



# Rivers from Volcanic Island Arcs: The subduction weathering factory

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## ABSTRACT

Here the focus is on the geochemistry of rivers draining volcanic arc regions. Although data are rather sparse, first order estimates show that volcanic arc settings are amongst the faster eroding regions of the Earth because they combine high precipitation regimes with high hydrothermal contributions in which increased temperature and increased acidity favor water–rock interaction. The hydrothermal contribution tends to obliterate the effect of climate and shows the importance of better evaluating the hydrothermal input from subduction zones, and the parameters that control it.

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## 1. Introduction

The interaction of volcanic acids (produced by degassing of the planet) and rocks is a giant neutralization reaction producing secondary products (clays and oxides) and releasing into the hydrosphere base anions that may (or not) recombine in the form of chemical sediments in the ocean (Ebelmen, 1845). The amount of limestone in the ocean indicates that the weathering factory has led to the sequestration of almost all the CO<sub>2</sub> present in the early Earth's atmosphere. Although the annual amount of acidity consumed by rock weathering is relatively low (0.4 PgC/a, Gaillardet et al., 1999), over Earth's history, the role of chemical weathering has been fundamental.

As many recent papers have shown, the weathering of volcanic rocks is probably responsible for 30% of the modern day global flux of acidity consumption, although these rocks represent only 5% of the Earth surface area (Dupre et al., 2003). Among volcanic rocks however, chemical weathering of volcanic arcs have not received much attention. This is despite the fact that subduction zone volcanism is the most active volcanism on Earth, delivering most of the CO<sub>2</sub> and other acids and ashes to the atmosphere and having essentially an explosive character. In particular, oceanic volcanic arcs form chains of volcanoes receiving very high precipitation (e.g. Indonesia). Surprisingly and unfortunately, the number of weathering studies on volcanic arc islands is somewhat low. In this paper, the available data are reviewed and it is shown that volcanic island arcs all share common characteristics and are in turn characterized by the highest chemical denudation rates on Earth.

## 2. River data base and methods

River chemistry data has been collected from numerous of recent works on volcanic island arcs. River data from the Lesser

Antilles are from Goldsmith et al. (2010), Gaillardet et al. (2011) and Jones et al. (2010), for Dominica, Martinique (Mount Pelée), Guadeloupe and South-Montserrat, respectively. Data from the Philippines (Indonesia) are from Schopka et al. (2011). Kamchatka rivers have been studied by Dessert et al. (2009) and additional data from New Zealand (Taranaki volcanic province) are from Goldsmith et al. (2008). A data base for major elements, temperature and pH was constituted. In the above studies, runoff values (i.e. water discharge divided by watershed surface area), which are critical for determining chemical denudation rates were collected from gauging stations and correspond to long-term average data. In Indonesia, hydrological data are not available and average runoff values were estimated from a few gauged watersheds and are therefore constant by definition. Overall runoff data range from a few hundreds to 5000 mm/a in Guadeloupe and 8000 mm/a in New Zealand. Mean air temperature vary from a few degrees in Kamchatka to 30 °C in tropical regions of Philippines and the Lesser Antilles.

The method for calculating chemical denudation rates from river data is now classic and consists of first removing the atmospheric contribution, then estimating the mass of dissolved solutes/L of water derived from chemical weathering reactions and finally multiply it by runoff in order to get a rate. The critical step in the procedure is the determination of the atmospheric contribution. Classically, this correction is based on Cl<sup>-</sup> in the river being derived from the atmosphere (Clcrit) and assuming that rainwater is of marine origin and, therefore, has marine X/Cl ratios. The only exception where data were corrected from rainwater data and not seasalt dissolution is Kamchatka where long-term averages of rainwater inputs are available. Atmospheric input-corrected concentrations were used to calculate the total dissolved cations (TDS<sub>at</sub> = Na + K + Ca + Mg in mass) and total dissolved solutes (TDS = Na + K + Ca + Mg + SiO<sub>2</sub> in mass). The cationic weathering rates (CWR) and total weathering rates (TWR) were determined in t/km<sup>2</sup>/a by multiplying these concentrations by runoff. The

