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# Steep spatial gradients of volcanic and marine sulfur in Hawaiian rainfall and ecosystems





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### HIGHLIGHTS

· Sources of sulfur in Hawaiian ecosystems were investigated via sulfur isotopes.

· Basalt, sea-salt, volcanic and marine biogenic emissions have distinct isotope ratios.

· Atmospheric deposition sources of sulfur dominated all but one site investigated.

· Steep gradients of marine vs. volcanic atmospheric deposition were found.

• Gradients occurred with distance to the coast and elevation.

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### ABSTRACT

Sulfur, a nutrient required by terrestrial ecosystems, is likely to be regulated by atmospheric processes in welldrained, upland settings because of its low concentration in most bedrock and generally poor retention by inorganic reactions within soils. Environmental controls on sulfur sources in unpolluted ecosystems have seldom been investigated in detail, even though the possibility of sulfur limiting primary production is much greater where atmospheric deposition of anthropogenic sulfur is low. Here we measure sulfur isotopic compositions of soils, vegetation and bulk atmospheric deposition from the Hawaiian Islands for the purpose of tracing sources of ecosystem sulfur. Hawaiian lava has a mantle-derived sulfur isotopic composition ( $\delta^{34}$ S VCDT) of -0.8%. Bulk deposition on the island of Maui had a  $\delta^{34}$ S VCDT that varied temporally, spanned a range from + 8.2 to + 19.7‰, and reflected isotopic mixing from three sources: sea-salt (+ 21.1‰), marine biogenic emissions (+15.6‰), and volcanic emissions from active vents on Kilauea Volcano (+0.8‰). A straightforward, weathering-driven transition in ecosystem sulfur sources could be interpreted in the shift from relatively low (0.0 to + 2.7%) to relatively high (+17.8 to + 19.3%) soil  $\delta^{34}$ S values along a 0.3 to 4100 ka soil age-gradient, and similar patterns in associated vegetation. However, sub-kilometer scale spatial variation in soil sulfur isotopic composition was found along soil transects assumed by age and mass balance to be dominated by atmospheric sulfur inputs. Soil sulfur isotopic compositions ranged from +8.1 to +20.3% and generally decreased with increasing elevation (0–2000 m), distance from the coast (0–12 km), and annual rainfall (180–5000 mm). Such trends reflect the spatial variation in marine versus volcanic inputs from atmospheric deposition. Broadly, these results illustrate how the sources and magnitude of atmospheric deposition can exert controls over ecosystem sulfur biogeochemistry across relatively small spatial scales.

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#### 1. Introduction

Sulfur is essential for plant growth and therefore the functioning of ecosystems, but many aspects of sulfur cycling and biogeochemistry set it apart from other nutrients. Concentrations of sulfur in most bedrock

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parent materials of soils are low (Migdisov et al., 1983), and most primary mineral hosts are rapidly weathered (Doner and Lynn, 1989). Sulfate is the dominant inorganic form of sulfur in well-drained soils where reducing conditions are not sustained (Freney and Williams, 1983) and it is easily leached by excess water. As a result, in many well-drained, upland settings, ecosystem sulfur is dominantly supplied as sulfate in atmospheric deposition (Bern and Townsend, 2008: Hasan et al., 1970: Tisdale et al., 1986; Yi-Balan et al., 2014). Of the forms of sulfur retained in soils, organic forms usually dominate in surface soil (Freney and Williams, 1983; Houle

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and Carignan, 1992; Tanikawa et al., 2014). Below the surface, sulfate can be retained by sorption (Harrison et al., 1989; Hasan et al., 1970) and less commonly by precipitation in secondary sulfate minerals (Delfosse et al., 2005; Mayer et al., 2001). Sulfur has six oxidation states, and inorganic sulfur compounds of oxidation states lower than + 6 might occur in reducing microsites or during temporary reducing conditions but are generally considered negligible in well-drained, upland soils (Freney and Williams, 1983).

Sulfur availability can limit primary production, but this fact is both better recognized and more problematic in agriculture because of the export of sulfur by crop removal (Tisdale et al., 1986). Even in agriculture, the commonality of sulfur limitation is often masked by nitrogen and phosphorus fertilizers that contain incidental sulfur (Scherer, 2001). The patterns of sulfur limitation in agriculture correlate generally with atmospheric deposition rates (McGrath and Zhao, 1995). In coastal settings and locations downwind from anthropogenic activities like fossil fuel burning, sulfur limitation is less likely; inland areas and zones where greater rainfall promotes greater leaching are more likely to experience sulfur deficiency (Tisdale et al., 1986). In undisturbed ecosystems, atmospheric deposition in excess of demand should result in rapid 'flow-through' losses of sulfur (Likens et al., 2002), whereas if demand exceeds atmospheric deposition, more efficient recycling should result.

