



Controls on chemical weathering on a mountainous volcanic tropical island: Guadeloupe (French West Indies)

C. Dessert^{a,b,c,*}, E. Lajeunesse^{a,b}, E. Lloret^d, C. Clergue^a, O. Crispi^{a,b,c},
C. Gorge^a, X. Quidelleur^e

^a Institut de Physique du Globe de Paris (IPGP), Sorbonne Paris Cité, Université Paris-Diderot, UMR 7154, CNRS, 75205 Paris, France

^b Observatoire de l'Eau et de l'Erosion aux Antilles (OBSERA), IPGP, UMR 7154, CNRS, 75205 Paris, France

^c Observatoire Volcanologique et Sismologique de Guadeloupe (OVSG), IPGP, UMR 7154, CNRS, Le Houëlmont, 97113 Gourbeyre, Guadeloupe

^d Laboratoire Génie Civil géo-Environnement (LGCgE), Université Lille 1, 59655 Villeneuve d'Ascq, France

^e Equipe Géochronologie et Dynamique des Systèmes Volcaniques (IDES), UMR 8148, CNRS-UPS, Université Paris-Sud 11, Orsay, France

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Abstract

Guadeloupe Island is a natural laboratory, ideally suited to the study of biogeochemical processes in tropical and mountainous volcanic environments. The island's east–west rainfall gradient (1200–8000 mm/yr) is superimposed on a north–south age gradient (2.7 Ma to present), providing a unique opportunity to investigate the influence of rainfall and rock age on the chemical weathering of volcanic terrains. Taking advantage of this configuration, we present the first temporal survey (2007–2013) of the geochemical composition of the dissolved load of rain and river waters in Guadeloupe.

Our data demonstrate that the chemical composition of river water is influenced by rainfall abundance, hydrothermal alteration (from active or fossilized volcanic systems) and interactions between water and minerals during chemical weathering processes. The contribution of rain to the overall chemical balance is especially significant in the older northern part of the island, where the ferrallitic soils are base-cation-depleted. Between 15% and 65% of the Ca or Mg riverine budgets comes from atmospheric deposits, highlighting the major role of rainfall in the geochemical budgets of small tropical and mountainous watersheds. The river water dataset indicates that different chemical weathering processes dominate the budget depending on the age of the local bedrock. In the younger, southern part of the island, a pool of easily-weatherable andesitic minerals from the bedrock dominates. The contribution from this pool decreases significantly (to 5–15 wt.% of the bulk soil) towards the older terrains in the north. The northern rivers are characterized by low Ca/Mg ratios (0.5–1.0), intermediate between those of fresh rocks (1.7–3.3) and soil (0.1). Weathering in the northern part of the island is therefore dominated by the dissolution of depleted secondary minerals into soils. The Ca/Mg ratio of the river water increases from north to south, eventually reaching values similar to those of the bedrocks, arguing for congruent dissolution of the youngest volcanic rocks.

The magnesium isotopic composition of river water ($\delta^{26}\text{Mg}$) reflects inputs from both rain and weathering processes. In southern and central rivers, the Mg isotopic value of waters after correction for rain inputs ($\delta^{26}\text{Mg}_{\text{wea}}$) is systematically depleted in heavy isotopes (mean value of -0.34‰) relative to that of the bedrock (-0.24‰ to -0.15‰). In the north, the $\delta^{26}\text{Mg}_{\text{wea}}$ of the river water (-0.09‰) is heavier than that of the andesitic bedrock, possibly reflecting the dissolution of ^{26}Mg -rich secondary minerals (ferrallitic soil measured around $+0.13\text{‰}$). The robustness of $\delta^{26}\text{Mg}$ and Ca/Mg as proxies of the degree of soil weathering should be investigated further via more detailed sampling campaigns in the future.

* Corresponding author at: Institut de Physique du Globe de Paris (IPGP), Sorbonne Paris Cité, Université Paris-Diderot, UMR 7154, CNRS, 75205 Paris, France.

E-mail address: dessert@ipgp.fr (C. Dessert).

By combining high-frequency monitoring of river discharge with measurements of concentration–discharge relationships for a wide range of chemical elements, we estimate the mean annual chemical weathering fluxes for three rivers that belong to the OBSERA critical zone observatory. Fluxes vary from 51.7 to 91.8 t/km²/yr north to south along the bedrock age gradient, and are among the highest recorded in volcanic tropical regions. Flash floods can explain 21–31% of the annual chemical weathering fluxes. The results highlight the importance of monitoring rivers over periods of several years in order to obtain accurate estimates of chemical exports in tropical and mountainous environments.

