggests that the weathering timescale in this area is much shorter than 300 ka. It has been shown (see Sections 4.1 and 4.2) that sands (bedload) and suspended sediments have very similar chemical compositions. Therefore, when possible, U-series data obtained for sands have been used for calculating steady-state TSS, considering that their composition can also be representative of the river sediment load. Comparison of TSS obtained with the sand data and with suspended sediment data can be compared for Hvita-S and Jökulsa a Fjöllum Rivers (#2 and #15), and show very similar TSS within analytical uncertainties (Table 3).

Fig. 4 illustrates first that TSS in Iceland are highly variable relative to previously studied areas. Steady-state TSS, calculated with U-series disequilibria, can only be compared with measured TSS for a small number of rivers. However, the few results obtained here indicate no systematic behaviour and, for most of the considered basins, close to steady-state conditions prevail for the weathering processes. This is a priori surprising for a high latitude area where weathering processes are likely to have been strongly affected by the last glaciation. For example, the Mackenzie Basin in Canada [23], also completely covered by an ice sheet (the Laurentide) until the Last Glacial Maximum (LGM), displays steady-state TSS that are different from TSS estimations based on field measurements. This has been interpreted as enhanced weathering rates, since deglaciation, of a fine-grained material previously accumulated under the ice sheet [23]. The discrepancy between Iceland and Canada may be first due to significant underestimation of measured TSS in the Mackenzie Basin, due to the lack of data when compared with Iceland. Another possibility is that in Iceland, steady-

state is reached quicker. Indeed, limited sediment trapping during glaciation has been highlighted, as ice streams from the central ice sheet to the Icelandic shelves have allowed the transport of eroded material into the ocean [63–65], in contrast to Canada. In addition, the continued presence of ice sheets in Iceland currently maintains high physical erosion rates (Fig. 3d), which may counterbalance the high chemical erosion rates observed in this region.

Complications of the steady-state model could arise due to Th and/or U exchange between the river dissolved phase and sediments, or to a non negligible contribution of groundwater to the river water. Such possibilities need to be considered here even if close to steady-state conditions for the considered rivers and the trend shown in Fig. 4 suggest little disturbance relative to the model hypotheses.

Significant U and Th adsorption onto sediments can indeed affect calculations and have been highlighted in

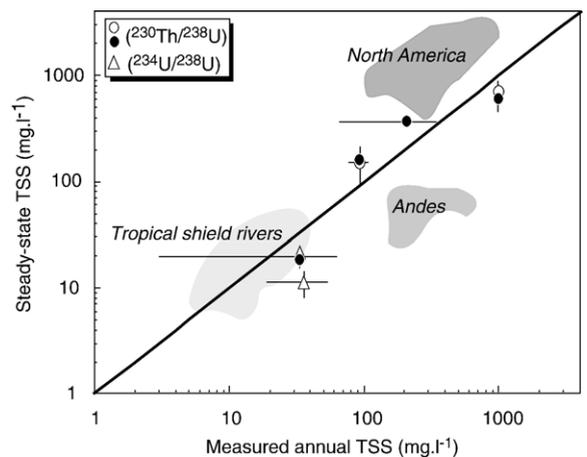


Fig. 4. Steady-state concentration of suspended sediment (TSS) estimated with U-series (using either ^{230}Th – ^{238}U or ^{234}U – ^{238}U system, see Table 3) versus TSS estimated based on [45] database (Table 1). Black circles display TSS calculated using bedload sediment data and open symbols using suspended sediments data.

Section 4.2 for the Jökulsa i Fljötösdal and Hvita-S suspended sediments (#17 and #2, respectively). We therefore avoided sediments which show U or Th enrichments. Nevertheless, the good agreement of the results obtained using suspended sediments data on one hand, and bedload data on the other hand, for the Hvita-S and the Jökulsa i Fjöllum (Table 3) suggest that adsorption does not significantly affect the calculations in these two cases. It has also been calculated that a significant difference of the ($^{230}\text{Th}/^{238}\text{U}$) ratio of the dissolved phase, for example due to Th adsorption, would not significantly affect the calculated TSS [23]. Similarly, a change of $\sim 10\%$ in the U content of suspended sediments of the Hvita-S (#2) would change the calculated TSS by $\sim 11\%$.

