Letters

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

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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 CO2 to the ocean. The watersheds studied here contain only silicate rocks, so the flux TAlk is a measure of atmospheric CO2 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., 2009) impact the stable isotope composition of dissolved silica, and investigate the
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 × 106 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 along 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

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 long Hawaiian-Emperor Volcanic Chain that formed by the interaction of the Hawaiian mantle plume with the Pacific Plate. The oldest dated rocks are 5.1 × 106 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 along 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.
incipient soil and some vegetation are present on the lava surface, some rainwater is retained on the surface. Ephemeral streams are found on the thin soils of Mauna Loa, on bedrock only a few hundred to a few thousand years old. These streams are only active for a few days every year and contribute negligibly to the overall weathering budget of the island. They are therefore omitted from this study. In contrast, perennial streams, arranged radially on the slopes of the volcano, have developed on the windward side of Mauna Kea, under heavy rainfall and on bedrock < 30 ka old. Kohala volcano is the oldest part of the island of Hawai‘i. It is the site of a large landslide that most likely accelerated valley formation on the windward side of the peninsula (Lamb et al., 2007). Thick soils mantle the high plateau, and the lowest Cl evidence by a water level much higher than in surrounding wells (Schopka et al., 2011). Only one of the groundwater samples collected for this study is from a perched aquifer (Pahala Well, sample HI-06-59), which is the remnant shield surface. Dense vegetation covers the walls and floors of the valleys that have been cut into the volcanic shield. Kaua‘i is similar to the Kohala Peninsula in this respect, although millions of years separate the two islands.

Groundwater in Hawai‘i is present either as a thin freshwater basal lens overlying sea water that has penetrated the lava layers, or as perched aquifers confined by dikes and/or tephra and soil layers that are much less permeable than basalt (Juvik and Juvik, 1998). Only one of the groundwater samples collected for this study is from a perched aquifer (Pahala Well, sample HI-06-59), evidenced by a water level much higher than in surrounding wells and the lowest Cl−-concentration of all wells used in this study.

2. Data and methods

We split the study area into four regions. The island of Hawai‘i comprises three regions: Kohala (Kohala Peninsula), Hamakua-Hilo (the windward slopes of Mauna Kea) and Kilauea (the eastern flanks of Mauna Loa and Kilauea volcanoes) (see Fig. 1b, and Fig. A1 for orientation); the island of Kaua‘i is the fourth region. Water samples were collected for chemical analyses on Kaua‘i and the island of Hawai‘i in 2005 and 2006, and on the island of Hawai‘i in 2008 (sampling locations are shown in Figs. A1 and A2).

Landscape analysis was performed using ArcGIS 9 (ESRI, 2009) on a National Elevation Dataset (NED) Digital Elevation Model (DEM), obtained from the USGS seamless data warehouse (http://seamless.usgs.gov/). The DEM has a resolution of 10 m.

2.1. Chemistry

A total of 56 streams and tributaries were sampled, 32 on the island of Hawai‘i and 24 on Kaua‘i. Some streams were sampled multiple times. Given the importance of SGD in Hawai‘i (e.g. Juvik and Juvik, 1998; Peterson et al., 2009), a total of 12 groundwater wells were also sampled on the island of Hawai‘i in 2005 and 2006. Chemical data for five more groundwater wells on Maui, O‘ahu and Kaua‘i were obtained from the USGS online database (http://waterdata.usgs.gov/usa/nwis/qwdata). The chemical composition of stream water and groundwater is presented in Tables A1 and A2, respectively.

Methods for sampling and chemical analyses are described in Schopka et al. (2011). Briefly, filtered samples were analyzed for DSI by molybdate blue spectrophotometry (Mortlock and Froelich, 1989). Alkalinity in samples from 2006 was determined by charge balance and in all other samples by Gran titration. Alkalinity is a measure of the capacity of a filtered water sample to neutralize strong acids and consists of the sum of titrable carbonate and non-carbonate chemical species in the sample (Round, 2006). Chemical analyses of our samples (not shown) show that carbonic acid is the most important anion contributing to alkalinity in our samples, and given the pH (~8.5), TALK ≈ [HCO3−]. Other contributions to the titrated alkalinity were minor or negligible (e.g. organic anions, borates, etc.). All samples were measured for major anions and cations. These data are the subject of a paper in preparation and will not be discussed here. We do note, however, that we corrected all data for atmospheric (stream data) and seawater (groundwater data) inputs, using Cl− as a tracer and X/Cl-ratios of seawater, X=[Na+, K+, Ca2+, Mg2+]. The results indicate that seawater contamination of our groundwater samples is <10% in all cases. Consequently the impact on alkalinity fluxes is also <10%, and probably much less for DSI since coastal seawater has very low silica concentrations relative to Hawaiian groundwater.

2.2. Hydrology

Long-term stream discharge data (defined here as five years or more of continuous data), collected by the USGS (http://waterdata.usgs.gov/nwis/dv/?referenced_module=sw), are available for 27% (15 out of 56) of the streams sampled. Stream discharge in the remaining watersheds was estimated by a geospatial statistical technique (kriging) applied to runoff from neighboring streams (Schopka, 2011). This allows us to estimate total stream discharge across an entire region even if only a subset of streams in that region were gauged. The kriging technique has advantages compared to simple linear interpolation or extrapolation, including more robust estimates in data-sparse regions and improved estimates of uncertainties (e.g. Nielsen and Wendroth, 2003). Yearly mean stream discharge was used to calculate the annual export of chemical weathering products from each watershed studied.

