

Chemical weathering in high-sediment-yielding watersheds, New Zealand

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[1] We have determined the chemical erosion yields for fifteen watersheds in New Zealand, ranging in size from 12.2 to 2928 km². These rates, coupled with previously measured physical erosion yields, allow us to compare these two modes of landscape denudation. The physical erosion yields are some of the highest measured in the world. Although in most instances the chemical erosion yields are only a small fraction of the total erosion yields, the absolute values are very high. Our data strongly support the notion that chemical erosion rates are greatly influenced by the yield of physical erosion and that the rapid production of fresh surfaces as a result of high physical erosion rates and subsequent denudation is critical to the high chemical erosion yields observed.

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1. Introduction

[2] Over the past decade, a debate has occurred regarding the ultimate controls on chemical weathering and chemical erosion rates at Earth's surface. Numerous recent works have demonstrated that the control of chemical weathering is directly related to the rates of physical or mechanical erosion, or that enhanced chemical erosion occurs primarily in regimes of the world where mechanical denudation (i.e., erosion) is high [Louvrat and Allègre, 1997; Gaillardet et al., 1999a; Millot et al., 2002]. Yet this tenet continues to be strongly debated. For example, Bluth and Kump [1994], Edmond et al. [1995], Gaillardet et al. [1999a, 1999b], and Anderson et al. [2002] have stressed the importance of physical erosion in determining chemical weathering and this connection between physical and chemical processes is enhanced in active orogenic regions. Others have argued as strongly that the tectonics is a secondary factor [Harris and Mix, 2002] or that there is little coupling between physical and chemical landscape denudation processes [France-Lanord et al., 2002; Mortatti and Probst, 2003].

[3] From a geomorphological point of view, increased relief leads to increased erosion through fluvial incision and mass wasting [Ahnert, 1970; Willett and Brandon, 2002;

Vance et al., 2003]. In general, the net, large-scale erosional potential of a landscape is thought to increase with precipitation, drainage area and slope [Montgomery et al., 2001]. In New Zealand, the highest erosion rates and sediment yields are also associated with the erodibility of the bedrock and climate factors such as rainfall [Hicks et al., 1996]. The extreme orographic precipitation in the western Southern Alps results from New Zealand's maritime location and the westerly atmospheric circulation [Fitzsimons and Veit, 2001]. The western Southern Alps have been subjected to intense fluvial erosion and debris avalanches which have led to the development of highly dissected, steep slopes [Whitehouse, 1988] but of relatively modest topography due to the high erosion rates [Fitzsimons and Veit, 2001].

[4] The combination of friable bedrock and high rainfall can lead to high landslide frequencies and the rapid removal of soil. The continual removal of unconsolidated material exposes bedrock that is more susceptible to chemical weathering. In these environments, soil depths are shallow, drainage density is extremely high, and there is rapid throughput of water [Tonkin and Basher, 1990]. Thus the rapid removal of soils and sediments by mass wasting allows for the production of new material from bedrock weathering. Stallard [1985] suggested that there is an optimal soil thickness for chemical weathering and more recent work has support that notion [Anderson et al., 2002].

[5] Even though a case has been made for the ultimate control of chemical weathering being related to the occurrence of physical erosion, there has been little correlation observed of chemical erosion rates to relief [Gaillardet et al., 1999a]. In addition much of the previous work has been

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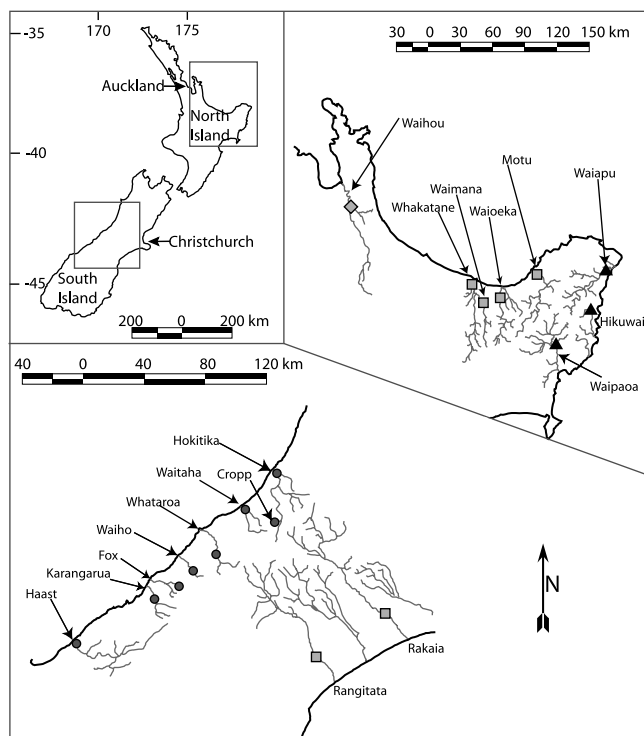


Figure 1. Map of New Zealand with insets showing the location of the East Cape on North Island and of the Southern Alps on South Island. The inset maps show the stream locations sampled for this study. Sampling locations on rivers are indicated by circles for alpine schist lithologies, by squares for greywacke/argillite lithologies, by triangles for weak marine sediments, and by diamonds for tephra/rhyolite lithologies. The same symbols are used for the respective lithologies in Figures 2 and 3. All locations represent single grab samples used for geochemical analysis. Exceptions are locations on the Cropp, Hokitika, and Haast Rivers. On the Hokitika and Haast Rivers, automated samplers were deployed from November 1998 until November 1999, and on the Cropp River the automated sampler was deployed from November 1998 until May 1999. All chemical weathering yields were calculated for the areas upstream of the sampling locations.

done on large river systems that contain a vast diversity of landforms, slopes and gradients.

[6] Herein we present chemical erosion yields determined for fifteen watersheds in New Zealand (Figure 1), including some with the highest known physical erosion yields in the world [Hicks *et al.*, 1996]. These data from both North and South Island watersheds, of diverse geologies, relief/topography and precipitation/runoff, allow us to assess the importance of physical erosion on the rates of chemical erosion (Table 1). In addition, because oceanic high-standing islands such as New Zealand are now recognized as major sources of sediments to the world ocean [Milliman and Syvitski, 1992], these data add to the overall understanding of the factors controlling sediment input to the oceans.

[7] For our purposes, “weathering” is the process of the solubilization and breakdown of rocks and minerals and

“erosion” is the flux of these breakdown products. Chemical erosion is the flux of the dissolved components, while physical erosion is the flux of particulate material. In this paper, we shall compare chemical erosion yields to physical erosion yields (mass per unit area per unit time).