Groundwater U and Th contribution to river waters is usually difficult to estimate and could affect the calculated TSS if this water resided for a significant time within the basin. As outlined in Section 2, groundwater contributions are greater in low surface runoff and permeable areas, which correspond to the volcanically active area largely avoided during the sampling. Moreover, [18] have shown that the residence time of groundwaters in the rift zone close to the glaciers is less than ~ 100 days, which is negligible relative to the half life of ^{230}Th . As a consequence, it can be assumed that a negligible amount of ^{230}Th has been produced in the waters by radioactive decay.

Overall, these observations suggest that the U-series constraints are a priori robust and indicate that weathering processes in Iceland globally operate in close to steady-state conditions, with a very recent onset of weathering (< 300 ka) for the sediments currently carried by the rivers.

5.2. Weathering timescale and rates

Other lines of evidence also indicate a short weathering timescale in Iceland. River sediments (suspended and bedload) generally constitute material that is little weathered (see Section 4). Sediment U/Th ratios are close to those of fresh rocks, and ($^{234}\text{U}/^{238}\text{U}$) and ($^{238}\text{U}/^{230}\text{Th}$) are close to secular equilibrium. In parallel, the corresponding dissolved phase is far from equilibrium (see Fig. 4), while the first U to be released into water is expected to be highly enriched in ^{234}U [41]. With two pairs of U-series nuclides measured for both phases of the river (sediment and dissolved), it is possible to determine more precisely the age of the nuclide fractionation induced by weathering. This fractionation results from the preferential mobility of some nuclides (^{234}U and ^{238}U) relative to others (^{238}U and ^{230}Th respectively), as outlined in Section 4.2. Assuming a simple model of continuous release of nuclides into waters, following the method developed in [23], it is possible to estimate the time during which sediments have

been leached, i.e. the weathering timescale. Sampled river sediments are assumed to have been initially part of a bedrock in secular equilibrium, and then to have resided in the watershed where they were continuously subjected to leaching and weathering by waters, until their transport out of the basin (Appendix B, [23,24]).

In the studied watersheds, the mean ages for the bedrocks are greater than 300 ka, implying all fresh rocks are effectively in ^{230}Th – ^{238}U secular equilibrium. For the ^{234}U – ^{238}U system, all unweathered basalts are assumed to be in secular equilibrium. Calculated ^{238}U release rates (k_g) range between $0.3 \cdot 10^{-4} \text{ yr}^{-1}$ and $3.2 \cdot 10^{-4} \text{ yr}^{-1}$ (Table 3). This is about one to two orders of magnitude greater than for granite located at similar latitudes (e.g. Canada [56,57]), consistent with the enhanced weathering susceptibility of basalts. More interestingly, this is also one order of magnitude greater than U leaching coefficients obtained for the Deccan Traps in India [22], a basaltic plateau located in a tropical area. This is however in agreement with lower silicate weathering rates estimated for the Deccan region based on major element data [58]. In fact, because U is an incompatible trace element during basalt fractionation, it becomes concentrated in the melt phase, which, on solidification, corresponds to the groundmass and associated glass. Consequently, the U and Th contents in phenocryst phases are very low compared with the groundmass and glass (for example, 0.01 ppm U is measured in the plagioclase of Ardoukoba tholeiites, Asal rift, against 0.2 ppm for the groundmass and whole rock, [59]). It can be calculated that, for tholeiites, $\sim 99\%$ of U is located in the glassy part of the groundmass. The high U releasing rates found in Iceland could therefore, at a first approximation, be attributed to the enhanced weathering susceptibility of the glass because of the large amounts of hyaloclastites reported in the volcanically active area that was covered with ice [60–62].

The duration for weathering calculated for the Hvita-S (#2), Nordura (#5), Öxnadalsa (#11), Skjalafaflljot (#12) and Jökulsa a Fjöllum (#15) Basins is very short, with a mean value of ~ 3000 yr (Table 3), and ranges between 980 yr for the Jökulsa a Fjöllum and 6300 yr for the Nordura. By considering the same range of leaching coefficients obtained from these calculations, it is also possible to estimate the weathering timescales for the other basins (Fig. 5). Estimated timescales range from a few tens or hundred years for the Sog (#1), Hvita-W (#4) and Holmsarvatn (#25) Basins, to a few thousands years for the Vestari Jökulsa (#8) and Geithellnadalur (#21) Basins. The greatest timescales roughly correspond to the glacial retreat in Iceland, dated at 10.3 ka [65]. Indeed, the majority of Iceland was covered with ice during Younger Dryas and glaciers attained their present positions about