SGD fluxes from the Hawaiian Islands are poorly quantified, having been modeled in a few discrete locations only (Johnson et al., 2008; Knee et al., 2008; Street et al., 2008; Peterson et al., 2009), but none of these efforts have targeted the total SGD flux from an entire island or the archipelago as a whole. The USGS has performed whole-island water budget studies for all the major Hawaiian Islands except for the island of Hawai‘i, where the water budget has been described in several regional studies (performed by the USGS, the State of Hawai‘i and private companies), which together cover the entire island. We used these studies to assess the magnitude of SGD from Kaua‘i and the island of Hawai‘i (see Fig. A3). Importantly, the results of these water-budget studies are in general agreement with the results of the more recent studies that directly measure or model SGD.

Most of these studies (and all the ones cited in this paper) treat groundwater recharge (G) as the residual in the water balance equation:

\[
G = P-DR-\Delta E-\Delta S
\]

where \(P\) = precipitation, \(DR\) = direct runoff, \(\Delta E\) = actual evapotranspiration and \(\Delta S\) = changes in soil moisture storage (e.g. Shade, 1995). G, in the sense employed in the cited water budget studies, can be discharged into rivers and streams (termed “base flow” (BF)), or directly into the ocean as SGD. DR is, in this formulation, the fraction of stream flow that derives from overland flow. G, as reported in the USGS reports, is therefore not equivalent to SGD, but rather represents the sum of SGD and BF:

\[
G = SGD + BF
\]

Introducing the term “stream discharge”, \(Q\), we define:

\[
Q = BF + DR
\]

Assuming \(\Delta S = 0\) when \(t > 1\) yr, and re-casting Eq. 1, we get:

\[
SGD = P - Q - \Delta E
\]

Q was kriged over the study area (see above and Schopka, 2011). The total kriged Q on Kaua‘i is a minimum value (the kriging surface does not extend over the entire coastal zone of the
island) and the calculated SGD from Kaua‘i is therefore a maximum value. On the island of Hawai‘i, data from Oki (2004) show that 6F is a minor (−6%) component of groundwater recharge; we therefore consider the DR-values from the water budgets representative of Q on the island of Hawai‘i. The results from the water budget studies cited and our calculation of SGD are reported in Table 1.

2.3. Uncertainties

We seek to estimate the total weathering fluxes delivered to the oceans by surface stream runoff and groundwater. The surface runoff is composed of many streams, and those are constrained either by direct observation or by geostatistical estimation. For the streams with more than five years of observations, we simply calculated the mean annual discharge (Qmean) and standard deviation (σQ) based on daily observations, expressed as the coefficient of variation:

\[ CV_Q(\%) = \frac{\sigma_Q}{Q_{mean}} \times 100 \]  

(5)

For the modeled streams, the kriging variance measures the spatial variability of the input variable but is not a measure of the reliability of the kriging estimate (Nielsen and Wendroth, 2003). To provide a conservative estimate of the variance in the modeled streams we propagated the variance on the measured input variable with the kriging variance using standard error propagation methods (Bevington and Robinson, 2002).

In order to estimate the overall uncertainty on the stream discharge from each island we propagated the uncertainties associated with the summation. The standard form for error propagation for a sum of the fluxes \( F = Q_1 + Q_2 \) depends on the correlation coefficients between rivers as well as their standard deviations \( \sigma_1 \) and \( \sigma_2 \):

\[ \sigma_F^2 = \sum \sigma_i^2 + \sum \rho_{ij} \sigma_i \sigma_j \]  

(6)

The terms in covariance matrix \( \text{COV} \) can be expressed as \( \text{COV}_{ij} = \rho_{ij} \sigma_i \sigma_j \). Where \( \rho_{ij} \) are the pairwise correlation coefficients. Let \( \rho_{ii} = 1 \). Then the variance for the summed stream discharge flux depends on the correlation coefficients between rivers as well as their standard deviations:

\[ \sigma_F^2 = \sum \sigma_i^2 + \sum \rho_{ij} \sigma_i \sigma_j \]  

(7)

The correlation coefficient matrix \( R \) is symmetric about the diagonal (i.e. \( \rho_{ii} = \rho_{jj} \) and \( \rho_{ij} = 1 \)). Then Eq. (7) can be expressed in matrix form:

\[ \sigma_F^2 = S \cdot R \cdot S \]  

(8)

where \( S \) is the vector of \( \rho_{ij} \) values. A degree of correlation in stream discharge time series is expected because they all tend to respond similarly to a common forcing (i.e. rainfall events). The covariance structure has a significant impact on the estimated uncertainty. The gauged streams in the study area do not have the same record lengths or sampling intervals, but there are enough overlapping data to estimate the degree of correlation. Values for \( \rho_{ij} \) are typically 0.6–0.9. The modeled streams are by definition strongly correlated with the others, a function of the kriging technique. Because of the data limitations we cannot compute \( R \) directly but its terms can be estimated. We consider both a mean \( \rho_{ij} = 0.8 \) (but assume normally distributed variation about this mean), and the limiting cases of either no or perfect correlation of all stream discharges (\( \rho_{ij} = 0 \) or 1).