2. Methods

[8] Water samples were collected in new, deionized water (18 M Ω) soaked low-density polyethylene (LDPE) bottles which were rinsed 3 times with river water prior to sample collection. The samples were stored at room temperature in the dark until return to the laboratory for filtration using dedicated and prerinsed polyetherimide funnels and a polycarbonate bell jar, and filtered directly into sample bottles. Samples were filtered through 0.4 μm pore-size NucleporeTM polycarbonate filters, with cation aliquots going into acid-washed LDPE bottles and anion aliquots into 18 M Ω washed LDPE bottles. Collection and cleaning procedures are detailed by Welch *et al.* [1996]. Cation samples were acidified with Ultrex HNO₃ prior to analysis. Anions (Cl⁻ and SO₄²⁻) were determined by ion chromatography (IC) using either a Dionex DX-300 or DX-120 instrument using the methods of Welch *et al.* [1996]. The major cations and Si were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The precision of the IC measurements were $\pm 2\%$ or better, while the precision of the ICP measurements was always $\pm 8\%$ or better, with most better than $\pm 3\%$. HCO₃⁻ concentrations were determined by the difference between Σ cations in equivalents minus Σ anions in equivalents [Lyons *et al.*, 1992]. These are low to relatively low total dissolved solids (TDS), circumneutral pH and noncolored waters for which we have assumed there is little contribution of any other species to alkalinity. Total dissolved solids were calculated as the total of these ions in mg L⁻¹ in each sample. The raw geochemical data for the rivers are given in Table 2.

[9] For the determination of chemical erosion, river water samples (one sample at each location) were collected during base flow conditions, by hand, from South Island, New Zealand in late March and early April 1999. In March 2000 a single water sample was collected at each site during base flow conditions by hand from the rivers of North Island. Between November 1998 and November 1999, series of water samples were collected from the Cropp, Hokitika, and Haast watersheds on South Island. On the Cropp River, 5 base flow samples and 12 storm runoff samples (aggregated to 5 samples to provide sufficient mass for geochemical analysis) were collected between November 1998 and June 1999. On the Hokitika River, 5 base flow samples and 38 storm runoff samples (aggregated to 12 samples) were collected between November 1998 and March 1999. On the Haast River, 10 base flow samples and 41 storm runoff samples (aggregated to 8 samples to provide sufficient mass for geochemical analysis) were collected between November 1998 and November 1999. Our data from the Haast River are very similar to those obtained by previous investigations [Kim *et al.*, 1999; Jacobson and Blum, 2003]. The chemical erosion yields were determined by first subtracting the TDS contribution from precipitation and then multiplying the subsequent TDS values by the mean annual stream water discharge. The TDS values include the dissolved Si concentration. The precipitation

Table 1. Chemical and Physical Erosion Yields and Environmental Data for New Zealand Watersheds Sampled for This Study

Watershed	Physical Erosion Yield, t km ⁻² a ⁻¹ (± Standard Error of Estimate, %) ^a	Chemical Erosion Yield, t km ⁻² a ⁻¹	Percent Chemical	Area Upstream of Spot Sampling Location, km ²	Lithology	Gradient, m km ⁻¹	Precipitation, cm a ⁻¹
<i>South Island Watersheds</i>							
Cropp	32,120 (±12)	442	1	12.2	AS ^b	522	1007
Hokitika	6313 (±25)	145	2	352	AS	38	940
Haast	4500 (±29)	218	5	1020	AS	27	650
Waitaha	10,325 ^c (±32)	480	4	223	AS	60	704
Whataroa	10,325 (±32)	413	4	445	AS	50	792
Rangitata	946 (±26)	93	9	1606	GA ^d	22	230
Rakaia	1981 (±28)	105	5	2808	GA	17.5	300
<i>North Island Watersheds</i>							
Motu	2531 (±16)	152	6	1393	GA	12.5	270
Waipaoa	6810 (±10)	163	1	1580	37% WS ^e	13	160
Hikuwai	14,200 (±40)	344	2	550	WS	12	190
Waiapu	20,520 (±42)	400	2	1559	36% WS	16	240
Waiouka	988 (±38)	80	7	750	GA	18	229
Waimana	660 (±16)	64	9	440	GA	19	212
Whakatane	381 (±29)	101	21	1557	GA	10	160
Waihou	55 (±11)	62	53	1606	T ^f	6	157

^aError in physical yield estimate based on error of estimate from sediment rating curve (as by *Hicks et al.* [2000]).

^bAlpine schist.

^cEstimated using suspended sediment data collected at nearest suspended sediment gauge (on the Whataroa River).

^dGreywacke/argillite.

^eWeak marine sediments.

^fTephya/rhyolite.

contribution was estimated by assuming that all the Cl⁻ present in the samples was due to precipitation and then using sea salt ratios of Cl to the other major elements to calculate their respective contributions from precipitation. The exception to this was SO₄²⁻, for which we used twice the seawater SO₄²⁻:Cl⁻ ratio, as suggested by *Stallard and Edmond* [1981] for Amazon basin rainfall. We acknowledge that this is a conservative approach and that the actual TDS from chemical erosion may be greater than our precipitation-corrected values, as some of the Cl⁻ present in the stream water may indeed be due to weathering.

[10] In addition to the calculation of chemical erosion for each watershed, we have also determined the silicate yields and the total cation yields from silicate chemical weathering only (Table 3). The silicate yields were determined in a similar manner as were the total chemical erosion yields for each watershed, except just using our dissolved Si data from each river. The total cation yields from silicate chemical weathering were compiled using the techniques of *Gaillardet et al.* [1999b], in which a Ca:Na ratio of 0.35 was used to determine how much of the total Ca²⁺ is derived from silicate weathering. Any Ca²⁺ in excess of that molar ratio is interpreted to be from CaCO₃ dissolution and the “corrected” Ca²⁺ values are summed along with the precipitation-corrected Na⁺, K⁺ and Mg²⁺ to calculate the yield of these cations from silicate weathering alone. The gradient of each watershed (Table 1) was calculated simply by dividing the watershed length (i.e., the long axis of the watershed) by its elevational change (total relief).

