The denudation of ocean islands by ground and surface waters: The effects of climate, soil thickness, and water contact times on Oahu, Hawaii

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Abstract

Ease of access, size, and basalt as the dominant bedrock make Oahu an ideal locality for investigating chemical weathering-driven denudation rates as a function of climate (rainfall varies by an order of magnitude), water–rock contact time, and soil thickness. New and compiled surface and groundwater solute data permit calculation of mass balances for solute fluxes from Oahu, revealing that groundwater dominates surface water solute fluxes by a factor of 3–12.

Weathering reactions were written consistent with the mineralogy of Oahu soils, permitting denudation rates to be partitioned between dissolved and suspended loads. Total denudation rates, indexed to the leaching of SiO₂, vary from 0.016 to 0.063 m/ka, with about 70% of Si transport due to dissolved loads. Drier regions of Oahu have distinctly lower denudation rates, and areas with thick weathering profiles have suppressed surface-water solute loads.

Indexing denudation in basaltic terranes to dissolved SiO₂ rather than other solutes leads to improved estimates of weathering rates. Other approaches require correction for the atmospheric depositions of sea salts based on Cl⁻/Ca⁰ abundances in waters that are assumed to derive solely from the ocean via atmospheric deposition.

Recent work indicates that Oahu is tectonically emerging at 0.060 m/ka. As long as this uplift continues, the net size of the island will slowly increase and the Koolau Range should persist as an orographic trap to precipitation, maintaining relative aridity in the Waianae Range. Comparing emergence and denudation rates suggests that growth of the island will be non-uniform, with arid regions experiencing the greatest emergence with wet regions in balance with denudation. More importantly, however, this work offers an increased appreciation of the controls on the rates and mechanisms of denudation in basaltic and intermediate composition terranes in the tropics.

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1. INTRODUCTION

An enormous literature details the growth history of the Hawaiian and other ocean islands. Less is understood regarding the mechanisms and rates of erosion by which ocean islands are denuded and eventually converted to seamounts, although there is a growing interest in this topic. The purpose of this study is to clarify the processes of chemical weathering and associated mass fluxes from tropical ocean islands in order to develop a sense of how rapidly and by what mechanisms they disappear once their constructional and gravitational collapse phases have ended. In particular, we evaluate the relative importance of ground and surface water solute fluxes and associated soil development. Although other studies have recently addressed this (e.g., Rad et al., 2007, 2011; Schopka and Derry, 2012), we present a forward model that balances dissolved and suspended loads. In addition to estimating mass fluxes and denudation rates of ocean islands (and basaltic terranes in general), we evaluate the influence of local climate variation and other variables on these fluxes. Oahu is an ideal natural laboratory due to excellent access, the availability...
of pre-existing data, bedrock is dominantly basalt, and precipitation rates and soil thicknesses vary greatly.

1.1. Background

1.1.1. Geology of Oahu

The remnants of two shield volcanoes comprise the island of Oahu (Fig. 1). Both the western side of the Waianae and eastern side of the Koolau Volcanoes have collapsed into the ocean, such that the island is constructed of their overlapping remnants (e.g., Sherrod et al., 2007). The Waianae volcano was active from \(\sim 4.0 \) to \(2.6 \) Ma, whereas the Koolau shield developed between \(\sim 3.2 \) to \(1.8 \) Ma. Beginning at about \(1.0 \) Ma until as recently as \(40 \) ka the mafic to ultramafic alkaline volcanic rocks known as the Honolulu Series were emplaced over the Koolau shield remnant in the southeastern portion of the island. By surface area, Oahu is dominated by the tholeiitic lavas of the Koolau shield (Sherrod et al., 2007).

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**Fig. 1.** Index map of Oahu illustrating the 5 hydrologic zones (Shade and Nichols, 1996) used in this study. Triangles represent water samples and shaded circles represent wells. Stiff diagrams (all at the same scale) of average ground and surface waters are presented, along with pie diagrams indicating the proportion of \(\text{SiO}_2\) in the solute load (black) on a mass basis. Red contours represent mean annual rainfall in mm.
1.1.2. Hydrogeology of Oahu

A comprehensive summary of the hydrology of the Hawaiian Islands can be found in Lau and Mink (2006). In addition, Nichols et al. (1996), Hunt (1996), and Shade and Nichols (1996) provide comprehensive summaries of the hydrogeology of Oahu. In terms of subsurface flow, fractures, intergranular textures and gas exsolution features of the lavas control the large-scale porosity and permeability of basaltic bedrock.

On a large scale, two features deserve special mention. First, steeply dipping impermeable dikes partition aquifer systems such that water levels across dike systems can vary significantly, disrupting local and regional potentiometric trends (Hunt, 1996). Second, aquifer systems comprise both fresh and saline systems. In essence, fresh water beneath the island is a large, low-density lens that sits buoyantly above seawater. The pressure exerted by the freshwater lens depresses and displaces saline water such that many water supply wells in Oahu produce water from horizons well below sea level. This is especially true near the coast where sedimentary caprock forms a confining unit (Hunt, 1996). Most fresh water exits the island via direct submarine discharge rather than runoff (Shade and Nichols, 1996).

1.1.3. Precipitation, weathering horizons, and vegetation

Annual precipitation varies by more than an order of magnitude on Oahu (Lau and Mink, 2006), thereby producing a wide range of climate and vegetation zones. Annual precipitation on the crest of the northern Koolau Range locally exceeds 7 m, whereas portions of southern and western Oahu receive <0.6 m (Fig. 1). Fairly steady rainfall occurs due to orographic effects exerted on trade wind moisture over mountain ranges, punctuated by high-intensity storms related to hurricanes, cold fronts, and convective systems. Precipitation is seasonal, with ~70% of precipitation being received between October and April (Hunt, 1996; Lau and Mink, 2006).

In a strict sense, soils are limited to <1–2 m depth, although the thickness of the weathering horizon (saprolite) can be much greater. Soil mapping (Fig. 2) shows the steep slopes of the Koolau and Wai’anae Ranges as underlain by bedrock, whereas oxisols, ultisols, inceptisols, vertisols, and mollisols dominate much of the remainder of the island. Portions of Oahu with high rainfall and gently sloping surfaces can develop thick saprolite horizons. Where annual precipitation is <130 cm, saprolite thickness is generally <30 m, and 30–90 m thick where precipitation exceeds 130 cm. Locally saprolite may be even thicker (Hunt, 1996), although steep slopes are usually devoid of soil regardless of rainfall totals (Fig. 3). Although much of the land surface of Oahu has been modified for sugarcane and pineapple cultivation, over much of the island native and wild invasive plant communities can be found inhabiting dry, mesic, and wet environments, corresponding to <120, 120 to 250, and >250 cm annual precipitation (Fig. 2). Plant communities can be quite dense, even in areas classified as dry, and year round warm temperatures ensure that soil pCO₂ values will be high. A comprehensive list of indigenous and endemic plants, including height and spread, was compiled by the Honolulu Board of Water Supply (HBWS, 2004).

1.1.4. Weathering in the Hawaiian Islands

Weathering products in the critical zone range from primary igneous minerals, to oxide and clay-rich soils to saprolite. Weathering is most rapid in permeable units and proceeds downward or inward where steep slopes are present (Hunt, 1996). However, steep slopes in both the relatively dry Waianae and wet Koolau Ranges cannot hold much soil, even where considerable vegetation is present (Figs. 2 and 3).