For Kaua‘i, the propagated coefficient of variation (CVf) for stream discharge is 36% (\( n = 32 \)). The limiting cases (\( \rho_{ij} = 0 \) or 1) yield CVf = 10% and 40%, respectively. For the island of Hawai‘i CVf for stream discharge is 38% (\( n = 42 \)). The limiting cases (\( \rho_{ij} = 0 \) or 1) yield CVf = 14% and 43%, respectively.

Uncertainty on SGD estimates is poorly constrained; none of the reports cited here deal with uncertainty explicitly. In her study of the water budget of Moloka‘i, Shade (1997) arrived at two different values for G using two methods for calculating the water budget—one method allocated excess soil-moisture to G before AE while the other allocated excess soil moisture first to AE and then the G. We use the difference between the two G estimates (~35%) as our measure of uncertainty on the G-values, and by extension SGD-values, from the Hawaiian Islands. Two further studies validate this approach: Oki (2002) performed a rigorous error analysis on his revised assessment of the water budget of the Hawi aquifer on the Kohala Peninsula and found that G could be estimated with at least 21% error. This low uncertainty is achieved using daily water budgeting, which dramatically improves the model’s ability to correctly estimate soil moisture storage and actual evapotranspiration compared to the monthly or even yearly budgeting used in the other reports. We interpret this as the lower limit on the error with which G can be estimated in Hawai‘i.

Gambelluca et al. (1996) found that errors on estimates of G on land under cultivation on O‘ahu are 49–58%, which we consider the upper limit on the errors of estimates of G in Hawai‘i.

Reproducibility on our DSI measurements and alkalinity measurements are generally less than 2% and 15%, respectively (Schopka et al., 2011). These uncertainties were propagated with the hydrologic uncertainties when estimating the geochemical fluxes and uncertainties.

3. Results

3.1. Water fluxes

Fluxes of water via SGD and Q are presented in Table 1. The ratio SGD/Q describes the relative importance of submarine groundwater...
discharge and total stream discharge in delivering water from land to the ocean.

Considering the whole of the island of Hawai‘i, SGD is nearly four times larger than stream discharge, accounting for 79% of the total water flux from the island. SGD/Q in the aquifers of Kilauea and Mauna Loa volcanoes (Fig. A3) approaches infinity, since nearly no stream discharge is observed in those areas (Takasaki, 1993), while in the Onomea aquifer just north of Hilo, the ratio is < 1 due to extremely heavy precipitation.

The USGS water budget report for Kaua‘i treats the island as a single aquifer and shows that around 84% of the total water discharge from the island leaves via streams, with SGD accounting for 16% of the total water flux.

3.2. Water chemistry

Our data show that there is a clear difference between groundwater and surface water in terms of chemistry (Fig. 2): groundwater has significantly higher concentrations of both TAlk (95% confidence interval (C.I.) for the mean is 1328–2162 µmol/L in groundwater vs. 307–477 µmol/L for streams) (Fig. 2a) and DSi (95% C.I. for the mean is 802–973 µmol/L in groundwater vs. 220–316 µmol/L in stream water) (Fig. 2b).

We calculate a recharge-weighted average concentration for TAlk and DSi in groundwater, assuming that the chemistry of the sampled wells is representative for the aquifer in which it is located (Table 2). Groundwater in the Kilauea region is significantly more dilute with respect to both DSi and TAlk than groundwater elsewhere (DSi: Kilauea = 697 ± 46 µmol/L (mean ± 1 s.e.); elsewhere: 928 ± 79 µmol/L; TAlk: Kilauea = 718 ± 159 µmol/L; elsewhere: 1913 ± 275 µmol/L). The Kilauea aquifers have extremely high groundwater recharge rates, and ~45% of all groundwater recharge that occurs in the archipelago flows through them (Table 1). We therefore use a separate recharge-weighted average TAlk and DSi for the Kilauea region (see above) for flux calculations.

3.3. Chemical fluxes

We compare total chemical weathering fluxes from the surface and subsurface (Table 2, Fig. 3) by calculating $R_{\text{sub/sur}} = F_{\text{gw}}/F_{\text{sw}}$, where $F_{\text{r}}$ = total flux, $gw$ = groundwater and $sw$ = surface water. This ratio indicates the relative importance of SGD and Q in delivering products of chemical weathering to the ocean.