3. Representativeness of the Data

[11] Except for the Hokitika and Haast Rivers (as noted above) the chemical weathering fluxes are computed using mean annual discharge and our chemical data from each

river. How representative are the other samples? In order to answer this question, we must first examine the hydrology of these rivers. *Duncan* [1992] has classified the rivers draining the Southern Alps as ones having slightly variable flow (as defined by the coefficient of variation of the flow). These rivers drain high-rainfall regions, have high base flow, but also have frequent large flooding events. The average flow of the Hokitika is 101 m³ s⁻¹. Our data set ($n = 12$) includes samples taken at flows as large as 787 m³ s⁻¹ and as low as 43 m³ s⁻¹. The precipitation corrected TDS of these samples are 34.3 and 48.4 mg L⁻¹, respectively, a difference of 29%. The average difference of the TDS between base flow and storm flow samples is 25%. We can also compare concentration values collected at different times to evaluate the representativeness of our data. When we compare our mean values to the mean values of *Kim et al.* [1999] which they obtained from two different times (November 1996 and February 1997) for the Haast River, our Ca²⁺ value of 244 μmol kg⁻¹ is within their range of 224 and 273 μmol kg⁻¹. Our Si value of 57 μmol kg⁻¹ is also similar to their two values of 76 and 59 μmol kg⁻¹, respectively. Our Na⁺ value is slightly higher, however (71 vs. 47 and 54 μmol kg⁻¹). Given this information, we believe that our fluxes for the South Island rivers are accurate to ±25–30%.

[12] The river systems in the northeast portion of the North Island have what *Duncan* [1992] terms intermediate variable flow, with higher coefficients of variation of their mean annual flow. Because we have no other solute data to compare to the flow records, it is much more difficult to evaluate the representativeness of our chemical fluxes and hence our chemical weathering yields. *Close and Davies-Colley* [1990] have pointed out that all New Zealand rivers, even at base flow conditions, have lower TDS values compared to river systems globally. However, the North

Table 2. Dissolved Load of New Zealand Rivers^a

River	Sample #	Sampling Date	Mean Flow, m ³ /s	TDS, µg/kg	Na, µmol/kg	K, µmol/kg	Ca, µmol/kg	Mg, µmol/kg	Cl, µmol/kg	Si, µmol/kg	NO ₃ , µmol/kg	SO ₄ , µmol/kg	HCO ₃ , µeq/kg
<i>South Island Rivers</i>													
Hokitika	1/1	7 Dec. 1998	483	31,790	44	62	119	18	29	41	0.0	22	309
Hokitika	1/2–3	19 Dec. 1998	572	24,674	34	47	93	14	21	33	0.0	12	249
Hokitika	1/4–5	20 Dec. 1998	523	26,259	34	55	99	13	25	34	0.0	14	260
Hokitika	1/6–7	29 Dec. 1998	511	25,313	33	60	91	11	18	32	0.0	13	254
Hokitika	1/8–9	30 Dec. 1998	523	25,929	33	61	94	12	19	36	0.0	14	258
Hokitika	1/10–13	17 Jan. 1999	537	24,442	31	54	90	11	19	32	0.0	12	245
Hokitika	1/14	31 Jan. 1999	517	34,292	43	64	136	18	31	38	8.2	26	323
Hokitika	1/15–26	31 Jan. 1999	787	34,285	32	69	137	18	20	33	4.8	19	347
Hokitika	1/27–29	5 March 1999	487	26,995	38	46	109	12	29	33	1.4	17	262
Hokitika	1/30–38	6 March 1999	638	24,116	30	51	92	11	18	29	2.1	11	244
Hokitika	1/39	30 March 1999	670	23,959	95	29	67	22	78	50	0.0	14	196
Hokitika	1/40	31 March 1999	372	35,106	47	38	154	15	20	51	0.0	26	350
Hokitika	1A	4 Nov. 1998	97	39,434	59	33	175	17	26	65	0.0	31	387
Hokitika	1B	23 Dec. 1998	121	37,000	53	30	168	15	23	55	0.0	33	360
Hokitika	1C	26 Jan. 1999	43	48,401	68	39	223	18	26	62	0.0	44	476
Hokitika	1D	4 March 1999	52	49,104	71	43	222	18	25	63	0.0	42	487
Hokitika	1E	25 March 1999	62	45,590	61	41	207	18	23	62	0.0	37	454
Fox		1 April 1999		53,721	35	56	269	26	7	26	0.5	104	463
Haast	2.1	2 April 1999	361	46,964	56	32	220	23	26	61	0.0	37	473
Haast	2.2	2 April 1999	361	50,864	48	22	254	25	18	54	1.2	43	521
Haast	2.3	2 April 1999	361	79,581	215	30	320	54	102	80	1.0	34	822
Haast	2.4	2 April 1999	361	28,706	36	13	136	14	14	45	0.0	26	283
Haast	NZ 3G	21 July 1999	67	65,953	60	343	38	31	68	0.0	53	684	
Haast	NZ 3I	21 Sep. 1999	116	63,000	51	44	301	35	31	59	0.0	18	700
Haast	NZ 3J	17 Nov. 1999	1889	29,332	29	43	134	14	31	35	0.0	52	233
Karangarua		1 April 1999		28,142	60	39	100	17	36	76	0.0	30	237
Waiho		1 April 1999		81,516	180	76	349	26	41	39	1.9	65	833
Waitaha		1 April 1999		61,881	59	81	286	20	30	59	1.7	55	612
Whataroa		1 April 1999	189	43,649	45	29	218	11	17	43	2.5	33	448
Rakaia		4 April 1999		44,454	69	20	198	24	13	85	3.5	38	440
Rangitata		4 April 1999	74	57,005	122	24	212	57	31	124	53.2	49	504
Cropp	NZ 2B	16 Jan. 1999	3.4	33,482	26	57	154	8	24	30	0.0	30	323
Cropp	NZ 2D	2 May 1999	1.18	46,974	42	63	224	12	34	42	0.0	44	454
<i>North Island Rivers</i>													
Motu (headwaters)	NZ00-1	15 March 2000	4.3	71,362	265	43	185	63	128	367	0.0	52	570
Waipaoa	NZ00-2	16 March 2000	32	370,080	1282	80	1485	266	266	187	0	911	2775
Mangatu	NZ00-3	16 March 2000	2.96	330,463	676	65	1622	125	155	171	1	576	2927
Uawa	NZ00-5	17 March 2000	2.41	30,770,727	369,730	1581	2811	7468	72956	210	0	5272	308368
Hikuwai	NZ00-6	17 March 2000	1.17	526,725	2652	86	1633	512	470	150	0	1405	3747
Makarika (Mata tributary)	NZ00-7	17 March 2000		823,718	7569	106	2234	265	8115	160	0	796	2966
Makatote (Mata tributary)	NZ00-8	17 March 2000		296,720	863	59	1335	180	271	176	0	869	1945
Mata	NZ00-9	17 March 2000	10.0	310,220	882	55	1372	165	247	159	0	541	2681
Mangaporo (Waipapu tributary)	NZ00-10	17 March 2000		187,168	571	49	796	113	119	113	0	439	1442
Waipapu	NZ00-11	17 March 2000	20.4	226,758	831	48	881	165	218	157	0	523	1706
Motu	NZ00-12	17 March 2000	32	85,091	243	34	309	70	133	234	0	90	724
Waioeke	NZ00-14	18 March 2000	8.6	68,922	243	34	193	74	145	292	0	57	552
Waimana	NZ00-15	18 March 2000	7.4	82,469	274	43	224	96	155	386	0	78	646
Whakatane	NZ00-16	18 March 2000	8.4	97,324	355	55	249	107	191	449	0	63	803
Waihou	NZ00-17	19 March 2000	26	91,183	385	110	67	57	166	1185	0	16	545
Waihou	NZ00-18	19 March 2000	26	97,162	458	116	81	73	212	1051	7	27	609
Waihou	NZ00-19	19 March 2000	26	102,087	480	125	88	77	225	1077	4	33	640
Waihou	NZ00-20	19 March 2000	26	116,925	478	91	346	161	343	252	0	401	440