Weathering rates obviously depend on temperature and precipitation, or more directly, soil pCO₂, as most weathering reactions require the availability of H⁺. On the island of Hawaii precipitation >1.4 m/yr on a 170 Ka bedrock substrate has resulted in nearly complete leaching of Si, Ca, Mg, Na and K from soil (Chadwick et al., 2002). As a result, thick laterites blanket gentle slopes of the Hawaiian Islands where the climate is mesic to wet.

Although we note some exceptions to the following, previous studies suggest that over the first 20 ka after eruption, primary minerals in basalt within the weathering zone will be consumed (Vitousek et al., 1997). Over the first 150 ka in humid settings, non-crystalline metastable phases such as imogolite, allophane, and ferric hydrous increase in abundance only to ripen later to crystalline materials such as halloysite, gibbsite and hematite over time scales on the order of 1 Ma, although the process is more rapid in drier regimes (Torn et al., 1997; Chadwick et al., 2002).

1.2. Approach

In order to understand the mass fluxes from Oahu we have measured or compiled the solute content of representative surface and groundwaters over as much of Oahu as practical. The resulting data were coupled to a published water budget (Shade and Nichols, 1996), from which we have calculated the mass solute flux for surface and groundwater waters from each of five hydrologic zones (Fig. 1). Mass balances of solute fluxes alone may neglect the formation of soil minerals by hydrolysis and oxidation reactions. These minerals are subsequently transported off of the island by streams, and over long time frames soil production rates should equal erosion rates in streams by storm events, an assumption employed in complementary studies (e.g., Gaillardet et al., 1995, 1997; Louvat and Allègre, 1997; Louvat and Allègre, 2002; Rad et al., 2006). However, rather than an inverse approach (e.g., Gaillardet et al., 1995), a forward mass balance model for soil formation was developed based upon an idealized mineralogy for Koolau basalts, checking the model against observed soil mineralogy and inferred mineral stabilities based on solute data.

Although applied specifically to Oahu, the approach has the advantage of permitting the quantitative examination of weathering rates as a function of climate, evaluating the relative importance of surface water and groundwater solute fluxes, neutralization of atmospheric CO₂, and the removal
of soil by streams in any terrane dominated by intermediate or mafic rocks.

2. METHODS

Bulk soil mineralogy was determined at Brigham Young University (BYU) using a Scintag XDS-2000 X-ray diffractometer with a Ge-detector and Cu radiation followed by data reduction to semi-quantitative estimates of mineralogy using RockJock v. 7 (Eberl, 2003). Bulk soil chemistry on selected samples was measured by wavelength-dispersive X-ray fluorescence spectroscopy (Siemens 303 instrument) at BYU on calcined soils incorporated into glass disks fused in a Li-metaborate flux. Soils with very high Al₂O₃ and Fe₂O₃ are difficult to analyze, but employment of fundamental-parameter matrix corrections produced totals ranging from ≈95 to 101%, after which samples were normalized to 100% on an anhydrous basis.

Cation and anion water splits were filtered with a 0.45 μm filter and stored in acid-washed bottles. Cation splits were treated with 5–6 drops of 7 N of trace-metal grade nitric acid. Temperature, pH, and conductivity were determined in the field using an IQ instruments IQ170 multi-meter equipped with a temperature compensating ISFET pH and conductivity probes. HCO₃⁻ concentrations were determined by acid titration to a pH of 4.5 using Hach digital titrators and calibrated acids.

Fig. 2. Map of Oahu soils with soil sample localities and soil mineralogy. Modified from USDA (1972). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
Anion concentrations were determined at BYU using a Dionex ICS90 ion chromatograph. Major cation abundances were measured with a PerkinElmer 5100C atomic absorption spectrometer. Except as described below, Si and Fe were analyzed at the University of Georgia Center for Applied Isotope Studies by inductively coupled plasma atomic emission spectroscopy. In all cases we attempted to achieve charge balances to <5% for samples collected by us. However, dilute Hawaiian waters often pose an analytical challenge and balance to this level of precision was not always achievable, nor did we have control over the charge balance of data compiled from the literature.

Filtration experiments on Hawaiian stream and spring waters sampled in 2011 were conducted to examine the contribution of silica particulate fluxes at base flow conditions. Five samples were collected in plastic bottles and analyzed for Si and Al contents in both filtered (<0.45 μm) and unfiltered water. Waters were loaded by pipette onto Rigaku UltraCarry Light sample holders, weighed, and dried at room temperature in HEPA-filtered air and analyzed against calibration standards with a Rigaku ZSX Primus II X-ray fluorescence spectrometer at BYU. Unfiltered waters were agitated to re-suspend particulates prior to loading.

Water was analyzed for $^3$H at BYU with a PerkinElmer Quantulus liquid scintillation counter. Tritium concentrations are reported in tritium units (TU; 1 TU = 3.2 pCi/L). Due to low $^3$H abundances, all samples were electrolytically enriched and enrichment factors were determined from the enrichment of NIST standards. $^3$H measurement uncertainties are $\sim$0.1 TU. Soil CO$_2$ concentrations were recorded at three localities during July 2008 in 50 cm deep soil-gas wells in windward Oahu using a Vaisala CARBO-CAP CO$_2$ meter, model GM70, with factory calibrated probes.

3. RESULTS

3.1. Soil chemistry

The major element chemistry of soils reflects the progressive weathering of parent material. When normalized to an average Koolau basalt (calculated from Haskins and Garcia, 2004), soils exhibit similar depletions in SiO$_2$, MgO, CaO, Na$_2$O, and K$_2$O (Fig. 4). This is especially true of CaO and MgO, which may be reduced from 8.86 and 10.08 wt.%, respectively, to as little as 0.039 and 0.03 wt.%. Less mobile elements like Fe, Ti, and Al increase in concentration, whereas one sample from the relatively dry Waianae area of western Oahu exhibits relatively muted depletions and enrichments (Fig. 4). Measured soil gas CO$_2$ abundances ranged from 5500 to 10,200 ppmv.

3.2. Soil mineralogy

Although the mineralogy of Hawaiian soils has been reported previously (e.g., Jones et al., 2000; Chadwick et al., 2002), we have conducted a mineralogical investigation of soils from widely dispersed regions of Oahu (Fig. 2). Although these data augment what is known about the soils of Hawaii, the primary purpose of this work is to assess the validity of weathering reactions presented below in order to evaluate the transport of suspended loads from Oahu.

Except for prominent quartz peaks, an otherwise representative X-ray diffraction pattern is presented in Fig. 5a. The clay mineralogy of soils and thick saprolites from mesic and wet regions of Oahu are dominated by halloysite ± kaolinite with lesser quantities of other phases such as gibbsite. With the exception of one dry-climate vertisol from the Waianae area, smectite group clays were absent in all soils, including those from southeastern Oahu where they were reported by Johnsson et al. (1993). However, we sampled inceptisols near the coast rather than the verticalsols that line canyon bottoms on this part of the island (Fig. 2).

