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Chemical weathering fluxes from volcanic islands and the importance of groundwater: The Hawaiian example

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ABSTRACT

We investigated the products and rates of chemical weathering on the Hawaiian Islands, sampling streams on Kaua'i and both streams and groundwater wells on the island of Hawai'i. Dissolved silica was used to investigate the flowpaths of water drained into streams. We found that flowpaths exert a major control on the observed chemical weathering rates. A strong link exists between the degree of landscape dissection and flowpaths of water through the landscape, with streams in undissected landscapes receiving water mainly from surface runoff and streams in highly dissected landscapes receiving a considerable fraction of their water from groundwater (springs and/or seepage). Total alkalinity in Hawaiian streams and groundwater is produced exclusively by silicate chemical weathering. We find that fluxes of total alkalinity (often called "CO_2 consumption rate" in the geochemical literature), from the islands are lower than those observed in basaltic regions elsewhere. Groundwater is, overall, the major transport vector for products of chemical weathering from the Hawaiian Islands. On the youngest and largest island, submarine groundwater discharge (*SGD*) transports more than an order of magnitude more solutes to the ocean than surface water and on the youngest part of the youngest island, *SGD* is the only link between the terrestrial weathering system and the ocean. These results suggest that groundwater, and particularly *SGD*, needs to be included in geochemical weathering budgets of volcanic islands.

1. Introduction

Recognition of the importance of weathering fluxes in volcanic terranes has led to a renewed focus on the processes that control these fluxes and how they may differ from those in continental settings. Chemical weathering fluxes from rivers draining basaltic terranes are among the highest recorded worldwide (Gislason et al., 1996; Louvat and Allègre, 1997; Dessert et al., 2003, 2009; Das et al., 2005; Pokrovsky et al., 2005, 2006; Eiríksdóttir et al., 2006; Rad et al., 2006; Schopka et al., 2011, etc.). Despite its relative accessibility, there has been little work on chemical weathering fluxes from the Hawaiian archipelago.

An early study of the chemical denudation of Hawai'i is that of Li (1988), who used stream chemistry data from the USGS to investigate chemical and physical denudation in Hawai'i. Li (1988) found that carbonic acid is the most important weathering agent on the islands and that chemical denudation rates on all the islands are higher on the wet windward side than on the dry, leeward side of the islands. He also investigated weathering fluxes by groundwater and found them to be roughly comparable to weathering fluxes by streams. In a survey of stream weathering fluxes from basaltic terranes worldwide, Dessert et al. (2003) used available USGS stream chemistry data to estimate surface weathering fluxes from Hawai'i. They found that inferred weathering rates in Hawai'i were anomalously low relative to other basaltic terranes in broadly similar climates, but they did not consider groundwater fluxes.

Recent work has highlighted the large flux of submarine groundwater discharge (*SGD*) to the global ocean from continents (e.g. Moore, 1996; Burnett et al., 2003; Moore et al., 2008) and islands (e.g. Cardenas et al., 2010; Huang et al., 2011). In particular, it has been demonstrated that *SGD* is a very important component of the hydrological balance of volcanic islands (e.g. Kim et al., 2003). Several studies provide evidence that *SGD* is widespread in Hawai'i as well. Street et al. (2008) used multiple chemical tracers (salinity, dissolved silica and Ra-isotopes) to quantify *SGD* in several locations in Hawai'i, Johnson et al. (2008) used thermal infrared imagery to demonstrate the presence of large, cold freshwater plumes along the west coast of the island of Hawai'i and Peterson et al. (2009) quantified the discharge via these plumes using salinity and Ra-isotopes. *SGD* is not only an important pathway for the delivery of water from land to ocean; it also transports significant amounts of dissolved solids from

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weathering on land directly to the global ocean (Rad et al., 2007; Georg et al., 2009).

In this paper, we compare the magnitude of chemical weathering fluxes via surface runoff and *SGD*, and investigate the control that bedrock age, climate and degree of landscape development exert on the relative magnitude of these fluxes. Here we use data on dissolved silica (*DSi*) and total alkalinity (*TAlk*), along with constraints on hydrologic fluxes, to estimate silicate weathering fluxes and associated transfer of atmospheric CO_2 to the ocean. The watersheds studied here contain only silicate rocks, so the flux *TAlk* is a measure of atmospheric CO_2 consumption associated with silicate weathering (e.g. Dessert et al., 2003). *DSi* is unaffected by atmospheric contribution and is treated here as a record of the dissolution of primary silicate minerals. Cycling of Si by vegetation (Derry et al., 2005; Ding et al., 2005, 2008, 2009) and clay precipitation and/or dissolution (Georg et al., 2007) impact the stable isotope composition of dissolved silica but not the export flux, unless the system is out of steady state. The Si-cycle is, perhaps somewhat simplistically, treated as a steady state system in this study.