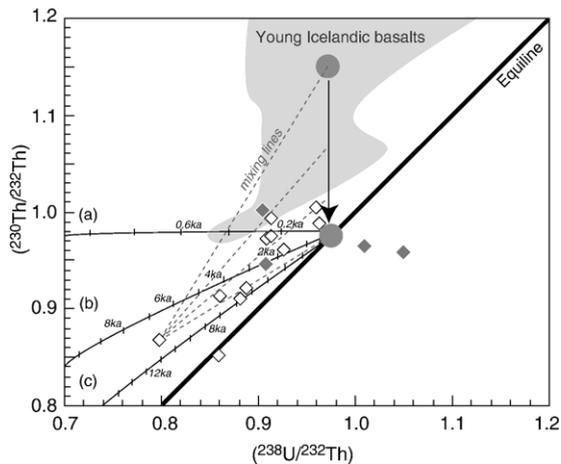


Fig. 5. ($^{230}\text{Th}/^{232}\text{Th}$) versus ($^{238}\text{U}/^{232}\text{Th}$) for sediments (symbols as in Fig. 3) of the Icelandic rivers. The arrow indicates closed system evolution of fresh basalts towards secular equilibrium, by simple radioactive decay [36–38]. Model curves reflect the continuous leaching evolution of sediment activity ratios as a function of time from initial secular equilibrium at $t=0$. Curves (a), (b) and (c) are calculated with release rates $k_8=2\cdot 10^{-5}$ and $k_0=1.4\cdot 10^{-5}$ ($k_8/k_0=1.4$); $k_8=3.3\cdot 10^{-5}$ and $k_0=1.4\cdot 10^{-5}$ ($k_8/k_0=2.4$); $k_8=3\cdot 10^{-4}$ and $k_0=5.7\cdot 10^{-7}$ ($k_8/k_0=526$). The chosen range corresponds to the range obtained when solving equations for each river (Table 3). Mixing lines between a sediment being weathered since the onset of deglaciation in Iceland (10 ka) and fresh tephra of various ages are shown in grey dashed lines.

9 ka ago. It is also interesting to note that, despite significant uncertainties, the shortest estimated weathering timescales are for basins located in the youngest basaltic terrains—North of Vatnajökull and South of Langjökull—(0.3–1.3 Ma), while the longer timescales correspond to the older basalt areas (2.4 Ma–5.9 Ma). North of Vatnajökull and South of Langjökull are characterized by sandy deserts and the highest deposition rates of aeolian material (up to 1 mm yr^{-1} , [25]). This material mainly comes from volcanic eruptions (tephra) in the active zone and also from glacier flood plains, and can therefore contribute to the sediment reservoir located within these catchments. As a consequence, the shortest estimated weathering timescales could be explained by a significant contribution of fresh tephra to sediment. As illustrated in Fig. 5, mixing lines between a sediment being weathered since 10 kyr and a fresh basalt—either in secular equilibrium or freshly erupted—would lead to decrease the apparent weathering timescales.

5.3. Assessing links between erosion rates and U-series

It has been shown in Iceland that the highest chemical erosion rates are located in the youngest areas and could be due to hyaloclastite, but the wide variability of the

chemical composition (in major and trace elements) of Icelandic basalts and their constituent phases limits direct comparison with river chemistry. Nevertheless, it is possible to better constrain the controls on weathering with U-series. Indeed, there is a striking inverse trend between ^{234}U – ^{238}U disequilibria measured in river waters and physical erosion rates (Fig. 6), that is inconsistent with recent observations: ($^{234}\text{U}/^{238}\text{U}$) measured in New Zealand river waters have been found to correlate positively with the uplift rate, and therefore have been inferred to be linked to physical erosion rates at the scale of a watershed [66]. ^{234}U release into water due to alpha-recoil effects are expected to be more significant when the particle radius is small and therefore when physical grinding has been significant (see review in [41]). However, in Iceland, such a covariation is not observed (Fig. 6). Rivers characterized by high dissolved ($^{234}\text{U}/^{238}\text{U}$) are associated with low physical erosion rates (for example the Fossa River, #20, with ($^{234}\text{U}/^{238}\text{U}$)=1.68 and a physical erosion rate equal to $34\text{ t km}^{-2}\text{ yr}^{-1}$). Lower ($^{234}\text{U}/^{238}\text{U}$) rivers correspond to relatively high physical erosion rates (Ytri Ranga River, #27; Skjalfafljot River, #12). This strongly suggests that some other process is acting to dominate ($^{234}\text{U}/^{238}\text{U}$) in Iceland waters. Low ($^{234}\text{U}/^{238}\text{U}$) ratios in rivers draining the younger terrains likely result from the close-to-congruent release of U isotopes into water. This congruency of the weathering process highlighted by U isotopes, associated with other observations previously detailed—(1) U and Th are mainly located in the glass/groundmass phase; (2) glass leaching experiments show a close-to-congruent process at the onset of weathering;