Because Fe and Ti are both relatively immobile and enriched in basaltic bedrock, oxide minerals are abundant and include maghemite (in particular), with lesser hematite, goethite, and ilmenite, which is common in soils developed on highly weathered tholeiitic basalt (Goulart et al., 1998). Although difficult to quantify, pseudobrookite was also recognized as a trace constituent in the diffraction patterns of many soils.

Soils developed in dry regions or on a very young volcanic substrate can vary quite remarkably from the mineralogy described above. Soils from dry regions of Oahu, especially at the base of steep slopes, often contain a large fraction of primary basaltic material. Plagioclase with pyroxene ± olivine occurs with halloysite in thin soils developed from tholeiitic basalts of northwestern and southeastern Oahu (Fig. 2).

Some soils developed on Honolulu Series substrates exhibit abundant glass and olivine ± pyroxene in diffraction patterns, even in fairly wet climates. This assemblage was confirmed by optical inspection of smear slides. In general, abundant halloysite ± kaolinite is indicated by broad peaks at $\sim$4.4 and $\sim$7 Å. Where these clays are less abundant in arid soils, a broad peak a $\sim$4.4 Å is accompanied by a small hump or a subtle flattening of the background at $\sim$7 Å. Such patterns indicate the formation of halloysite, even in arid regions where primary basaltic constituents are also present.
The presence of quartz is of particular interest, although quartz tholeiites, by definition, may contain this phase in the fine-grained groundmass. Quartz is observed in the differentiation patterns of samples from all climate zones, although it is quantifiable only in mesic and wet regions. Although quartz is present in many surface samples, we observed a maximum content of about ~9 wt.% (Figs. 2, 5a) in saprolite taken from a road cut on the eastern flank of the Koolau Range near Kailua. Notably, quartz-bearing samples are found in a weathering profile that developed in place along a ridge top on a remnant of the northern flank of the Koolau shield, precluding stream deposition of quartz-bearing sediment. These samples contain quantifiable quartz only at depths >1 m (Fig. 2).

3.3. Solute data

Solute data for this study come from mixed sources. We have collected ~45 new streams samples, along with ~30 springs and wells. These have been combined with published data from 45 wells (Hunt, 2004), as well as stream and well data retrieved from the National Water Information System maintained by the U.S. Geological Survey. In total, we have assembled solute data for nearly 170 spring, well, shaft or tunnel samples and nearly 130 stream samples distributed across Oahu (Fig. 1).

In order to avoid the effects of seawater contamination in deep wells, or spring and streams near sea level, 17 groundwater and 3 surface water samples with Cl abundance >1% of apparent seawater were eliminated from mass balance calculations. Windward Oahu streams, for example, exhibit a low and narrow range of seawater or sea salt contribution at 0.09 ± 0.02%, with none exceeding 1%. By contrast, South Central Oahu groundwater has a broad range of seawater components at 0.65 ± 1.34%, although the 1% cutoff is somewhat arbitrary, it limits the influence of seawater by significantly impacted samples without greatly reducing the size of our data set.

The large and spatially distributed data set provides confidence that mean solute values used in denudation calculations are reasonably representative of the hydrologic zones of Oahu (Fig. 1). Exceptions to this are scant surface water data from the leeward part of Oahu, where surface water fluxes are low and sampling opportunities are few. Surface water data are lacking altogether from southeastern Oahu where there are no perennial streams. Summary solute data for the 5 hydrological zones of Oahu are given in Table 1 and illustrated in Fig. 1. In a few cases, multiple measurements were available for the same stream or well. Separate analyses were retained in order to help capture temporal variability in solute content.

Oahu waters tend to have mixed anions and cations (Fig. 1), where Ca²⁺ and SO₄²⁻ are usually subordinate, and Cl⁻ is often dominant. Given the setting, Cl⁻ and Na⁺ are likely enriched due to the atmospheric deposition of sea salts. Surface waters are more dilute than nearby groundwater counterparts. SiO₂ is a major component, comprising from 10 to nearly 25% of the solute load on a mass basis (Fig. 1).

Mineral stability diagrams (Fig. 6) indicate that nearly all groundwaters are quartz saturated and in equilibrium with kaolinite. Surface waters, by contrast, exhibit a greater range of compositions, such that many waters are undersaturated in quartz and in equilibrium with gibbsite in addition to kaolinite.

Filtration experiments showed that, with one exception, Si abundances of filtered and unfiltered waters were nearly identical. One stream had an unfiltered water Si content that was approximately 2.8 times higher. However, its Al abundance was also much higher in unfiltered water, sug-
Fig. 5. (a) X-ray diffraction pattern of a saprolite from windward Oahu near Kailua. This pattern, except for abundant quartz, is representative of many weathering products from mesic and wet regions of the island. See text for discussion. Insets show saprolite in outcrop (right) as well as secondary electron (left, black and white) and X-ray maps (left, color) images of crushed saprolite. Purple image indicates the distribution of Al, where Si (yellow) was superposed. Yellow–green areas represent quartz embedded within saprolitic clay. (b) X-ray diffraction pattern of two Hawaiian tholeiites, one with gypsum-filled vesicles. Note the possible presence of a quartz peak at 26.65° on the shoulder of an adjacent plagioclase reflection. The inset is a back-scatter image showing fine-grained groundmass material of low atomic number. Some of this material has SiO2 contents of up to 93 wt.% SiO2, where the presence of other elements may reflect interferences with adjacent phases. See text for discussion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
suggesting that much of the drop in Si after filtering was due to the elimination of Si-bearing clay particles.

3.4. Tritium content

We have measured $^3$H abundances for 57 waters collected from rain, streams, springs, wells, tunnels and shafts collected in 2008, and all have less than 3 TU. Summary statistics are presented in Table 2a, and Table 2b presents student’s T probabilities that these waters represent the same population. It is clear that streams and wells, as well as rain and wells, have distinct mean $^3$H abundances from one another. Tritium abundances <3 TU are expected in waters from low latitudes 45 years after the cessation of above ground nuclear tests.

4. DISCUSSION

In order to estimate total denudation rates by a mass balance method, it is important to partition weathering into its dissolved and suspended load components. We approach this by a direct estimate of the solute flux, from which we infer a soil production term based on weathering reactions. We also assume the rate of soil removal by streams is in a long-term steady state with soil formation (e.g., Gaillardet et al., 1995, 1997; Louvat and Allegre, 1997; Louvat and Allegre, 2002; Rad et al., 2006; Schopka and Derry, 2012). This includes any mass movements that may transport debris to the base of steep slopes that is subsequently transported by streams to the ocean. Our approach, however, is that weathering reactions are validated by observed weathering zone mineralogy rather than inferred mass balances of water chemistry and fluxes, suspended load compositions and fluxes, and calculated bedrock compositions.

A published water budget (Shade and Nichols, 1996) divides Oahu into 5 distinct and useful hydrological zones (Fig. 1). This water budget has explicit runoff and recharge terms, the latter of which we assume is in a steady state with groundwater discharge to the ocean. We note that except during large storm events, the base flows to streams reflect groundwater discharges. In this sense, Hawaiian surface waters are the manifestation of shallow flow systems, although they are accounted for separately in water and mass balance budgets. However, groundwater that sustains streams at elevations significantly above sea level (>100 m) represents shallow, perched systems. Throughout much of the island the top of the main freshwater lens is well below stream elevations (e.g., Hunt, 1996) and they are therefore treated separately.