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CO<sub>2</sub> consumption rates were calculated by multiplying runoff by HCO<sub>3</sub> concentrations. An important parameter is  $\Phi = \text{TDScat}/\text{SiO}_2$  which quantifies the amount of dissolved matter transported as dissolved cations compared to that transported as dissolved silica. Chemical weathering advance rates were calculated using an andesite average chemical composition and density according to Navarre-Sitchler and Brantley (2007).

### 3. Results and discussion

#### 3.1. Atmospheric contribution

The determination of Clcrit is not easy in particular because of the limited knowledge of both Cl concentration in rainwater and the evapo-transportation factor in most of the sites. When geological evidence shows that there is no hydrothermal input in the watershed, it is possible to constrain Clcrit by only considering rivers which are not influenced by hydrothermal inputs. In the Lesser Antilles, for example, Clcrit ranges between 200  $\mu\text{mol/L}$  and 600  $\mu\text{mol/L}$  depending of runoff values (Gaillardet et al., 2011). In Kamchatka, by contrast, Clcrit are much lower, never exceeding a few  $\mu\text{mol/L}$ . For rivers impacted by hydrothermal inputs the use of both Cl and SO<sub>4</sub> concentrations allows separation of rivers impacted by hydrothermal inputs and non-impacted rivers which have Cl/SO<sub>4</sub> in agreement with the rainwater ratio. The distance to the sea and the abundance of seasalts in the atmosphere or local wind patterns probably explain these important differences of Clcrit. Following Goldsmith et al. (2008), in New Zealand, all riverine Cl was attributed to atmospheric input, which is probably an oversimplification. The determination of Clcrit in rivers from volcanic settings could probably be improved by the use of isotopic tracers such as Sr, Cl or Br isotopes.

The correction of atmospheric input represents a significant part of the dissolved load, ranging from a few% to 50–60% in dilute rivers from the Lesser Antilles. Among the different regions, the Kamchatka rivers show the lowest atmospheric contribution.

#### 3.2. Water–rock interactions and water composition

Once corrected from atmospheric inputs, the concentration of dissolved solutes show an important range of variation at regional and global scales. This variability is imposed by variable runoff values and the contribution of hydrothermal inputs particularly in the most active volcanic provinces (Montserrat, Jones et al., 2010). In Guadeloupe, the range of TDScat is between 1 and 83 mg/L with a median value of 11 mg/L. In the Kamchatka peninsula, about the same range of variation is found, with a median value of 20 mg/L. In the Philippines, TDScat range from 8 to 236 mg/L with a median value of 30 mg/L. The highest values of TDScat are found in Montserrat and correspond to the active part of La Soufrière volcano which is still erupting. In Montserrat, TDScat values range from 4 to 290 mg/L with a median value of 56 mg/L. Rivers draining volcanic island arcs generally have high dissolved silica concentrations. The  $\Phi$  ratio has a median value of 0.5 (twice as much silica as cations) and a highly asymmetric histogram toward higher values ( $\Phi = 2$ –3). High values of  $\Phi$  are clearly observed in the rivers most influenced by hydrothermal inputs. This is particularly true in the Lesser Antilles where Montserrat groundwaters, much influenced by hydrothermalism, can have  $\Phi$  values up to 10. The elemental ratios such as Ca/Na, Mg/Na, Ca/Mg are relatively constant among the different provinces and have median values close to 1.2, 0.6 and 2, respectively. These values of the elemental ratios are roughly similar to the bedrock ratios considering a mean andesitic composition. This surprising result tends to indicate that cations are released congruently from the rocks by chemical

weathering. The  $\Phi$  ratio in bedrock is by contrast close to 0.2, indicating a significant removal of solution Si during chemical weathering, most probably in clay minerals.