We calculate $R_{\text{sub/sur}}$ for the island of Hawai‘i as a whole using total island-wide chemical fluxes via SGD and total surface

![Fig. 2. Comparison of solute concentrations in groundwater and surface water. Both alkalinity (TAlk) and dissolved silica (DSi) are consistently higher in groundwater than in surface water. (a) Alkalinity and (b) dissolved silica. The data plotted in this figure are from this study and the USGS, see Table A2.](image)

<p>| Table 2 | Fluxes of TAlk and DSi via surface water and submarine groundwater discharge (Kaua‘i, island of Hawai‘i) and groundwater (other Hawaiian islands). See text for explanation of calculations. Errors given are ± 1 standard deviation. |
|---------|-------------------------------|-------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|</p>
<table>
<thead>
<tr>
<th>Region</th>
<th>Groundwater $^a$ µmol/L, mean ± 1 s.e.</th>
<th>SCD $^b$ 10$^6$ m$^3$/yr</th>
<th>Area $^c$ km$^2$</th>
<th>Groundwater $^d$ 10$^6$ mol/yr</th>
<th>Surface water $^e$ 10$^6$ mol/yr</th>
<th>$R_{\text{sub/sur}}$, TAlk</th>
<th>$R_{\text{sub/sur}}$, DSi</th>
</tr>
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<tbody>
<tr>
<td>Kaua‘i</td>
<td>1913 ± 275 928 ± 79 390 ± 137 1437 510 ± 186 271 ± 96 965 ± 394 642 ± 244 0.5 ± 0.3$^f$ 0.4 ± 0.1$^f$</td>
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<td>Island of Hawai‘i</td>
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<tr>
<td>Hamakua-Hilo</td>
<td>961 ± 336 910 1752 ± 638 929 ± 328 475 ± 194 271 ± 103 1.4 ± 0.8$^f$ 1.3 ± 0.5$^f$</td>
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<tr>
<td>Kohala</td>
<td>366 ± 128 706 667 ± 243 354 ± 125 143 ± 58 111 ± 42 1.5 ± 0.8$^f$ 0.9 ± 0.3$^f$</td>
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<tr>
<td>Kilauea $^e$</td>
<td>718 ± 159 697 ± 46 4901 ± 1715 3750 3519 ± 1281 3416 ± 1208 0 0</td>
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<tr>
<td>Rest of island $^e$</td>
<td>1913 ± 275 928 ± 79 1501 ± 525 5090 2736 ± 996 1450 ± 513 0 0</td>
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<tr>
<td>Total</td>
<td>7729 ± 2705 10456 8674 ± 3157 6149 ± 2174 618 ± 252 382 ± 145 14 ± 8$^f$ 16 ± 6$^f$</td>
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<td>Other islands</td>
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<tr>
<td>O‘ahu</td>
<td>1095 1542 1996 1058 n.a.$^g$ n.a. n.a. n.a.</td>
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<tr>
<td>Moloka‘i</td>
<td>264 675 482 256 n.a.$^g$ n.a. n.a. n.a.</td>
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<tr>
<td>Maui</td>
<td>1517 1888 2764 1466 n.a.$^g$ n.a. n.a. n.a.</td>
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$^a$ SCD-weighted average concentration of TAlk and DSi. Groundwater in the Kilauea region of the island of Hawai‘i is significantly more dilute than groundwater elsewhere on the islands and we therefore calculate a separate SCD-weighted concentration for that region. See Section 3.2 for further discussion.

$^b$ SGD on Kaua‘i and the island of Hawai‘i, otherwise G.

$^c$ Arithmetic average of area-normalized fluxes from studied watersheds multiplied by area of island.

$^d$ $R_{\text{sub/sur}}$ on Kaua‘i and in individual regions on the island of Hawai‘i is calculated using area-normalized subsurface fluxes ($F_{gw}/\text{Area}$) and the arithmetic average of area-normalized weathering fluxes from the streams in each region (see Table A1). See Section 3.3 for further discussion.

$^e$ Surface discharge is approximately zero for these regions (Schopka, 2011).

$^f$ $R_{\text{sub/sur}}$ for the island of Hawai‘i as a whole is calculated using total island-wide chemical fluxes via SGD and total surface weathering fluxes from the Hamakua-Hilo and Kohala regions. Since we did not sample all streams on the island, the resulting $R_{\text{sub/sur}}$ is a maximum value. See Section 3.3 for further discussion.

$^g$ n.a. = data not available.
Fig. 3. Ratios of subsurface to surface chemical fluxes (Rsub/sur), by region. The y-scale is broken for clarity. For reference, Rsub/sur=1 is displayed with a heavy black line. Rsub/sur diminishes rapidly as the bedrock through which the groundwater percolates ages and permeability is reduced. In Hamakua-Hilo and Kohala, groundwater contributes more to the overall flux than does surface water. In contrast, stream flow is more important for solute fluxes than groundwater is on Kaua‘i.

weathering fluxes from the Hamakua-Hilo and Kohala regions. Since we did not sample all streams on the island, the resulting $R_{\text{sub/sur}}$ is a maximum value (we sampled most streams in Hamakua-Hilo and around 40% of the runoff-active area on Kohala, see Fig. A1). $R_{\text{sub/sur}}$ for TAlk is $14 \pm 8$, and $R_{\text{sub/sur}}$ for DSi is $16 \pm 6$ on the island of Hawai‘i.

$R_{\text{sub/sur}}$ on Kaua‘i and in individual regions on the island of Hawai‘i is calculated using area-normalized subsurface fluxes ($F_{\text{sub}}$/Area) and the arithmetic average of area-normalized weathering fluxes from the streams in each region (see Table A1). On Kaua‘i, an average of ~30% of solutes comes from subsurface weathering ($-15$% for TAlk, $-65$% for DSi). In the runoff-active parts of the island of Hawai‘i, groundwater is a larger vector for chemical fluxes than on Kaua‘i, where $R_{\text{sub/sur}}$ is as low as ~0.4. On average, ~60% ($-20$% for TAlk-fluxes from Hamakua-Hilo and Kohala, and ~50% ($-10$% for DSi-fluxes from these same regions, come from subsurface weathering. This percentage increases to ~94% ($-75$% for TAlk, $-35$% for DSi) for the island of Hawai‘i as a whole.