1.1. Study site

The 600 km long, NW–SE trending Hawaiian archipelago lies at the edge of the tropics (19–22°N) and consists of five main islands and several smaller ones (Fig. 1). The islands, composed exclusively of basalt, are the youngest volcanoes in the 6000 km long Hawaiian-Emperor Volcanic Chain that formed by the interaction of the Hawaiian mantle plume with the Pacific Plate. The climate is warm, with pronounced differences in rainfall between the windward (< 6000 mm/yr) and leeward (100–1000 mm/yr) sides of each island. A thermal inversion layer is present at 1500–3000 m a.s.l. and above this layer, precipitation is negligible. We investigated chemical weathering fluxes via stream water and groundwater on Kaua'i and on the island of Hawai'i (Fig. 1a). The two islands represent the extremes in age and landscape development in the Hawaiian archipelago.

The island of Hawai'i (Fig. 1b) ranges in age from zero years on the currently active Kilauea volcano to $\sim 700 \times 10^3$ years (kyr) on Kohala volcano (Dalrymple, 1971; McDougall and Swanson, 1972). The island retains considerable constructional volcanic topography, with the exception of the NE-coast of the Kohala peninsula where a large flank collapse occurred around 250 ka (Lamb et al., 2007). The leeward side of the island of Hawai'i receives much less precipitation than the wet windward side and has no permanent streams. The lack of surface runoff results from the combination of low rainfall and the high permeability of fresh lava, which allows rapid infiltration of rainwater into the groundwater reservoir (Macdonald et al., 1983). Even when active, leeward streams typically cease to flow prior to reaching the ocean. Soil development is largely a function of precipitation, and substantial elemental loss on the oldest soils (Kohala) occurs only where mean annual precipitation (MAP) > 1100 mm/yr (Chadwick et al., 2003), with smaller losses in younger soils. Because of the combination of the orographic rain shadow and regional inversion only a small fraction of the leeward side of the island has rainfall that exceeds this value, on the upper slopes of Kohala and in south Kona where thermal convection generates slightly higher MAP (Giambelluca et al., 2011). While weathering and leaching takes place in these smaller areas, the presence of only ephemeral streams indicates that the majority of solutes exported from the weathering zone must reach the ocean via groundwater. Stream water geochemical fluxes from the leeward portions of the island of Hawai'i are therefore negligible contributors to the island-wide flux.

Kaua'i (Fig. 1c) is the oldest of the large Hawaiian Islands (the oldest dated rocks are 5.1×10^6 years (Myr) old, McDougall, 1979). Kaua'i is heavily impacted by tectonic gravitational landsliding. It is deeply eroded and retains only a small fragment of the original volcanic shield morphology in the headwaters of the Waimea Canyon. Deep valleys separated by knife-edge ridges characterize the remainder of the island, and soils are deeply weathered (Vitousek et al., 1997). The central high plateau on Kaua'i is also one of the wettest places on Earth with MAP in excess of 11000 mm/yr. Rainfall diminishes towards the coast all around the island and is the lowest on the leeward (SW) side.

As lava flows weather, their permeability decreases due to collapse of the original permeable lava structure (primary mineral dissolution, bioturbation), secondary minerals filling in empty vesicles, etc. As a consequence, flowpaths of water change (Lohse and Dietrich, 2005; Jefferson et al., 2010). On young, unweathered surfaces most rainfall percolates uninterrupted to the groundwater table, and streams do not occur on the surface. This is the case on most of the leeward side of the island of Hawai'i. When

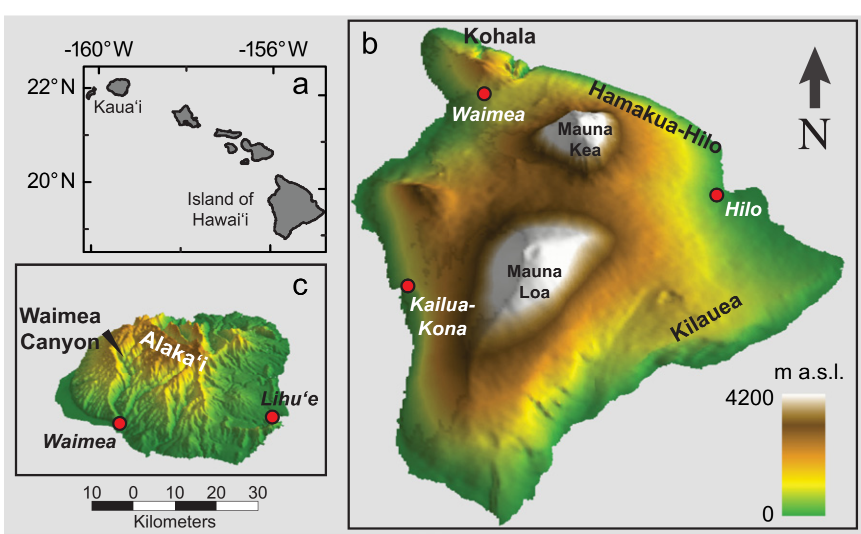

Fig. 1. Overview of the study area. (a) The Hawaiian Archipelago. Kaua'i and the island of Hawai'i are the oldest and youngest, respectively, of the islands and lie in the NW and SE extreme of the archipelago. Shaded relief maps of the island of Hawai'i (b) and Kaua'i (c) illustrate the striking difference in topography of the two islands. Place names in regular bold font indicate locations and regional division discussed in text, place names in italics indicate main towns. The elevation scale bar applies to both islands.