[American Journal of Science, Vol. 311, December, 2011, P. 851–894, DOI 10.2475/10.2011.02]

OROGRAPHY-DRIVEN CHEMICAL DENUDATION IN THE LESSER ANTILLES: EVIDENCE FOR A NEW FEED-BACK MECHANISM STABILIZING ATMOSPHERIC CO_2

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ABSTRACT. In this paper we present chemical composition data for major elements in rivers from three islands of the Lesser Antilles. The Lesser Antilles are a tropical volcanic subduction arc and are characterized by steep gradients of relief, bedrock age and precipitation. They constitute a natural laboratory where the response of the weathering engine to large variations of runoff can be understood. Data indicate that the Lesser Antilles are characterized by extremely variable chemical weathering (40-430 t/km^2/a) and CO_2 consumption (300-3500.10^3 mol/km^2/a) rates, amongst the highest found on Earth and consistent with the previous studies on the weathering of volcanic rock. A noteworthy observation is that, along the runoff gradient, concentrations of rock-derived solutes do not follow a pure dilution law and that a buffering mechanism exists stabilizing solute concentrations. As a result concentrations vary much less than runoff and chemical weathering rates are mainly controlled by runoff. Precipitation patterns in the Lesser Antilles are essentially orographic and controlled by the adiabatic decompression of the water-saturated Atlantic air masses. The production of acidity by volcanic degassing is an additional factor that modulates the runoff effect. Two main conclusions can be drawn from this study. First, chemical weathering fluxes of oceanic islands are strongly dependent upon relief repartition, which cautions the use of regional mean values to compare volcanic islands. Second, volcanic activity in the Lesser Antilles subduction arc, by creating relief, promotes high orographic precipitation and/or infiltration regimes, that in turn results in elevated chemical weathering and atmospheric CO_2 consumption fluxes. This feedback mechanism, implying mainly precipitation and relief, is proposed to act in complement to the temperature-related feedback proposed by previous authors for stabilizing the atmospheric CO_2 content of the atmosphere in response to volcanic CO_2 degassing. This study highlights the importance of the water cycle in controlling chemical weathering of volcanic arc islands and associated CO_2 consumption rates.

Key words: Subduction Arc, weathering, CO_2 consumption, runoff, orographic precipitation, hydrothermal input

INTRODUCTION

The interaction between rocks and water is one of the most important geological processes on Earth, responsible for the transformation of bedrocks into secondary products (mainly clays and Al-Fe oxides) and water dissolved components. Chemical weathering produces sediments of lower density compared to the initial bedrock and the detritus is transported to the oceans when physical erosion is active. Chemical weathering initiates the geological cycle. Water rock interaction is also a giant neutralization reaction where the acidity of the atmosphere, ultimately derived from volcanic degassing, is consumed by its reaction with rock minerals (Berner, 2004).

It is now widely accepted that, at the surface of the Earth, the chemical weathering of volcanic rocks is of major importance in the global production of solutes to the ocean, sediment formation and consumption of atmospheric acidity (Louvat and Allègre, 1997; Dupré and others, 2003; Gislason and Oelkers, 2011). Previous studies

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have suggested that 30 to 35 percent of the global atmospheric CO_2 consumption by weathering is attributable to chemical weathering of volcanic rocks (Gaillardet and others, 1999; Dessert and others, 2003). Although this figure represents a very crude estimate based upon an estimate of the geographic surface area of volcanic rocks exposed to chemical weathering and the assumptions that the volcanic rocks behave like basaltic rocks during chemical weathering and that weathering rates follow an Arrhenius relationship with temperature. A particularly large unknown is the importance of weathering of volcanic rock in subduction zone settings. A couple of studies have started to estimate rates of chemical weathering and water composition in subduction settings, in particular volcanic arcs (Louvat, ms, 1997; Dessert and others, 2003; Gaillardet and others, 2003; Anazawa and Ohmori, 2005; Goldsmith and others, 2008; Dessert and others, 2009; Goldsmith and others, 2010; Schopka and others, 2010; Jones and others, 2010), but there is still much to be done. In particular, subduction zone volcanism is characterized by calc-alkaline rocks that, due to their structure and relatively silica-rich composition compared to basalts, may weather more slowly (Wolff-Boenisch and others, 2006). Subduction zone volcanism is also more explosive, due to the abundance of volatiles resulting in production of volcanic ash that is rich in glass and to the production of sulfuric and hydrochloric acids that accelerate chemical weathering (Varekamp and Thomas, 1998; Jones and others, 2010; Flaathen and others, 2010).

At a regional scale, understanding the balance between production of magmatic rocks and consumption by weathering and erosion is important to understand the long term stability of volcanic arcs and the input of sedimentary material that nourish the subduction factory (Carpentier and others, 2008). The major chemical and isotopic fractionation that occur during the weathering of subduction zone rocks are then of critical importance for estimating the role of first-cycle chemical weathering on the mobility of elements, on the composition of sediments entering the subduction factory and sedimentary recycling (Labanieh and others, 2010).

For theses reasons, the weathering of subduction zone areas requires attention.

Guadeloupe, Martinique and Dominica are part of the Lesser Antilles volcanic arc. Recent studies (Samper and others, 2007; Samper and others, 2009; Germa and others, 2010) have proposed estimates of the rate of magmatic production in the Lesser Antilles. Depending on the duration of the period considered, these numbers vary from 0.04 km^3/a for the North of Martinique Island to 0.47 km^3/a for the Axial Chain in Guadeloupe. So far, precise and systematic estimates of volcanic arc erosion by riverine chemical and physical processes have not been determined. Considerable volumes have been eroded in the Lesser Antilles by flank destabilization as shown by Boudon and others (2007) over the last 300 ka, but the long-term mean erosion rate represented by these discrete events is difficult to estimate and can not be compared to estimates of fluvial erosion. Sediment accumulation rates during the late Quaternary (Reid and others, 1996) in the Caribbean have been estimated but they poorly record the aerial erosion rates because of the input of other external sources such as the Saharian dust.

This paper is part of an effort to estimate present day chemical and mechanical erosion rates of the Lesser Antilles (Rad and others, 2007; Sak and others, 2010; Lloret and others, 2010; Chatanantavet and others, 2010) and report chemical analyses of rivers sampled at several periods of Martinique, Dominica and the volcanic part of Guadeloupe Island. In this paper, we show that chemical weathering rates in the Lesser Antilles are controlled by runoff essentially because concentrations of rock-derived solutes are not purely diluted at high runoff. Runoff is controlled by relief via orographic precipitation. Other important parameters are the input of acidity from volcanic degassing and hydrothermal alteration. Two important consequences arise from this work. First, chemical weather-

ing rates are dependent upon island geometry in the volcanic arc islands of the trade wind belt and second is the existence of a negative feedback mechanism relating CO_2 degassing by volcanic activity to CO_2 consumption by chemical weathering reactions which is triggered by orographic precipitation.

GEOLOGICAL, PEDOLOGICAL AND CLIMATIC CONTEXT

Guadeloupe, Martinique and Dominica are part of the Lesser Antilles volcanic arc created by the oblique subduction of the North American plate under the Caribbean plate at a rate of 2 cm/a (DeMets and others, 2000; Feuillet and others, 2001, 2002, and references therein). The Lesser Antilles Arc is an active volcanogenic and seismogenic zone (fig. 1) spanning >850 km from St. Vincent Island in the south to Anguilla in the north. The volcanic arc splits into two subparallel volcanic arcs at the present day position of Martinique. The western arc is comprised of flat-topped islands of Miocene to Plio-Quaternary aged deposits that are capped by coral reef platforms. The Eastern Arc is still active and contains more than 15 active volcanoes. Their maximum elevation is 1467 m (La Soufrière in Guadeloupe). The explosion of the Montagne Pelée Volcano killed 28,000 people in 1902 and a plinean eruption is still ongoing in Montserrat, 70 km north to Guadeloupe Island. Geologic descriptions and the timing of volcanism of the three islands discussed here can be found in Feuillet and others (2002), Lindsay and others (2003), Samper and others (2007), Komorovski and others (2008), Samper and others (2009), and Germa and others (2010). All islands are comprised of composite volcanoes of andesitic or basaltic-andesitic compositions that form lava flows, lava domes and pyroclastic deposits. The pyroclastics dominate the other lithological types (Komorovski and others, 2008). Plinian activity has been associated to production of dacite domes (Soufrière of Guadeloupe, Pelée in Martinique and Northern Dominica) and considerable amounts of volcanic ashes disseminated onto the Caribbean region. The trois Pitons-Micotrin volcanic center on Dominica produced large volumes of ignimbrite that can be considered as the most differentiated material of the studied zone. Construction periods are associated to destruction phases by collapse and flank-collapse, creating large calderas and debris avalanche deposits such as those that destroyed the Carmichael volcano in South Basse-Terre, 13.5 and 11.5 ka ago (Deplus and others, 2001; Komorovski and others, 2005; Boudon and others, 2007; Samper and others, 2009).

The three islands studied here are located under a wet tropical climate with high mean annual temperatures (24 °C) and air humidity (75%), and high rainfall throughout the year. The cyclonic period occurs [approximately from July to November (Zahibo and others, 2007)] and is characterized by heavy rainfall periods caused by tropical storms (several a year) and hurricanes (recurrence interval of ~10 years) that are responsible for extreme flood and landslide events. Most of physical erosion transport occurs during these periods of time. A well-known climatic feature of the Lesser Antilles islands is the asymmetry of precipitation regime between the western (leeward) and eastern (windward) sides due to the dominant trade wind pattern. Precipitation also varies as a function of elevation and exceeds 10 m/a at the summits of the active volcanoes. In contrast, the driest parts of the islands receive <1 m/a of precipitation. Accordingly, the drainage intensity is important in the Lesser Antilles.

Vegetation is naturally adapted to the pronounced precipitation gradients. Rainforest is the natural vegetation (Rousteau, 1996) and has been preserved in the National Parks that occupies most of Basse Terre Island and in the Pelée region in Northern Martinique. Vegetation varies with elevation. From low altitude to high altitude, the different biomes are decidous tropical forest (especially developed in the leeward coast), evergreen tropical forest, mountain and submountain rainforest and altimountain forest.

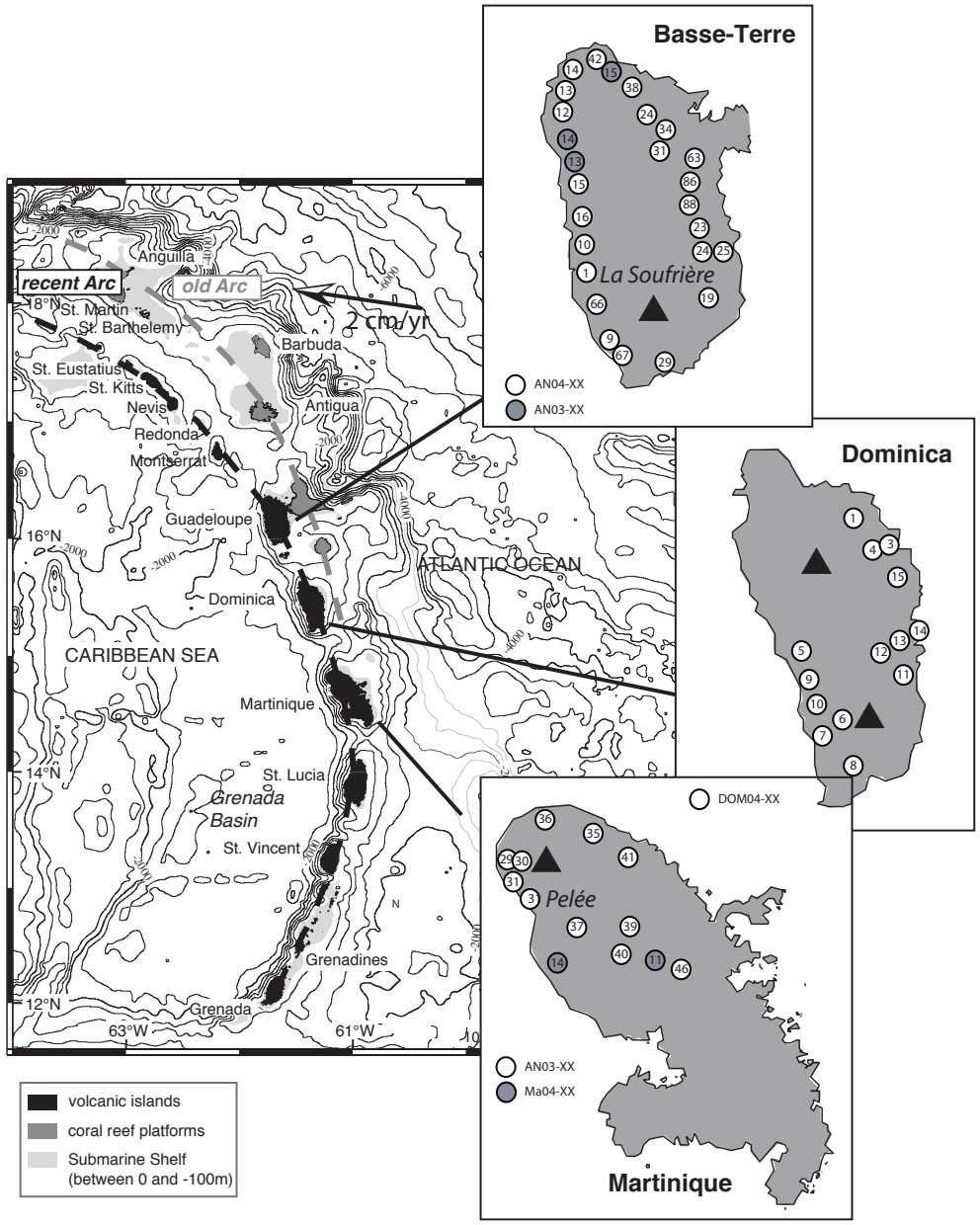

Fig. 1. Geographical setting and sampling location.

Soils in the Lesser Antilles are well-developed and follow the vegetation and bedrock age gradients. Ferralitic soils cover the more ancient parts of Lesser Antilles islands while andisols are developed in the most recent volcanic parts (Colmet-Daage, 1969; Buss and others, 2010; Lloret and others, 2010). The dry leeward slopes are covered by a very poorly developed soil system.

SAMPLING AND RESULTS

Samples from Guadeloupe, Martinique and Dominica were collected in February 2003, February 2004, and October 2004 (fig. 1). February samples correspond to dry season and October samples to the rainy season. It is important to keep in mind that our sampling was conducted in periods with no big (hourly or daily) discharge variations and did not capture extreme events (tropical storms or hurricanes). Although such events are more frequent during the rainy season, none occurred during our sampling interval. As a result, our chemical database is biased toward relatively high concentrations as flood episodes tend to dilute the dissolved concentrations. By contrast, the discharge data taken from several governmental agencies from Guadeloupe and Martinique Island are long term estimates that take extreme events into account (see discussion section).

Samples were taken in areas with minimum anthropogenic impact. The most extensive sampling was done in Basse-Terre in Guadeloupe where most of the rivers flowing to the sea were sampled. In Basse-Terre, rivers were sampled in the protected area upstream to the cultivated zone. In Dominica and Martinique, it was more difficult to find rivers with low human impact and this is the main reason why we focused in Martinique on the Northern part of the Island. In addition to "large rivers," a number of small streams were sampled in order to capture the spatial variability. Hydrothermal springs in the vicinity of the active volcanic centers were also sampled.

Between 1 and 7 liters of water were collected in the field and pH and temperature were immediately measured. Filtration through 0.2 μm cellulose acetate filters (142 mm or 47 mm) was done within a day to separate the suspended and dissolved phases. Some samples (from the smallest rivers) were filtered in the field with 0.2 μm syringue filter holders. Alkalinity was determined using the Gran technique. Filtered waters were acidified at pH 2 with distilled 16N nitric acid for cation analysis. Non-acidified samples were used for analysis of anions (Cl^-, SO_4^{2-}, NO_3^- and HCO_3^-). Anions, cations and dissolved silica were measured by HPLC Dionex in Paris, with a precision better than 5 percent. Concentrations of major elements in rivers and hydrothermal springs are given in table 1. Thermal waters were filtered on site to avoid précipitation of iron oxides.

Most of the rivers draining the Lesser Antilles are characterized by neutral pH values ranging from 6.3 (Blanche, Martinique) to 7.73 (Goyave, Guadeloupe). Only a few rivers, all located around La Soufrière volcano have significantly lower values (between 4 and 5). Total dissolved solids (TDS) range from 48 mg/l for the less concentrated rivers to 300 mg/l for rivers close to active volcanic centers. The most abundant dissolved species in the Lesser Antilles is silicic acid (H_4SiO_4) with concentrations ranging from 140 μmol/l to 1000 to 2000 μmol/l, much higher than dissolved Si concentrations found in La Reunion, Azores and Iceland. The mean value is not significantly different among the individual islands with concentrations around 450 to 500 μmol/l (or 50 mg/l). The second more abundant species is bicarbonate (HCO_3^-) with typical values ranging from almost 0 in the acidic rivers to 1500 μmol/l. The median value is about 400 μmol/l with no detectable differences among the three islands. Rivers from the Lesser Antilles are chloride-rich, due to their proximity to the sea, with a median value of 200 to 300 μmol/l. We observe, for most of the rivers from the database, a decrease of Cl^- concentration with runoff, from 600 μmol/l in the driest part of the Lesser Antilles to 200 μmol/l in the wettest. Rivers impacted by hydrothermal processes are an exception to this rule.

Many of the rivers of the Lesser Antilles are characterized by high concentrations of sulfate (SO_4^{2-}). There is no relation between pH and the amount of sulfate in solution. A histogram of sulfate concentrations is highly asymmetric with a median value of about 100 μmol/l and a tail towards values up to 2000 μmol/l (not shown).