4. Discussion

4.1. Water chemistry and chemical fluxes

We attribute the higher concentrations of both TAlk and DSi in groundwater to two factors: (1) Soils in Hawai‘i are rapidly depleted of primary minerals during weathering (Vitousek et al., 1997) while groundwaters may contact a much larger reservoir of fresh minerals, and (2) longer residence time ($\tau$) of water in the subsurface than in the surface environment. For example, a groundwater $\tau$ of $\leq 35$ years in the Kilauea East Rift Zone was reported by Scholl et al. (1996), while a much shorter $\tau$ of $\leq 20$ day has been reported for water in streams on O‘ahu and the island of Hawai‘i (Fagan and Mackenzie, 2007; Paquay et al., 2007). The relatively dilute character of the groundwater in Kilauea is most likely a consequence of the very high flux of water through the aquifers.

We make the simplifying assumption that the weathering system in Hawai‘i is in steady state. All sampled streams are undersaturated with respect to amorphous Si and calcite. Our groundwater samples are all but one undersaturated with calcite and all are undersaturated with amorphous Si. The undersaturation indicates that Si and alkalinity are not being removed from the water to any great extent. Based on previous work on silica in Hawaiian streams (Mortlock and Frohlich, 1987; Derry et al., 2005), DSi varies by about a factor of two even when stream discharge varies by one to two orders of magnitude, and the correlation between DSi and stream discharge is very weak. Consequently hydrologic variability is the strongest control and also the largest source of uncertainty in our flux estimates. While we do not have long term DSi or TAlk data (and this would clearly be desirable), longer time series are unlikely to substantially modify the estimated fluxes.

We find that groundwater chemical fluxes are an important component of chemical weathering budgets on the Hawaiian Islands. Groundwater transports anywhere from 30% (Kaua‘i) to 95% (island of Hawai‘i) of the total flux of chemical weathering products from the islands. In other words, chemical weathering fluxes transported to the oceans via groundwater are up to an order of magnitude larger than via surface water.

Rad et al. (2007) also estimated the chemical weathering flux carried as groundwater discharge from two islands in the Lesser Antilles volcanic arc and the hotspot Reunion Island. They used stream discharge data and island-wide estimates of evapotranspiration to estimate ground water infiltration. They also used limited data from geothermal springs and wells to estimate the composition of groundwaters. Silica and bicarbonate (calculated by charge difference) in subsurface samples from Guadeloupe and Martinique are higher than reported here from Hawai‘i, consistent with the hydrothermal temperatures of the sampled fluids in the Antilles samples. Silica data are not available from Reunion, but HCO$_3^-$ concentrations reported in two aquifer samples are similar to values from Hawai‘i.

There is little evidence that most Hawaiian groundwater is impacted by hydrothermal activity. For example, SGD from the island of Hawai‘i has a temperature of ~19–21° C (Johnson et al., 2008; Peterson et al., 2009), and Conrad et al. (1997) showed that groundwater in deep drill holes on the east flank of Kilauea volcano is the same temperature from sea level down to ~500 m below sea level—~20–25 °C. The results from Rad et al. (2007) are therefore not directly comparable with our work. Conrad et al. (1997) do report much higher temperatures deeper in the drill-holes, but our sampling did not tap any of this water. Local geothermal sources are known from the NE Rift zone of Kilauea but we did not sample these waters. Such sources probably enhance the silica and bicarbonate fluxes delivered to the oceans in SGD but the island-wide impact is probably modest.

Rad et al. (2007) found that groundwater fluxes accounted for 45–70% of the total HCO$_3^-$ fluxes from the three studied islands, and 65–95% of cation fluxes. For the two islands for which Rad et al. (2007) report dissolved silica values, 45–80% of the silica flux was via groundwater. No uncertainties were calculated, but given the reconnaissance nature of the sampling and water balance data they are probably large. Overall, the data of Rad et al. (2007) are consistent with the results from Hawai‘i although yielding a slightly smaller contribution from subsurface alteration. All the data imply that weathering fluxes delivered by groundwater significantly exceed stream (surface) water discharges and are the main pathway for the delivery of weathering solutes to the ocean from young volcanic islands. The new data in this study
demonstrate that this conclusion holds even in the absence of high temperature water rock interaction.