^aEmpty cells indicate that geochemical data were not collected or that the stream is not gauged.

Island rivers have higher TDS values than the South Island rivers, suggesting that during storm flow events the North Island systems may undergo more rainfall dilution than experienced in the Southern Alps rivers. This would, in turn, decrease the chemical erosion yields greater than the 25–30% estimated above for the South Island systems. Using the base flow solute data of *Close and Davies-Colley* [1990], we calculated precipitation-corrected

TDS for base flow samples from the Waimana ($n = 6$), the Waipaoa ($n = 2$), and the Waioeke ($n = 2$), three North Island rivers which we also sampled. The average TDS of *Close and Davies-Colley's* [1990] base flow samples collected in 1987 were 16%, 63%, and 102% higher than our grab samples, respectively. Thus our chemical weathering yields from the North Island rivers may be underestimates at these base flows.

Table 3. New Zealand Watersheds Silicate Chemical Erosion Weathering Calculated From Cation Yields and Calcium Carbonate Weathering Yields

New Zealand Watershed	Silicate Weathering Yield, kmol ha ⁻¹ a ⁻¹	Carbonate Weathering Yield, kmol ha ⁻¹ a ⁻¹
Hokitika	4.4	5.9
Haast	3.6	9.7
Cropp	9.2	21.5
Waitaha	11.5	22.0
Whataroa	7.7	20.2
Rangitata	3.5	3.0
Rakaia	2.9	4.2
Waipaoa	0.81	0.51
Hikuwai	2.5	0.6
Waiapu	1.9	1.2
Motu	5.3	3.3
Waioeke	3.4	2.0
Waimana	2.8	1.5
Whakatane	4.7	2.1
Waihou	3.1	1.9

[13] The physical erosion yields for these watersheds have been determined previously [Hicks and Griffiths, 1992; Hicks *et al.*, 1996] from gauged suspended sediment loads, and the values used here derive from the most recent analysis of the data set. The flow and suspended sediment load data are long-term records that range in length from 7 years for the Waitaha to 47 years for the Whakatane. These multiyear averages have been used to determine physical erosion yields. We consider these data to be of the highest quality and extremely representative of the yields from these watersheds. The standard error of the estimates of the suspended solids, calculated in the manner of Hicks *et al.* [2000] range from a low value of $\pm 10\%$ for the Waipaoa to $\pm 40\%$ for the Hikuwai. We have used these same error estimates for the physical erosion yields calculated from the suspended matter data.

4. Results

[14] Our calculated chemical erosion yields (Table 1) and the previously determined physical erosion yields for each of these watersheds [Hicks and Griffiths, 1992; Hicks *et al.*, 1996] are some of the highest known (i.e., 32,120 t km⁻² a⁻¹ for the Cropp). The range among the physical erosion yields is large, with differences of a factor of ~ 600 (Table 1). Because of the lack of storage within the hillslopes and flood plains for physical weathering products, essentially all the material is transported rapidly from its original location and removed from the basins. Hicks *et al.* [1996] demonstrated that the sediment yields in New Zealand are primarily controlled by rainfall in the South Island, but by lithology on North Island. For example, for a given rainfall amount, sediment yields from watersheds underlain by Tertiary marine mudstones (such as the Waipaoa, Hikuwai and Waiapu) are 100 times those in other rock terrains. In addition to the fissile bedrock found in the mudstone watersheds of the East Cape, the Waipaoa watershed has been subjected to extensive anthropogenic alterations. Deforestation for agriculture by the Maori began there approximately 650 years ago [Gomez *et al.*, 1999] but widespread land clearing has only occurred since about 1820 [Hicks *et al.*, 2000]. Only 3% of the basin is currently forested and it is

estimated that the erosion rate has increased fivefold to tenfold since European deforestation [Orpin *et al.*, 2002]. The conversion of forest to pasture in this region of North Island has decreased the size of a rainfall event required to trigger slope failure which has led in turn to greater landslide activity [Brooks *et al.*, 2002].

[15] Thus for New Zealand as a whole, there is no rainfall–sediment yield relationship generally, but there is a relationship within each lithology. Greywacke/argillite:alpine schist:soft marine sediments produced a relationship such that sediment production can be expressed as a power law function of annual precipitation where $S = aP^{2.3}$ (where S is sediment yield in t km⁻² a⁻¹ and P is mean annual precipitation in mm) and the coefficient a varies 15:25:900 for the respective lithologies mentioned above (greywacke/argillite:alpine schist:soft marine sediments) [Hicks *et al.*, 1996]. The relationships between lithology and physical erosion can easily be explained. The highest sediment yields occur in the watersheds underlain by the alpine schist (AS) and the Tertiary marine sediments (WS) (Table 1). The high yields from the alpine schist relate to the frequency of extremely high intensity rainfall events in this region and to a lesser degree, to the fissile nature of some of the schist [Hicks and Griffiths, 1992; Hicks, 1999]. The high sediment yields from the East Cape of North Island are related to the soft and unconsolidated nature of the bedrock [Hicks and Griffiths, 1992]. Hicks *et al.* [1996] have speculated that “tectonics” may also be an important factor controlling sediment yields (i.e., physical erosion) because on both North and South Islands, the watersheds with the highest yields tend to cluster along the boundary of the Australian and the Pacific plates. The maximum uplift rates in the Southern Alps (South Island) and in the East Cape (North Island) are within a factor of 2–3 of each other, at 4–12 mm yr⁻¹ [Pillans, 1986; Basher *et al.*, 1988].