4.1. Model soil

We present a model for the mineralogical development of a lateritic soil from basaltic bedrock. The model was guided by patterns emerging from observed enrichments and depletions of elements in soil relative to bedrock, as well as soil mineralogy and water chemistry. Although the observed mineralogy of Hawaiian soils is complex, mature weathering profiles (laterites) are dominated by a mixture of kaolinite-like clays and iron oxides.

In order to write weathering reactions consistent with soil mineralogy, an estimate of expected primary basalt mineralogy, including specific formulas for solid-solution minerals, was needed. Haskins and Garcia (2004) report major elements for a thick section of the Koolau shield volcano from material recovered through drilling, permitting the calculation of a mean rock composition. Given the average Koolau basalt composition, use of MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) permitted estimation of primary mineralogy. Initial calculations were conducted at 1 kbar at the QFM buffer with 0.5 wt.% water. Magma was allowed to crystallize to 11% to approximate observed mean phenocryst abundances of ~13% (Haskins and Garcia, 2004). Groundmass
mineralogy was estimated by allowing the remaining liquid to crystallize nearly to >90% at 1 bar at the QFM buffer. The resulting mineralogy is given in Table 3.

The following weathering reactions approximate the observed soil mineralogies of Fe-oxides and an Al–Si phase (especially halloysite). The reactions for phenocrysts are:

Table 2a
Summary statistics for tritium abundances (TU).

<table>
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<th>Precipitation</th>
<th>Streams</th>
<th>Springs</th>
<th>Wells a</th>
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</thead>
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<td>Maximum</td>
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<td>2.7</td>
<td>1.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Minimum</td>
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<td>0.8</td>
<td>0.1</td>
<td>0.0</td>
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<tr>
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<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Mean</td>
<td>1.6</td>
<td>1.2</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>1 σ</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
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<tr>
<td># of observations</td>
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<td>40</td>
<td>6</td>
<td>26</td>
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</table>

* Includes samples from tunnels and shafts.

Table 2b
Student’s T-test comparisons of tritium for various Oahu water sources.

<table>
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<th>Wells a</th>
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<td>Wells</td>
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</table>

* Includes samples from tunnels and shafts.

Fig. 6. Activity diagrams for Hawaiian waters and selected clay minerals. Diagram modified from Li (1988). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
appears to be relatively immobile in our soils. By contrast, Fe continues to leach as intermediate authigenic phases mature towards halloysite and, ultimately, gibbsite. Mg continues to leach as the primary mineralogy breaks down. Mg can become soluble by complexing with organic acids or in very wet anoxic soils, iron may be reduced to the more soluble ferrous state during weathering. There is little evidence, however, for significant leaching of ferrous iron in wet regions of Oahu. X-ray diffraction data show that except ilmenite, Fe-bearing phases are exclusively ferric-iron minerals. Contrary to expectation, dry regions show the lowest Fe–Ti oxide abundances (Fig. 2). Also, intensely weathered soils reach >50% Fe₂O₃ abundances at <10% SiO₂ (Fig. 7). Well waters analyzed by us have Fe concentrations below detection limit and streams have very low but variable concentrations with a mean of 0.13 ± 0.20 mg/L. Regarding Ti, its solubility may be limited by ilmenite, and simple speciation calculations (PHREEQC, Parkhurst and Appelo, 1999) indicate that equilibrium Ti concentrations should be on the order of only μg/L. Thus, we treat these elements conservatively.

Al exhibits initial enrichments as halloysite accumulates. However, as halloysite breaks down in favor gibbsite, additional Si and some Al are released. Al₂O₃ concentrations reach a maximum at ~15% SiO₂. This value is consistent with the model soil as it equals ~30% retention of SiO₂ (Table 4) from a beginning composition of ~50%. This is discussed further in a subsequent section. Brimhall and Deitrich (1987) present a methodology for the evaluation of elemental leaching by indexing to an immobile element. When indexed to Ti, the soils in Fig. 7 show a mean leaching for SiO₂ of 72% for soils across the weathering spectrum (Fig. 7).

These variations suggest that an Fe₂O₃ phase (maghemite) and gibbsite should be the ultimate weathering components in Oahu laterites. However, in none of our near-surface samples is gibbsite the dominant clay mineral, suggesting that halloysite is most common in the near-surface environment and therefore prone to removal by streams. Mineral-stability diagrams suggest that kaolinite-like clays with some gibbsite are expected in Hawaiian soils (Fig. 6). In summary, the idealized mineralogy of halloysite (or kaolinite) and hematite (or maghemite) seems to provide a good model of Oahu laterite development.

Some discussion the presence of quartz in Hawaiian soils is warranted as it may affect mass balance estimates based

| Table 3: Model basalt mineralogy calculated from Melts. |
|----------------|----------------|----------------|
| Mineral        | Vol. abundance (%) | Formulae       |
| Phenocrysts    |                 |                |
| Olivine        | 3.2             | Mg₁₀Fe₀.₄₀SiO₄  |
| Orthopyroxene  | 6.2             | Ca₁₀Fe²⁺₀.₃₆Mg₂SiO₆ |
| Plagioclase    | 2.0             | Na₂₀.₂₆Ca₀.₇₃Al₁.₇₅Si₂.₂₇O₈ |
| Groundmass     |                 |                |
| Clinopyroxene 1 (pigeonite) | 18.8   | Ca₀.₂₂Fe²⁺₀.₄₀Mg₀.₉₆SiO₆ |
| Clinopyroxene 2 (augite)   | 23.6         | Ca₀.₈₂Fe²⁺₀.₄₀Mg₀.₇₆SiO₆ |
| Plagioclase     | 42.2            | Na₀.₅₃Ca₀.₄₇Al₁.₄₇Si₁.₅₃O₈ |
| Fe-oxide       | 4.0             | Fe₂O₃          |

* oxide phase was assumed to be pure magnetite to simplify writing of weathering reactions.
on Si transport. Quartz has previously been attributed to eolian transport (Jackson et al., 1971; Chadwick et al., 1994; Chadwick et al., 2002; Jones et al., 2000; Whipkey et al., 2002; Chorover et al., 2004; Chadwick et al., 2009). If all quartz were eolian, then its presence plays little role in denudation estimates as the accumulation of loess is expected to be in a long-term steady state with its removal by streams.
Quartz should be most abundant in wet regions where rainfall removes it from the troposphere and leaching of the weathering horizon leaves this phase in the residuum (Jackson et al., 1971; Johnsson et al., 1993). We do not dispute that most or nearly all of the observed quartz in Hawaii, especially in near-surface materials, is eolian in origin. However, certain observations suggest that some quartz could be: (a) authigenic, (b) a relict groundmass phase of quartz tholeiite, or (c) the result of low-temperature hydrothermal alteration prior to weathering. In northern Oahu, quartz is present in one weathering profile at depths >1 m (Fig. 2). As this locality is a ridge top on a remnant flank of the Koolau volcano, quartz-bearing material has not been buried by the deposition of younger quartz-free sediment. Only eluviation of quartz out of the near surface could reflect an eolian origin.