Much of the research on ecosystem sulfur sources and biogeochemistry has focused upon sites impacted by anthropogenic sulfur deposition and ecosystem acidification because this was a widespread problem, though it is now generally declining (Houle and Carignan, 1992; Likens and Bormann, 1974; Mitchell et al., 2001; Novák et al., 1996). Less research has been done on sulfur sources in relatively unpolluted ecosystems (Yi-Balan et al., 2014). In this study, sulfur isotopes are used to trace the mixing of natural sulfur sources of volcanic (basalt and vent emissions) and marine (sea-salt and biogenic) origin in Hawaiian atmospheric deposition and ecosystems. Bulk deposition from three sites on the island of Maui provides insight into the composition and variability of atmospheric deposition. The sulfur isotopic composition of lichens has been used to trace the composition of atmospheric deposition (Wadleigh, 2003) and two samples of lichen from the northern end of Hawaii Island are used for the same purpose here. Strontium isotopes are used to confirm lichen dependence on atmospheric inputs. Soil and vegetation from sites comprising an age-gradient, differing in volcanic substrate age from 0.3 to 4100 ka but otherwise similar, are used to examine the idea that progressive weathering and element leaching drives ecosystems to depend on atmospheric sulfur inputs. Transects are used to evaluate the importance of elevation, rainfall, and distance to the coast relative to ecosystem sulfur sources. Wide ranges in the sulfur isotopic composition of Hawaiian soils and crops have been observed (Mizota and Sasaki, 1996; Rodrigues et al., 2011), and there is potential for sulfur limitation in Hawaiian agriculture (Hasan et al., 1970; Hue et al., 1990). The results presented here shed light on the role of spatial gradients of atmospheric sulfur deposition on such patterns, and suggest that similar gradients exist in other coastal settings.

#### 2. Materials and methods

#### 2.1. Bulk deposition sampling

Bulk deposition (rainfall plus dry deposition) was collected at three locations on the island of Maui (Fig. 1). All three locations were colocated with U.S. Geological Survey (USGS) rain gaging sites. The first site was at West Wailuaiki Stream near Keanae (USGS 16518000), located at 20.81436°N, 156.14297°W at 472 m asl and about 3.0 km from the coast. West Wailuaiki is on the wetter windward side of Maui and averages 5000 mm of annual rainfall. The second site was at Oheo Gulch at a dam near Kipahulu (USGS 16501200), located at 20.66837°N, 156.05222°W, 128 m asl, and about 1.2 km from the coast. Oheo Gulch is on the southeastern corner of Maui and averages 2800 mm of annual rainfall. The third site was at Kepuni Gulch (USGS 203721156151601) located at 20.61950°N, 156.25189°W, 226 m asl, and about 1.5 km from the coast. Kepuni Gulch is on the dry, leeward side of Maui and averages 530 mm of annual rainfall.

Bulk deposition was collected by means of plastic funnels covered with nylon screening material connected via plastic tubing to polyethylene reservoirs. The reservoirs were protected from sunlight inside stream gage equipment boxes. All collector materials were soaked overnight in, and then thoroughly rinsed with, 18 M $\Omega$ /cm water. Samples were collected from the reservoirs in acid-washed, 18 M $\Omega$ /cm waterrinsed, polyethylene bottles approximately once every two months from September 2007 to December 2009. Samples were shipped to Denver, Colorado and then kept frozen until analysis.

#### 2.2. Soil and vegetation sampling

Soil samples analyzed for this study were obtained from previous studies' archives or by resampling sites from those studies. The soil samples fall into two categories. First is a series of soil depth profiles collected from substrates spanning a gradient of ages (0.3, 20, 150, 1400, 4100 ka), and therefore time for soil development, along the island chain (Fig. 1; Table 1). At each site the soils are derived from basaltic volcanic material with a reasonably similar chemistry, are colonized by similar vegetation dominated by *Metrosideros polymorpha*, have similar climate with approximately 2500 mm annual rainfall, and have low gradient topography that minimizes gains or losses by erosion (Vitousek et al., 1997). Two samples of *M. polymorpha* leaves from canopy emergent trees were collected at each site.