Table 1

	Name	Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
BASSE-TERRE, GUADELOUPE														
Feb. 2003	**River Name**													
AN03-1	Vieux Habitant River @ maison du café	2/2/03	4800	n.d	450	157	130	3	29	400	238	14	65	127
AN03-2	St-Louis Riv.	2/2/03	4000	n.d	442	172	130	9	40	429	260	24	82	156
AN03-3	Rivière Rouge	2/2/03	4000	n.d	557	131	130	3	583		268	21	94	325
AN03-5	Rivière Noire (cascade Vauchelet)	2/3/03	4000	n.d	1075	404	130	0	1586	250	809	103	508	1300
AN03-6	Gallion Riv. upstream	2/3/03	4000	n.d	841	511	130	6	830	278	590	73	314	690
AN03-7	Grand Carbet Riv. Second Fall	2/4/03	6000	n.d	648	700	130	0	803	243	616	79	382	697
AN03-8	Grand Carbet Third Fall	2/4/03	5400	n.d	431	1113	130	0	406	242	637	70	317	530
AN03-9	Grand Carbet at mouth	2/4/03	4600	n.d	599	906	130	24	272	684	547	67	286	569
AN03-10	Capesterre Riv. Upstream (National Park)	2/4/03	5000	n.d	391	163	163	21	20	340	237	16	65	132
AN03-11	Beaugendre Riv.	2/5/03	1575	n.d	654	258	220	2	63	892	455	29	112	295
AN03-12	Grande Plaine Riv. at Saut D'Acomat	2/5/03	2000	n.d	607	440	250	0	982		606	40	296	646
AN03-13	Petite plaine Riv.	2/5/03	1600	n.d	519	447	350	4	72	1048	559	29	211	333
AN03-14	Fenche-Fougères Riv.	2/5/03	1500	n.d	604	415	350	0	470	402	529	27	246	431
AN03-15	Nogent Riv.	2/5/03	850	n.d	615	584	584	2	49	426	650	32	134	126
AN03-16	Losteau Riv.	2/5/03	1860	n.d	399	344	250	0	86	859	535	25	149	264
AN03-17	Bras David riv. at Maison Forêt	2/6/03	3000	n.d	521	244	244	0	18	429	334	15	88	139
AN03-18	Baron Riv.	2/6/03	3000	n.d	424	202	202	0	11	691	373	20	85	207
AN03-19	Ecrevisses Riv.	2/6/03	3000	n.d	369	208	208	0	9	451	337	24	72	127
AN03-20	Riv. Bras Saint-Jean	2/6/03	3000	n.d	284	198	198	0	12	420	304	21	67	130
AN03-21	Grande Rivière à Goyave (upstream)	2/6/03	2900	n.d	387	160	160	0	11	300	227	8	54	95
AN03-22	La Lézarde Riv. at Saut Lézarde	2/6/03	3750	n.d	380	190	190	0	10	430	304	23	68	127
AN03-23	Grande Rivière à Goyave at Baindridge	2/6/03	3000	n.d	448	324	324	6	15	300	370	34	82	89
AN03-24	Rivière à Sables	2/6/03	1600	n.d	371	311	311	0	21	383	403	21	84	108
AN03-25	Grande Rivière à Goyave at Bonne Mère	2/6/03		n.d	426			0	0		396	541	208	266
AN03-26	Moustique Riv. Near Sofia Spring	2/6/03	1850	n.d	522	331	300	9	50	287	371	18	101	107
AN03-27	Sofia Spring	2/6/03		n.d	276	382		2	304		406	32	71	94

TABLE 1
(continued)

	Name	Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
BASSE-TERRE, GUADELOUPE														
Feb. 2004	**River Name**													
AN04-1	Vieux Habitant Riv. at Barthole	1/31/04	4800	n.d	466	218	130	11	168	351	300	14	77	179
AN04-2	Ravine Bernardine	1/31/04	4800	7.7	484	168	140	0	26	540	280	13	71	143
AN04-3	Soil water near AN04-02	1/31/04		n.d	375	159	159	15	24	462	254	5	67	122
AN04-4	Soil Water near AN04-03	1/31/04		n.d	1081	462	462	0	39	1433	890	62	331	320
AN04-5	Triburary of AN04-01	1/31/04		n.d		309	200	14	85		659	77	187	232
AN04-6	Riv. Noire at Cascade Vauchelet	1/31/04	4000	7.46	1041	428	150	0	1655	220				
AN04-7	Saut d'eau Matouba Riv.	1/31/04	4000	7.7		172	150	12	30	142	361	38	109	280
AN04-8	Ravine Blondeau	2/1/04	2000	7.41	521	961	961	15	48	1358	1192	93	321	395
AN04-9	Rivières des Pères	2/1/04	3100	n.d	751	302	150	43	493		475	38	195	452
AN04-10	Beaugendre Riv.	2/1/04	1575	7.94	522	285	220	14	77	795	469	18	105	291
AN04-11	Caillou Riv.	2/1/04	1200	7.9	653	596	500	22	213	684	793	69	228	288
AN04-12	Baille-Argent Riv.	2/1/04	1100	7.9	592	583	500	0	666	313	808	71	307	457
AN04-13	Deshaies Riv.	2/1/04	1000	7.76	587	599	500	11	140	281	706	62	135	128
AN04-14	Ferry Riv.	2/1/04	1040	7.12	661	572	500	0	205	559	772	76	201	255
AN04-15	Grande Plaine Riv. at Saut D'Acomat	2/1/04	2000	5.05	602	442	250	12	988		641	53	274	554
AN04-16	Losteau Riv.	2/1/04	1860	7.85	602	348	250	13	100	657	541	42	132	239
AN04-17	Petit Carbet Riv. at Trois Rivières	2/2/04	3000	7.33	210	171	171	4	18		194	16	29	57
AN04-18	Tributary of the Grand Carbet Second Fall	2/2/04		7.49	636	757	130	0	640	609	1005	105	359	576
AN04-19	Grand Carbet Riv. Second Fall	2/2/04	6000	7.38	419	300	130	0	575	171	407	37	207	422
AN04-20	Tributary of the Grand Carbet Second Fall	2/2/04	5000	7.1	696	148	130	0	34	613	282	27	79	172
AN04-21	Tributary of the Grand Carbet Second Fall	2/2/04	5000	7.55	140	141	130	0	25	110	149	6	31	39
AN04-22	Soil Water nea Grand Carbet Second Fall	2/2/04		7.25	533	167	130	0	23	525	258	20	62	160
AN04-23	Pérou Riv. Upstream (National Park)	2/2/04	4000	n.d	380	146	130	10	44	310	221	16	50	97
AN04-24	Capesterre Riv. Upstream (National Park)	2/2/04	5200	8.05	410	189	130	42	32	427	230	14	44	102
AN04-25	Capesterre downstream (village)	2/2/04	4900	n.d	344	149	130	12	30	345	263	13	67	140
AN04-26	Rouge Riv.	2/3/04	4000	4.7	518	128	128	4	537		275	25	85	292
AN04-29	Grande Anse Riv. at trois Rivières	2/3/04	1700	7.65	557	313	300	72	75	688	436	33	148	269
AN04-30	Bambou Riv.	2/3/04		7.83										

Table 1
(continued)

	Name	Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
BASSE-TERRE, GUADELOUPE														
Feb. 2004	**River Name**													
AN04-31	Bras David riv. at Maison Forêt	2/4/04	3000	7.1	432	271	271	0	30	515	376	28	85	134
AN04-32	Corossol Riv.	2/4/04	3000	7.65	374	223	223	0	24	467	333	19	61	122
AN04-33	Ecrevisses Riv.	2/4/04	3000	7.56		234	234	0	11		363	27	67	117
AN04-34	Grande Rivière à Goyave (upstream)	2/4/04	3000	7.73	285	192	192	0	22	379	266	12	55	101
AN04-35	Grande Rivière à Goyave (at Montauban)	2/4/04		n.d	344	312	200	16	32	496				
AN04-36	Tributary of Moreau Riv.	2/5/04	4500	6.6	187	236	236	3	10	105	236	9	42	30
AN04-37	Rose Riv.	2/5/04	2850	7.44	405	263	263	5	12	460	356	29	73	124
AN04-38	Moustique Riv. at Sainte Rose	2/5/04	1850	7.44	459	362	362	2	29	351	404	35	98	110
AN04-39	Tributary of the Moustique Riv.	2/5/04	1850	n.d	308	386	386	3	35	154	397	31	73	53
AN04-40	Tributary of Rivière salée	2/5/04	1850	6.5	327	388	388	6	20	228	389	32	80	58
AN04-41	Sofia Spring	2/5/04		3.8							433	18	68	91
AN04-42	Vieux Fort Riv.	2/5/04	900	6.69	581	613	613	8	30	466	695	64	135	104
Oct. 2004														
AN04-43	Deshaies Riv.	10/18/04	1000	7.43	515	592	500	5	103	376	625	33	115	110
AN04-44	Ferry Riv. at captage	10/18/04		7.2	574	451	451	3	190	317	475	31	132	162
AN04-45	Ferry Riv.	10/18/04	1040	7.56	567	621	500	7	177	487	671	36	150	197
AN04-46	Baille-Argent Riv.	10/18/04	1100	7.39	543	649	500	13	448	293	625	33	205	272
AN04-47	Caillou Riv.	10/18/04	1200	7.62	536	604	500	8	125	514	650	38	158	177
AN04-48	Beaugendre Riv.	10/18/04	1575	7.61	498	282	220	10	60	624	421	26	81	237
AN04-49	Grande Plaine Riv. at Saut D'Acomat	10/19/04	2000	4.66	648	536	250	8	1081	14	604	32	299	586
AN04-50	Moustique Riv. Near Sofia Spring	10/19/04	1850	7.42	324	344	300	2	53	191	304	15	64	67
AN04-52	Vieux Fort Riv.	10/19/04	900	7.29	568	573	573	8	29	407	571	23	115	95
AN04-53	Rivière du 2ième bras	10/19/04	2000	n.d	471	364	364	5	20	428	367	23	98	117
AN04-54	Homard Riv.	10/19/04	2000	n.d	274	319	319	10	19	242	296	15	51	100
AN04-55	Janikeete Riv.	10/19/04	2000	n.d	376	341	341	5	17	302	338	20	77	87
AN04-56	Grande Rivière à Goyave (upstream)	10/19/04	2900	n.d	338	228	228	2	20	366	275	13	60	117
AN04-57	Blondeau Riv.	10/20/04	1200	8.03	509	680	680	15	51	914	821	33	201	267
AN04-58	Ravine Sèche Riv.	10/20/04	1200	7.62	398	595	595	79	104	573	875	43	158	167

TABLE 1
(continued)

	Name	Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
BASSE-TERRE, GUADELOUPE														
Oct. 2004	**River Name**													
AN04-59	Comar Riv.	10/20/04	1200	7.51	526	587	587	42	68	1055	1008	46	214	292
AN04-60	La Ravine Riv.	10/20/04	1200	7.8	655	623	623	36	48	1103	788	28	222	344
AN04-61	Corrosol Riv.	10/21/04	3000	7.54	300	175	175	0	14	278	221	8	47	82
AN04-62	Bras David riv. at Maison Forêt	10/21/04	2750	7.5	319	220	220	0	24	269	242	10	51	82
AN04-63	Lézarde at Clède	10/21/04	3750	7.04	241	158	158	0	16	321	204	13	47	97
AN04-64	Quiock Riv.	10/21/04	3000	7.05	285	271	180	2	88	134	279	18	51	82
AN04-65	Corossol Riv.	10/21/04	3000	7.23	335	183	183	0	13	301	233	10	47	87
AN04-66	Baillif Riv.	10/22/04	1910	7.5	244	245	200	37	35	383	279	54	77	127
AN04-67	Gallion Riv. at mouth	10/22/04	2000	7.51	380	254	150	10	390	237	313	36	137	299
AN04-68	Soil Water in a landslide at Col des Mamelles	10/22/04		n.d	714	183	183	10	22	39	204	26	17	12
AN04-70	Bains Jaunes Spring	10/23/04		4.23	868	416		4	1063	14	490	38	256	667
AN04-71	Bain Jaunes Spring	10/23/04		7.04	631	987		0	1693	270	892	79	573	1055
AN04-72	Tributary of Vieux Habitant Riv.	10/24/04		6.9	422	181	150	2	114	267	242	13	64	137
AN04-73	Vieux Habitant Riv. at Barthole	10/24/04	4800	7.3	552	172	130	0	19	375	229	13	64	115
AN04-74	Ravine near AN04-73	10/24/04		7.4	618	367	250	8	27	698	500	18	150	207
AN04-75	Ravine ruse	10/24/04		7.15	781	248	150	5	30	388	325	23	73	122
AN04-76	Ravine at la Gibelière	10/24/04		7.58	686	446	200	31	94	690	567	41	201	247
AN04-77	Petit David (Trib. of Bras David Riv.)	10/25/04		n.d	344	324	200	0	88	10	296	13	64	80
AN04-78	Grande Rivière à Goyave (upstream)	10/25/04	3000	n.d	288	178	178	35	13	281	221	8	56	92
AN04-79	Capesterre downstream (village)	10/26/04	4900	7.49	486	254	254	76	25	461	275	18	90	170
AN04-80	Capesterre Riv. Upstream (National Park)	10/26/04	5200	n.d	463	183	183	35	20	392	242	15	77	145
AN04-81	Capesterre at mouth	10/26/04	4900	n.d	411	212	212	68	25	452	254	31	90	195
AN04-82	Bras David riv. at Maison Forêt, Tributary	10/27/04	3000	6.76	317	296	296	0	11	212	292	8	60	52
AN04-83	Bras David riv. at Maison Forêt, Tributary	10/27/04	3000	6.64	146	265	265	2	11	47	229	8	34	20
AN04-84	Quiock Riv.	10/27/04	3000	7.15	318	310	200	0	48	199	283	15	60	80
AN04-85	Bras David riv. at Duclos	10/27/04	3000	7.42	358	592		0	21	320	271	15	68	122
AN04-86	Rose Riv.	10/28/04	2800	7.62	179	147	147	11	14	459	146	58	43	193
AN04-87	Perou Riv. upstream (National Park)	10/28/04	4000	7.43	488	169	150	3	46	326	213	15	64	107

TABLE 1
(continued)

	Name	Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
BASSE-TERRE, GUADELOUPE														
Oct. 2004	**River Name**													
AN04-88	Moreau Riv.	10/28/04	4500	7.37	299	150	150	5	11	278	188	8	43	85
AN04-89	Bouteiller Riv.	10/28/04		7.72	461	231	231	5	9	454	317	13	81	147
AN04-90	Vieux Habitant Riv. at Barthole	10/28/04	4800	7.4	472	192	130	0	31	396	258	15	73	132
AN04-91	Grand Carbet Riv. Second Fall	10/28/04	5000	7.53	710	430	130	57	919	306	490	58	310	617
AN04-92	Baille-Argent Riv.	10/28/04	1100	7.37	509	649	500	15	451	303	771	43	239	322
MARTINIQUE														
Feb. 2003														
AN03-29	Couleuvre Riv.	2/9/03	1500	n.d	644	506	506	23	51	1057	693	30	184	382
AN03-30	Céron Riv.	2/9/03	1500	n.d	614	336	336	8	37	906	492	29	142	327
AN03-31	Précheur Riv.	2/9/03	1500	n.d	915	251	251	2	70	955	476	56	186	291
AN03-32	Claire Riv.	2/9/03	1500	n.d	1415	377		25	278	1180	1021	99	208	313
AN03-33	Roxane Riv.	2/9/03	2000	n.d	1246	375	300	118	50	1115	643	62	200	387
AN03-34	Grande Rivière	2/10/03		n.d	838	289	289	7	31	739	425	69	127	240
AN03-35	Capot Riv.	2/10/03	2500	n.d	835	322	200	94	74	791	451	74	178	317
AN03-36	Macouba Riv.	2/10/03	1500	n.d	1121	451	300	168	74	841	613	60	227	347
AN03-37	Carbet Riv.	2/11/03	2000	n.d	516	235		1	98	705	232	11	57	81
AN03-38	Sulphide rich spring	2/11/03		n.d	213	232		5	282		259	3	57	81
AN03-39	Alma Riv.	2/11/03	4300	n.d	449	229	229	0	17	847				
AN03-40	Duclos Riv.	2/11/03		n.d	521	260	260	0	25	644	360	49	129	212
AN03-42	Lorrain Riv.	2/12/03	2800	n.d	366	233	233	2	175	274	318	32	120	266
AN03-43	Cold Spring	2/12/03		n.d	533	216	216	3	15	788	322	15	136	252
AN03-44	Iron rich Spring	2/12/03		n.d	2041	434		0	29		4872	314	4043	5583
AN03-45	Grand Carbet Riv.	2/13/03	2000	n.d	482	251	251	2	92	699	381	22	144	296
AN03-46	La Lézarde Riv.	2/13/03	2600	n.d	354	233	233	5	25	333	277	16	80	127
AN03-47	Spring water	2/13/03		n.d	242	219	219	1	11	96	231	15	38	32
AN03-48	Lorrain spring	2/13/03		n.d	307	265	265	0	16	257	272	14	56	102
AN03-49	Coulée Blanche Riv.	2/14/03	1500	n.d	1643	752	400	0	647	4145	3036	435	611	1039

Table 1

(continued)