#### 3.3. Chemical denudation rates

The cation weathering rates and total weathering rates in  $\text{t}/\text{km}^2/\text{a}$  calculated for rivers draining volcanic island arcs are very variable. TWR range from a few  $\text{t}/\text{km}^2/\text{a}$  to 700  $\text{t}/\text{km}^2/\text{a}$  in the high runoff, active regions of the Lesser Antilles and Philippines. The median value of CWR and TWR are 20 and 50  $\text{t}/\text{km}^2/\text{a}$ , respectively. In Fig. 1 it is shown that weathering rate increases from the high latitude province of Kamchatka to the tropical regions but it is

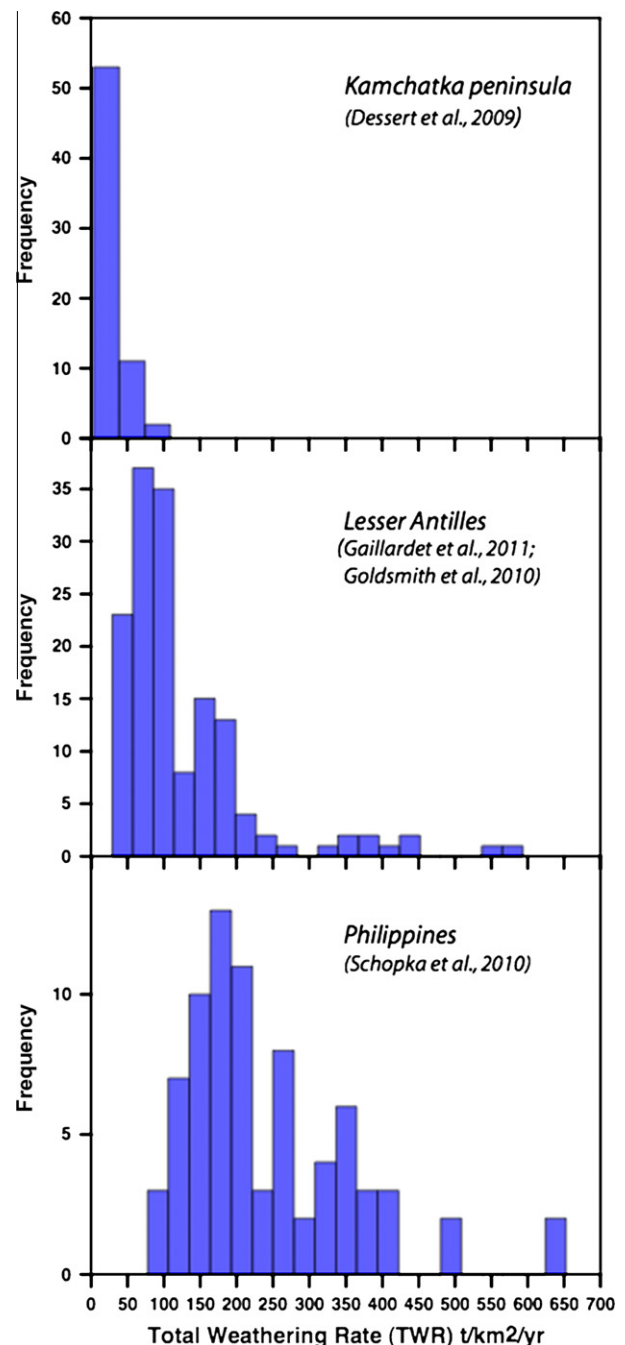


Fig. 1. Histograms of chemical denudation rates (TWR) in different volcanic arc provinces.