[16] Dadson *et al.* [2004] have recently established that earthquake-triggered landslides greatly increased the sediment flux to rivers in Taiwan. The seismic weakening of the slopes caused increased sediment movement during subsequent high rainfall events. This process probably takes place as well in the Southern Alps, which are seismically active [Fitzsimons and Veit, 2001]. Because there is such little storage in these regions, any mass movement of soil material by landsliding is rapidly lost from the hillsides [Hovius *et al.*, 1997]. The entrainment and downstream movement of these sediments can lead to channel overloading and increased stream sediment yields [Korup *et al.*, 2004].

[17] Our calculated chemical erosion yields range from 62 to 480 t km⁻² a⁻¹ (a variation of approximately eightfold), a much narrower range than for the physical erosion yields discussed above. In general, the chemical erosion yields follow the sediment yields in that the lowest chemical erosion yields were in the greywacke/argillite lithologies (Table 1). There is a general increase in chemical erosion yields with precipitation, but this increase is clearly lithologically influenced (Figure 2). There was a general correlation between chemical erosion yields and physical erosion yields (Figure 3). Note that the same flow records were used for calculations of both physical and chemical erosion yields. As also seen in the earlier work of Hicks *et al.* [1996], there are lithologic differences in physical

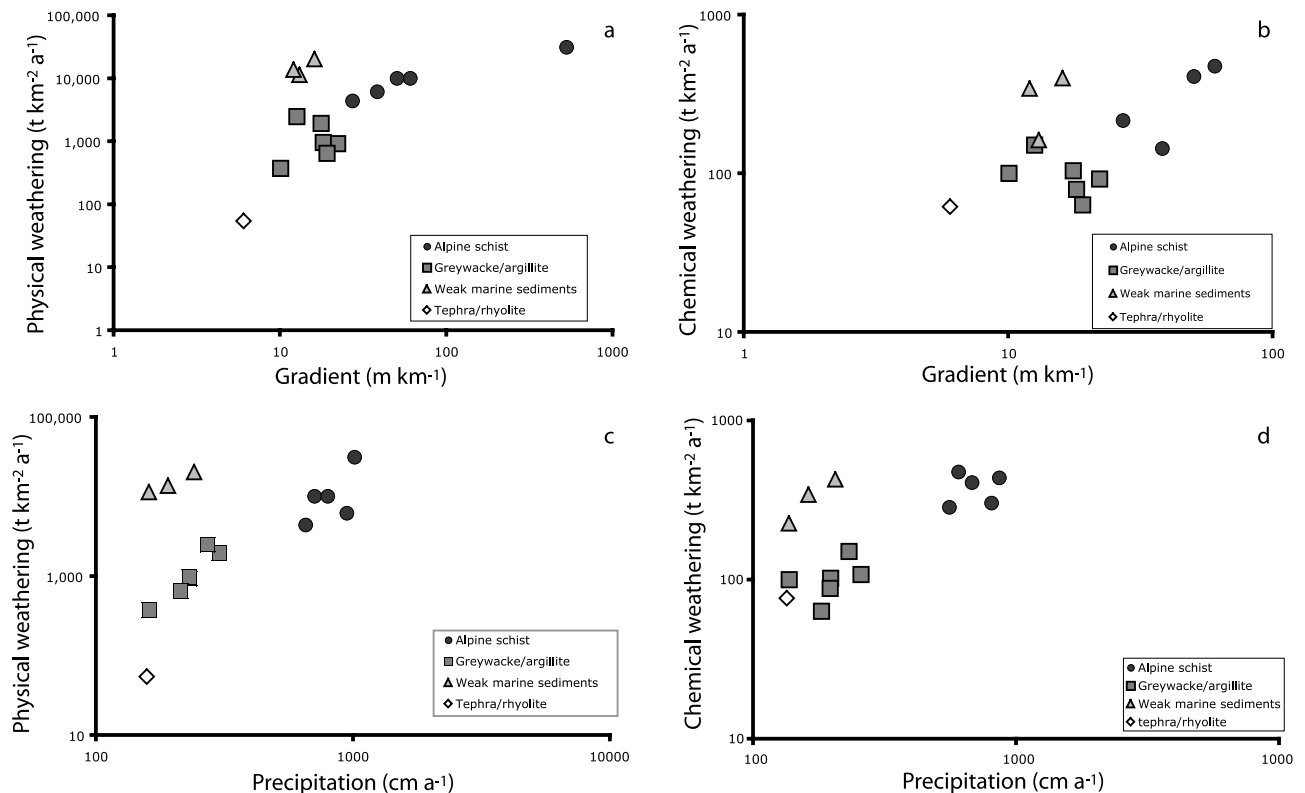


Figure 2. Chemical and physical weathering in New Zealand watersheds as functions of watershed gradient or amount of annual precipitation in the watersheds. Symbols used to represent different lithologies are the same as used in Figure 1. (a, b) Chemical and physical weathering yields in New Zealand watersheds of different geologies. Chemical weathering yields were calculated using geochemical analysis of samples from locations indicated in Figure 1 and use the same symbols as in Figure 1. Physical weathering yields were calculated using the most recent analysis of data from *Hicks and Griffiths* [1992] and *Hicks et al.* [1996] of samples collected at NIWA gauging stations and the watershed areas upstream of the gauges. (c, d) Physical and chemical weathering in New Zealand watersheds of different geologies as a function of the annual precipitation. (Physical weathering data are from *Hicks and Griffiths* [1992] and *Hicks et al.* [1996].)

erosion for a given chemical erosion yield (Figure 3). The greywacke/argillite and alpine schist terranes yield less sediment per given chemical yield.

5. Discussion

[18] Chemical and physical erosion yields show little relationship to watershed gradient (Figures 2a and 2b). The gradient effect is more pronounced for physical erosion in the Southern Alps at gradients >40 m km⁻¹. However, the general steepness of the watershed does influence chemical erosion yields as shown by a closer look at the variation of these yields in the Hokitika drainage along its flow path. The Cropp is one of the highest elevation (gauge at ~ 860 m) subwatersheds in the Hokitika and it has a chemical erosion yield of 442 t km⁻² a⁻¹, while the Hokitika River at a location ~ 33 km upstream from its mouth at an elevation of ~ 140 m has a yield of 307 t km⁻² a⁻¹, and the entire Hokitika watershed has a yield of 145 t km⁻² a⁻¹. Clearly the addition of the lower lying areas of the watershed reduces the overall chemical erosion yield. In the Cropp, the smallest and the steepest watershed we studied, soils are thinly developed, particularly on the steepest slopes. Despite

the thin soils, most of the basin is vegetated by forest, subalpine scrub or alpine grasslands, depending upon elevation. The vegetation does not significantly affect the water balance through transpiration in the higher-elevation regions due to the very high rainfall amounts, perpetual saturation, steep slopes and continual runoff [*Chinn, 1979; Weingartner and Pearson, 2001*]. The maximum age for the postglacial land surfaces has been determined to be $10,250 \pm 150$ years BP, with 2370 ± 70 years BP determined as the minimum age for deglaciation in the Cropp watershed [*Basher et al., 1988*]. There also, mass wasting is continuous and the mean residence time of the soils is thought to be as little as 100 – 200 years [*Basher et al., 1988*]. Strong orographic forcing and the very high physical erosion yields help to attain a steady state topography balancing the uplift [*Fitzsimons and Veit, 2001; Willett, 1999*].