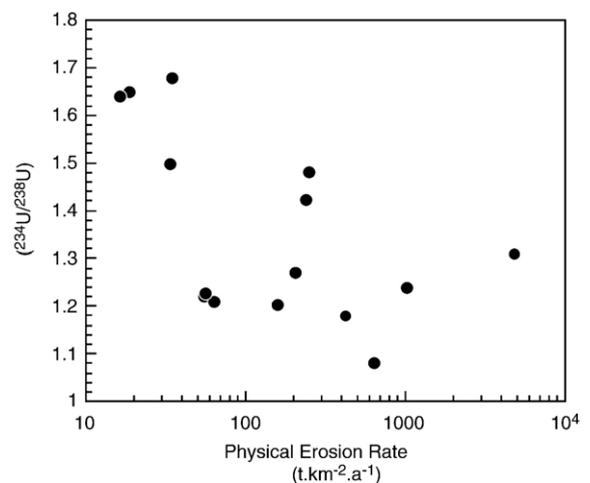


Fig. 6. ($^{234}\text{U}/^{238}\text{U}$) measured for the dissolved phases of Icelandic rivers (except for Jokulsa I Fljotsdal River, #17, see Section 4.2) versus the physical erosion rates estimated based on measured TSS (Table 1).

(3) chemical erosion rates in Iceland are higher in young and hyaloclastite rich areas; (4) Iceland weathering rates are higher than in the Deccan—reinforces the role of the age and the glass fraction on basalt weathering rates. This study also illustrates the primary control of chemical erosion rates on ($^{234}\text{U}/^{238}\text{U}$) in Icelandic river waters, even when physical erosion rates are high. In areas where hyaloclastites are less abundant or the basalt already weathered, recoil effects from more resistant or secondary phases are likely to dominate over congruent U isotope release. It seems therefore that ^{234}U – ^{238}U disequilibria in silicate river waters depend on a balance between physical and chemical erosion rates at the scale of the watershed. Where this balance is a function of climatic or tectonic parameters such as runoff, temperature and uplift, ^{234}U – ^{238}U disequilibria should also depend on the same parameters, as shown for New Zealand [66].

Weathering timescales have recently been shown to be a fundamental parameter for explaining weathering rates of silicate phases [67,68] but are rarely taken into account in the modelling of the CO_2 cycle. Most published data correspond to experimentally controlled or soil scale conditions, and demonstrate that weathering rates decrease rapidly in the early stages of weathering [68]. By comparing U-series and major element results published for several areas, it is possible to address the role of weathering duration on weathering rates at larger scales. Recent studies have shown that tropical areas little affected by the last glaciation yield long weathering timescales, linked to significant soil thicknesses (50–100 kyr for the Deccan [22], 100–300 kyr for the Amazon shield [24]). By contrast basins potentially strongly affected by the last glaciation are characterized by shorter weathering timescales and thinner soils (10–20 kyr for the Mackenzie in Canada, 5 kyr for the Andes and 3 kyr for Iceland). Fig. 7 shows that for these basins where chemical erosion was significantly limited during glaciation, there is a negative trend between the silicate weathering rate estimated from major elements measured in river waters, and weathering timescales derived independently from riverine U-series disequilibria. The Mackenzie Basin, characterized by greater weathering timescales for sediments (20 kyr), exhibits the lowest silicate weathering rates while basins where particles have been leached for a shorter time display greater weathering rates (Andes and Iceland). Moreover, this correlation can be fit using power functions similar to that of White and Brandtley [68] obtained from both experimental and field studies (Fig. 7). This agreement strongly suggests that, despite differences in lithology,