The second category consists of shallow soil collected along transects of elevation, rainfall and distance from the coast, but developed on lava flows of a common age (Fig. 1; Table 1). In most cases, a single 0-30 cmdepth integrated sample was taken, but in some cases samples representing one or more A horizons from similar depths were analyzed. From the Kohala Peninsula on the northern end of the island of Hawaii, 22 samples were analyzed from two transects on Hawi volcanics, assigned an age of approximately 150 ka (Vitousek et al., 2004). Supplementing those are samples from another three sites on the Hawi volcanics, assigned an age of 170 ka (Chadwick et al., 2003). Together, the transects span elevations from 160 to 1150 m, annual rainfall from 180 to 2500 mm, and distances from the coast of 1.7 to 9.4 km. Also from the island of Hawaii, 21 soil samples from two transects on the 350 ka Pololu volcanics were analyzed (Vitousek et al., 2004). Together, the transects span elevations from 13 to 569 m, annual rainfall from 626 to 1829 mm, and distances from the coast of 0.1 to 7.0 km. Estimates of annual rainfall come from Giambelluca et al. (2013). To expand the range covered by these transects, we analyzed two samples of soil (12-20 and 38-43 cm) from another site on the Pololu volcanics at 1800 m elevation, 3500 mm annual rainfall, and at 11.6 km from the coast (Marin-Spiotta et al., 2011). In addition to the soil, samples of the epiphytic cyanolichens Pseudocyphellaria crocata and Flavoparmelia caperata collected from the 3500 mm rainfall site in March of 2008 were also analyzed.

Soils from transects on the south flank of Haleakala Volcano on the island of Maui were also analyzed (Fig. 1; Table 1). The samples were initially collected as part of an investigation of environmental constraints on Polynesian agriculture (Kirch et al., 2004). From 53 ka flows of the Hana volcanics (Sherrod et al., 2003), nine samples spanning an elevation range from 152 to 790 m, annual rainfall from 545 to 780 mm, and distance from the coast of 0.7 to 4.0 km were analyzed. From 226 ka flows of the Kula volcanics (Sherrod et al., 2003), 13 samples spanning an elevation range from 154 to 2126 m, annual rainfall from 757 to 885 mm, and distances from the coast of 0.7 to 8.3 km were analyzed.

Finally, soils from three sites on the 5000 ka Na'Pali member of the Waimea Canyon Basalt on the island of Kauai were analyzed (Chadwick



Fig. 1. Map showing collection locations for soil, vegetation and bulk deposition, with sites of volcanic emissions and dominant trade wind direction shown for reference. Symbols representing sampling sites are identified by labels in the figure.

et al., 2009). These sites span an elevation range from 632 to 1153 m, annual rainfall from 500 to 1800 mm, and distances from the coast of 2.0 to 6.0 km (Fig. 1; Table 1).

#### 2.3. Bulk deposition analysis

The first few samples from each collector may have been contaminated and therefore no data are reported for those samples. The pH of bulk deposition was measured by using a model 290A pH meter and model 9157BN electrode (Thermo Fisher Scientific, Waltham, Massachusetts). A calibration suitable for low ionic strength waters was confirmed by measuring a pH of 4.00  $\pm$  0.02 for a solution of  $5 \times 10^{-5}$  M H<sub>2</sub>SO<sub>4</sub> (Davison, 1990).

Bulk deposition was filtered to <0.2  $\mu$ m by using Acrodisc syringe filters (Pall Corporation, Cornwall, United Kingdom). Cations (Ca, Mg, Na, K, Sr) were analyzed by inductively coupled plasma-mass spectrometry (DRC-e, Perkin Elmer, Waltham, Massachusetts) and anions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) by ion chromatography (Dionex DX-120, Sunnyvale, California)

(Lamothe et al., 2002; Theodorakos et al., 2002) in research laboratories at USGS in Denver, Colorado (USA). When concentrations in some samples were initially below the calibration range, those samples were evaporated at 60–90 °C on a hot plate in a laminar flow hood and concentration factors up to  $12 \times$  were determined gravimetrically. Standard reference samples of precipitation from the USGS (http://bqs.usgs.gov/srs/) were analyzed along with unknowns and measured concentrations of analytes were 81-100% of expected values.

Sulfur concentrations and volumes of rain water samples were too small to precipitate a solid sulfate for analysis by isotope ratio mass spectrometry (IRMS). Therefore, sulfur isotopic compositions for collected rain water samples were determined using a Nu Instruments HR®, double focusing multi-collector-inductively coupled plasmamass spectrometer (MC-ICP-MS), at the USGS in Denver, Colorado (USA). Isotopic mass bias fractionation was corrected using standardsample bracketing (Albarède and Beard, 2004), utilizing in-house reference materials calibrated to Vienna Canyon Diablo Troilite (VCDT). Samples and reference material were introduced to the MC-ICP-MS using a

Table	1

Summary of gradients and sites for which soil  $\delta^{34}\!S$  VCDT was measured.