[19] In the East Cape region of North Island (Figure 1), in the weakly held marine sediments, the physical erosion yields are greater than the uplift rates in the Waipaoa, suggesting that the landscape is reequilibrating to a change in climate [*Berryman et al., 2000*]. In the Southern Alps of South Island, landsliding and rapid soil loss continually

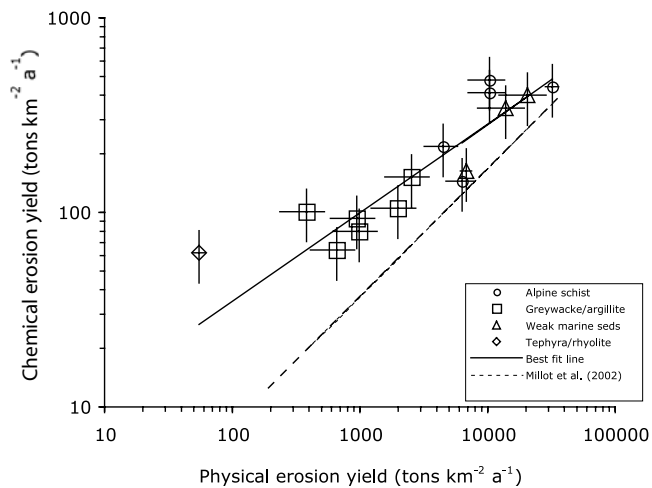


Figure 3. Plot of chemical and physical denudation rates and the best fit line for watersheds hosted in alpine schist, greywacke/argillite, and weak marine sediments. The best fit line shown through the data was calculated omitting the point from the tephra/rhyolite watershed. The equation of the line shown is $C = 3.89S^{0.465}$, with an r^2 of 0.822. If the one point in the tephra/rhyolite watershed is included, then the equation of the best fit line through all the data is $C = 8.91S^{0.367}$, with an r^2 of 0.764. Also shown is the regression line determined by *Millot et al.* [2002] for rivers from the Canadian shield. The error bars shown are $\pm 30\%$ for the chemical weathering yields, the maximum likely uncertainty on the chemical yields, as discussed in the text. The error bars on the physical weathering yields (\pm the standard error of the measurement) are given in Table 1 and are based on the most recent analysis of the suspended sediment ratings curves, following the method of *Hicks et al.* [2000].

supply fresh mineral surfaces for chemical weathering [*Tonkin and Basher*, 1990; *Hovius et al.*, 1997]. On North Island, gully erosion and shallow landsliding, exacerbated by deforestation, transport soils rapidly to riverine floodplains [*Gomez et al.*, 1999; *Hicks et al.*, 2000]. These processes allow ample water through the thin soils, greatly enhancing the chemical erosion yields. High rainfalls alone, however, do not lead to high chemical erosion yields. Over time, the material undergoing weathering would be depleted of easily weatherable cations unless they are replaced [*Stewart et al.*, 2001]. The equally rapid removal of weathering residue, leaving fresh bedrock surfaces, is the key to the high chemical erosion yields in these New Zealand watersheds.

[20] We believe that the correlations between physical and chemical weathering rates result from the following processes. The rapid loss of soils from the landscape continually supplies fresh mineral surfaces to be weathered. Little development of the soil profiles occurs at higher elevations like the Cropp watershed [*Tonkin and Basher*, 1990]. In addition, evapotranspiration affects the water balance very little in the high-elevation regions [*Chinn*, 1979] due to the very high rainfall amounts. In addition, the drainage density on the steep, rectilinear slopes is extremely high [*Tonkin and Basher*, 1990]. The small percentage of water loss via transpiration and the rapid throughput of

water through the thin soils increases the thermodynamic affinities of weathering reactions [*White and Blum*, 1995]. Although thin soils usually have less moisture retention within the soil profiles and hence lower weathering rates [*White and Blum*, 1995], in the higher elevations of the Southern Alps this is compensated for by such extreme rates of precipitation that the soils are continuously saturated, as well as continuously flushed [*Chinn*, 1979; *Weingartner and Pearson*, 2001]. So we hypothesize that these high chemical weathering yields are due to a combination of a continuous supply of fresh, easily weatherable mineral surfaces via enhanced erosion and the presence of an endless supply of corrosive, dilute precipitation in contact with the fresh minerals.

[21] Using the approach of *Millot et al.* [2002], we have represented the relationship between physical and chemical erosion yields (yields expressed as $t\ km^{-2}\ a^{-1}$) as a power function (Figure 3), with chemical erosion yield, C , given by $C = 3.9S^{0.47}$. This means that a factor of ten increase in physical erosion will result in a factor of 2.9 increase in chemical erosion. This relationship was determined using the data from the watersheds hosted in the alpine schist, the greywacke/argillite and the weak marine sediments. The one point from the volcanic watershed was omitted, as it does not fit the relationship as well. If it is included, the slope is only slightly different and a tenfold increase in the physical weathering rate would result in a 2.4-fold increase in the chemical weathering rate. *Millot et al.* [2002] determined for a number of the granitic and basaltic watersheds they studied that chemical erosion was described as $C = 0.39S^{0.66}$ where a tenfold increase in physical weathering yield would increase the chemical weathering yield by a factor of 4.6. Their yields were determined in larger watersheds of igneous rocks where the erosion yields were generally lower than those we determined for New Zealand watersheds. The difference between their results and ours may suggest that there is some critical residence time either in soils or floodplains where chemical erosion is enhanced but cannot go above a certain limit. Lower physical erosion rates imply a longer residence time for the soils/sediments that in turn leads to lower chemical erosion rates. This could be due either to a change in mineralogy (i.e., conversion of primary minerals to weathering product minerals such as clays) or to reduced chemical weathering due to saturation state effects. Clearly, storage should increase the extent of chemical weathering of freshly produced bedrock particles, but the rapid transport and loss of these materials minimize the production of soluble products.