Name		Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
MARTINIQUE														
Oct. 2004	**River Name**													
Ma 04-1	Fond Lahaies riv.	10/22/04		7.2	514	431	431	22	38	479	552	36	113	135
Ma 04-5	Précheur Riv.	10/22/04	1500	7.9	861	253	253	13	71	702	416	45	168	254
Ma 04-6	Couleuvre Riv	10/22/04	1500	n.d	714	554	554	22	48	1013	663	35	188	377
Ma 04-7	Céron Riv.	10/22/04	1500	n.d	649	355	355	15	34	763	451	29	136	303
Ma 04-8	Soil Water solution	10/22/04		n.d	840	259	259	0	36	445	393	36	61	235
Ma 04-8'	Cold Spring	10/22/04		7.3	870	274	274	0	36	473	397	38	61	235
Ma 04-9	Lézarde Riv.	10/23/04	2600											
Ma 04-10	Lezarde upstream	10/23/04	2600	7.02	297	252	252	19	26	268	262	19	77	95
Ma 04-11	Blanche Riv.	10/23/04	4300	6.37	386	259	259	17	26	455	301	25	101	152
Ma 04-12	Didier Spring	10/23/04		6.9	2076	680	680	3	64	12586	5359	318	4200	4332
Ma 04-13	Soil Solution	10/23/04		n.d	745	497	497	23	31	741	650	50	146	254
Ma 04-14	Capot Riv.	10/24/04	2500	7.73	709	432	432	83	32	940	554	42	216	319
Ma 04-15	Lorrain Riv.	10/24/04	2800	n.d	538	186	186	2	259	320	294	25	107	250
Ma 04-16	Lorrain Riv. (flood)	10/24/04	2800	n.d	398	370	370	70	34	454	391	30	136	178
Ma 04-17	Lézarde Riv. (flood)	10/24/04	2600	n.d	432	320	320	40	30	500	361	29	116	176
DOMINICA														
Oct. 2004														
Dom 04-1	Melville Hall Riv.	10/17/04		7.4	336	162	160	6	36	317	233	20	67	129
Dom 04-3	Pagua Riv.	10/17/04		7.12	257	177	165	1	115	235	211	11	64	144
Dom 04-4	Tributary of Pagua Riv.	10/17/04		7.13	258	225	165	1	186		212	10	74	176
Dom 04-5	Layou Riv.	10/17/04		6.91	385	168	165	26	38	323	236	21	67	129
Dom 04-6	Trafalgar Riv.	10/18/04		7.49	664	167	165	40	140	808	342	34	211	303
Dom 04-7	Roseau Riv.	10/18/04		7.2	717	477	165	17	134	962	591	52	199	343
Dom 04-8	Pichelin Riv.	10/18/04		7.69	1020	313	165	46	70	699	457	57	130	254
Dom 04-9	Belfast Riv.	10/18/04		6.74	643	247	247	22	22	533	334	39	86	175
Dom 04-10	Springfield Riv.	10/19/04		7.38	659	216	165	13	44	729	331	31	152	252
Dom 04-11	Rosalie Riv.	10/19/04		8.53	520	195	165	17	29	405	269	26	71	142

Table 1
(continued)

	Name	Sampling date	Runoff mm/a	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM
DOMINICA														
Oct. 2004	**River Name**													
Dom 04-12	Triburaty of the Rosalie Riv.	10/19/04		7.7	388	195	195	6	20	420	235	18	74	145
Dom 04-13	Brousse Castel Riv.	10/19/04		7.33	289	166	165	4	21	410	219	13	64	153
Dom 04-14	Calish Riv.	10/19/04		7.11	294	170	165	2	31	351	212	13	68	137
Dom 04-15	Madjini Riv.	10/19/04		7.08	462	312	312	12	21	594	378	15	101	228

Such a distribution is consistent with the presence of sulfate-enriched point sources. The least abundant anion measured in the river water of the Lesser Antilles is nitrate (NO_3^-), ranging from 10 to 20 μmol/l for median values. These low values validate our sampling strategy to avoid human contamination.

Dissolved sodium (Na^+) is the most concentrated cation with a median concentration of 400 μmol/l and no difference among the three islands. Concentrations of Na^+ are relatively well correlated to Cl^-, although the Na^+ is 100 to 200 μmol/l greater than the Cl^- concentration. This discrepancy is attributed to non-marine input of Na^+, essentially silicate weathering. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) concentrations are centered around 200 μmol/l and 100 μmol/l respectively and are well correlated in the three islands. This correlation defines a mean Ca/Mg of about 1.5 to 1.7, consistent with waters draining silicates. Potassium (K^+) is, as expected, less concentrated than Na^+ but well correlated to Na^+ (mean Na/K of 0.07) and Mg^{2+} (mean Mg/K of 6).

Data do show significant seasonal variations between the wet and dry seasons with concentrations generally diluted during the rainy season. For example, riverine concentrations in Bras David catchment (Guadeloupe) are 30 to 40 percent lower during the rainy seasons. When concentrations are plotted as a function of the water discharge of the sampling day (http://www.hydro.eaufrance.fr/) typical decreases of concentrations are observed, although the data set is too small to calculate regression lines and annual discharge averaged concentrations (figure not shown).

Our river chemistry data are consistent with recently published data for Guadeloupe (Lloret and others, 2010) and for Dominica Island (Goldsmith and others, 2010). These data are also consistent with data for river and hydrothermal waters in Montserrat (Jones and others, 2010), except that the Montserrat data fall into the upper range of concentrations reported here. The higher concentrations in Montserrat are anticipated given the very young age of the weathered material. Compared to other studies in volcanic areas, the river concentration data from the Lesser Antilles are very close or slightly higher than those found in the Kamchatka rivers (Dessert and others, 2009), although mean runoff value is about 4 times lower that in the Lesser Antilles. The concentrations reported in the Lesser Antilles are broadly consistent with solute concentrations measured in La Réunion island (Louvat and Allègre, 1997). Compared to the data from the Philippines (Schopka and others, 2010), rivers from the Lesser Antilles of comparable runoff show lower concentrations of Ca^{2+} and Mg^{2+} (by a factor of two) and alkalinity (by a factor of 4).

Only a few hydrothermal springs were sampled for this study. In agreement with previous studies (that is Brombach and others, 2000; Villemant and others, 2005), the hydrothermal springs have relatively high concentration levels (for example 1000 μmol/l $< Na^+ <$ 4000 μmol/l). Chemical types are either Ca-SO_4-type waters corresponding to interaction between oxidized sulfur and minerals, or Ca-Na HCO_3-type waters corresponding to shallow heated groundwaters. Sulfate concentration may reach 10,000 μmol/l. Springwater temperature and pH range from 27 °C to 57 °C and from 3.8 (Sofaia spring) to 6.7 respectively.

DISCUSSION

Runoff Estimates

Runoff is a critical parameter for the calculation of chemical weathering rates. Runoff water is the water available for chemical reaction and transport. Water discharge data have been recorded by two governmental agencies in Guadeloupe and Martinique Island (ORSTOM up to 1990 and then DIREN). Monthly average data can be downloaded at http://www.hydro.eaufrance.fr/. Data from table 1 have been extracted from this database for the rivers that have been monitored for water

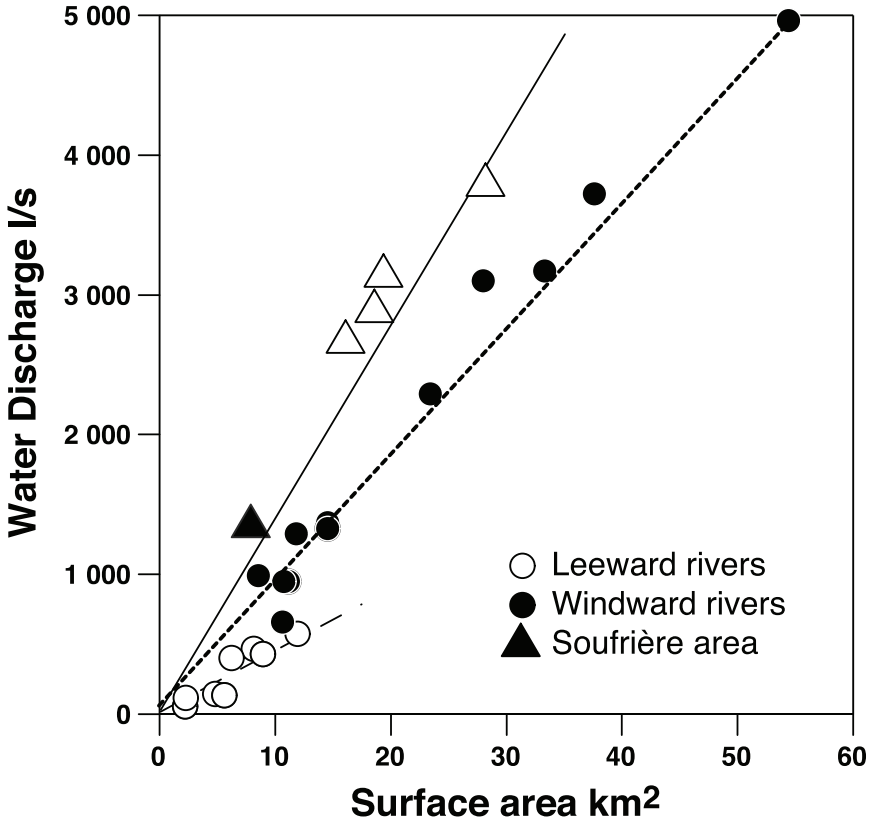

Fig. 2. Relation between river water discharge values and drainage basin area in Guadeloupe for the gauged rivers. The rivers from the leeward and windward show clearly different patterns as well as the rivers draining the Soufrière Massif. These empirical relationships have been used to estimate water discharge for un-gauged rivers.

discharge. This represents about 18 rivers in Guadeloupe and 6 rivers in Martinique. For the non-gauged rivers, we have extrapolated runoff values based on the closest monitored watersheds and based on the first order correlation that we observe, using the gauged basins, between runoff values and drainage basin area (fig. 2). Although this extrapolation introduces significant uncertainty we consider it small enough for the purpose of estimating chemical weathering rates. The largest rivers on both Martinique and Guadeloupe have a documented catalog water discharge data for the pre-1980 interval. Monitoring along these rivers has been significantly reduced since 1980. As a consequence, while some rivers have been monitored for more than 30 years, others have only been monitored for a couple of hydrological cycles. For the longest available time series, the variability of water discharge data is very important and data tend to show significant decrease of water discharges over the last 30 years (for example 30% for Vieux Habitant, Guadeloupe).

Runoff is calculated by dividing the water discharge by the surface area of the drainage basin and is expressed in mm/a in table 1. Runoff integrates evapotranspiration as well as infiltration processes. Like many tropical islands, runoff is very variable spatially. The rivers draining La Soufrière volcano on Guadeloupe and Piton du Carbet–Pelée volcanoes on Martinique are characterized by runoff values as high as

5000 mm/a for the Capesterre, Vieux Habitant, Grand Carbet and Blanche Rivers. Runoff decreases sharply along a south to north gradient on Guadeloupe and along the northwest side of Pelée volcano where infiltration becomes dominant. The lowest runoff values observed in this study are ~800 to 1000 mm/a for the Vieux Fort, Nogent, Céron and Coulée Blanche Rivers on Martinique. Runoff data broadly mimic precipitation patterns. The recent high relief volcanoes of La Soufrière (Guadeloupe) and Montagne Pelée-Piton des Carbets (Martinique) receive ≤10 m/a of precipitation. Additionally, runoff values vary from drainage basins draining the windward and leeward sides of islands. The trade winds coming from the East and the orography imply contrasted precipitation regimes. The windward coast receives about 2 times more water than the leeward coast. This is particularly pronounced on Guadeloupe because of the meridian orientation of the volcanic chain. Orographic effects are subdued on Martinique because recent, high relief, volcanoes do not fall along a north-south line but rather show a triangular repartition (Montagne Pelée, Piton du Carbet and Morne Jacob) at the north of the Island where rainfall is the highest. Another difference between the northern portions of Martinique and Guadeloupe is that the highest runoff values do not coincide with the regions with the greatest precipitation rates. This is probably due to infiltration of rainwater into the volcanic pile. The abundance of pyroclastic formations in the Pelée volcano favors infiltration and recharge of groundwaters that discharge directly into the sea (Rad and others, 2007). As highlighted by Goldsmith and others (2010), there is no water runoff data available for Dominica but given the geomorphic similarities between Guadeloupe and Dominica islands (relief and the north-south orientation of the volcanic range), runoff values are likely to be in the same range as those measured at the southern end of Guadeloupe and the northern portions of Martinique.

Rainwater Contribution

Rivers draining small oceanic islands are characterized by high atmospheric contributions due to their small surface area and the influence of seasalt aerosols. Seawater aerosols decrease with increased elevation and distance from the ocean (Gislason and others, 1996 and references therein) and Na^+, Mg^{2+}, and K^+ versus Cl^- ratios in rainwater are essentially the same as in the ocean. It is classically assumed that chloride is the conservative element that is best adapted to correct for atmospheric inputs. However, volcanic islands are affected by hydrothermal processes that may have a considerable impact on the water chemistry (Louvat and others, 1997). Chloride and SO_4^{2-}, which are associated with volcanic hydrochloric and sulfuric acid respectively, are particularly sensitive to hydrothermal inputs. While hydrothermal inputs are part of the weathering budgets, atmospheric inputs have to be subtracted from riverine dissolved load to estimate denudation rate. To distinguish between atmospheric and hydrothermal inputs, we used both Cl^- and SO_4^{2-} concentrations (fig. 3). For a number of rivers, we observe a good correlation between Cl^- and SO_4^{2-} concentration with a slope not centered on the marine Cl^-/SO_4^{2-} value (20), but slightly lower. This range of Cl^-/SO_4^{2-} values is consistent with coastal and oceanic rainwater analyses from 20 islands in the Pacific and Atlantic oceans (Kroopnick, 1977), from Guyana (Chetelat and others, 2005) and from Guadeloupe (Dessert, personal communication) that indicate a Cl^-/SO_4^{2-} typically ranging between 10 and 23, with a median value significantly lower than seawater Cl^-/SO_4^{2-} ratio, indicative of SO_4^{2-} enrichment in rainwater relative to seawater. Assuming that SO_4^{2-} and Cl^- behave conservatively, we used figure 3 to separate rivers that have SO_4^{2-} and Cl^- in rainwater proportion from those that are clearly enriched in SO_4^{2-}. The rivers with significant contribution of SO_4^{2-} and Cl^- from hydrothermal activity are designated as hydrothermal-impacted rivers or H-impacted rivers. This graph implicitly assumes that hydrothermal activity provides much more SO_4^{2-} ion than Cl^- ion, a hypothesis that is justified

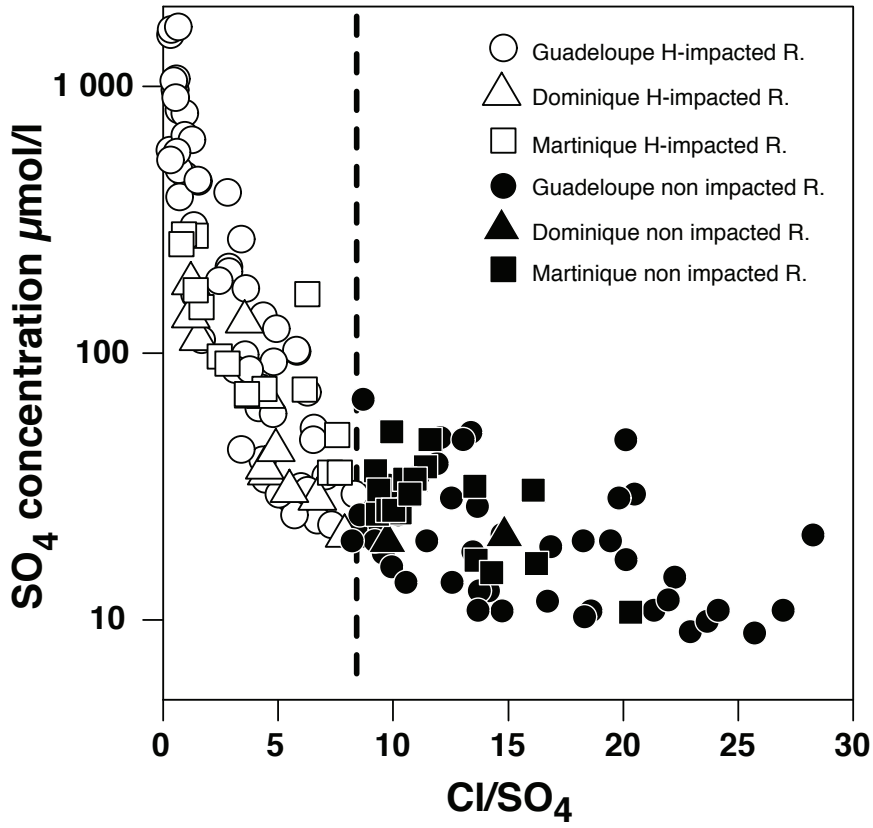

Fig. 3. Cl^-/SO_4^{2-} as a function of SO_4^{2-} in all the stream and river samples from this study. This diagram is used to separate the rivers significantly impacted by hydrothermal inputs (H-impacted rivers) from the others (non H-impacted), mainly controlled by atmospheric inputs for Cl^- and SO_4^{2-}. The cutting values of the Cl^-/SO_4^{2-} ratio and SO_4^{2-} concentration are 8–10 and 25–50 µmol/l respectively. Cl^-/SO_4^{2-} lower than 8 are classified as H-impacted rivers. These values are to be considered as approximate values.

by the relative abundance of sulfuric acid compared to hydrochloric acid in subduction volcanic arc settings.

The non H-impacted rivers show absolute chloride concentrations decreasing linearly from 600 to 150 when runoff values increase from 1000 mm/a to 3000 mm/a (fig. 4). The Cl^- concentration stabilizes at about 150 to 200 µmol/l when the runoff values exceed 3000 mm/a. This pattern suggests that the concentrating effect of evapo-transporation processes is only effective for runoff values <3000 mm/a. The 4 fold increase in Cl^- concentration observed from the high relief zones to the relatively dry regions of northern Guadeloupe is consistent with the observed range of runoff variations, although a simple dilution of seasalt aerosols would lead to Cl^- concentration in the high runoff zones of Soufrière and Pelée volcanoes close to 100 µmol/l, lower than the observed value. At high runoff values, a small but significant atmospheric Cl^- enrichment seems to characterize river waters. The origin of this enrichment remains unclear but it will not impact the calculation of weathering rates in this study given the high cation concentration found in the rivers draining the active volcanic area.