More critically, a saprolite sample from Windward Oahu, contains ~9% quartz (Figs. 2 and 5). Figure 5a indicates that this saprolite exhibits relict igneous textures in outcrop; thus, it is unlikely that the 9% quartz has been embedded into its matrix by eolian processes. Additionally, elemental X-ray maps of crushed saprolite show that the quartz is intimately embedded within clay, which also casts doubt on an eolian origin.

This saprolite is not far from a documented occurrence of quartz in amygdules produced by hydrothermal alteration (Fujishima and Fan, 1977; White, 1984). Quartz in Hawaiian surface soils has a δ18O value of ~ +18‰ (Rex et al., 1969), which could represent a low-temperature origin via interaction with continental meteoric waters, consistent with subsequent eolian transport. However, low-temperature hydrothermal alteration of basalt (100–150 °C) with Hawaiian meteoric waters (−2‰ to −3‰) could produce, in situ, a similar composition (e.g., calibration of Sharp and Kirschner, 1994).

Quartz tholeiite lavas, dominating the shield-building phase of Hawaiian volcanoes, may crystallize quartz in the groundmass (e.g., McBirney, 1993). If so, saprolitic quartz may simply be a relict groundmass phase. Fig. 5b shows X-ray diffraction patterns of two Hawaiian tholeiites, one from Mauna Loa and the other from the Koolau series, where the most intense quartz peak may be present on the shoulder of adjacent plagioclase peaks. Reconnaissance microprobe analysis reveals groundmass phases with up to ~93% SiO2, ~0.75% TiO2, and 4.3–4.5% Al2O3. Far too rich in SiO2 to represent glass, these analyses probably reflect quartz along with the excitation of Al x-rays from adjacent or subjacent feldspar, whereas TiO2 may reflect rutile inclusions. Although the origin of quartz in Hawaiian saprolite is not central to understanding the processes associated with denudation, it is important to note that non-eolian processes may be responsible for its presence in some locations.

### 4.2. Denudation rates

#### 4.2.1. Indexing to Si-fluxes

The use of Si to track silicate mineral weathering has recently been used on the island of Hawaii and Kauai (Schopka and Derry, 2012). Conceptually, the partitioning of Si can act as a proxy for tracking the weathering and ultimate removal of a unit volume of basalt (e.g., Navarre-Sticher and Brantley, 2007) from Oahu and is relatively insensitive to anthropogenic effects and atmospheric inputs (Bluth and Kump, 1994; Schopka and Derry, 2012); thus, our calculations are indexed to this element, assuming Si release is in a steady state. In other words, when all of the Si from a unit volume of basalt has been eroded, all mass associated with primary and authigenic phases is assumed to be removed as well. Six of 7 weathering reactions are tied directly to Si, and reaction (7) represents a volumetrically minor constituent in basalt (4%; Table 3).

#### Calculations showing partitioning of soil production versus SiO2 releases in dissolved loads.

<table>
<thead>
<tr>
<th>Phase weathered</th>
<th>Vol. abundance (%)</th>
<th>Reaction</th>
<th>Weighted moles SiO2 liberated</th>
<th>Weighted moles SiO2 retained</th>
<th>Total weighted moles SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine phenocrysts</td>
<td>3.2</td>
<td>(1)</td>
<td>3.2</td>
<td>0.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Orthopyroxene phenocrysts</td>
<td>6.2</td>
<td>(2)</td>
<td>12.3</td>
<td>0.0</td>
<td>12.3</td>
</tr>
<tr>
<td>Plagioclase phenocrysts</td>
<td>2.0</td>
<td>(3)</td>
<td>2.1</td>
<td>6.9</td>
<td>9.0</td>
</tr>
<tr>
<td>Total phenocrysts</td>
<td>11.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Groundmass clinopyroxene (augite)</td>
<td>18.8</td>
<td>(4)</td>
<td>18.8</td>
<td>0.0</td>
<td>18.8</td>
</tr>
<tr>
<td>Groundmass clinopyroxene (pigeonite)</td>
<td>23.6</td>
<td>(5)</td>
<td>188.9</td>
<td>0.0</td>
<td>188.9</td>
</tr>
<tr>
<td>Groundmass plagioclase</td>
<td>42.2</td>
<td>(6)</td>
<td>89.5</td>
<td>124.1</td>
<td>213.6</td>
</tr>
<tr>
<td>Magnetite</td>
<td>4.0</td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total groundmass</td>
<td>88.7</td>
<td></td>
<td>314.8</td>
<td>131.0</td>
<td>445.8</td>
</tr>
</tbody>
</table>

% of total: 70.6% 29.4%
Relative to Cl\(^-\), the SiO\(_2\) abundance of seawater is small enough to be neglected. Holland (1978) and Nordstrom et al. (1979), showed that seawater SiO\(_2\) abundances are <10 mg/L, and may be as low as 1 mg/L (Abe, 2007). SiO\(_2\) concentrations in Oahu waters, especially groundwaters, are generally elevated by comparison (Table 1), suggesting that the assumption that all SiO\(_2\) is liberated from water–rock interaction is proper.

4.2.2. Role of biogenic silica

Phytoliths and diatoms are potential sources of amorphous silica particulate fluxes, which if unaccounted for, could lead to underestimation of the role of streams in denudation. Free-floating diatoms may be discharged to the ocean, whereas phytoliths may be transported in plant debris, as suspended particles following the decay of plant matter, or their silica may be recycled via dissolution in the soil zone and re-uptake in plants. At low soil pH, phytoliths tend to be preserved (Fraysse et al., 2006), and Derry et al. (2005) concluded that most silica released to streams had passed through a biogenic silica cycle.

Five lines of evidence suggest that neglecting biogenic silica in stream denudation calculations is justified. First, groundwater fluxes, Si, and TDS concentrations are much larger than that of streams; thus, stream contributions to denudation by dissolution are small and errors in their silica budgets are unimportant. Second, although vascular plant debris is transported to the ocean by streams, the phytolith silica flux is undoubtedly small relative to dissolved fluxes or to the amount of plant litter that decays in place. Third, the work of Derry et al. (2005) suggested that the biogenic cycling of silica could reach a steady state where mineral–water reactions ultimately control Si availability despite being cycled through plants. Fourth, as described later, calculated stream denudation rates indexed to TDS abundances agree well with those indexed to silica.

Finally, filtration experiments suggest that there is little actual particulate transport of Si. Three of four stream samples examined had virtually identical Si concentrations before and after filtration, whereas the remaining had an Si content that was 2.8 times higher in unfiltered water. However, both Si and Al were removed by filtration, suggesting that Si particulate fluxes were dominated by transport of clay particles, rather than phytoliths or diatoms.

4.2.3. Denudation calculations

Denudation calculations were accomplished as follows. The density of basalt was estimated at 2600 kg/m\(^3\), accounting for the presence vesicles, joints, and other discontinuities. The mass of SiO\(_2\)/m\(^3\) is:

\[
\text{SiO}_2/m^3 = 0.5074 \times 2600 = 1319 \text{ kg/m}^3
\]

0.5074 = wt. fraction SiO\(_2\) in Koolau basalt

We multiply this value by the respective surface area of each of the 5 hydrological provinces (Shade and Nichols, 1996). For south central Oahu.

\[
\left( 1.319 \times 10^{11} \text{ kg/m}^2 \right) \left( 6.745 \times 10^5 \text{ m}^2 \right) = 8.899 \times 10^{16} \text{ kg/m}
\]

is the mass SiO\(_2\) in fresh basalt per meter depth.