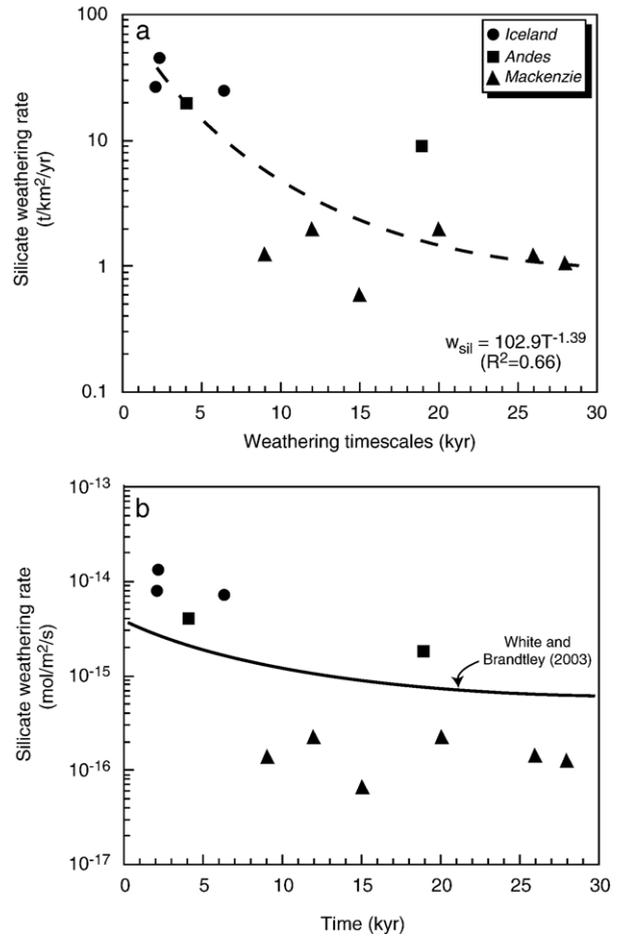


Fig. 7. (a) Silicate weathering rates calculated using major and trace elements data versus weathering timescales estimated with U-series, for Iceland (this study), the Andes [24] and the Mackenzie basin [23,70]. (b) Silicate weathering rate in mol/m²/yr have been estimated assuming a surface area of 1 m²/g [67] and soil thickness of 20 cm, 50 cm and 30 cm for the Iceland basins, the Mackenzie basins and the Andes basins, respectively. The black curve represents the White and Brandtley [68] power law where $R = 3.1 \cdot 10^{-13} t^{-0.61}$ (with R =average silicate weathering rate and t =time).

the time during which particles have been weathered plays a key role on large scale weathering rates.

Several parameters have been proposed to explain the decrease of rates with time, in particular reactive surface area, the saturation state of the solution in contact with the silicates, as well as clay and oxide formation. With time, waters can reach equilibrium and saturation (relative to mineral phases), which in turn slow down in-situ weathering. Also, thicker soils in lower physical erosion terrains can be characterized by a significant fraction of material that is already weathered and depleted in mobile elements, and consequently will release on average fewer cations into waters. Overall, this trend suggests that thicker

soils slow down weathering [1,69]. Since the weathering time is a key parameter even over short period of time (0–20 kyr), a likely implication is that any recent significant disturbance of soil thicknesses, either by anthropogenic factors or by climatic events, should therefore affect large scale silicate weathering rates and hence potentially atmospheric CO₂ levels.

6. Conclusions

Iceland provides a unique opportunity to compare U-series disequilibria measured in rivers with chemical and physical erosion rates estimated independently. Chemical and physical erosion rates in Iceland are found to be surprisingly high for a cold and glaciated area, ranging between 13 and 33 t km⁻² yr⁻¹ and between 21 and 4864 t km⁻² yr⁻¹, respectively.

River waters display (²³⁴U/²³⁸U) and (²³⁸U/²³⁰Th) that are systematically higher than secular equilibrium while river suspended and bedload sediments display close to secular equilibrium values. Weathering processes in Iceland appear to operate in steady-state conditions, and an age of sediment weathering of ~10 kyr maximum is estimated with a simple model of continuous weathering. In Iceland, high physical erosion rates are associated with high chemical erosion rates and low (²³⁴U/²³⁸U) ratios in waters. Rapid weathering of glassy basalts in young areas plays a major role, and high physical erosion rates are not associated with higher ²³⁴U/²³⁸U ratios. By contrast, ²³⁴U is released significantly preferentially compared with ²³⁸U in old areas characterized by the presence of mineral phases more resistant to weathering.