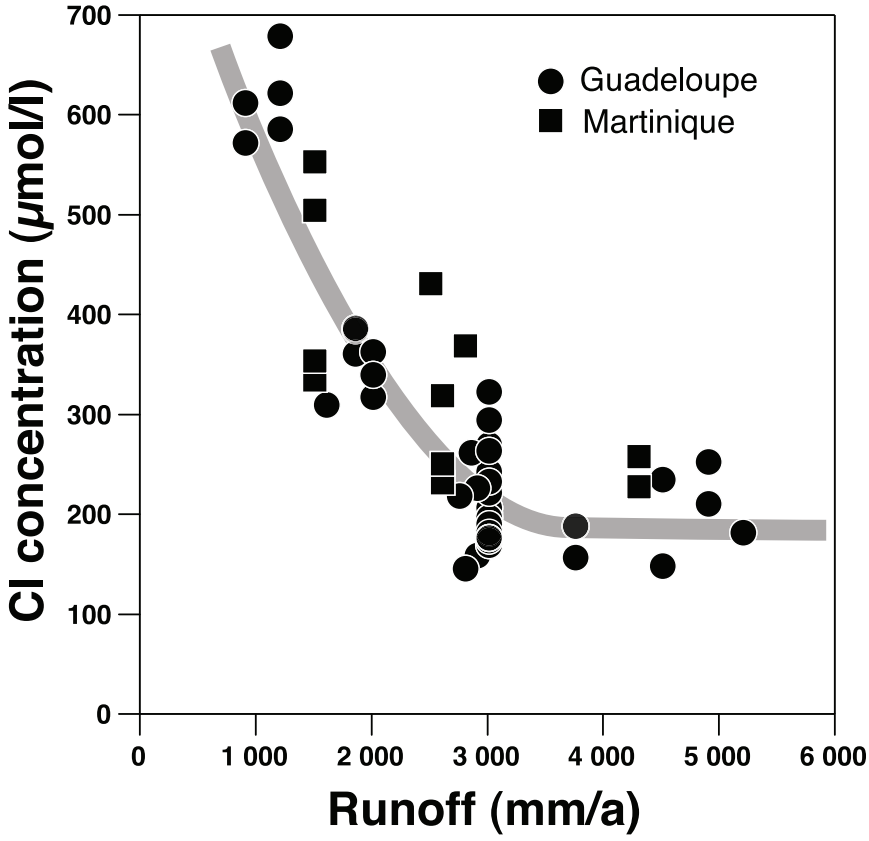

Fig. 4. Diagram showing the atmospheric chloride concentration in the non H-impacted rivers as a function of runoff. At low runoff, Cl^- is 4-5 times concentrated in rivers compared to high runoff sites, mainly due to evapo-transporation (assuming Cl^- behaves conservatively). At runoff values higher that 3000 mm/a, evapo-transpiration does not seem to influence stream Cl^- concentration, which remains constant.

For the non H-impacted rivers the Cl^- concentration is called the critical (or cyclic), Cl^- (Cl_{crit}) and is used to correct from atmospheric inputs using

$$[X]^* = [X] - \left(\frac{X}{Cl}\right)_{rain} Cl_{crit}. \quad (1)$$

Here [X] and [X]* denote the riverine concentrations of any element X measured in river water and corrected from atmospheric inputs respectively, and $(X/Cl)_{rain}$ is the molar ratio in the rain. The marine ratios were used in order to correct cations from atmospheric inputs. The proximity of seawater and the few available rainwater chemical datasets suggest that the non-marine contribution of atmospheric input to rivers is small. The rivers in this study are corrected from a marine atmospheric input but their dissolved load may include elements not derived from the bedrock but rather from the dissolution of aeolian dust transported by the atmosphere. The inherent uncertainties that make the weathering rates calculations of this paper first order estimates (runoff estimate, critical chloride determination, average river chemistry) imply that a non-marine atmospheric contribution is probably not detectable. A better correction would

require the knowledge of the long-term atmospheric inputs and that record does not exist.

For the H-impacted rivers, the Cl_{crit} value is estimated based on the comparison with neighboring non-impacted rivers and the general relationship between Cl_{crit} and runoff values observed for non-impacted rivers (fig. 4). On Dominica, Cl_{crit} is difficult to estimate due to the absence of runoff values. Consequently, for the Dominica rivers Cl_{crit} concentration is estimated using the lowest riverine Cl^- concentrations.

H-Impacted rivers are mainly found in the recent volcanic zones such as the Soufrière and Pelée Massifs where numerous thermal springs have been described and partly monitored for volcanic activity. The largest hydrothermal input is found in the rivers draining the Soufrière Volcano, with Cl^- and SO_4^- loads >1000 μmol/l (Cascade Vachelet, Noire River). On Basse-Terre, Guadeloupe, H-impacted rivers far from the modern volcanic centers also exist (for example Grande Plaine river) especially in the vicinity of Bouillante. This district is an exploited geothermal zone and numerous hot springs rich in sulfate ions are known (Brombach and others, 2000). Throughout the Island of Basse-Terre, field observations have reported the existence of hydrothermal deposits such as iron sulfides, silica concretions and carbonates. Well-developed pyrite veins and hydrothermal weathering features were observed by the authors after a large landslide at the Col des Mamelles, Western Basse–Terre, in 2005. The dissolution of hydrothermal minerals may thus also explain the excess of sulfate observed in the H-impacted rivers. The proportion of H-impacted rivers is especially high on Dominica as is consistent with recent volcanic activity on the island.

Note that a few rivers show evidence of anthropogenic impact. This is particularly evident when the Grande Rivière à Goyave on Guadeloupe is compared between the outlet of the National Park and 20 km away in the cultivated area because Cl^- and NO_3^- concentrations increase significantly. Ravine Gachet and Grand Carbet (AN03-28 and AN03-08) as well as Vieux Fort River (AN04-42 and AN04-52) show Cl^- enrichments with no SO_4^{2-} enrichment and are likely impacted by anthropogenic activities. The relatively low runoff value makes these rivers particularly sensitive to pollution.

As shown by the above calculation, constraining the atmospheric contribution to rivers in active volcanic setting, where both Cl^- and SO_4^{2-} have several possible origins remains difficult and our calculations are probably first-order estimates. A challenging issue for the low-T weathering studies is the need of developing a more robust tracer of hydrothermal and atmospheric inputs in volcanic (or metamorphic) contexts.

River Composition Versus Rock Composition

Once the atmospheric contribution to the river has been corrected, the river chemical load is attributed to the weathering of rock minerals. Petrology and chemistry of the Lesser Antilles bedrock have been extensively described in the literature (Blanc, ms, 1983; Samper and others, 2007, 2009; Sak and others, 2010). All rocks from the Lesser Antilles fall in the category of low- to medium-K andesitic basalts and andesites on the K_2O vs. SiO_2 diagram. Dacites and rhyolites are rare and are confined to the volcanic domes. Typical cation base concentrations vary as a function of partial crystallization of parent magmas. The database of Samper and others (2007, 2009) reports chemical analyses for lava flows of variable age from Basse-Terre island, Guadeloupe. These data show that $Na_2O + K_2O$ weight percent concentrations are positively correlated with SiO_2 concentration, an index of chemical differentiation, while CaO and MgO are inversely correlated with SiO_2. On Guadeloupe, $Na_2O + K_2O$ ranges from 2.5 to 5.5 percent (corresponding to variations in SiO_2 between 47% and 62%) with a mean value of 4.1 percent. Calc-alkaline elements vary from 5 to 12 percent for CaO and from 1.5 to 6 percent for MgO. Mean values for bedrock CaO and MgO are 7.9 percent and 3.2 percent respectively (for a mean SiO_2 value of 56%).

These numbers, characterizing the lava flows of Basse-Terre, are in very good agreement with the unweathered core of the volcanic clast from Bras David catchment in Guadeloupe studied by Sak and others (2010). From the database of Samper and others (2007, 2009), the mean bedrock molar cation ratios and associated standard deviations are Ca/Na = 1.4±0.5 (36), Mg/Na = 0.83±0.42 (50), K/Na = 0.18±0.04 (22) and Ca/Mg = 1.9±0.7 (37). In parentheses is variability defined as the percent ratio of standard deviation over mean value. Once corrected from atmospheric inputs, the same ratios and their variability can be calculated in the rivers. Elemental ratios are less sensitive to precipitation or evaporation processes because both numerator and denominator are affected by the same concentration or dilution factor. The corresponding water-discharge weighted ratios in water (calculated on the largest rivers) are Ca/Na = 1.3±0.5 (38), Mg/Na = 0.6±0.2 (33), K/Na = 0.16±0.09 (56) and Ca/Mg = 2.2±0.5 (23). It is worth highlighting that calculated ratios do not show significant difference between H-impacted and non H-impacted rivers. These calculations show that, within standard deviation, there is no clear difference between the river chemistry and the rock chemistry in the Lesser Antilles, with the possible exception of Mg, which is slightly less abundant in rivers than in the bedrock. In addition to mean values, the variability in river composition is consistent with the variability observed in the bedrock. These similarities suggest that the variability in river chemical composition is essentially inherited from the chemical variability of the bedrocks, which is, itself, inherited from magmatic processes. This result suggests the formation of secondary minerals capable of incorporating dissolved cations is quantitatively negligible in the Lesser Antilles. It also suggests that vegetation uptake does not affect the chemistry of river waters for major cations.

However, a slight but interesting increase of Ca/Na ratio (from 0.7 to 1.2) with runoff (lower runoff are found for the leeward rivers) is observed for the non H-impacted rivers from Guadeloupe. This trend remains to be more fully documented but would indicate that the formation of clay minerals (uptaking Ca preferentially) is more important on the leeward side of the Island.

The case of Si is somewhat different. The cation/silica ratios are clearly different from those of the bedrock. For example, Na/Si and Ca/Si water-discharge weighted ratios in the dissolved load (calculated on the largest rivers) are 0.35±0.14 and 0.44±0.19 respectively, while the same ratios calculated from the bedrock database are 0.09±0.02 and 0.12±0.03 respectively. The preferential mobility of Ca and Na compared to Si clearly shows the uptake of Si in the weathering zone, most probably in secondary clay minerals.

We can define the ratio Φ (g/g) of total cation concentrations over Si abundances as

$$\Phi = ([Ca]^* + [Mg]^* + [K]^* + [Na]^*)/[SiO_2]. \quad (2)$$

For source rocks, the parameter, $\Phi_{bedrock}$ equals 0.19±0.04 (20%). For river waters, Φ_{River}, is calculated as $TDS_{cat}/[SiO_2]$ in g/g where $[SiO_2]$ is the concentration of dissolved silica and TDS_{cat} is the sum of the atmosphere-corrected cation concentration. Φ_{River} equals 0.56±0.24, indicating the preferential mobilization of cations, or the retention of Si compared to cations. Therefore, in mass, secondary products reincorporate 3 times more Si than cations. In contrast to cation elemental ratios, Φ_{River} is lower in the non-impacted rivers (0.45±0.05).

From a petrological point of view, the rocks (from lavas to pumices) of the Lesser Antilles have a porphyritic texture. Major phenocrysts are plagioclase ($>An_{50}$) and clinopyroxene (augite). Orthopyroxene, amphibole, biotite, oxides are less frequent and olivine and quartz are only found occasionally. The pumices are particularly quartz-rich. The groundmass is mostly composed of plagioclase, pyroxene and glass

(Germa, ms, 2008). Sak and others (2010) have studied a volcanic clast from Bras David watershed and proposed the following modal abundances for the unweathered core: 53% groundmass + glass, 26% plagioclase (An_{70}), 9% pyroxene (augite), 9% porosity and <2% ilmenite, rutile and apatite. According to Sak and others (2010), the weathering reactions of plagioclase and pyroxene phases on that particular clast can be written as

$$Na_{0.3}Ca_{0.7}Al_{1.7}Si_{2.3}O_8 + 6.3H_2O + 1.7H^+ \rightarrow 0.3Na^+ + 0.7Ca^{2+} + 2.3H_4SiO_4 + 1.7Al(OH)_3$$

$$Ca_{0.8}Mg_{0.8}Fe(II)_{0.2}Fe(III)_{0.1}Al_{0.3}Si_{1.8}O_6 + 0.05O_2 + 1.85H_2O + 3.2H^+ \rightarrow 0.3FeO(OH) + 0.15Al_2Si_2O_5(OH)_4 + 1.5H_4SiO_4 + 0.8Ca^{2+} + 0.8Mg^{2+}.$$

Pedogenic descriptions of a soil profile in Bras David watershed in Guadeloupe confirm that the prominent minerals are halloysite, kaolinite, plus Fe and Al oxides that do not contain soluble cations (Buss and others, 2010). Ndayiragije and Delvaux (2004) described the evolution of soil mineralogy and geochemistry in a topo-sequence (with an annual rainfall varying between 2500 mm and 4000 mm) and reported a strong decrease in total alkaline and alkaline-earth elements with increasing chemical weathering (glass to allophane to halloysite). According to these authors, the only cation that seems to be slightly retained in the soils is K^+, but our comparison between bedrock and river water does not suggest K^+ retention.

These petrologic and pedogenic descriptions are consistent with the similarities observed between water chemistry and rock composition and the shift in the Φ ratio. The significant difference in the Φ_{River} ratio between the H-impacted and non H-impacted rivers and the trend of increasing Φ_{River} with hydrothermal contribution (see fig. 10) probably reflect Si precipitation in the hydrothermal conduits or the enhanced precipitation of Si in the form of hydrothermal clays. At the scale of the Lesser Antilles, the parameter Φ_{River} is thus a good proxy for hydrothermal contribution. Finally, although the above reactions are only examples of plausible reactions occurring at the base of the soil profiles in the Lesser Antilles they demonstrate that chemical weathering reactions consume CO_2 and O_2 from the atmosphere. The origin of the protons can be the dissolution of atmospheric, biogenic or volcanogenic CO_2 or the dissociation of other acids produced in the volcanic system like sulfuric acid or hydrochloric acid and/or oxidation of sulfides. This will be discussed below.

Chemical Weathering and Weathering Advance Rates in the Lesser Antilles

Quantification of rock chemical weathering rate based on river chemistry can be done using different parameters. The cationic dissolved load (TDS_{cat} in mg/l) and total dissolved load (TDS in mg/l) are defined respectively as:

$$TDS_{cat} = [Na]^* + [K]^* + [Ca]^* + [Mg]^* \quad (3)$$

and

$$TDS = TDS_{cat} + [SiO_2]. \quad (4)$$

These two numbers do not include sulfate ions derived from the oxidation of sulfide minerals, or from thermal springs or contributions of hydrochloric acid. The dissolved load TDS_{hyd} that include these two hydrothermal components is defined as

$$TDS_{hyd} = TDS + [Cl]^* + [S]^* \quad (5)$$

where [Cl]* and [S]* are the concentrations of Cl and S (in mg/l) of volcanic origin. Note that TDS_{hyd} does not take into account the contribution of volcanically derived

carbonic acid, which is significant in the most H-impacted rivers (Rivé and others, 2012[1]). The hydrothermal impact on the rivers from Guadeloupe range from 0 (rivers from the North) to 35 percent for the rivers draining the active volcano. The mean value for Guadeloupe of the hydrothermal contribution is 10 percent.

The total dissolved solutes can be converted into denudation fluxes, or rates in $t/km^2/a$, when multiplied by runoff,

$$CWR = TDS_{cat}*Runoff \quad (6)$$

$$TWR = TDS*Runoff \quad (7)$$

$$TWR_{hyd} = TDS_{hyd}*Runoff. \quad (8)$$

We are unable to do these calculations for Dominica due to the absence of runoff data. These rates have been first calculated for the whole database, using the estimated runoff for streams and non-gauged rivers. Histograms of the distribution of CWR and TWR are shown on figure 5. These histograms are asymmetric with very high values found in the H-impacted rivers, particularly on the active volcanoes. Median values of CWR and TWR are 30 $t/km^2/a$ and 95 $t/km^2/a$, respectively.

In order to get a representative view of chemical denudation rates at the scale of the Lesser Antilles Islands we then focus on the largest rivers (table 2). Most of the large rivers have been sampled three times on Guadeloupe and two times on Martinique. The mean TDS concentrations were calculated by arithmetically averaging the dry and wet season values. In the instances where two analyses were available for the dry season (February 2003 and 2004 on Guadeloupe), they were first averaged. This calculation likely overestimates the concentrations because it gives an equal weight to the dry and wet seasons and because the flood events are not included. As already stated, the chemical denudation rates presented here are to be considered as first order estimates given the numerous sources of uncertainties.

Based on large rivers, cationic and total weathering rates in the Lesser Antilles vary from about 10 $t/km^2/a$ and 40 $t/km^2/a$ in the northern rivers of Guadeloupe to 230 $t/km^2/a$ to 430 $t/km^2/a$ for the rivers draining La Soufrière volcano. Chemical denudation rates in the Lesser Antilles therefore vary by a factor of 10. The arithmetic mean of CWR and TWR for Guadeloupe are 50 $t/km^2/a$ and 140 $t/km^2/a$ respectively. The range of variation is lower in Martinique (80 $t/km^2/a$ to 350 $t/km^2/a$ for TWR) than in Guadeloupe but the mean CWR and TWR values are similar. The median CWR and TWR values for the large rivers on Martinique and Guadeloupe are 32 $t/km^2/a$ and 95 $t/km^2/a$, respectively. Although computed differently, these values are in agreement with recently calculated chemical weathering rates (TWR) of 6 to 106 $t/km^2/a$ for Dominica (Goldsmith and others, 2010).