After appropriate unit conversions, the groundwater flux multiplied by the average silica concentration yields the SiO\(_2\) flux from this portion of Oahu as follows:

\[
\frac{4.964 \times 10^{11} \text{ L} / \text{yr}}{10^9 \text{ kg} / \text{L}} = 2.864 \times 10^7 \text{ kg/yr}
\]

This leads directly to the denudation rate:

\[
\frac{2.864 \times 10^7 \text{ kg/yr}}{8.899 \times 10^{17} \text{ L/ka}} = 3.219 \times 10^{-9} \text{ m yr}^{-1} \approx 0.032 \text{ m ka}^{-1}
\]

These calculations were repeated for the other hydrological provinces of Oahu for both ground and surface waters. Table 5 reports calculated denudation rates with uncertainties for dissolution based upon the 1\(\sigma\) variation in SiO\(_2\).

The fraction of soil produced can be estimated from the weathering reactions discussed above. Table 4 gives estimated moles of Si released to solution or retained in soil minerals. The stoichiometry of weathering reactions describes the fate of Si in igneous silicate minerals in terms of the proportion of Si fixed in halloysite versus that leached into the aqueous phase. The abundance of each mineral, calculated from MELTS, is in turn used to weight the release and secondary fixation of Si as a result of weathering.

From the weathering reactions, halloysite clearly dominates Si-bearing phases in the soil, and ~30% of Si should be retained in clay. This permits us to estimate the contribution to denudation by dissolution of Si contributing in streams during base flow and storm events, assuming that over long time intervals stream transport is in a steady state with soil formation (Table 5).

Although we apply the value of 30% Si retention across Oahu, local variations in the degree of leaching could be applied to adjust for differences in physical erosion rates. There are two possible approaches for the local adjustment Si retention. One is to examine the mineralogy of local weathered material and rewrite weathering reactions accordingly. The other is to measure the major element composition of weathering products and use degree of silica leached following the Brantley and White (2009) methodology.

Fig. 2 indicates that model soil development and removal should be valid within wet and mesic portions of Oahu as the mineralogy in these regions is dominated by halloysite and Fe–Ti oxides. With the exception of soils developed on very young Honolulu Series substrates, soils of the dry regions of the island are also dominated by clay and iron oxides, although some primary igneous minerals are locally preserved. Thus, although the model soil is less well suited for dry portions of the island, we believe that relatively little error is introduced into the analysis as mature soils such as oxisols, mollisols, ultisols, and vertisols are quite widespread (Fig. 2).

Our denudation rates overlap with the lower to middle range of previous estimates of 0.04–0.19 m/ka for the Hawaiian Island chain (Moberly, 1965; Li, 1988; Dessert et al., 2003; Rad et al., 2007; Navarre-Sitchler and Brantley, 2007), although dry portions of the island yield rates as low as 0.016 m/ka (Table 5). Li (1988) and Moberly (1965) ap-
proached the problem on a different scale by evaluating individual drainages or a restricted set of drainages to produce estimates extrapolated to entire islands, whereas our rates are averages over five broad regions of Oahu with very different climates.

When the dissolved load calculations of Rad et al. (2007) for all of Hawaii, including ground and surface waters, are converted from mass fluxes (t/km²/yr) to denudation rates, the contribution of surface water dissolved loads equals 0.013 m/ka, which is nearly double our highest rate (0.007 m/ka) for windward Oahu. However, their groundwater rate of 0.037 m/ka falls well within our range (Ta-

By contrast, Navarre-Sitchler and Brantley (2007), after conversion, give a denudation rate of 0.059 m/ka in-
dexed to Si-fluxes. Overall, these values agree well with our calculations although they lack the resolution to ac-

4.3. Controls on denudation rates

Examination of the variation in denudation on the scale of a single island leads to three important conclusions. First, the ratio of subsurface to surface water denudation (Table 5) shows that erosion of Oahu is dominated by groundwater, a conclusion expected from the results of Rad et al. (2007) (2011), at least as far as dissolved loads are concerned. Second, variations in these rates across Oahu are significant and are influenced by climate and attendant soil thicknesses, as well as the slope of land sur-
faces, processes that are unaccounted for in other studies. Finally, integration of 3H data suggests that water-aquifer contact times are important.

4.3.1. Groundwater solute fluxes

As indicated in Table 5, the importance of groundwater in dissolved-load fluxes is 3–12 times larger than surface water. This result was inevitable because groundwater fluxes are uniformly larger than surface water flows (Shade and Nichols, 1996), and solute loads in groundwater exceed those of surface waters in all hydrological zones. In fact, solutes are elevated in groundwaters by factors as high as >4.

4.3.2. Variation in physical erosion rates

Although the dominance of dissolved mass fluxes by groundwater has recently been emphasized (e.g., Rad et al., 2007, 2011), its recognition has important conse-
quences for mass balance calculations of suspended load fluxes. After we convert from mass flux to denudation rates, Louvat and Allegre (1997) figures infer total erosion rates for Reunion Island of 0.49–3.57 m/ka, of which physical erosion dominates solute removal by factors of 7–140. By contrast, physical erosion is subordinate in Oahu, although Reunion Island bears many climatic and geological similarities. Both were created by hot-spot volcanism, exhibit large variations in rainfall due to orographic effects on tradewind moisture, and have locally perched and large basal aquifers that discharge to the ocean (Rad et al., 2007).

Louvat and Allegre (1997) did not account for dissolved fluxes in groundwater. When dissolved-load denudation rates that include groundwater for Reunion (Rad et al., 2007) are calculated, they are ~0.15 m/ka. Assuming the weathering reactions of Oahu apply to Reunion, the soil erosion term is ~0.06 m/ka, for a total rate of ~0.21 m/ka. Thus, when groundwater is added to calculations, physical erosion rates are reduced but are still on the order of 0.30–3.35 m/ka. The low end of this range is 5 times the rate inferred for Reunion using our approach.

Louvat and Allegre (1997) recognized the large difference in physical erosion rates in Hawaii versus Reunion, attributing the mechanical removal of material as a limiting factor in Hawaii, whereas chemical weathering rates are the limiting factor in Reunion. Comparison of these islands suggests that physical denudation rates may vary greatly depending on local controls, even where the geological and climatic settings are similar.

Inferred denudation rates on the order of >1 m/ka (>1 km/Ma) are nonetheless puzzling for islands like Re-
union and Oahu. For example, two shield volcanoes comprise Reunion Island: The 2–0.35 Ma, 3070 m Ma Piton des Neiges and the 0.53–0 Ma, 2600 m Piton de la Four-

_normalized_solute patterns (Fig. 8) illustrate why sur-
face water solute fluxes are low in central Oahu relative to groundwater. The Waianae and Koolau volcanoes dominate the middle of the island as represented by broad plains of their relatively intact remnant interior flanks (e.g., Sher-
rord et al., 2007; Fig. 1). As a result, thick lateritic weathering profiles up to 100 m thick have developed in the middle of the island. Shallow groundwater systems that feed base flows of central Oahu streams contact highly weathered materials and few solutes are mobilized (Bluth and Kump, 1994). By contrast, wells in central Oahu are completed deep within less-weathered basalt flows as the top of the water table is <30 m above sea level (Nichols et al. (1996)) and surface elevations in the center of the island
reach ~300 m. SiO₂ and other solute enrichment in central Oahu groundwaters (Fig. 1) reflects contact with bedrock rather than laterite.