[22] The Waiho and the Fox Rivers are the two most extensively glacier dominated of these watersheds, with the Fox River originating from the Fox Glacier and the Waiho River from the Franz Josef Glacier. These rivers can be compared to the nearby Waitaha River, a watershed of similar size, which has several small cirque glaciers in its headwaters [*Hicks et al.*, 1990] but only 1.5% of its total area glacierized. All three watersheds have similar lithology, as they are located within the Haast schist. The Waiho and Fox rivers have lower Si:cation ratios than does the Waitaha (Table 2) suggesting that Si weathering rates are lower in the glacier covered catchments as previously shown by *Anderson et al.* [1997, 2000] and *Hodson et al.* [2002]. However, the precipitation-corrected K:Na ratios of all three

Table 4. Weathering Yields in Other Locations

Location	Physical Erosion Yield, t km ⁻² a ⁻¹	Chemical Erosion Yield, t km ⁻² a ⁻¹	Percent Chemical
Sierra Nevada ^a	77–680	3–110	3–29
Brahmaputra ^b	3450	289	8
Ganga ^b	2500	245	9
Congo ^c	5	8	62
Loire ^d	8	14	64

^aRiebe *et al.* [2001].^bGaly and France-Lanord [2001].^cGaillardet *et al.* [1995].^dGrosbois *et al.* [2000].

rivers vary greatly. The Fox and the Waitaha have very similar ratios. The average precipitation-corrected K⁺ value for all the rivers draining the Southern Alps to the west is 43 μmol kg⁻¹, but the Fox and the Waiho are 56 μmol kg⁻¹ and 75 μmol kg⁻¹, respectively. We have also analyzed the Fox water for its dissolved strontium isotopes. The ⁸⁷Sr/⁸⁶Sr ratio for Fox water is 0.709724, while ratios from the nearby nonglaciated Karangarua, Whataroa and Hokitika Rivers were 0.70931, 0.71083 and 0.711238, respectively. This suggests that little preferential weathering of biotite is taking place in the Fox River, in contrast with other glacierized watersheds [Anderson *et al.*, 1997]. It is likely that in these glacierized watersheds, such as the Fox, the Sr originated from enhanced carbonate mineral weathering as suggested by Jacobson *et al.* [2003], as the Waiho does have the highest precipitation-corrected Ca²⁺ concentration of any of the Southern Alps rivers (Table 2). Thus all the information gathered to date from glaciated watersheds indicates enhanced CaCO₃ dissolution when compared to nonglaciated watersheds [Anderson *et al.*, 1997, 2000; Jacobson *et al.*, 2003]. The Fox River is not currently gauged but the Waiho River is gauged. The chemical erosion yield from the Waiho watershed is 1190 t km⁻¹ a⁻¹, the highest we have observed and ~2.5 times that of the Waitaha. The physical erosion rate of the Waiho watershed is estimated to be 10,325 t km⁻¹ a⁻¹ (D. M. Hicks, unpublished data). Thus the Waiho system has the highest ratio of chemical to physical erosion (11.5%) of any of the rivers in the Southern Alps, including the rivers draining the eastern slopes. These data suggest that the glacierized watersheds may produce the highest chemical weathering fluxes, as previously demonstrated by Sharp *et al.* [1995], but much of this, as mentioned above, is undoubtedly from carbonate weathering.

[23] The physical and chemical erosion yields from these New Zealand watersheds can be compared to yields from various landscape types and ages (Table 4). Our chemical erosion yields are some of the highest ever reported, orders of magnitude higher than continental averages [Garrels and Mackenzie, 1971] and comparable to those of the Ganga and Brahmaputra. In general, they are two orders of magnitude greater than larger rivers draining geologically older and more subdued terrains such as the Loire and Congo (Table 4). In addition, even though the absolute values of chemical erosion are extremely high in many of these New Zealand watersheds, the percentage that chemical erosion constitutes of the total denudation is small, with chemical erosion consisting of only ~1% of the total material loss in the Cropp watershed, for instance. In general, only in the

greywacke/argillite drainages are the chemical erosion yields greater than 5% of the total yield (Table 1). In the greywacke/argillite or tephra/rhyolite watersheds of lower elevation or of larger area (i.e., the Whakatane and the Waiho) the chemical erosion yields are more than 20% of the total erosion yield. In addition, because the Whakatane watershed is dominated by tephra and rhyolite, the enhanced chemical erosion is due in part to a more weatherable rock type dominating the watershed. The reason that the greywacke/argillite and alpine schist watersheds yield less sediment per given chemical yield is unknown but it could be due to differences in mineralogy and rock type, or due to the lesser cohesion of the Tertiary marine sediments.

[24] The chemical erosion yields in these New Zealand watersheds are higher than those reported for other active margin areas such as the west coast of the USA where yields of 21–98 t km⁻² a⁻¹ have been reported [Dethier, 1986; Phillips and Rojstaczer, 2001]. Total cation yields from silicate chemical weathering only (Table 3) for some of the watersheds on the western slope of the Southern Alps are 2–3 times higher than for small watersheds within the Himalaya, which range from 1.02 kmol ha⁻¹ a⁻¹ for the Lirang watershed to 3.8 kmol ha⁻¹ a⁻¹ for the Bore watershed [West *et al.*, 2002].

[25] Although the chemical erosion fluxes are high, for the most part the silicate fluxes are relatively low (Table 3). These data are supported by recent work by Jacobson *et al.* [2003] on South Island streams and rivers and by our own calculations (Table 3) indicating that chemical weathering of CaCO₃ is a major process in these watersheds even though the CaCO₃ content of the rocks is small. Much recent work in other regions has demonstrated unequivocally that the dissolution of CaCO₃ in igneous and metamorphic terrains is an important process [Blum *et al.*, 1998; White *et al.*, 1999; Horton *et al.*, 1999; Anderson and Dietrich, 2001]. If we assume that the high Ca²⁺ fluxes come from nonstoichiometric weathering of plagioclase (Ca released at a faster rate relative to Na than the Ca:Na ratio of the mineral [Staufer and Whittchen, 2002]) instead of from CaCO₃ [Staufer and Whittchen, 1991], the silicate chemical erosion yields would be considerably higher. The highest ratios of Si weathering to chemical erosion yield occur in the greywacke/argillite watersheds, but there is no correlation between these. The low Si to total cation flux ratios indicate these are superficially weathered systems [Huh and Edmond, 1999], which also emphasizes the importance of physical erosion and the short residence times of soils and sediments in these environments. The Si yields from these New Zealand watersheds are within the range of values from the western USA, yields which vary between 2.4 and 15.3 t km⁻² a⁻¹ [Dethier, 1986; Anderson *et al.*, 2002].