The relationship between CWR and TWR is shown in figure 6A. The H-impacted rivers clearly exhibit the highest chemical denudation rates. We observe that all non-impacted rivers lie on a straight line expressing the constancy of the TDS_{cat}/SiO_2 (Φ_{River}) ratio. The H-impacted rivers define another trend marked by a lower Φ_{River} ratio than that of non-impacted rivers. Figure 6 also shows that TWR_{hyd} is only significantly different (that is, higher) than TWR for strongly H-impacted rivers such as the Gallion and Grand Carbet rivers, draining the active volcano of La Soufrière. In these rivers, TWR_{hyd} can reach 600 $t/km^2/a$ and locally 800 $t/km^2/a$, 2 orders of magnitude greater than the lowest chemical denudation rates found in northern

[1] Rivé, K., Agrinier, P., Gaillardet, J., and Rad, S., 2012, Magmatic CO_2 as a weathering agent in the rivers of the Lesser Antilles: Earth and Planetary Science Letters, submitted.

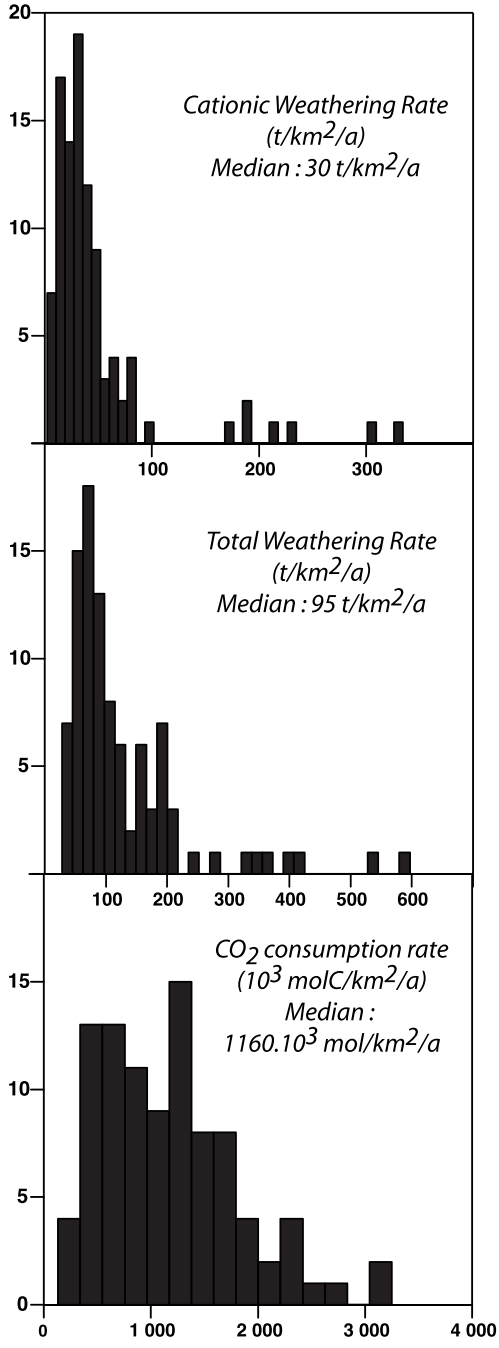

Fig. 5. Histograms of cationic weathering rates (CWR), total chemical denudation rates (TWR) and CO_2 consumption rates in the Lesser Antilles calculated using the whole database. The asymmetric shape of the histograms is due to the point contribution of hydrothermal inputs. The median values of CWR, TWR and CO_2 consumption rates are 30 t/km^2/a, 95 t/km^2/a and 1160.10^3 molC/km^2/a respectively.

TABLE 2

	Longitude	Latitude	Runoff mm/a	Age Ma	Relief m	Surface area km^2	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM	TDS_{cat} mg/L	CWR t/km^2/a	TDS mg/L	TWR t/km^2/a	Φ g/g	TDS_{hydr} mg/L	TWR_{hyd} t/km^2/a	CO_2 cons. 10^3 mol/km^2/a
Basse-Terre. Guadeloupe																									
Gallion Riv.	61°41'35.2O	16°00'24.0N	4000	0.02			n.d	841	511	130	5.7	830	278	590	73	314	690	47.9	192	98	393	0.95	138	552	1112
Riv. des Pères	61°44'21.3O	16°00'38.4N	3100	0.02	1410	25.2	n.d	751	302	150	43	493		475	38	195	452	31.2	97	76	236	0.69	97	301	
Grande Anse Riv.	61°39'34.3O	15°57'47.3N	1700				7.65	557	313	300	72	75	688	436	33	148	269	18.3	31	52	88	0.55	54	92	1170
Grand Carbet (second fall)	61°38'41.5O	16°02'38.8N	6000	0.03	1220	9.6	7.46	621	465	130	28	804	256	500	58	302	588	40.9	224	78	427	1.11	116	631	1386
Baillif Riv.	61°44'46.9O	16°01'21.7N	1910	0.63	1065	6.88	7.5	244	245	200	37	35	383	279	54	77	127	10.7	20	25	48	0.73	28	53	732
Vieux Habitant Riv.	61°43'39.7O	16°04'55.8N	4800	0.55	1060	19.32	7.35	489	200	130	5.5	96	368	271	14	73	151	11.4	55	41	195	0.39	46	221	1768
Beaugendre Riv.	61°45'27.1O	16°05'13.8N	1575	0.8	980	11.94	7.78	543	276	220	8.8	65	733	441	25	95	265	18.6	29	51	80.5	0.57	54	86	1156
Losteau Riv.	61°46'04.1O	16°09'39.8N	1860	1.46	1004	8.28	7.85	500	346	250	6.3	93	758	538	34	141	252	21	39	51	95	0.73	57	106	1410
Grande Plaine Riv.	61°45'39.2O	16°12'33.6N	2000	1.6	428		4.86	626	488	250	7.1	1032	7	613	39	292	593	39.9	80	78	155	1.06	119	237	14
Petite Plaine Riv.	61°47'01.5O	16°13'18.7N	1600	1.7	590		n.d	519	447	350	4.2	72	1048	559	29	211	333	23.8	38	55	88	0.76	61	96	1677
Fenche Fougères Riv.	61°44'53.3O	16°13'45.0N	1500	1.7	622		n.d	604	415	350		470	402	529	27	246	431	27.7	42	64	96	0.76	81	121	603
Baille-Argent Riv.	61°48'01.0O	16°15'37.4N	1100	1.6	720		7.55	538	632	500	10.5	504	303	743	47	247	343	26.5	29	59	65	0.82	79	87	333
Deshaies Riv.	61°47'37.7O	16°18'13.4N	1000	1.6	465	2.4	7.59	551	595	500	8.1	121	328	665	47	125	119	13.1	13	46	46	0.39	53	53	329
Caillou Riv.	61°46'58.0O	16°14'03.9N	1200	1.65	706		7.76	594	600	500	15	169	599	721	54	193	232	20.6	25	56	68	0.57	64	77	719
Ferry Riv.	61°48'07.7O	16°16'15.2N	1040	1.72	683	4.73	7.34	614	596	500	3.3	191	523	721	56	176	226	20.1	21	57	59	0.54	66	68	544
Vieux Fort Riv.	61°45'33.7O	16°19'39.6N	900	2.8	540		6.99	574	593	593	7.9	29	436	633	44	125	99	9.2	8.3	44	39	0.27	46	42	393
Nogent Riv.	61°44'48.8O	16°20'04.8N	850	2.6	560	5.17	n.d	615	584	584	1.9	48	426	650	32	134	126	10.6	9	48	40	0.29	48	41	362
Capesterre downstream	61°35'43.8O	16°04'02.5N	4933	0.42	1251	19.33	7.49	426	205	200	46	25	401	262	16	78	153	9.8	48	35	174	0.39	36	178	1977
Capesterre upstream (National Park)	61°33'58.5O	16°03'25.4N	5200	0.42	1132	16.56	8.05	436	186	156	38	26	409	236	15	60	124	8.6	45	35	181	0.33	36	189	2129
Capesterre at mouth			4900	0.42			n.d	411	212	212	68	25	452	254	31	90	195	11.8	58	37	179	0.48	37	181	2215
Perou Riv. (National Park)	61°36'43.9O	16°03'29.8N	4000		1169	9.33	7.43	434	157	140	6.7	45	318	217	15.5	57	102	7.7	31	34	135	0.3	36	142	1272
Moreau Riv.	61°36'09.1O	16°07'40.8N	4500	0.66	1079	7.55	7.37	299	150	150	4.8	11	278	188	7.7	43	85	5.4	24.5	23	105	0.3	24	106	1251
Rose Riv.	61°35'04.0O	16°08'52.9N	2825	0.7			7.53	292	205	205	8	13	459	251	43	58	159	10.2	29	28	79	0.7	28	79	1298
Lézarde Riv. at Clède	61°36'41.8O	16°12'08.8N	3750	0.8	749	8.37	7.04	310	174	174		13	375	254	18	57	112	8.2	31	27	101	0.44	27	101	1408
Bras David Riv. at Maison Forêt	61°41'34.7O	16°10'32.8N	3000	0.9	972	11	7.3	397	238	238		24	370	298	16	68	109	7.8	23	32	92	0.32	32	93	1078
Grande Riv. à Goyave upstream	61°40'12.1O	16°10'14.7N	2950	0.9			7.73	324	189	189	9.2	16	331	247	10	56	101	6.9	20	26	78	0.36	27	78	978
Riv. à Sable	61°40'17.2O	16°13'50.6N	1600				n.d	371	311	311	0	21	383	403	21	84	108	9.0	14.5	31	50	0.4	31	50	613
Moustique Riv.at Sainte Rose	61°42'03.8O	16°18'10.4N	1850	1.5	587	6.26	n.d	490	346	331	5.5	39	319	387	27	100	109	8.8	16	38	71	0.3	39.5	73	590

TABLE 2
(continued)

	Longitude	Latitude	Runoff mm/a	Age Ma	Relief m	Surface area km^2	pH	SiO_2 µM	Cl µM	Cl_{crit} µM	NO_3 µM	SO_4 µM	HCO_3 µM	Na µM	K µM	Mg µM	Ca µM	TDS_{cat} mg/L	CWR $t/km^2/a$	TDS mg/L	TWR $t/km^2/a$	Φ g/g	TDS_{hydr} mg/L	TWR_{hyd} $t/km^2/a$	CO_2 cons. 10^3 $mol/km^2/a$
Martinique																									
Claire Riv.	61°11'37.8O	14°46'34.0N	1500	0.05			n.d	1415	377		25.2	278	1180	1021	99	208	313									1770
Macouba Riv.	61°08'54.6O	14°52'19.8N	1500	0.02			n.d	1121	451	300	168	74	841	613	60	227	347	28.4	43	96	144	0.42	103	154	1262
Carbet Riv.	61°07'43.8O	14°43'54.9N	2000	2			n.d	516	235		1.1	98	705	232	11	57	81									1410
Alma Riv.	61°05'55.3O	14°42'53.9N	4300	1.5			n.d	449	229	229		17	847													3642
Duclos Riv.	61°06'01.1O	14°40'40.5N					n.d	521	260	260	0.2	25	644	360	49	129	212	15.5		47		0.5	47			
Grand Carbet Riv.	61°07'43.8O	14°43'54.9N	2000	2			n.d	482	251	251	1.6	92	699	381	22	144	296	18.7	37	48	95	0.65	50	100	1398
Précheur Riv.	61°13'30.7O	14°48'11.2N	1500	0.04			7.9	888	252	252	7.5	71	829	446	50	177	273	21.2	32	74.5	112	0.4	76	115	1243
Couleuvre Riv.	61°13'06.9O	14°50'27.5N	1500	0.64			n.d	679	530	530	22	50	1035	678	33	186	280	23.7	35.5	64	97	0.58	65	98	1553
Céron Riv.	61°13'31.4O	14°49'53.1N	1500	0.64			n.d	631	345	346	11	35	835	472	29	139	315	19.5	29	57	86	0.52	58	87	1252
Blanche Riv.	61°04'06.7O	14°41'58.6N	4300				6.37	386	259	259	17	26	455	301	25	101	152	10.2	44	33	143	0.44	34	146	1957
Coulée Blanche Riv.	61°11'00.8O	14°46'51.9N	1500				n.d	1643	752	400	0	647	4145	3036	435	611	1039	133	199	232	347	1.35	264	396	6218
Fond Capot Riv.	61°09'50.4O	14°40'47.3N	2500	0.01			7.73	709	432	432	83	32	940	554	42	216	319	21.9	55	64	161	0.51	65	162	2350
Capot Riv.	61°05'29.1O	14°50'27.1N	2500	0.01			n.d	835	322	200	94	74	791	451	74	178	317	25.3	63	75	188	0.5	82	204	1978
Lorrain Riv.	61°03'11.6O	14°47'51.5N	2800	4.3			n.d	434	263	263	25	156	349	334	29	121	231	14.6	41	41	114	0.57	45	127	978
La Lézarde Riv.	61°03'16.2O	14°43'13.5N	2600	0.37			7.02	361	268	268	21	27	367	300	21	91	133	8.8	23	30	79	0.4	31	80	954

TDS_{cat} = [Na]* + [K]* + [Ca]* + [Mg]*; CWR = TDS_{cat}*Runoff; TDS = TDS_{cat} + [SiO_2], TWR = TDS*Runoff, Φ_{River} = [Na]* + [K]* + [Ca]* + [Mg]*)/[SiO_2], TDS_{hyd} = TDS + [Cl]* + [S]*, TWR_{hyd} = TDS_{hyd}*Runoff, CO_2 cons. = [HCO_{3-}]*Runoff.

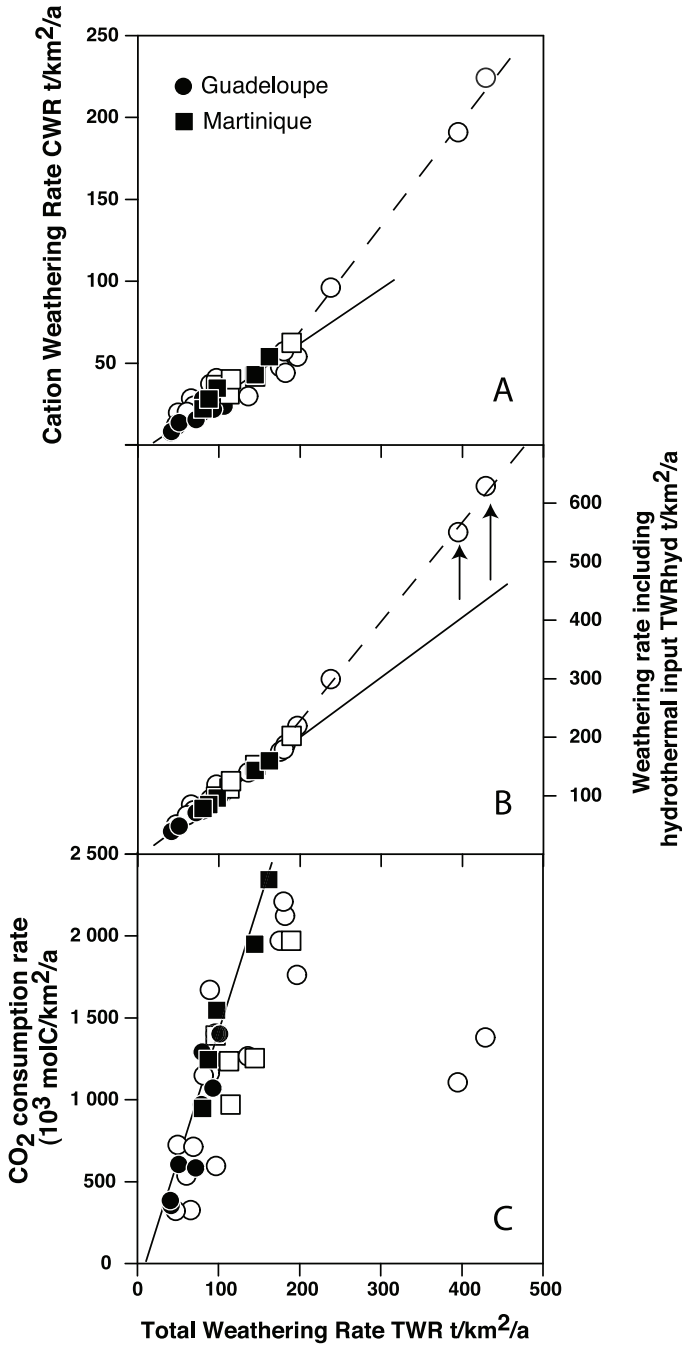

Fig. 6. Relationships, in the Lesser Antilles, between CWR, TWR and CO_2 consumption rates calculated on the largest rivers. Open symbols are for H-impacted rivers, plain symbols for non H-impacted rivers. The two linear trends in figures 6A and 6B reflect the depletion in SiO_2 in the H-impacted rivers. The highest CWR and TWR are found for the H-impacted rivers but this is no longer true when CO_2 consumption rates are considered (fig. 6C). This difference is due to the involvement of sulfuric acid as a weathering agent in the H-impacted rivers.

Guadeloupe (fig. 6B). This demonstrates that hydrothermal activity has a major influence on chemical weathering rates, at least at a regional scale.

At a global scale, it appears that the weathering rates found in the Lesser Antilles are amongst the highest measured (Louvat, ms, 1997; Louvat and Allègre, 1997, 1998; Dessert and others, 2001; Das and others, 2005; Dessert and others, 2009). The Java, Japan, Philippines and Kamchatka regions are the closest geological settings to Lesser Antilles because they are subduction volcanic arc systems. The TWR in the Lesser Antilles is equivalent to those found in Java (50 to 160 $t/km^2/a$ if the outlier river at 1075 $t/km^2/a$ is discarded) and about 3 times greater than the reported 15 and 85 $t/km^2/a$ with a mean value of 35 $t/km^2/a$ for the Kamchatka rivers. In the Philippines, the range of CWR and TWR is quite similar but the median values are two times greater than those of the Lesser Antilles with 70 $t/km^2/a$ and 200 $t/km^2/a$ respectively (Schopka and others, 2010). The recently published data for the Japanese Archipelago of TWR of silicate-dominated lithological classes reports that for the volcanic and pyroclastic lithologies, rates range from 10 to 80 t/km2/a for a runoff range varying from 500 mm/a to 1700 mm/a with a median value close to that of Kamchatka peninsula (Hartmann and Moosdorf, 2011).