The relative enrichment of SiO₂ in groundwater persists in windward Oahu, although subdued to a factor of ~1.5. Most of eastern Oahu is wet or mesic, yet soils are often thin to absent on the steep slopes of the windward Koolau Range (Fig. 3) where they are easily eroded. Thus, both surface and groundwaters contact relatively un-weathered material, muting the differences in solute content.

### 4.3.4. Aquifer-rock contact time

Tritium data allow us to infer longer water-rock contact times and deeper flow paths for wells compared to springs and streams, which contributes to the higher solute loads in groundwater. We assume that ground and surface-waters are decoupled, although there must be some mixing between the two. However, careful analysis of the time-series history of tritium in precipitation permits the recognition of longer mean water rock contact times in groundwater.

Fig. 9 presents a time series history of ³H abundances in precipitation from the Hawaiian Islands, augmented by data from other tropical localities, as well as a histogram of inferred ages from our ³H values. We have taken the total observed range of ³H abundances in 2008 and projected decay paths back in time to where they intersect the time-series curve for precipitation. We recognize 4 categories of water: >1.4 TU, 0.7–1.3 TU, 0.2 to 0.6 TU, and <0.2 TU. These correspond to semi-quantitative estimates of recharge 1975 to the present, 1970 to 1980, ~1960, and prior to 1960, respectively. When these intervals are assigned to their respective waters, streams have the expected shorter residence times compared to groundwaters. This would not normally be clear from the examination of raw tritium values where the oldest waters (before 1960) and youngest waters have lower tritium abundances than waters of intermediate age.

Our interpretation is consistent with data from Hufen (1974) (Fig. 10), where all streams sampled exhibit ³H and ¹⁴C activities impacted by bomb-pulse nuclides. By contrast, most wells and shafts were not affected by atmospheric nuclear testing.

### 4.3.5. Climate effects

The lowest denudation rates (Table 5) occur in leeward and southeastern Oahu, where the climate is dry, with some areas receiving < 600 mm annual precipitation (Fig. 1). The calculated rate here is one quarter that of the maximum rate in north-central Oahu. Leeward Oahu is in the trade wind rain shadow of both the Koolau and Waianae Ranges, whereas southeastern Oahu lacks an orographic trap for trade wind moisture. Denudation rates in dry portions of Oahu are much lower than wet and mesic regions. Intra-island climate variability clearly plays an important role in mass removal fluxes.

In spite of the relative aridity, solute abundances are high in Leeward and especially southeastern Oahu where Cl⁻ is elevated (Fig. 1; Table 1). This is likely due to atmospheric deposition of marine salts, leading to their accumulation in soil between recharge events.

### Table 5
Calculated denudation and CO₂ consumption rates for Oahu.

<table>
<thead>
<tr>
<th></th>
<th>Surface water m/ka</th>
<th>Groundwater m/ka</th>
<th>Soil m/ka</th>
<th>Total m/ka</th>
<th>CO₂ consumption (10⁶ mol/km²/yr)</th>
<th>Ratio groundwater/surface water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indexed to SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South central</td>
<td>0.003 ± 0.002</td>
<td>0.032 ± 0.008</td>
<td>0.015</td>
<td>0.050</td>
<td>1.09</td>
<td>11.7</td>
</tr>
<tr>
<td>North central</td>
<td>0.003 ± 0.002</td>
<td>0.041 ± 0.006</td>
<td>0.019</td>
<td>0.063</td>
<td>1.54</td>
<td>12.1</td>
</tr>
<tr>
<td>Windward</td>
<td>0.007 ± 0.002</td>
<td>0.023 ± 0.007</td>
<td>0.013</td>
<td>0.043</td>
<td>1.29</td>
<td>3.2</td>
</tr>
<tr>
<td>Leeward</td>
<td>0.002 ± 0.001</td>
<td>0.015 ± 0.003</td>
<td>0.007</td>
<td>0.024</td>
<td>1.02</td>
<td>6.5</td>
</tr>
<tr>
<td>Southeast</td>
<td>0.001 ± 0.0004</td>
<td>0.005</td>
<td>0.016</td>
<td>0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indexed to dissolved solids, corrected for seawater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South central</td>
<td>0.003 ± 0.002</td>
<td>0.024±.0010</td>
<td>0.010</td>
<td>0.037</td>
<td></td>
<td>8.5</td>
</tr>
<tr>
<td>North central</td>
<td>0.003 ± 0.002</td>
<td>0.032 ± 0.006</td>
<td>0.012</td>
<td>0.048</td>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td>Windward</td>
<td>0.007 ± 0.003</td>
<td>0.018 ± 0.005</td>
<td>0.009</td>
<td>0.034</td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>Leeward</td>
<td>0.002 ± 0.001</td>
<td>0.013 ± 0.008</td>
<td>0.005</td>
<td>0.02</td>
<td></td>
<td>5.7</td>
</tr>
<tr>
<td>Southeast</td>
<td>0.009 ± 0.001</td>
<td>0.009 ± 0.001</td>
<td>0.003</td>
<td>0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ratio of the two methods</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South central</td>
<td>0.96</td>
<td>1.32</td>
<td>1.35</td>
<td>1.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>North central</td>
<td>0.98</td>
<td>1.27</td>
<td>1.31</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Windward</td>
<td>1.06</td>
<td>1.28</td>
<td>1.26</td>
<td>1.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leeward</td>
<td>1.02</td>
<td>1.16</td>
<td>1.21</td>
<td>1.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Southeast</td>
<td>1.23</td>
<td>1.23</td>
<td>1.31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.6. Comparison of indexing methods

Finally, we compare denudation indexed to Si-leaching to approaches where solutes must be corrected for atmospheric deposition (e.g., Moberly, 1965; Li, 1988; Gaillardet et al., 1995; Dessert et al., 2003; Rad et al., 2007). By comparing the methodologies it is possible to gain insights into the strengths and weaknesses of various approaches.

Denudation rates in Table 5 were re-calculated based on total rock/soil derived solutes after subtracting the contribution of atmospheric deposition of sea salt, where all Cl was assumed to derive solely from the ocean, and all other solutes were corrected in proportion to their abundances in seawater.

For surface waters, denudation rates vary by <6% between the two methods (Table 5), an agreement we consider to be quite remarkable. By contrast, groundwater denudation rates are systematically suppressed by ~25% when correcting for sea salt. The source of this difference is unclear as it seems unlikely that basalts contain sufficient Cl to result in a systematic overestimation of atmospheric contributions.