On a more global scale, comparison with published data shows that, for basins strongly affected by the last glaciation, the time during which sediments have been weathered within the watershed is a key parameter that determines large scale silicate weathering rates.

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Appendix A

For constraining steady-state TSS (sediment content carried by the river), we use mass balance equations for U (between source rocks and river solutes and sediments), as detailed in e.g. [23,24], and where source rocks are assumed to be in secular equilibrium (activity ratios equal to 1):

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_p (1-X_w) + \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) X_w = 1 \quad (1)$$

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_p (1-X_w) + \left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right) X_w = 1 \quad (2)$$

X_w being the fraction of U carried by the river with the dissolved phase (w) and p referring to river particles. Also,

$$X_w = \frac{U_w}{U_w + \text{TSS} \cdot U_p} \quad (3)$$

with U_w and U_p being the U content in water and in particles (sands or suspended sediments, see text for more details), respectively.

Steady-state TSS (in g/l) can then be obtained either by combining Eqs. (1) and (3) (TSS₁), or (2) and (3) (TSS₂), depending on the activity ratio considered:

$$\text{TSS}_1 = \frac{U_w - \left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_w U_w}{\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_p U_p - U_p} \quad (4)$$

$$\text{TSS}_2 = \frac{U_w - \left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_w U_w}{\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_p U_p - U_p} \quad (5)$$

Both results (TSS₁ and TSS₂) are expected to be identical if weathering process operates at short time-scales, since loss of ²³⁴U and ²³⁰Th nuclides by radioactive decay is not considered in the mass balance Eqs. (1) and (2). Also, steady-state TSS₁ or TSS₂ can be compared with TSS estimated based on regular field measurements of suspended particles contents (see text and Table 3 for more details).

Appendix B

We present here the differential equations used for constraining weathering timescales for sediments currently carried by rivers. We have considered first order kinetics to describe the release of ^{238}U , ^{234}U and ^{230}Th from particles (following a method developed in [23]):

$$\frac{d^{238}\text{U}_p}{dt} = -k_8^{238}\text{U}_p \quad (6)$$

$$\frac{d^{234}\text{U}_p}{dt} = \lambda_8^{238}\text{U}_p - (k_4 + \lambda_4)^{234}\text{U}_p \quad (7)$$

$$\frac{d^{230}\text{Th}_p}{dt} = \lambda_4^{234}\text{U}_p - (k_0 + \lambda_0)^{230}\text{Th}_p \quad (8)$$

where $^{238}\text{U}_p$, $^{234}\text{U}_p$ and $^{230}\text{Th}_p$ refer to ^{238}U , ^{234}U and ^{230}Th abundance in the particles and k_8 , k_4 and k_0 the releasing rates or leaching coefficients [23] for ^{238}U , ^{234}U and ^{230}Th , respectively. λ_8 , λ_4 and λ_0 are the decay constants of ^{238}U , ^{234}U and ^{230}Th , respectively. The release rates for ^{238}U , ^{234}U and ^{230}Th represent the fractions of ^{238}U , ^{234}U and ^{230}Th released into water per unit of time, and result from several processes potentially involved during weathering: dissolution, either congruent or incongruent with precipitation of secondary minerals, leaching and adsorption/desorption processes.

We have also considered that the amount of ^{238}U , ^{234}U and ^{230}Th released by the particles is being carried by river dissolved phase such that:

$$^{238}\text{U}_w = \int_0^t k_8^{238}\text{U}_p(t) dt \quad (9)$$

$$^{234}\text{U}_w = \int_0^t k_4^{234}\text{U}_p(t) dt \quad (10)$$

$$^{230}\text{Th}_w = \int_0^t k_0^{230}\text{Th}_p(t) dt \quad (11)$$

The only unknowns are the leaching coefficients and the time (t) during which particles have been weathered. The only assumption for solving the equation systems is secular equilibrium for ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) in fresh particles at time $t=0$. For each river, all these parameters (k_8 , k_4 and k_0 and t) can be determined using a Matlab function that minimizes the difference between the measured and the modelled ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) ratios for sediments and dissolved phase.

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