Finally, following the approach of Navarre-Sitchler and Brantley (2007) and taking the mean rock composition deduced from the bedrock analyses published by Samper and others (2007) for Guadeloupe, the CWR can be converted to a weathering advance rate (WAR, in mm/a)

$$WAR = \frac{CWR}{\alpha\rho(1-\varphi)}. \tag{9}$$

Here α, ρ, and φ are the average mass of alkali and alkaline earth cations per g of parent andesite, the average bulk density of the andesite and the porosity of the parent material (considered here as 0), respectively. According to Samper and others' (2007) database, the cation concentration in the bedrock is 10×10^{-2} t/t. According to CWR numbers calculated above, we find that the weathering advance rates in the Lesser Antilles must range between 30 and 150 mm/ka. The median value of CWR leads to a mean WAR of 100 mm/ka. This weathering advance rate compares favorably with the compilation from Navarre and Brantley (2007) at characteristic watershed scale and is among the highest weathering advance rates found worldwide. The recently calculated weathering advance rate using U series in a volcanic clast from Bras David catchment is between 0.23 and 0.31 mm/ka, (Ma and others, 2012) and confirms the two order of magnitude difference in weathering rate between the watershed and the clast scales calculated in Guadeloupe (Sak and others, 2010).

Atmospheric CO_2 Consumption Rates by Chemical Weathering Reactions in the Lesser Antilles

Consumption of atmospheric/soil CO_2 is calculated for the large rivers using the concentration of dissolved bicarbonate (marine correction is not significant) and river runoff values as

$$CO_2 \text{ consumption rate} = [HCO_3^-]*\text{Runoff}. \tag{10}$$

For the non H-impacted rivers, there is a strong correlation (see fig. 6C) between the so-calculated CO_2 consumption rates and those calculated using the equivalent cationic load

$$CO_2 \text{ consumption rate} = ([Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}])*\text{Runoff}. \tag{11}$$

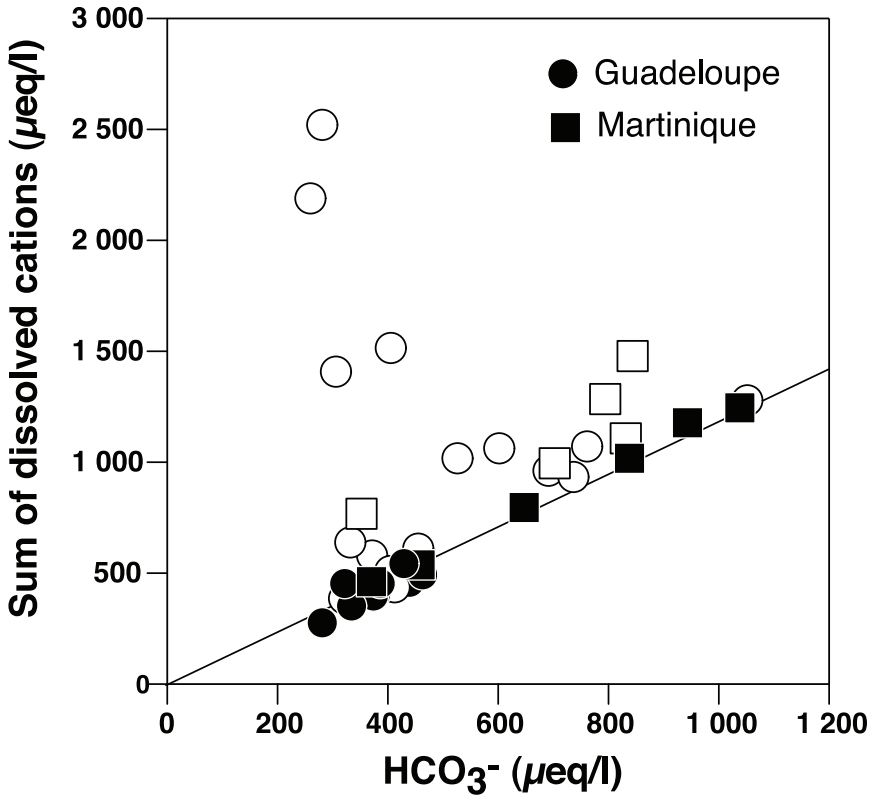

Fig. 7. Diagram showing that in the rivers of the Lesser Antilles, the sum of precipitation-corrected-cations ($[Na^+]+[K^+]+2[Ca^{2+}]+2[Mg^{2+}]$) is compensated by bicarbonate ions in the non impacted rivers but that the H-impacted rivers, as defined by the SO_4^{2-} vs. Cl^-/SO_4^{2-} plot (fig. 3), lie out of the 1:1 line. This is due to the contribution to sulfate ion to the charge balance.

The reason for this agreement is that in the non-impacted rivers, the cationic charge is only compensated by HCO_3^-. This is true as far as no hydrothermal SO_4^{2-} or Cl^- is present. As expected, in the H-impacted rivers the cationic load is compensated by the sum (in equivalent) of HCO_3^- and SO_4^{2-} as shown in figure 7. In the H-impacted rivers, a significant part of the protons are not provided by atmospheric CO_2 dissolution but by sulfuric acid dissociation. For a number of highly H-impacted rivers, hydrochloric acid is an additional significant source of protons.

The CO_2 consumption rates calculated based on the largest rivers range from $\sim 300\times10^3$ mol/km^2/a for the rivers of Northern Guadeloupe (for example AN04-12, AN04-13, AN04-14) to $\sim$2500 to 3500×10^3 mol/km^2/a for the rivers draining the Pelée and Soufrière volcanoes (for example AN04-19, AN04-67). The low pH of Grande-Plaine river (@ Saut d'Acoma) is an exception as cations are essentially compensated by SO_4^{2-}, indicating the importance of sulfuric acid weathering. The median value for the largest rivers is $\sim 1300\times10^3$ mol/km^2/a. The non H-impacted samples display only slightly lower CO_2 consumption rates, with a median value of $\sim 1100\times10^3$ mol/km^2/a. The small difference in terms of CO_2 consumption rate between the non-impacted and H-impacted rivers contrasts with the strong discrepancy observed for chemical weathering rates. Again, this reflects the impact of sulfuric

acid during weathering reactions as indicated by the high concentration of SO_4^{2-} ions (fig. 7).

The CO_2 consumption rates on Martinique are significantly higher than those on Guadeloupe, but we attribute this discrepancy to the distribution of sampled rivers on Martinique. Our data on Martinique are concentrated on rivers draining Pelée volcano and this sampling biases our results toward high CO_2 consumption rates.

All the CO_2 consumption rates calculated in this study compare well with recent rates calculated for the Dominica rivers by Goldsmith and others (2010) that reported values ranging from 500 to 1500×10^3mol/km^2/a. On a more global scale, the CO_2 consumption rates calculated for the Lesser Antilles are comparable to those found in La Réunion ($1300\text{-}4400\times10^3$mol/km^2/a) in a similar climate (Louvat, ms, 1997). Compared to similar regional geological contexts, these rates are significantly lower than the rates found in Java (Louvat, ms, 1997, and Dessert and others, 2003) and are between 2 and 3 times higher than the CO_2 consumption rates found on the Kamchatka Peninsula, situated in a similar volcanic arc context. The CO_2 consumption rates found in the Lesser Antilles are amongst the highest CO_2 consumption rates by chemical weathering reactions ever found on Earth, confirming the importance of weathering in tropical island settings.

What controls the chemical denudation rates in the Lesser Antilles?

The different drainage basins investigated here all have about the same mean annual temperature and therefore we conclude that temperature is not a factor playing a role in the chemical denudation rates within the Lesser Antilles. We examine here the potential effects of runoff, volcanic acidity, and bedrock age on chemical denudation rates. Physical denudation may potentially exert a control on chemical erosion rates and that topic will be discussed in a companion paper.

Runoff Control

Chemical denudation rates are sensitive to the runoff. Runoff represents both the amount of water in the drainage catchment that is potentially interacting with the parent material, and the amount of fluid exporting the dissolved and solid products of erosion out of the drainage basin. At the scale of the Lesser Antilles, runoff values fluctuate widely from the low relief zone of North Guadeloupe (~900 mm/a) to the high relief active volcanoes of La Soufrière, Pelée and Dominica (≤5000-6000 mm/a). Runoff values in non-sampled parts of Martinique or in Montserrat (Jones and others, 2010) confirm the very large variability that is observed even at the scale of a few km^2 in volcanic islands. The origin of this variability is directly linked to the precipitation and evaporation regimes and to the infiltration/runoff partitioning. The windward side of the Lesser Antilles receives more rain than the leeward side and rivers draining the windward side have the highest runoff values.

The specifics of the relation between chemical denudation rates and runoff are shown in figure 8A. One must keep aware of the inevitability of this representation. Denudation rates, calculated by multiplying a concentration (for example, in g/l) by runoff, are examined here as a function of runoff. A straight line in this diagram means that concentration is constant over the range of considered runoff. This, in turn, means that concentration is not diluted at high runoff and consequently runoff does increase chemical denudation. This is the reason why we also plotted TDS in mg/l as a function of runoff in figure 8B. Two major linear trends between TWR and runoff characterize the Lesser Antilles. The line with the lower slope applies to the non H-impacted rivers while the H-impacted rivers are characterized by a steeper slope. By considering Guadeloupe samples only, the relationship between TWR in t/km^2/a and runoff is

$$\mathrm{TWR} = 0.019*\mathrm{Runoff} + 25. \quad (12)$$

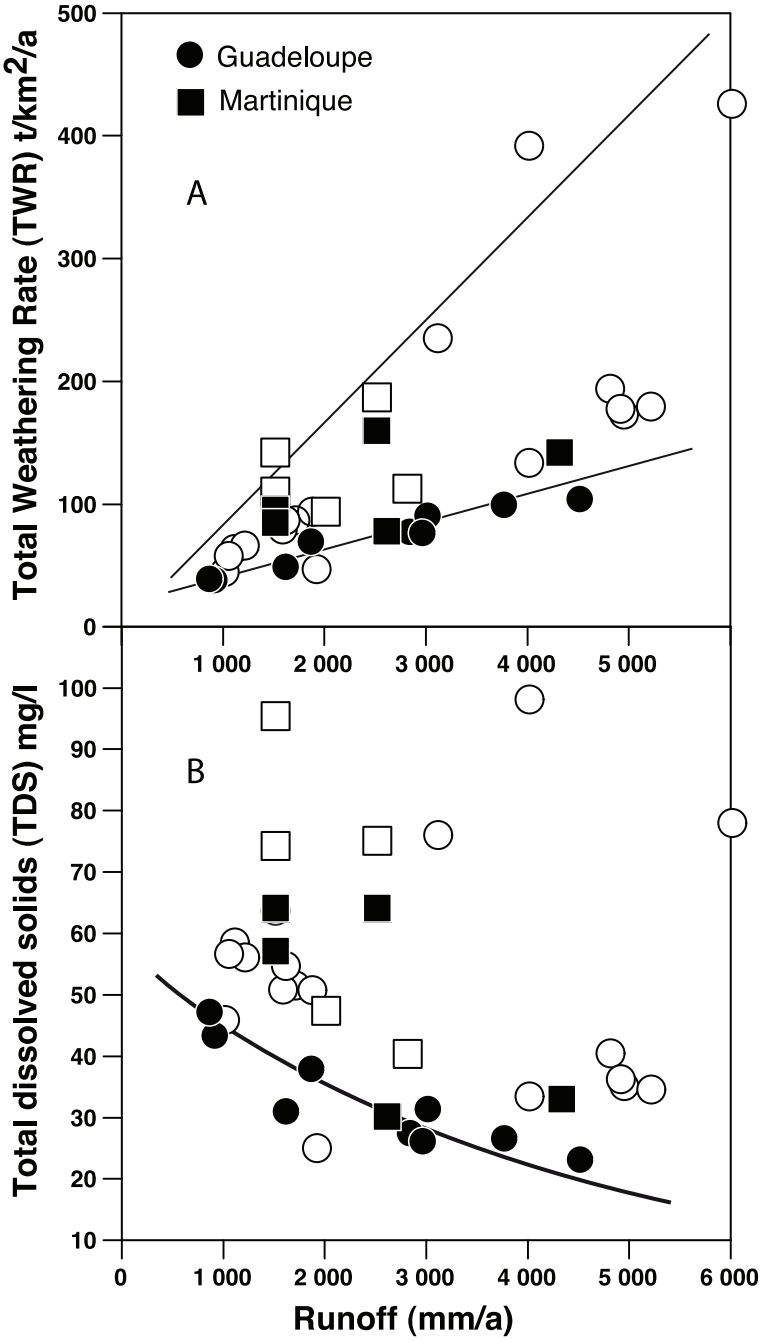

Fig. 8. Total weathering rate (TWR, fig. 8A) and Total Dissolved Solutes (TDS_{cat}, fig. 8B) as a function of runoff for the largest rivers of the Lesser Antilles. Symbols are the same as in previous figures. Non H-impacted rivers from Guadeloupe define a linear relationship indicating that dissolved solutes are not purely diluted at high runoff. This is an example of the "chemostatis" concept proposed by Godsey and others (2009). Rivers impacted by hydrothermal activity (open symbols) show different control relationships with runoff, indicative of the contribution of sulfuric acidity.

In terms of concentrations, the TDS of non H-impacted rivers decrease slightly with runoff but it is important to note that this decreasing trend is not a dilution (and this is the reason why the slope in fig. 8A is not 0 for these rivers). A pure dilution law would be in the form of TDS proportional to R^{-1}. For non H-impacted Guadeloupe samples, TDS (mg/l) as a function of runoff rather gives a relation in the form:

$$\mathrm{TDS} = 590\ \mathrm{Runoff}^{0.4}. \quad (13)$$

The exponent of -0.4 (> -1) means that increased chemical weathering at high runoff compensates for water dilution. The situation is more ambiguous for Martinique indicating that other controlling parameters play a role. H-Impacted rivers show no relationship between TDS and runoff, although in figure 8A, TWR of H-impacted rivers appears to correlate with runoff. This correlation is indicated by the relatively small range of variation in TDS concentration relative to runoff at the scale of the Lesser Antilles.

This analysis highlights the importance of runoff variability on tropical islands and partly explains the observed co-variation between total weathering rate and runoff. This correlation has no geochemical significance other than documenting that concentrations are not purely diluted at high runoff. The relative constancy of concentrations with runoff in catchments is defined as "chemostasis" by Godsey and others (2009) and is a universal process reported for numerous catchments worldwide. Possible mechanisms are an increased dissolution of minerals and glasses with increasing discharge (Gislason and others, 2009) or hydrological buffering. Our study shows that non H-impacted rivers from the Lesser Antilles do show that increased runoff leads to increased weathering rates but that the concentration of total dissolved solids of H-impacted rivers does not vary significantly as a function of runoff. This result is not surprising as the hydrothermal contribution probably depends primarily on the proximity to the active volcanic or tectonic centers more than precipitation.

When CO_2 consumption rates are considered, slightly different conclusions arise. Two relationships between CO_2 consumption rates and runoff with very different slopes exist (fig. 9). The line with the lower slope (about 1000×10^3 molC/km^2/a for 3000 mm/a) corresponds to H-impacted and non H-impacted rivers whose HCO_3^- concentrations are constant over the whole range of runoff. The line with the higher slope (2500×10^3 molC/km^2/a for 3000 mm/a) corresponds to rivers from North Martinique.

In summary our findings demonstrate that runoff exerts a first order control on the calculated chemical denudation rates for the drainage basins with no-hydrothermal inputs, the highest runoff values are associated to the highest chemical denudation rates. In contrast, in drainage basins where a hydrothermal component is detected, that signal clearly dominates the river chemistry and is independent of runoff.