Dessert et al. (2003) investigated chemical weathering fluxes from Hawaiian streams and calculated the mean CO$_2$ consumption rate (essentially equivalent to TALK in this paper) in Hawai‘i as 0.66 x 10$^8$ mol/km$^2$/yr. This is on the low end of CO$_2$-fluxes from basaltic regions worldwide (Dessert et al., 2003). They did not include groundwater fluxes in their study and our results are therefore not directly comparable to theirs. However, we did calculate the arithmetic average of area-normalized $F_{\text{TA}}$ (the CO$_2$ consumption rate) from stream discharge in individual watersheds (Table A1). On Kaua‘i, $F_{\text{TA}}$=0.59 x 10$^8$ mol/km$^2$/yr and on the island of Hawai‘i, $F_{\text{TA}}$=0.88 x 10$^8$ mol/km$^2$/yr, comparable to the value for Hawai‘i previously reported by Dessert et al. (2003). They noted that CO$_2$ consumption in Hawaiian surface waters was lower than predicted from correlations with either runoff or temperature applied to other basaltic regions (Bluth and Kump, 1994; Dessert et al., 2003). Consideration of the large SGD flux eliminates the apparent discrepancy between CO$_2$ consumption rates in Hawai‘i and those from other basaltic regions. However, estimates of the SGD contribution to the overall chemical weathering flux are not available from most other locations, and it is likely that inclusion of groundwater data would increase the total chemical weathering flux estimates for at least some of the basaltic provinces summarized by Dessert et al. (2003). The observation that Hawaiian weathering fluxes including SGD fall on the global trends for other regions that do not include groundwater may be fortuitous, or may suggest that the importance of groundwater in Hawai‘i is greater than some other places. Different age surfaces and different eruptive styles may impact the extent to which groundwater is an important carrier of weathering solutes from volcanic islands, in addition to climate variables.

The very large fluxes of weathering solutes delivered to the oceans via SGD have implications not only for the overall chemical weathering fluxes from volcanic islands but also for the role of volcanic island weathering in ocean chemical budgets. Weathering rates of volcanic islands are high as measured in stream fluxes (Louvat and Allegre, 1997; Dessert et al., 2003; Rad et al., 2007; Schopka et al., 2011), but the results of this study and of Rad et al. (2007) imply weathering rates derived only from stream fluxes will substantially underestimate the total CO$_2$ consumption in these settings. Groundwater geochemical fluxes range from being roughly equal to the stream fluxes on Kaua‘i and O‘ahu (Table 2 and Li, 1988) to more than an order of magnitude greater on Hawai‘i (Table 2).

4.2. Groundwater chemical fluxes and geomorphology

The Hawaiian Islands exhibit a striking landscape evolutionary sequence, and aspects of this are well-illustrated on the island of Hawai‘i (Fig. 4). Roughly, the windward side of the island of Hawai‘i can be divided into three geomorphic sectors. All have developed under similar trade wind dominated conditions with high rainfall, although there have been glacial-interglacial climate variations (Hotchkiss et al., 2000). The constructional shield volcano surfaces of Kilauea (<4 ka) and Mauna Loa (<30 ka) are practically un-eroded (Fig. 4a). Streams are ephemeral, even in regions of high rainfall (>4000 mm/yr). Further NW, on older Mauna Kea surfaces (50–120 ka, Sherrod et al., 2008) an incised drainage pattern develops, although with low order branching (Fig. 4b). Finally, on Kohala volcano deeply incised amphitheater-headed canyons dissect the windward escarpment (Fig. 4c). The Kohala escarpment was initiated by the Pololu slump, a giant landslide constrained to have occurred between 385 and 173 ka, and possibly between 250 and 230 ka (Lamb et al., 2007). The escarpment would have been considerably higher relative to sea level at the time, given continual subsidence of the northern part of the island of ca. 2.6 mm/yr (Ludwig et al., 1991).

To investigate the extent of landscape maturity in our study regions, we extracted topographic profiles approximately parallel to the coast, along the somewhat continuous low-relief volcanic surface that has been locally incised by multiple streams. Profile “a” in Fig. 4 is from the flanks of Kilauea and Mauna Loa volcanoes. Profile “b” is from Mauna Kea (Hamakua-Hilo region) and the last profile, profile “c”, is from Kohala (Fig. 4). These profiles were created by visually estimating the location of the 200 and 500 m a.s.l. contours of the inferred pre-incision surface and plotting the present-day elevation along these pre-incision contours. We chose the 200 and 500 m a.s.l. contours because comparing the two illustrates the striking differences in the degree of incision in the different regions, as explained below.

The constructional shield volcano surface of Kilauea and Mauna Loa shows little incision (Fig. 4a). The deepest channels observed are 10–20 m deep and we cannot tell from the elevation dataset alone if these are original features in the lava surface or if some fluvial erosion has occurred. The 200 m a.s.l. profile has not undergone significantly more erosion than the 500 m a.s.l. profile. The older Mauna Kea surface is in general considerably more incised than Mauna Loa (Fig. 4b). Erosion has removed up to ~150 m of lava (e.g. Laupaho‘ehoe Stream) along the paleo-200 m a.s.l. contour and a maximum of 100 m of lava along the paleo-500 m a.s.l. contour. This is significantly more erosion than on Kilauea/Mauna Loa, but much less than in parts of Kohala (Fig. 4c), where the transition to a highly dissected valley-and-ridge landscape is already well under way on the windward side of the peninsula. Streams in the N section of the profile drain the 120–260 kyr Hawai‘i Volcanics, while the S part of the profile is underlain by the 260–500 kyr Pololu Volcanics (Sherrod et al., 2008). The degree of erosion seen in Fig. 4b and the N section of Fig. 4c is similar, which is not surprising given the similar substrate ages in these two regions. Incision has proceeded significantly further in the older Pololu Volcanics of Fig. 4c, carving the streambed both deeper and further upstream than in profiles “a” and “b”. Along the section of coast truncated by the giant Pololu slump it is not uncommon for streams to have incised almost down to sea level along the paleo-500 m a.s.l. contour. Some of these valleys, most notably Pololu and Waipio valleys were cut deeper during periods of Pleistocene low sea level stands and have since been filled with alluvial sediments as base levels rose (see Lamb et al., 2007 and references therein).