[26] Tectonics and lithology have been argued previously as the governing factors in determining CO₂ uptake [Edmond and Huh, 1997; Huh and Edmond, 1999]. Only silicate weathering affects long-term CO₂ levels. Net CO₂ fluxes related to chemical weathering have been shown to be threefold greater in orogenic zones than in stable basement regions [Huh and Edmond, 1999]. However, global models to evaluate CO₂ fluxes via silicate weathering have generally focused on large river systems. We have calculated the average basin-scale CO₂ consumption rates in

Table 5. Silicate Chemical Yields and CO₂ Consumption ($\bar{\text{O}}\text{CO}_2$) Based on Silicate Weathering From New Zealand Watersheds

	H ₄ SiO ₄ Yield, t km ⁻² a ⁻¹	CO ₂ Flux, × 10 ³ moles km ⁻² a ⁻¹
<i>North Island Streams</i>		
Waipaoa	2.4	170
Hikuwai	4.1	292
Motu	13.2	940
Waioeke	11.1	790
Waimana	9.7	690
Whakatane	15.1	1074
Waihou	4.7	336
Waiapu	8.0	570
<i>South Island Streams</i>		
Hokitika	4.2	296
Cropp	11.7	832
Haast	7.0	500
Whataroa	11.8	840
Waitaha	13.3	946
Rangitata	5.9	418
Rakaia	5.8	409

moles km⁻² a⁻¹ resulting from alumino-silicate weathering. This annual consumption rate is designated $\bar{\text{O}}\text{CO}_2$ by Edmond and Huh [1997] and is calculated as twice the dissolved Si yield from silicate weathering only (i.e., $\bar{\text{O}}\text{CO}_2 = 2\bar{\text{O}}\text{Si}$). We adopt their terminology (Table 5). For the Hokitika, Cropp, Haast, Whataroa and Waitaha, the streams draining the western slope of the Southern Alps, the basin-scale average $\bar{\text{O}}\text{CO}_2$ is 683×10^3 moles km⁻² a⁻¹. For the Rangitata and Rakaia, the longer streams draining the eastern slopes of the Southern Alps, the basin-scale average $\bar{\text{O}}\text{CO}_2$ is 414×10^3 moles km⁻² a⁻¹. For the Waihou, Whakatane, Waimana, Waioeke and Motu, the North Island streams draining the weak sedimentary rocks, the basin-scale average $\bar{\text{O}}\text{CO}_2$ is 344×10^3 moles km⁻² a⁻¹. For the Waipaoa, Hikuwai and Waiapu, the North Island streams draining the greywacke/argillite, the basin-scale average $\bar{\text{O}}\text{CO}_2$ is 874×10^3 moles km⁻² a⁻¹. These values are similar to those calculated for rivers from the Andes ($220\text{--}1000 \times 10^3$ moles km⁻² a⁻¹) and are generally higher than those for the Himalayan rivers ($100\text{--}320 \times 10^3$ moles km⁻² a⁻¹), shield/basement rivers ($15\text{--}555 \times 10^3$ moles km⁻² a⁻¹) determined by Edmond and Huh [1997] and for tributaries of the Amazon [Mortatti and Probst, 2003]. Recently Dalai et al. [2002] determined CO₂ drawdown via weathering during the monsoon season in the Himalaya to be as high as $400\text{--}700 \times 10^3$ moles km⁻² a⁻¹. Clearly many of the New Zealand watersheds have very high CO₂ consumption rates when compared to other systems. Thus even though the Si weathering in these watersheds is a small fraction of the total weathering, the high-elevation Southern Alps watersheds and the greywacke/argillite watersheds have high CO₂ consumption rates.

[27] If our data are combined with those of Dethier [1986] and Anderson et al. [2002], it is clear that CO₂ consumption via chemical weathering associated with island arcs and oceanic-continental plate boundaries is higher than in most other geological environments. Particularly, the weathering of volcanic rocks produces high amounts of dissolved Si [Dethier, 1986] and hence higher CO₂ consumption

[Louvat and Allègre, 1997]. Although the chemical erosion of, and hence CO₂ consumption by, basaltic terrain is generally high, e.g., $580\text{--}2540 \times 10^3$ moles km⁻² a⁻¹ for the Deccan Traps [Dessert et al., 2001], for active tectonic areas with steep slopes and high rainfall the CO₂ consumption is even higher, e.g., $1300\text{--}4400 \times 10^3$ moles km⁻² a⁻¹ for Réunion Island [Louvat and Allègre, 1997]. Yet the influence of physical erosion on high chemical erosion, even in basaltic terrain, cannot be overemphasized [Louvat and Allègre, 1997]. These data would suggest that island arc settings such as Indonesia and the Philippines with a higher percentage of their landscape covered by volcanic rocks would be important regions of chemical erosion and CO₂ consumption.

[28] The rapid removal of soils minimizes soil thickness and maximizes water through flow, and hence contact with fresh mineral surfaces. This enhances chemical weathering, as the accumulate of solutes in soil solutions may significantly retard weathering [White and Blum, 1995]. The geochemistry of the particles being eroded from these tectonically active environments demonstrates little difference from their original bedrock [Carey et al., 2005], suggesting that little chemical weathering per unit mass of material has taken place. The large absolute chemical weathering yields observed in New Zealand reflect the tremendous amount of solids being produced within these watersheds. So in these very active tectonic regions, weakly chemically weathered sediments are produced, but the chemical weathering yields are large compared to other geological regions simply because the sediment yields are so high [Gaillardet et al., 1999a]. For example, in the Cropp watershed the erosion rate is thought to be essentially equal to the uplift rate [Tonkin and Basher, 1990]. This steady state has led to no significant difference between the soil evacuation interval and the residence time of the soil mantle over the majority of the watershed [Tonkin and Basher, 1990].

6. Conclusions

[29] The seminal work of Milliman and Syvitski [1992] and more recently that of others [Restrepo and Kjerfve, 2000; Mertes and Warrick, 2001; Lyons et al., 2002; Campbell and Church, 2003] clearly indicate that high-standing islands associated with plate boundaries, island arcs and andesitic mountain chains close to the ocean provide the largest flux of sediments to the marine environment. Our data suggest that these very high physical weathering erosion yields are associated with high chemical erosion yields. Therefore past long-term fluctuations in atmospheric CO₂ may have been influenced by weathering of these types of geological provinces, and not just by weathering in more continental mountainous regimes. Our results also strongly support the earlier work of Gaillardet et al. [1999b]: that to produce high chemical weathering and hence chemical erosion, active physical erosion is required.

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