important to note that a considerable overlap exists between the different provinces. This overlap is particularly true for cation weathering rates between the Lesser Antilles and Kamchatka peninsula. The enrichment in dissolved silica of tropical rivers reduces the overlap when TWR are compared. In contrast to a series of previous studies (e.g. Louvat, 1997), no correction was made here from any hydrothermal input. The rates calculated here deliberately integrate a hydrothermal component and this is the reason why CWR in the tropics can be similar to CWR at high latitude. The chemical denudation rates calculated for the volcanic island arcs are in the upper range of those reported for rivers draining volcanic rocks (Louvat, 1997; Dessert et al., 2003; Dupre et al., 2003) from non-volcanic arc settings. A correlation is observed between TWR and CWR (Fig. 2), with a slope changing towards high values of chemical denudation. This is due to significant hydrothermal input in the rivers having high denudation rates with lower  $\Phi$  values. In detail, the cold climate province of Kamchatka clearly shows the lowest denudation rates (Fig. 1) while the highest TWR values are calculated for the Philippines and Lesser Antilles. This result is a consequence of the higher runoff and temperature observed in the tropical zone and is in agreement with the global control found by Dessert et al. (2003). The highest chemical denudation rates are found around the Pinatubo and Soufriere de Guadeloupe volcanoes and reach 600 t/km<sup>2</sup>/a.

The advance weathering rates vary between 15 mm/ka for rivers from Kamchatka and the Lesser Antilles, up to 1.5 m/ka in the most volcanic active regions.

### 3.4. Acidity consumption rates

The major agent of chemical weathering is carbonic acid whose dissolution in soil water produces the protons necessary for chemical weathering of minerals. The consumption rates of CO<sub>2</sub> found in the volcanic arc islands are the highest worldwide. Consumption rates of CO<sub>2</sub> up to 6000 × 10<sup>3</sup> mol/km<sup>2</sup>/a are found in New Zealand and the Philippines. The Lesser Antilles, have lower consumption rates not exceeding 3000 × 10<sup>3</sup> mol/km<sup>2</sup>/a. Kamchatka peninsula has the lowest consumption rates of CO<sub>2</sub> with a maximum of 1000 × 10<sup>3</sup> mol/km<sup>2</sup>/a.

In a volcanic arc context, two other important sources of acidity are contributing to chemical weathering reactions: H<sub>2</sub>SO<sub>4</sub> and HCl. Their contribution can be calculated once concentrations in rivers

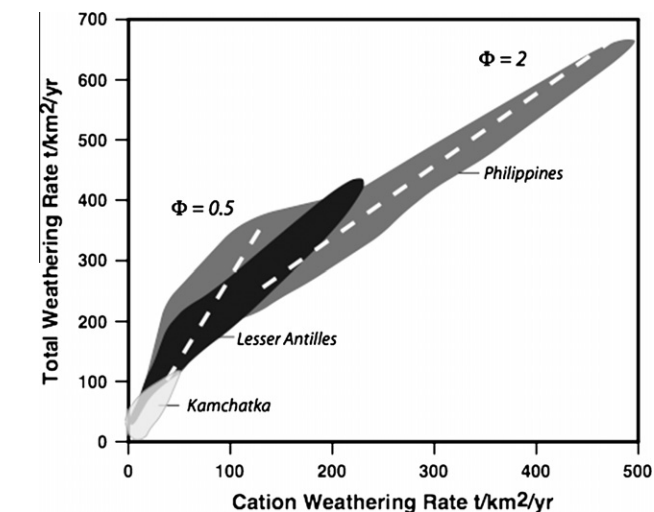


Fig. 2. Cationic weathering rates vs. Total denudation rates in the different volcanic arc provinces of the world. The parameter  $\Phi$  is the ratio of dissolved cation concentration over dissolved silica concentration.

have been corrected for atmospheric inputs. For example, in the Lesser Antilles, Gaillardet et al. (2011) calculated that 25% of the protons are derived from H<sub>2</sub>SO<sub>4</sub> and 5% from HCl, the rest being provided by H<sub>2</sub>CO<sub>3</sub>. The worldwide data base shows that the main acids involved in chemical weathering in island arcs are H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>CO<sub>3</sub> with a contribution of H<sub>2</sub>SO<sub>4</sub> that can be dominant near active volcanoes. The median values for each of the volcanic provinces here show that Kamchatka peninsula, despite relatively low runoff values, shows the most important contribution of H<sub>2</sub>SO<sub>4</sub> to chemical weathering (40%). The database, therefore, shows that the dominant control of chemical weathering rates in island arcs is the input of volcanic acids. This control tends to hide the temperature-control on chemical weathering rates.