Influence of Volcanic Emissions of Acidity

Active volcanoes such as La Soufrière release into the atmosphere acid gases that may favor rock chemical weathering. The oxidation of volcanic gases SO_2 and H_2S produces sulfuric acid (H_2SO_4, a strong acid) while other gases are directly released as strong acids. Only CO_2, once released in the atmosphere, will combine with water to form carbonic acid, a weak acid. According to Varekamp and Thomas (1998), volcanic acid emissions are either subaerial gas fluxes from craters, fumaroles of diffuse gas seepage, or adsorbed gases on fine ashes, or dissolved gases in volcanic lakes and shallow hydrothermal systems. This is particularly true in the Lesser Antilles, where the volcanic gases are dominated by SO_2, H_2S, HCl, CO_2 and water (Bernard and others, 2006; Villemant, personal communication), and where shallow groundwaters are

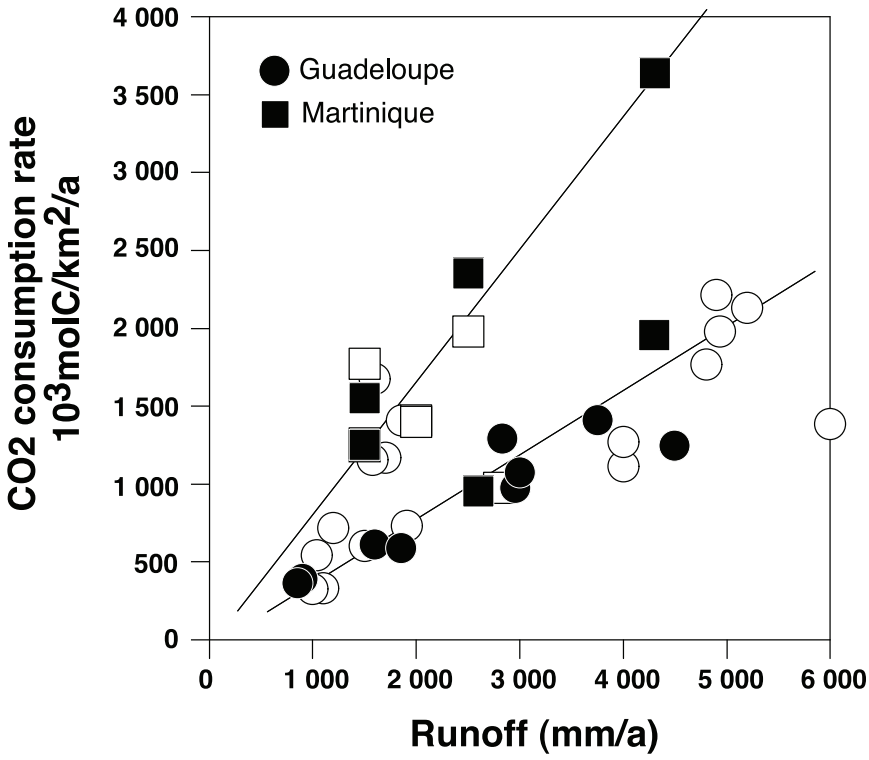

Fig. 9. CO_2 consumption rate during silicate weathering as a function of runoff for the largest rivers of the Lesser Antilles. Symbols are the same as in previous figures.

influenced by sulfuric and carbonic acids derived from passive degassing (Villemant and others, 2005). For example, the anions of the thermal springs around the Soufrière volcano on Guadeloupe are dominated by Cl^- and SO_4^{2-}, indicating that the main acids involved in rock weathering are hydrochloric and sulfuric acid respectively. The reactions of hydrochloric and sulfuric acid formation are respectively

$$HCl = H^+ + Cl^-$$

$$SO_2 + 1/2O_2 + H_2O = 2H^+ + SO_4^{2-}.$$

Hydrofluoric acid does not seem to be a significant source of acidity as shown by the very low concentrations of F^- in thermal springs on Guadeloupe (Villemant and others, 2005). However Hydrofluoric acid may play a role during initial stages of weathering when F^- is leached from the fresh ash (White and Hochella, 1992; Wolff-Boenisch and others, 2004). Total cation load of the southern Guadeloupe hot springs reach 15 to 30 meq/l, an order of magnitude higher than in the riverwaters. These hotsprings are subdivided into two major groups: Ca-SO_4 rich waters formed by the reaction of meteoric waters and sulfuric acid (the dominant water type) and Ca-Na-HCO_3 rich waters derived from shallow geothermally heated groundwater. Carbon isotopic analyses of thermal springs in the Lesser Antilles (Aubaud and others,

2007; Rivé and others, 2012[2]) show that most of the carbonic acid involved in chemical weathering is of magmatic origin. All these processes of water-rock interaction are facilitated by the steep geothermal gradient near the active volcanic center. However, low-temperature springs and shallow groundwaters are also present (Rad and others, 2007) in inactive parts of the Lesser Antilles and are potentially rich in sulfate ions. The oxidation of volcanic sulfide deposited at depth when exposed to the oxic surface waters creates acid mine drainage conditions and is another potential source of sulfuric acid in regions where hydrothermal activity is ceased. This is the likely origin of sulfuric acid in the Grande Plaine River, Guadeloupe, which is draining an area away from the active volcanism, but the drainage basin contains ancient hydrothermal deposits (visible at the Col des Mamelles). One possible reaction explaining the formation of this "low-temperature" sulfuric acid may be

$$FeS_2 + 3.75O_2 + 3.5H_2O = 4H^+ + Fe(OH)_3 + 2SO_4^{2-}.$$

The generation of "high-temperature" and "low-temperature" sulfuric acid is not unique to this system and was also shown to occur on the Kamchatka Peninsula (Dessert and others, 2009).

In rivers, hydrothermal (past or present) activity can be quantified using the SO_4^{2-} concentration or the SO_4^{2-}/Cl^- ratio. Figure 10 shows that the dissolved cationic load increases with the involvement of sulfuric acid, particularly on Guadeloupe Island. For an increase of SO_4^{2-} between 100 and 1000 μmol/l, cationic load is multiplied by a factor of 2 to 3. Alternatively the significance of sulfuric acid as a weathering agent can be assessed on a plot of total dissolved cations as a function of the concentration of HCO_3^- (fig. 7). Here, rivers with cation loads <1000 μmol/l, plot along the 1:1 line, indicating that carbonic acid is the only significant acid involved, but not the rivers with higher chemical cationic load. For these rivers, cationic and anionic loads can only be balanced if SO_4^{2-} is taken into account. When the CWR or TWR are plotted against SO_4^{2-} concentration or SO_4^{2-}/Cl^- ratio, then only a trend on increasing chemical denudation with hydrothermal activity is visible. This, in turn, means that the catchments with the highest water runoff are not necessarily those with the highest hydrothermal contribution or that the hydrothermal input is being diluted at high runoff regimes.

In the Lesser Antilles, the production of acidity by volcanism exerts a first order control on the chemical denudation of an island. For example, we calculate that, using a runoff-weighted average, for Basse-Terre Island, 25 percent of the protons consumed by chemical reactions are provided by sulfuric acid, 5 percent by hydrochloric acid and the remainder by carbonic acid. As shown by Rive (2008), between 23 and 40 percent of the carbonic acid involved in chemical weathering reactions are of magmatic origin. These "hydrothermal" contributions originate from passive degassing or dissolution of volcanic deposits at depth.

Age Control

Based on the K-Ar dating of lava flows, the recent papers by Samper and others (2007, 2009) have led to a complete reinterpretation of the evolution of subaerial effusive volcanism in Guadeloupe. These data record the southward migration of volcanism on Basse-Terre at a rate of 18 to 25 km/Ma. The oldest rocks are found in the Northern part of the Island (Basal complex) where the Vieux Fort or Nogent rivers have been sampled. The activity of the "Septentrional chain" and "Central chain" is dated between 1.8 to 1.15 Ma and 1.0 to 0.4 Ma respectively, while the Southern part of

[2] Rivé, K., Agrinier, P., Gaillardet, J., and Rad, S., 2012, Magmatic CO2 as a weathering agent in the rivers of the Lesser Antilles: Earth and Planetary Science Letters, submitted.

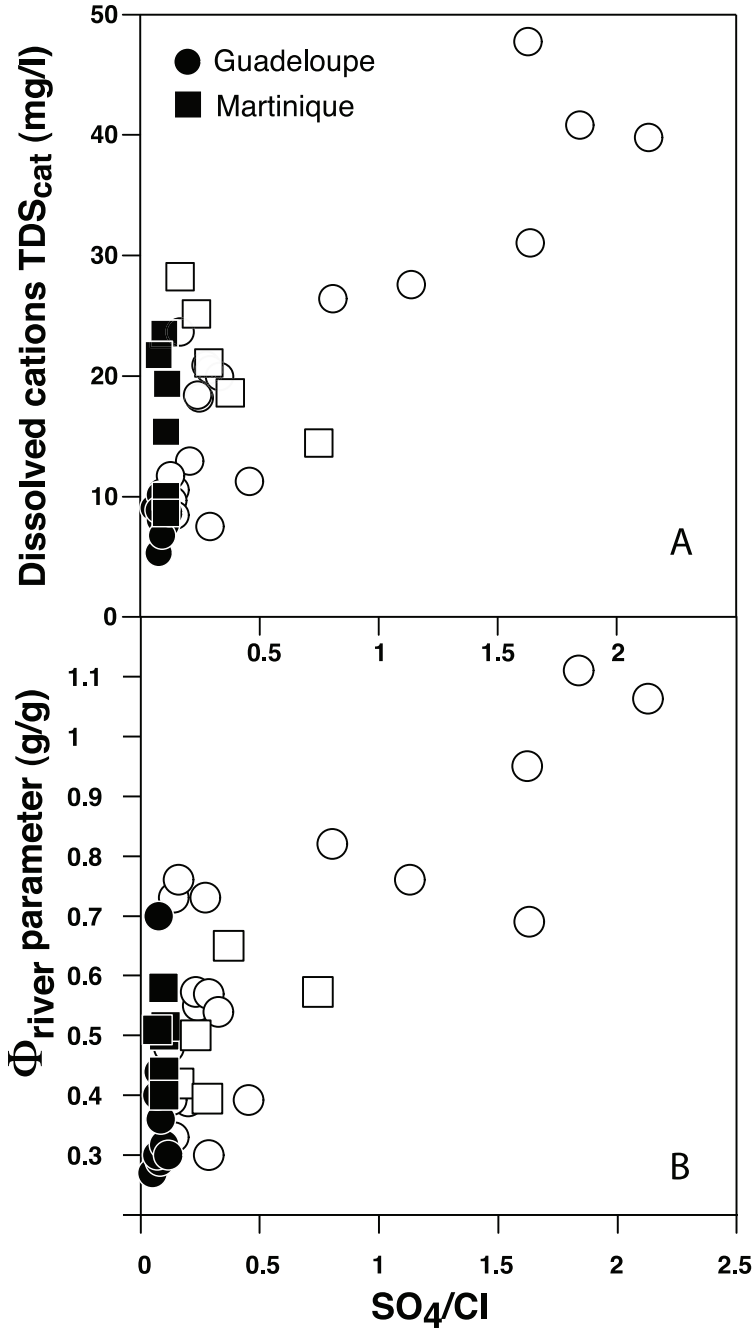

Fig. 10. Diagram showing the increase TDS_{cat} (A) and Φ_{River} (eq 2) (B) with increasing SO_4^{2-}/Cl^- ratio as an index for the relative abundance of SO_4^{2-} and thus the involvement of sulfuric acid in the weathering budget. Similar increases are obtained by simply plotting SO_4^- concentration on the X axis. If rates are plotted, no relationship is observed with sulfuric acid contribution. These diagrams demonstrate the importance of additional sources of acidity to enhance weathering rates particularly in Guadeloupe. Symbols are the same as in previous figures.

the Island (Grande Découverte complex volcano, including la Soufrière volcano) is dated between 0 and 0.4 Ma. Guadeloupe is therefore a well adapted setting to look at chemical weathering rates as a function of age as it has been done in Iceland (Gislason and others, 1996) or Hawaii (Chadwick and others, 1999). In contrast, in Northern Martinique, where most of the studied rivers were sampled, revised K-Ar dating (Germa and others, 2010) show that activity at the volcanic centers oscillated rather than migrating in a straightforward manner as on Guadeloupe. Specifically the Morne Jacob volcano started its effusive activity 5 Ma and then the Carbet and Conil complexes were built between 2.4 and 200 ka, in close proximity. The most recent effusive activity of Montagne Pelée volcano occurred in approximately the same location leading a less favorable case. The age of the drainage basins from this study were determined based on the geological map of Feuillet and others (2001) for the southern portions of Basse-Terre and the ages of lava flows determined recently by Samper and others (2007, 2009). This method assumes that the age of the lava flows disseminated in the basins is representative of subjacent bedrock of the whole drainage basin. In other words, the pyroclastics associated with the effusive volcanism are presumed to be the same age as the lava flows. This assumption is justifiable based on geological observations reported in Basse-Terre volcanic centers (Samper and others, 2009). However the age given here should be considered as a first order number given the scarcity of lava flows and the variability observed in the lava flow age determinations (Samper and others, 2007). On the islands of Martinique and Dominica this method of constraining bedrock age is further complicated by the superposition of volcanic terranes of different ages and extensive fluvial incision that makes the determination of a drainage basin age very difficult.

The first order trend that emerges from the inspection of the chemical denudation rates as a function of age is that the higher weathering rates calculated in the Lesser Antilles are associated with the most active parts of the islands. Figure 11 shows how TWR varies as a function of bedrock age for Martinique and Basse-Terre islands. This figure shows that TWR decreases sharply with parent bedrock age. This decrease affects both the H-impacted and non H-impacted rivers and is much more pronounced on Basse-Terre island in Guadeloupe than Martinique. In contrast to TWR in $t/km^2/a$, TDS_{cat} (or TDS) in mg/l does not display a regular decrease with increasing age. The rivers flowing through the youngest regions have high cation loads because of hydrothermal activity, but in Guadeloupe, rivers draining older terrains in Bouillante district also exhibit high solute concentrations derived from silicate weathering. The high concentrations observed in "old" terrains are, as shown above, due to the contribution of sulfuric acid from extinct hydrothermal systems. We conclude that high denudation rates are observed in the most active parts of the Lesser Antilles (similar to what is found for example in Iceland according to Gislason and others, 1996 for basalt weathering) and that the decrease of chemical denudation rates with rock age is more an effect of decreasing runoff than an effect of age.

The Interplay Between Runoff, Relief, Age and Volcanic Activity

Runoff and bedrock age are not independent parameters. Relief of each drainage basin was calculated using RiverTools GIS application. On Guadeloupe, runoff values, relief, and bedrock age are correlated (fig. 12). The lack of similar correlation on Martinique may be related to the lack of a clear age gradient. Figure 12 illustrates the decay of relief from the most recent, southern part of the Guadeloupe to older northern part. At a given bedrock age, rivers draining the leeward and windward sides of the divide show significant differences in runoff value but in both cases, runoff decreases with bedrock age. This confirms that the apparent decrease in chemical weathering rates with bedrock age reported above may be attributed to the decrease in runoff from the active part to the quiescent parts of Basse-Terre. Figure 12 and the

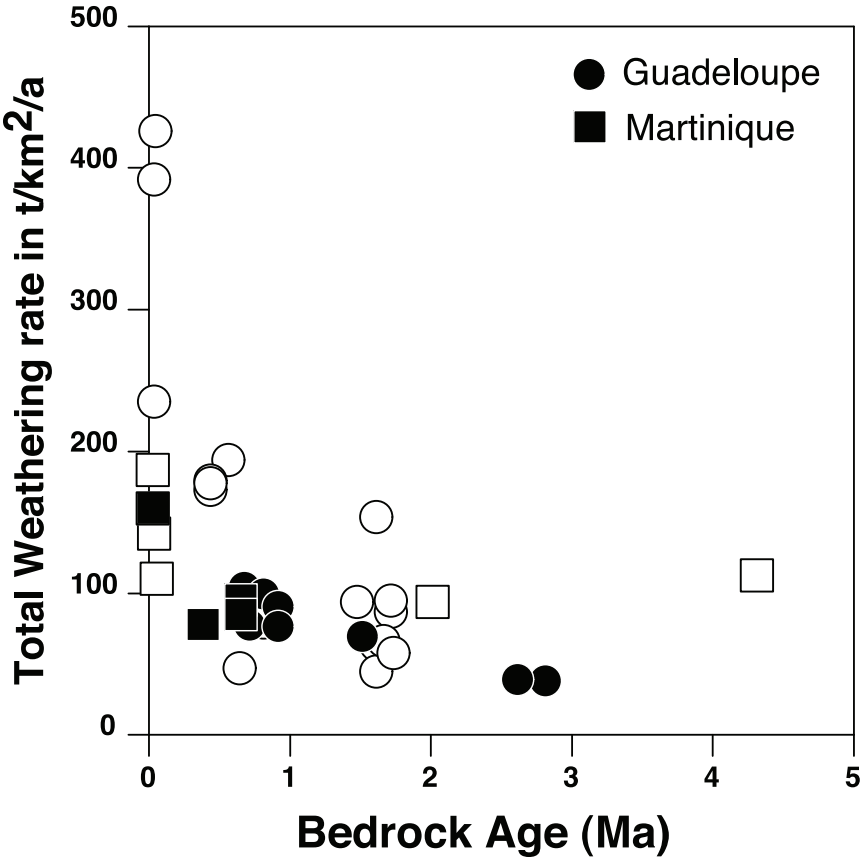

Fig. 11. Decrease of Total Denudation Rates inferred from the rivers of the Lesser Antilles with bedrock age, estimated based on the dating of lava flows disseminated within the drainage basin (Samper and others, 2007). The decrease with age is observed for both H-impacted and non H-impacted rivers. No significant relation between TDS_{cat} or TDS with age is observed.

conclusions from the previous sections strongly suggest that silicate denudation rates in the Lesser Antilles and associated CO_2 consumption are primarily controlled by the amount of runoff water, hydrothermal activity and the contribution of volcanic acidity.

As already pointed out, among the different drainage basins, runoff variations are much more important (by a factor of 6-7) than variations in concentration of dissolved cations, silica and alkalinity (factor of 2-3). This is due to the fact that with increasing water runoff, river concentrations do not decrease according to a dilution trend and therefore the product of concentration by runoff increases with runoff. The important result is that variations in the chemical denudation rate are most sensitive to variations in runoff. The same conclusion was reached by Godsey and others (2009) based on the analysis of concentration-discharge relationships in numerous streams in the US or Moosdorf and others (2011) by examinating the relationships between bicarbonate concentration and runoff in catchments from North America. The relative constancy of concentration versus runoff explains the correlation reported by many authors (Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; Hartman and Moosdorf, 2011) between catchment weathering rates and runoff at the global scale.