The dramatic differences in present stream dissection and topography suggest different water routing pathways in the three regions. We can use the silica content of stream water to gain some insight into the sources of stream water in different geomorphic settings. Streams with different geomorphic characteristics exhibit differences in the concentration and downstream evolution of D$_{Si}$ along the stream profile (Fig. 5).

A representative stream profile from the Hamakua-Hilo region (Manule Stream) on the windward slope of Mauna Kea hardly differs from the little eroded constructive volcanic landscape of the volcano (Fig. 5a). The measured [Si]$_{SW}$ of streams along the Hamakua-Hilo coast (Mauna Kea volcanics) is on the order of 100–200 μmol/L. This is on the lower end of Si-concentrations in surface water and much lower than any measured groundwater sample, suggesting that groundwater contributes very little to stream discharge in the region, even when incision is 100–150 m. A different picture emerges along the Kohala escarpment (Fig. 5b), where the upper reaches of the Wai‘oloa River and its tributaries drain gently sloping headwaters before plunging into the deeply dissected Waipio valley. In the headwater region, [Si]$_{SW}$ is
Fig. 4. Profiles through inferred paleo-contours at present-day 500 and 200 m a.s.l. illustrate the difference in the degree of erosion in the three study regions on the island of Hawai‘i. The top panel shows a shaded relief map of the island of Hawai‘i with 250-m contour intervals. The lines on the shaded relief map in the top panel show the approximate location of the present-day 500 (black) and 200 m a.s.l. (white) contours. We extracted topographic profiles (a–a’, b–b’ and c–c’) approximately parallel to the coast, along the somewhat continuous low-relief volcanic surface that has been locally incised by multiple streams. Due to the curvature of the volcanoes, streams do not always line up exactly in the contour profiles. For clarity, the gray dashed lines connect selected stream valleys. Kilauea Volcano is heavily impacted by tectonic gravitational landsliding on the seaward side. Reconstructing the original topography of the edifice in such regions is not straightforward and would furthermore target tectonic processes rather than erosion. The seaward flank of Kilauea was therefore omitted from the reconstruction. The same goes for Kaua‘i, where the landscape is indeed heavily eroded but also affected by large-scale faulting and gravitational collapse (e.g. Holcomb et al., 1997; Reiners et al., 1999). (a–a’) The Kilauea region is underlain in the south by lavas of Kilauea Volcano (< 4 kyr) and in the north by lavas of Mauna Loa (< 30 kyr, most surface lavas are < 7 kyr). The white arrows in the overview map and the profile indicate the boundary between the two volcanoes. Erosion is very minor in this region. (b–b’) The slopes of Mauna Kea (64–300 kyr) are significantly more incised than both Kilauea and Mauna Loa. Valleys reach a depth of ~100 m along the 500 m contour and nearly 150 m along the 200 m contour. Large areas between valleys are still little incised. (c–c’) The deep valleys in the southern (left) part of the profile on Kohala are eroded into substrate of 260–500 kyr. In the northern (right) part of the profile, the substrate is of roughly the same age as in (b), and the degree of erosion is very similar to the erosion in that profile.
generally very low (~50–150 μmol/L) but it rises abruptly to ~700 μmol/L when the streams enter the deep valley. This pattern is even more pronounced in the deeply incised Waimea Canyon on Kaua‘i (Figs. 5c, 1d). Before it enters the canyon, the Waimea River drains the Alaka‘i Swamp, a highly weathered high plateau, where the river has low [Si]sw of ~10–100 μmol/L. The tributaries entering the main trunk stream from the east drain this swamp and also have low [Si]sw, whereas ephemeral streams that originate near a knife-edge ridge on the west wall of the canyon generally have higher [Si]sw of ~500–600 μmol/L. Assuming that Si behaves conservatively and using the weighted average [Si] of groundwater (928 ± 79 μmol/L, Section...
3.2) and the measured [Si]wet of both tributaries and the trunk streams downstream, a simple mixing model reveals that groundwater contributes 15–50% of the water volume in the Waiau River and ~30% of the water volume of the Waimea River. We assume that the groundwater enters the streams both in discreet springs (e.g. “Tributary A” on Kauai) as well as via diffuse flow through the streamed. The downstream abrupt increase in silica below the major nick points in the Kohala and Waimea canyons indicates that groundwater is an important contributor to stream discharge in deeply incised valleys.

Jefferson et al. (2010) investigated the drainage development of a basaltic chronosequence in the Oregon Cascades, paying special attention to the partitioning of water among different flowpaths and how this partitioning evolves over time. There are some clear parallels between their observations and ours, although a direct comparison is not straightforward because of a lack of comparable metrics in the two studies—Jefferson et al. (2010) use hydrographs as a proxy for flowpaths whereas in this study, element concentrations are used to infer about flowpaths. Jefferson et al. (2010) found drainage density (km/km²) to be an excellent indicator of drainage development, showing a clear increase with age in their studied watersheds. No such trend was observed in our dataset. The constant drainage density we calculated for the Hawaiian watersheds is most likely a methodological issue—it is difficult to ascertain the exact contributing area to a watershed in the extremely porous rocks of Mauna Kea and Kohala, and the definition of channel length is subject to similar considerations (Schopka, 2011). We therefore developed alternate methods (incision along paleo-contours) to define the degree of drainage development in our study sites, as described above.