### 3.5. Importance of runoff variability

Runoff can change drastically from one valley to another as a function of orography, wind patterns and infiltration. This is very well illustrated by the Lesser Antilles, which are typical trade wind mountainous islands. The windward coasts receive up to 10 m of precipitation while the leeward sides have precipitation rates not exceeding 2000 mm/a. The rivers from the Pelée Volcanoe (Martinique) are dry most of the time due to high infiltration rates. In the Lesser Antilles, Gaillardet et al. (2011) showed that dissolved concentrations along the precipitation gradient only change by a factor of 2 while runoff changes by a factor of 5–6. As a consequence, the relationship between denudation rate and runoff is automatic and simply means that concentrations derived from chemical weathering reactions are buffered along the runoff gradient. This “chemo-static” behavior of rivers has already been reported by many authors (Godsey et al., 2009) and is really a mechanism that merits more attention.

The data base confirm the observation made in the Lesser Antilles that there is a strong control of chemical denudation rates with runoff because of the relatively low variability of TDS compared to runoff. On Fig. 3, it is shown that runoff and hydrothermal contributions both modulate the chemical denudation rates in the Lesser Antilles, New Zealand and Kamchatka provinces.

The importance of runoff variability in controlling the rate of chemical weathering shows that mean average regional values of chemical denudation rates has little significance as they strongly depend on runoff and infiltration patterns, and, therefore, on topography and lithology.

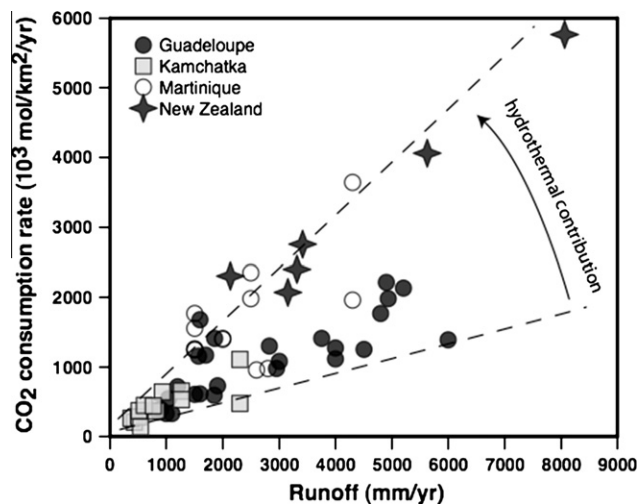


Fig. 3. Runoff and hydrothermal control of chemical denudation rates in volcanic arc provinces.

#### 4. Conclusions

This very rapid overview of data from rivers draining volcanic arcs shows how important these regions are in terms of chemical weathering budgets to the ocean and in terms of acidity consumption. This conclusion is reinforced by the importance of groundwater discharge to the ocean in these settings (Rad et al., 2007).

However, there is still a great need for work to be done, in particular, in the following areas. More data is needed on rivers draining volcanic arcs. The atmospheric input is a crucial component to be determined and specific tracers should be developed to better constrain it. Although most of the previous studies have discarded the hydrothermal contribution to rivers draining volcanic areas (and focused on the low-temperature chemical weathering rates), this is a really important component, if not the dominant, part of the weathering budget and there is need of understanding what controls the hydrothermal inputs on a global scale. More work should be undertaken to understand the relative constancy of river concentrations as a function of runoff. Finally, all these research perspectives need time series data to capture the temporal variability of river systems and need a good knowledge of the hydrological budget at the catchment scale. Well-designed hydro-geochemical observatories are the only way to go further.

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