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1. INTRODUCTION

The surface of the Earth evolves under the action of geological, chemical, physical and biological processes that are closely combined in the transformation of bedrock into secondary minerals. This complex engine controls the evolution of soils, the shape of landscapes, and the riverine transport of dissolved and particulate products from continents to oceans. Chemical weathering of Ca–Mg silicate rocks is a key process in the Earth's global geochemical cycles, and in the carbon cycle in particular (e.g. Berner et al., 1983; François and Walker, 1992; Godd eris and Fran ois, 1995; Beaulieu et al., 2012). Many studies have therefore focused on river geochemistry for the quantification of weathering fluxes and associated atmospheric CO₂ consumption fluxes (e.g. Stallard and Edmond, 1983; Probst et al., 1994; Gaillardet et al., 1999; Galy and France-Lanord, 1999; Dessert et al., 2001; Viers et al., 2007).

The importance of lithology has been considered by several authors, who have shown that basalt weathers at faster rates than other silicate rocks (e.g. Bluth and Kump, 1994; Gislason et al., 1996; Louvat and All gre, 1997; Dessert et al., 2001). These studies all confirm that the chemical weathering fluxes of rivers draining volcanic rocks are among the highest recorded worldwide, with the highest fluxes measured in humid tropical regions. Dessert et al. (2003) suggested that the atmospheric CO₂ consumption derived from basalt weathering might represent up to 30–35% of the global silicate weathering flux. This global estimate does not take into account chemical weathering induced by acidity from volcanic degassing and hydrothermal alteration. More recent studies have begun to assess the impact of hydrothermal alteration on the overall riverine budget in active volcanic settings (Dessert et al., 2009; Gaillardet et al., 2011; Louvat et al., 2011; Schopka et al., 2011; Riv e et al., 2013). These studies report that hydrothermal alteration induced by volcanic activity, either active or fossilized, forms a significant part of the cationic and carbon budgets. Parameters such as vegetation, which generates organic acids (Oelkers and Gislason, 2001; Pokrovsky et al., 2005), and the age of rock substrate (Gislason et al., 1996; Kennedy et al., 1998) may also strongly influence the chemical weathering of volcanic rocks.

Guadeloupe Island is an ideal natural laboratory in which to study weathering processes in a tropical volcanic environment. The east–west rainfall gradient is superimposed on a north–south age gradient, allowing us to inves-

tigate the different roles of a wide variety of parameters that influence alteration in volcanic terrains. This study forms part of a larger effort to characterize biogeochemical cycles and weathering rates in the Lesser Antilles (Rad et al., 2006; Goldsmith et al., 2010; Jones et al., 2010; Gaillardet et al., 2011; Lloret et al., 2011; Clergue et al., 2015). Preliminary field investigations performed in Guadeloupe have allowed us to show that most of the soil erosion is driven by tropical storms that occur on only a few days each year (Lloret et al., 2013; Allemand et al., 2014). Floods associated with such storms represent around 43% of the annual water flux, around 54% of the annual flux of dissolved organic carbon and at least 85% of the annual flux of particulate organic carbon. The exports of dissolved inorganic carbon (DIC) vary considerably with the intensity of hydrothermal alteration, increasing from north to south (Gaillardet et al., 2011; Riv e et al., 2013), and with the morphology/hydrology of watersheds (Gaillardet et al., 2011; Lloret et al., 2011, 2013). The southern catchments are generally younger, steeper and wetter than the northern ones and the highest levels of DIC export are correspondingly found in the south of the island. In our preliminary studies, we also showed that the export of DIC varies significantly during the year as a function of hydrological variability. We demonstrated, for example, that 25% of the annual DIC flux of the Capesterre River (which is unaffected by a hydrothermal input) is transported during floods (Lloret et al., 2013). Thus, neglecting to consider such transport during floods in tropical, mountainous island environments will undoubtedly lead to an underestimation of the annual budget.

In order to address the different factors that influence chemical weathering in Guadeloupe, we adopt an approach that combines measurement of major element concentrations in river water with determination of Mg isotope composition, which then allows us to test the potential of the latter as a proxy of chemical weathering intensity. Mg isotopic ratios (²⁶Mg/²⁴Mg and ²⁵Mg/²⁴Mg) are reported to be a useful tracer of weathering processes and biogeochemical pathways. For example, rivers that drain silicate rocks have distinctively lighter Mg isotope ratios than the parental silicate material (e.g. Tipper et al., 2006, 2012; Brenot et al., 2008; Pogge von Strandmann et al., 2008; Chapela Lara et al., 2014). However, the behavior of Mg isotopes during weathering is not well established. A number of different processes have been proposed to explain the preferential release of ²⁴Mg into solution, including preferential uptake of heavy Mg isotopes by vegetation (e.g. Bolou-Bi et al., 2010, 2012; Tipper et al., 2010), preferential incorporation

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