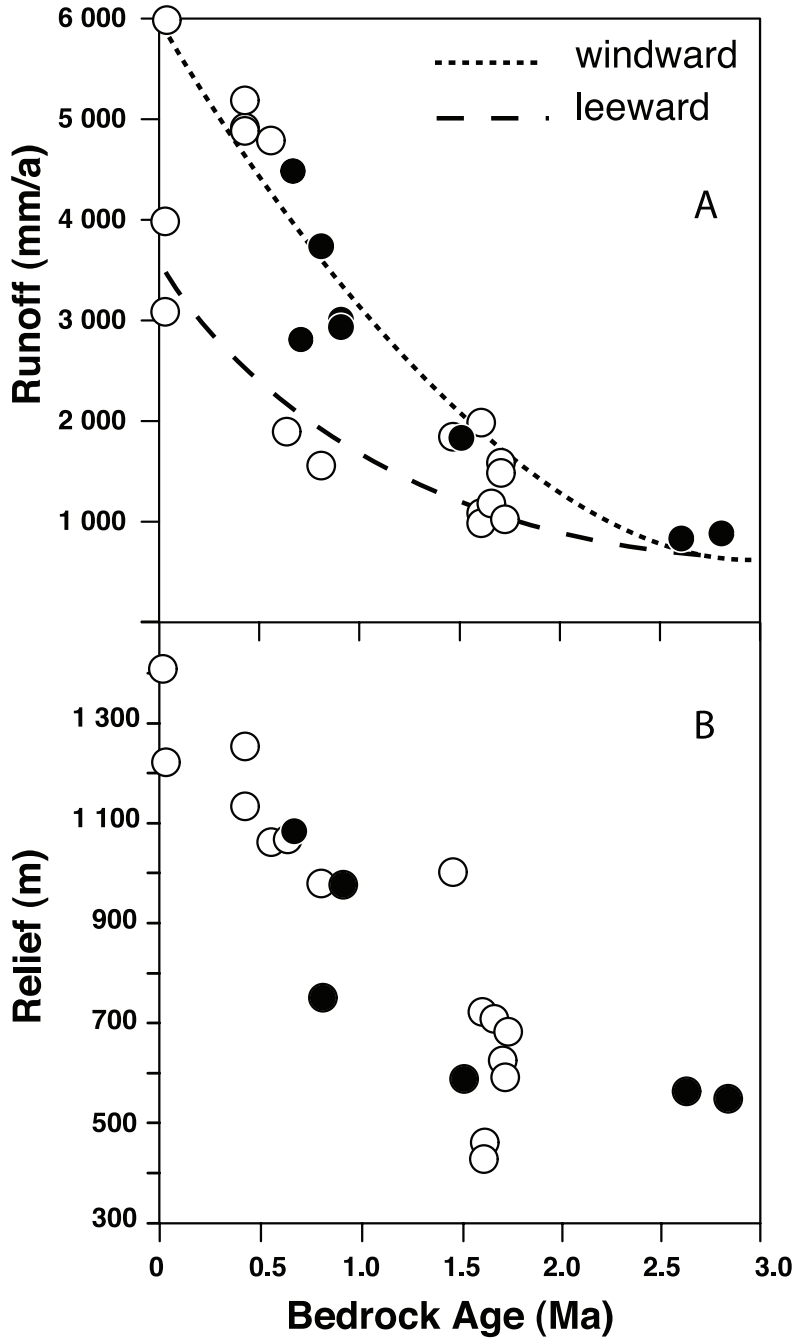

Fig. 12. Diagram showing the interplay between Runoff (A), relief (B) and bedrock age in the drainage catchments of Guadeloupe. Relief was calculated using RiverTools GIS application. These relationships are found in Guadeloupe because of North-South migration of volcanism during the Quaternary. In Dominica and Martinique the stagnation of volcanism activity through time does not allow us to delineate relations between runoff, relief and age.

The high runoff values and their variability are directly linked to the precipitation and evaporation regimes. The highest precipitation (and lowest evapo-transpiration) are observed in the high relief areas and are the consequence of orographic rains influenced by the Atlantic air masses coming from the east. The relief-forced rise of near-saturated warm maritime air, by cooling and expansion, implies water condensation and causes heavy rain on the windward side of the divide. On the leeward side, as the air descends, it compresses and warms and becomes drier. These features are not specific of Lesser Antilles and are observed in all the regions of the world associating high relief and water-saturated air masses. One of the best evidence of the importance of relief on precipitation rates is given by the contrast between the Basse-Terre and Grande Terre Islands in Guadeloupe. Although Grande Terre Island is windward, it is an uplifted Tertiary carbonate platform with low relief. Precipitation rates are ≤1500 mm/a, while precipitation rates on the higher relief Basse-Terre Island range from 2000 to >5000 mm/a in Basse-Terre.

As synthesized by Roe and others (2005), the simplest model that can be used to describe the total condensation rate in a vertical column of saturated air is derived from a Clausius-Clapeyron relationship relating the water vapor pressure to temperature in the form

$$e^{sat}(T) = 6.112\exp\left(\frac{17.67 \cdot T}{243.5 + T}\right), \tag{14}$$

where $e^{sat}(T)$ is saturation vapor pressure in millibars and T is temperature (°C). With the adiabatic decompression of an ascending air mass, water will reach saturation and it can be established that the mass of water vapor per unit of volume in saturated air decreases with elevation. A decrease of 500 m and 1000 m of z in the tropics typically decreases the atmospheric moisture content by 12 percent and 22 percent respectively. The rate of water condensation is imposed by the vertical velocity of the ascending air mass and the most straightforward expression that can be calculated for orographic rain condensation rate S (in mm/h) following Roe and others (2005) is

$$S = \rho_0 q_0^{sat} u \cdot \nabla z_s \exp(-z_s/H_m). \tag{15}$$

Here u is wind speed, z_s the surface elevation, ρ_0 and q_0^{sat} the air density and water vapor pressure per unit of air mass respectively. The subscript 0 denotes z=0 conditions and H is a characteristic scale of about 4000 m in the tropics. For typical tropical latitude (ground temperature of 26 °C, ρ_0 of 1.18 kg/m^3), applying equation (15) to a DEM of South Basse-Terre (La Soufrière volcano, Guadeloupe), averaging slopes onto 4×4 km^2 cells, with a typical u value of 6.6 m/s (Komorowski and others, 2008), we predict a precipitation rate increase by a factor of 5 between 50 m and 750 m of elevation. This calculation is a sensitivity calculation demonstrating the efficiency of relief in the tropics to remove atmospheric humidity. It is interesting to note that the same calculation performed for lower temperature (hence higher latitude) shows the same orographic enhancement factor but a reduction of precipitation rates by a factor of 4 between 25 °C and 5 °C. In a pure orographic system, the effect of temperature is thus equivalent to that of elevation (given that the mean average elevation of arc volcanoes is around 1000 m in the Lesser Antilles).

As outlined by Roe and others (2005) this model is too simplistic, in particular it does not account for the range of diverse meteorological processes in tropical islands. For example, in a recent study on Dominica (Smith and others, 2008) observations of rain gauges and radar scans showed that the orographic effect on precipitation rates is between 2 and 8. This range is attributed to repetitive convective triggering over the windward slope. As reviewed by Roe and others (2005), a number of models have been

developed, taking into account not only the basic thermodynamic principles but also topography, cloud microphysics, radiative processes and atmosphere-land surface interactions and they are able to reproduce the precipitation patterns on mountainous ranges, at least at the mesoscale. Models are limited by our knowledge of the physical processes and by computational constraints.

The above calculations predict precipitation patterns but not runoff + infiltration patterns. There is unfortunately no measurement on evapo-transpiration rates in the Lesser Antilles and only rough estimates of infiltration rates (Rad and others, 2007). Infiltration rates are particularly important in the youngest part of the Lesser Antilles and contribute to groundwater discharging directly into the sea (Rad and others, 2007). The partitioning between runoff and infiltration should however depend on soil properties and slope gradient. The observation that runoff values for the main catchments are at a first order correlated to precipitation rates estimated from the global precipitation map indicates that infiltration is a second order parameter in runoff control. From this study, we conclude that for rivers draining the Lesser Antilles, orographic precipitation causes the greatest variations in runoff and that runoff is a determinant of chemical denudation rates.

Despite the first order control that runoff exerts on chemical denudation rates in the Lesser Antilles, the chemistry of Lesser Antilles rivers suggests that volcanic acidity input is a viable mechanism capable of significantly increasing the dissolved load concentrations by a factor of 2 to 3. This is achieved through the action of sulfuric, hydrochloric and volcanic carbonic acids. The contribution of these additional sources of acidity compared to atmospheric CO_2 is preferentially playing a role in the most active (recent) parts of the volcanic islands but can also be generated in quiescent (old) volcanic areas by the dissolution of hydrothermal deposits. The infiltration of rainwater through porous volcanic layers or fault systems is then warmed at depth due to the steep geothermal gradient. High temperature favors chemical weathering as well as the addition of acids from magma degassing. Water is, of course, necessary to produce hydrothermal springs but is probably not limiting in the Lesser Antilles, given the relatively high precipitation rates. As shown earlier, there is no relationship between the hydrothermal contribution and runoff in the Lesser Antilles although such a relationship may exist at global scale (higher runoff would be associated to higher hydrothermal contribution). The links between hydrothermal contribution and runoff are probably complicated at regional scale because hydrothermal pathways of water are complex and strongly depend upon the hydrogeological setting (and geological structure). The hydrothermal and volcanic acidity are additional factors that may locally increase chemical denudation rates. Obviously, this is related to volcanic activity and precipitation regimes. Finally, the effect of the bedrock age that was mentioned earlier can be explained by the fact that relief is decreasing with age, as a result of chemical or physical erosion and also as a result of flank collapse events. As shown by Boudon and others (2007) and Samper and others (2007) such episodes of huge flank destabilization have occurred, for example, in the axial chain of Basse-Terre Island at 640 and 550 ka respectively. Relief is therefore strongly linked with bedrock age on Guadeloupe. Additional factors may play a secondary role to enhance the susceptibility of young volcanic rocks to chemical weathering. As outlined by Gislason and others (1996) in Iceland, the decrease of chemical denudation rates with age is explained by the glassy nature of young basalts compared to the crystalline texture of the older ones. As glass weathers more rapidly than minerals (Gislason and Eugster, 1987; Gislason and Oelkers, 2003), very young basaltic terrains are more susceptible to weathering. In the case of the Lesser Antilles, the abundance of pyroclastic rocks, glassy pumice layers in the most recent parts of the islands probably

favors chemical denudation in the early stages of water-rock interaction as indicated by figure 11.

Relief, which determines precipitation rates, thus runoff and infiltration, sulfuric and hydrochloric acid contributions and rock susceptibility to chemical weathering are factors all ultimately caused by volcanic activity. As a consequence, the chemical denudation rates and atmospheric carbon consumption in the Lesser Antilles are primarily controlled by volcanic activity in general. As volcanic activity is a consequence of plate tectonics this feedback loop is an example of the coupling between deep earth and surficial processes.

A Negative Climate Feedback Mechanism Involving Relief, Precipitation and Chemical Weathering

Following Walker and others (1981), Dessert and others (2001) suggested that the CO_2 injected in the atmosphere by volcanic degassing is particularly well balanced by a feedback mechanism involving CO_2 consumption by chemical weathering reactions and an Arrhenius-type dependency of basalt weathering CO_2 fluxes with temperature.

This study on the Lesser Antilles, as a study case, suggests the existence of another feedback mechanism linking volcanism and climate at geological timescale. Volcanic activity of tropical volcanic islands, by creating relief, is generating high precipitation regimes (due to water-saturated air decompression), thus high runoff and/or infiltration regimes associated with high geothermal gradients lead to high surface and subsurface chemical weathering fluxes and associated CO_2 consumption fluxes. This feedback is probably not specific to the Lesser Antilles and should apply at least at all volcanic arc settings of the tropical zone with mountainous topography in the trade wind belt. A recent study by Schopka and others (2010) from the Philippines indicates similar CO_2 consumption rates to those reported here in the Lesser Antilles. This feedback should also apply, although surface areas are much smaller, to tropical volcanic islands in general (for example, Réunion Island, Louvat and others, 1997). As arc volcanism is a significant source of CO_2 to the atmosphere (Marty and Tolstikhin, 1998), this feedback mechanism may be of importance for the Earth's atmosphere and climate regulation. A difference between the feedback mechanism suggested in this paper and the Arrhenius-controlled feedback is that it is based on a regional increase of the water cycle dynamics rather than on a global temperature effect. Note however that the regulation loop proposed here is also influenced by temperature though the dependence of vapor saturation with temperature according the Clausius-Clapeyron relationship (eq 14). Cold climates should lead to reduced orographic precipitation compared to warm climates, at a given relief. Future studies, extended to other volcanic arc settings will be necessary to assess the relative importance of these two feedback mechanisms. A key process here (that remains to be understood) for making this feedback possible is the non-dilution of dissolved concentrations at high runoff, both in low-temperature and high-temperature water-rock interaction, or chemostatic behavior of rivers.

With regards to the on going debate surrounding the importance of climate versus tectonic uplift on geological CO_2 sequestration (for example Molnar and England, 1990), the study of weathering rates in the Lesser Antilles clearly suggests that both "tectonics" (as a process creating relief and generating high runoff) and "climate" are controlling chemical denudation and associated CO_2 consumption of volcanic arc islands. Our results and the recently published results by Goldsmith and others (2008) Jones and others (2010) and Schopka and others (2010) in the Philippines, show that establishing the weathering budget of tropical volcanic arcs islands and deciphering the controlling parameters is crucial to improve our understanding of the weathering's engine and its global feedback mechanisms.

CONCLUSION

We have reported in this study the major element composition of rivers from three islands from the Lesser Antilles volcanic arc in order to estimate the chemical denudation rates in such settings. The Lesser Antilles are characterized by strong local to regional gradients of relief, precipitation, runoff and bedrock age. The main conclusions from this study are.

1. The rivers of the Martinique, Guadeloupe (Basse-Terre) and Dominica are relatively dilute rivers with a median Total Dissolved Solid value of 130 mg/l. Calculations show that 40 percent (in mass) of solutes are derived from the rocks, 60 percent from the atmosphere (precipitation and atmospheric/soil CO_2). Rivers from the Lesser Antilles are characterized by relatively high dissolved silica concentrations compared to cations. They contain on average 1.8 times more silica than cations (in mass). The main rock weathering agents are carbonic acid (accounting for 70% of the protons available for weathering reactions), sulfuric acid (25% of the protons) and hydrochloric acids (5% of the protons).
2. Elemental ratios of major cations in river waters from the Lesser Antilles are similar to those in the andesitic bedrock within uncertainties. River water is depleted in silica compared to cations. This has important implications for constraining the silicate weathering endmember for rivers draining mixed lithologies in the tropics (for example using inversion techniques).
3. The concentration of solutes derived from weathering reactions in the rivers spanning the runoff gradient are not purely diluted when runoff increases. This illustrates the concept of chemical chemostasis of rivers at a regional scale. The important consequence is that the spatial variability in chemical denudation rates in the Lesser Antilles is imposed by runoff variations and that catchment hydrology is a main driver. The variability of chemical denudation rates is mainly due to runoff variability, which is itself related to topography.
4. Chemical denudation rates (cations and silica) of the different catchments are highly variable and range from 40 $t/km^2/a$ to 430 $t/km^2/a$ with a median value for the largest rivers of 95 $t/km^2/a$. There is no detectable difference between Basse-Terre, Dominica and Martinique. Weathering advance rates average 100 mm/ka for Guadeloupe Island. The CO_2 consumption by rock weathering is variable ranging from 300×10^3 $mol/km^2/a$ to 3500×10^3 $mol/km^2/a$.
5. These values are among the highest chemical denudation rates reported globally and confirm the importance of subduction zone weathering in climatic regulation and oceanic inputs. This conclusion is strengthened when fluxes of dissolved organic matter and subsurface fluxes (discharging directly to the ocean) are taken into account (Rad and others, 2007; Lloret and others, 2010).
6. The controlling factors of chemical denudation rates in the Lesser Antilles appear to be runoff, hydrothermal activity (resulting from infiltrated waters) and the input of volcanic acidity. Runoff is controlled by relief through orographic precipitation and therefore all these factors are related to volcanic activity in general, creating relief, high thermal gradient and degassing of volcanic acids. On Basse-Terre, Guadeloupe, the migration of volcanic activity over the past 3 Ma created a unique natural laboratory of weathering processes along a N-S gradient. Due to the combination of the above factors, higher denudation rates are reported in the most recent terrains where runoff, infiltration, volcanic acidity and contribution of hydrothermal waters are maximum.
7. Our results suggest the existence of a negative feedback capable of stabilizing

atmospheric CO_2 concentrations and therefore climate as follows. The creation of relief in water-saturated air masses increases local precipitation rates (by adiabatic decompression), and thus runoff and or infiltration. It then increases surface, subsurface and hydrothermal weathering rates and consumes the CO_2 (and other acids) released by volcanic activity. This precipitation-related feedback complements with the temperature-related feedback proposed by Dessert and others (2001) for basalt weathering.

8. Our results emphasize the significance of relief as a parameter for generating runoff on mountainous islands of the trade wind belt. Our results illustrate how much the prediction of chemical denudation rates of volcanic rocks in island arc settings will be sensitive to the orographic precipitation regime and thus local relief configuration. The chemical denudation rates are expected to depend on the 3D geometry of the island. In particular, our conclusions caution the use of mean values of chemical denudation rates to compare volcanic island weathering intensities. Mean values (even runoff-weighted) should be taken with great care and instead of mean values, which are topography-dependent, histograms and median values should be utilized.
9. This study highlights the importance of studying catchment hydrology in complement to water chemistry in the high weathering rate regimes of the tropical volcanic arcs. Proper mass budgets imply the design of river observatories to monitor continuously water and chemical fluxes. In the mountainous islands of the trade wind belt, remote monitoring is particularly essential to sample the extreme events. This remains a technological challenge.

ACKNOWLEDGMENTS

This work was supported by the CNRS-INSU though the program Relief de la Terre and by the IPGP program on Potamology. Ph. D. thesis for SR was funded by the Commissariat à l'Énergie Atomique (CEA). Céline Dessert is thanked for discussion. We also thank the team from the Volcanological and Seismological Observatories in Martinique and Guadeloupe (OVSG) particularly Francois Beauducel and Sarah Bazin. Gilbert Hammouya is thanked for assistance in field work around La Soufrière massif. In Dominica, we benefited from the help of Eric Hypolite, director of Forestry, Wildflife and Parks of Dominica and Raphael Joseph of the Environmental Health Office in Dominica. Francois Metivier Anne Le Friand and Georges Boudon are thanked for discussion. Helène Bouquerel and Anne Lise Salomé helped in the field and Francois Capmas is thanked for lab assistance. This paper has benefited from helpful reviews from Damien Calmels, Peter Sak, Josh West, Jens Hartmann and Sigurdur Gislason. This is IPGP contribution 3270.

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