Derry and Chadwick (2007) noted that atmospheric deposition, even in coastal settings, seldom has the composition of sea salt, with Ca in particular being enriched by a factor of up to 4.5. Mg and Na behave in a nearly conservative fashion, whereas K can also be enriched by a factor of up to 2. K is a minor constituent in Hawaiian waters, so uncertainty in the enrichment of this parameter is unimportant. A simple sensitivity study shows that reported variations in the composition of Ca in atmospheric deposition is also trivial. North central Oahu has a sea-salt corrected groundwater denudation rate of 0.032 m/ka. A threefold increase in the correction for Ca decreases this rate to only 0.031 m/ka. Additionally, the true enrichment of elements like Ca in island atmospheric deposition can be highly uncertain, so it is difficult to choose anything other than sea salt unless a long record of reliable atmospheric deposition data is available. For example, Carrillo et al. (2002) report 6 annual mean values of Ca on the island of Hawaii. Their mean Ca/Cl ratio, normalized to sea salt, is 2.2 ± 1.7.

4.4. Atmospheric CO2 consumption

Dessert et al. (2003) estimated that basalt weathering globally consumes ~4.08 × 10^{12} mol-CO2/yr. Bicarbonate fluxes for Oahu alone total 1.83 × 10^9 mol-CO2/yr, or 0.04% of the total. Dessert et al. (2003) also estimated a CO2 consumption rate of 0.66 × 10^6 mol/km^2/yr for the Hawaiian Islands. Assuming there is no contribution of carbon from the bedrock substrate, silicate weathering neutralizes carbonic acid (dissolved CO2) derived directly from the atmosphere or indirectly from the plant-soil system. Thus, we calculate CO2 consumption directly from bicarbonate abundances (Dessert et al., 2003). Our values range from 0.51 to 1.54 × 10^6 mol/km^2/yr for the various regions of Oahu (Table 5), where the highest rates are in the center...
mediate rate of 1.2 mol/km²/yr moves the Hawaiian Islands to the regression line published by Dessert et al. (2003). See text for more discussion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 10. 14C and 3H activities of Hawaiian waters as reported by Hufen (1974). See text for more discussion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the island. Assuming an intermediate rate of 1.2 × 10⁶ mol/km²/yr applies for the entire Hawaiian Island chain, this amounts to ~2 × 10¹⁰ mol/yr, which is nearly 0.5% of the total CO₂ consumed by basaltic terranes.

As noted, bicarbonate and all other species are elevated in groundwater discharging directly to the ocean explain our higher values for CO₂ consumption. In fact, an intermediate rate of 1.2 × 10⁶ mol/km²/yr moves the Hawaiian Islands to the regression line published by Dessert et al. (2003).

4.5. Speculative landform evolution

In addition to speculation regarding future landscape development in Oahu, the purpose of this subsection is to illustrate how finer-scale denudation rate studies may promote a better understanding of geomorphic evolution. McMurtry et al. (2010) suggested that Oahu is undergoing uplift at 0.060 ± 0.001 m/ka, and that this rate has been constant over the last 500 ka. The large mass of younger islands to the southeast, Hawaii, Maui, and Molokai, deflect the lithosphere downward. As Oahu moves away from the locus of active volcanism and lithospheric depression it emerges (Watt and ten Brink, 1989).

The emergence rate of McMurtry et al. (2010) is nearly identical to the denudation rate of north-central Oahu, but greater than that of the remainder of the island. Long-term higher denudation rates in windward, north-central, and south-central Oahu could have contributed to the present higher elevation of the Waianae Range, which already exceeds that of the Koolau Range by ~300 m.

As long as a steady-state elevation or net emergence persists, the Koolau Range should remain an orographic barrier, trapping precipitation from the trade winds. Subaerial basalts appeared on Kauai at ~5.5 Ma (Sherrod et al., 2007), with tectonic uplift ceasing at ~0.75 Ma (Garcia et al., 2010). In other words, 4.75 million years (m.y.) elapsed between emergence of the island near the hot spot and cessation of uplift away from it. Waianae and Koolau volcanic rocks are as old as ~4.0 and ~3.0 Ma, respectively. To a first approximation, uplift of Oahu may persist for an additional 0.75–1.75 m.y.

Once Oahu is no longer emergent, erosion of the Koolau Range will decrease its effectiveness as an orographic barrier and experience lower weathering rates as less moisture is trapped. Inspection of rainfall patterns on windward facing slopes of Hawaiian Islands indicates that precipitation drops off rapidly at high elevation. For example, on the windward slopes of Hawaii, precipitation decreases at elevations above ~300 m (Giambelluca et al., 2011), the approximate elevation of the highest portions of the Koolau Range. At the same time, increasing fractions of trade wind moisture will pass over the Koolau Range to be trapped on the Waianae Range, accelerating weathering rates there.

5. CONCLUSIONS

Oahu represents an ideal natural laboratory to investigate denudation rates as a function of climate because it is composed of a dominant bedrock, has good access, and mean annual rainfall that varies by more than an order of magnitude. Although we have conducted an investigation of a single island, we believe that the approach used and insights gained are widely applicable to mafic to intermediate terranes, especially in the tropics in light of variation in mass fluxes due to climate.

Mass balance calculations reveal that dissolved groundwater mass fluxes flux are the single largest source of mass removal, exceeding dissolved surface water fluxes by a factor of 3–12. This results from larger groundwater fluxes, which also have greater solute loads. Higher solute loads in groundwater are also the result of: (1) longer water–rock contact times, and (2) because stream base flows in areas with thick weathering profiles have been in contact with materials that have been stripped of mobile components. Mass balance calculations show that climate causes denudation rates to vary by a factor of 4, from 0.016 to 0.063 m/ka, with relatively wet regions of the island eroding faster.

Comparison of this study to investigation of the Reunion Island (Louvat and Allegre, 1997; Rad et al., 2007) suggest that much uncertainty, or large variations, exist in the balance between physical erosion and solute transport in otherwise geologically and climatically similar settings. This contrast suggests that further investigation of this contrast may prove fruitful in understanding the balance between suspended and dissolved load fluxes in a wide variety of settings.

Indexing denudation and soil production rates to dissolved SiO₂ appears to be a superior approach to TDS-
based calculations because no correction for the atmospheric deposition of sea salt is required, and although the cycling of biogenic silica is important (e.g., Derry et al., 2005) at a process level in soils, it can assumed to be in a steady-state with mineral–water reactions (Schopka and Derry, 2012). Si-indexed denudation rates nonetheless compare reasonably well with TDS-based calculations and the differences in those rates (Table 4) give additional insight into the total uncertainty in these types of calculations.

Because Oahu is in an emergent state, this study indicates that denudation coupled to rock uplift permit speculation regarding future geomorphic states. McMurtry et al. (2010) showed that over the past 500 ka Oahu has undergone tectonic uplift at a rate equivalent to our highest denudation estimate. As long as this uplift continues, the net size of the island will slowly increase and the Ko‘olau Range will likely persist as an orographic barrier to precipitation in western Oahu. However, once uplift ceases, orographic precipitation will be increasingly transferred to the Waianae Range, which will become the locus for future denudation.

Finally, although it is of secondary interest to the goals of this study, we document the occurrence of quartz in the weathering zone of Oahu that is unlikely due to eolian processes. Although wind-blown dust is undoubtedly the primary source of most quartz in Hawaiian soils, it appears that quartz can occur due to other processes, including neof ormation, low-temperature hydrothermal alteration, or especially in relict igneous groundmass.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.09.046.

REFERENCES