In the youngest landscapes on Hawaii, all precipitation that does not evaporate or transpire goes to groundwater recharge and discharge as SGD. There is no permanent surface drainage or well-developed drainage network on the young Kilauea or Mauna Loa substrates, although a few channels are active during heavy precipitation events. In the Oregon Cascades young volcanic surfaces are drained by spring-fed streams whose discharge is relatively insensitive to rainfall events (Jefferson et al., 2010). In the Cascades, the hydrograph becomes flashier as streams age, the drainage network develops and surface flow takes over from baseflow as the main contributor to stream discharge. In Hawaii, the older age of the Mauna Kea surface on the windward side of the island leads to the development of stream channels but with only low order branching. Streams in the Hamakua-Hilo region of Hawaii are flashy and fed by surface runoff and shallow groundwater, similar to their counterparts in the Cascades. There is little chemical evidence of a deep, high silica groundwater source in streams from this intermediate stage of landscape development. In the deeply incised canyons from windward Kohala (island of Hawaii) and Waimea Canyon, Kauai, the deep groundwater source is clearly evident in the stream water chemistry.

The decrease in $R_{\text{sub/sur}}$ with bedrock age (island of Hawaii <700 kyr, Kauai~5 Myr) (Fig. 3) is coupled with a general decrease in the proportion of rainfall that discharges as SGD (43% on the island of Hawaii, 7% on Kauai, see Table 1). As mixing models of ground- and surface water show, this hydrological shift is accompanied by an increased contribution of groundwater to discharge in streams draining deeply incised valleys and canyons. For the purposes of geochemical budgets and weathering studies, this result implies that in these deep valleys, weathering reactions proceeding in the groundwater reservoir contribute solutes that may be erroneously reported as the products of weathering in soils and saprolite, i.e., in the surface environment. In fact, and assuming that our mixing models are valid, over 90% of DSi in the Waimea River on Kauai and up to 75% of DSi in Waialoa River on the Island of Hawaii comes from groundwater. Counting groundwater-derived solutes with subsurface fluxes would increase $R_{\text{sub/sur}}$ in both these regions. A similar result was found by Calmels et al. (2011) in a steep, rapidly eroding watershed in Taiwan.

Our results show that groundwater is a major pathway for the transport of chemical weathering products from the Hawaiian Islands to the ocean. The importance of groundwater fluxes evolves with time and the geomorphic evolution of the islands. On the geologically young island of Hawaii, groundwater discharge of weathering products to the oceans is around 15 times greater than stream fluxes. On the older island of Kauai, direct groundwater discharge of weathering solutes still contributes more than half of the total weathering flux to the oceans. Groundwater is an essential component of the weathering system during the entire life span of a volcanic island as observed in Hawaii. In very young volcanic systems where the high hydraulic conductivity precludes surface runoff, groundwater is the only link between the weathering system and the ocean. As the landscape matures, surface runoff is generated and stream channel incision occurs. During this initial stage of landscape development, streams remain relatively dilute. Stream solutes are derived from the weathering of regolith, with negligible contributions from deep groundwater. A large fraction of precipitation continues to feed groundwater recharge and most of that recharge discharges directly into the ocean. Chemical weathering fluxes via surface water are nonetheless higher than at other stages in the landscape evolutionary sequence due to reactive nature of the regolith minerals. As the landscape continues to evolve, stream channels incise down to the level of the groundwater table and groundwater becomes an important component of stream discharge. Deeply incised streams have much higher concentrations of weathering solutes than at earlier stages. Groundwater “captured” by stream incision into the water table is often the largest source of weathering solutes to stream discharge.

5. Conclusions

In this study we have shown that direct submarine groundwater discharge (SGD) is a major pathway for weathering solutes from Hawaii to the oceans. Weathering in soils and regolith consumes CO₂ and delivers solutes to Hawaiian stream, but subsurface weathering by groundwater is much more important, by a factor of approximately fifteen on the island of Hawaii. We obtain consistent results using either dissolved silica (DSi) or alkalinity (TAkk). The total CO₂ consumption from stream water analysis and surface water budgets are 965 × 10⁶ mol/yr on Kauai and 618 × 10⁶ mol/yr on the island of Hawaii. These values are comparable to those obtained by Dessert et al. (2003). However, using estimates of groundwater recharge based on water balance modeling and the chemistry of a suite of wells, we estimate that the total CO₂ consumption from surface runoff and SGD combined are near 1475 × 10⁶ mol/yr on Kauai and 9292 × 10⁶ mol/yr on Hawaii.

Large groundwater fluxes are characteristic of young volcanic landscapes in humid settings. Comparison with other examples suggests that groundwater is commonly a major vector of weathering products to the ocean in volcanic lands, and that weathering fluxes from volcanic terranes can be severely underestimated if direct groundwater discharge to the oceans is not accounted for.

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Appendix A. Supporting information

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References