Gradient type	Island	Volcanic suite	Substrate age (ka)	Elevation (m)	Mean annual rainfall (mm)	Distance to coast (km)	Number of sites
Age	Several	Several	0.3, 20, 150, 1400, 4100	1163-1238	2500	5.1-16.1	5
Spatial, elevation, rainfall	Hawaii	Hawi	150-170	160-1150	180-2500	1.7-9.4	25
Spatial, elevation, rainfall	Hawaii	Pololu	350	13-569	626-1829	0.1-7.0	21
High rainfall, lichen site	Hawaii	Pololu	350	1800	3500	11.6	1
Spatial, elevation, rainfall	Maui	Hana	53	150-790	545-780	0.7-4.0	9
Spatial, elevation, rainfall	Maui	Kula	226	154-2126	757-885	0.7-8.3	13
Spatial, elevation, rainfall	Kauai	Na'Pali	5000	632-1153	500-1800	2.0-6.0	3

desolvating nebulizer (DSN 100). The rain water samples consisted of a relatively low matrix and as such column separation was not required. Sample preparation for isotope analyses consisted of acidifying the samples using HNO<sub>3</sub> to approximately 2% HNO<sub>3</sub> by volume. The signals of <sup>32</sup>S and <sup>34</sup>S were measured using Faraday cups. In order to resolve the isobaric interferences of  ${}^{16}O-{}^{16}O$  on  ${}^{32}S$  and  ${}^{16}O-{}^{18}O$  on  ${}^{34}S$  all measurements were made using medium resolution mode (Bühn et al., 2012). A USGS Standard Reference Material (SRM) M-158 (major ion constituents, chlorinated water) was analyzed using the same preparation as the rain water samples. In addition a National Research Council of Canada certified reference material seawater standard, CAAS-4, processed through column separation was also analyzed as a secondary standard reference material (Craddock et al., 2008). Sulfur isotope data are generally reported in conventional  $\delta$  notation with respect to a standard or in-house reference material of known sulfur isotopic composition. The values of the sulfur isotope ratio  $\delta^{34}$ S VCDT are calculated as

$$\delta^{34}S = \left(R_{sample}/R_{standard} - 1\right) \times 1000 \tag{1}$$

where  $R = {}^{34}S/{}^{32}S$ . Values are expressed on a per mil (‰) basis and VCDT is the reference standard.

Triplicate analysis was carried out on both the USGS M-158 SRM and CAAS-4 which resulted in an average  $\delta^{34}$ S of + 1.5‰ ( $2\sigma = 0.2$ ) and + 21.2‰ ( $2\sigma = 0.3$ ) respectively. The USGS M-158 water sample was analyzed by IRMS at the USGS Stable Isotope Laboratory in Denver, Colorado and resulted in a  $\delta^{34}$ S of + 1.4‰ ( $2\sigma = 0.3$ ). Böttcher et al. (2006) reported an average sulfur isotopic composition of modern seawater sulfate  $\delta^{34}$ S of + 21.0‰. Both samples are within error to the reported  $\delta^{34}$ S values. Additionally, National Institute of Standards (NIST) SRM 8553 was analyzed as an unknown and resulted in a  $\delta^{34}$ S value of + 17.0‰ ( $2\sigma = 0.3$ ), comparable to the NIST certificate value of + 16.86‰ for  $\delta^{34}$ S.

#### 2.4. Soil and vegetation analysis

Soil samples were air dried and archived at room temperature. Vegetation collected for this study was air dried, rinsed with deionized water, air dried again, and milled prior to analysis. Soil and vegetation samples were screened for sulfur concentrations on a LECO SC-444 (LECO Corporation, St. Joseph, Michigan) at the USGS in Denver, Colorado prior to isotopic analysis.

Isotopic compositions ( $\delta^{34}$ S VCDT) of bulk sulfur (organic and inorganic) in soil and vegetation were measured at a USGS laboratory in Menlo Park, California, with sulfur concentrations determined simultaneously. Samples were analyzed in a Carlo Erba elemental analyzer configured as described in Fry et al. (2002) and connected to a GVI Optima IRMS. The target sulfur content per sample was 25 µg. A size series of working standard NIST 1577B bovine liver, which has been calibrated to Vienna Canyon Diablo Troilite for  $\delta^{34}$ S at + 7.6‰ (Fry et al., 2002), was analyzed at 10 sample intervals to bracket variation in sample size and correct for instrumental drift. In addition one working standard with a  $\delta^{34}$ S value of + 11.27 and NBS127 with a  $\delta^{34}$ S value of + 21.17 (Halas and Szaran, 2001) were run to correct for variations in delta value linearity. A tin capsule blank was analyzed with every run. Following analysis, chromatograms and standards were inspected for proper machine function and samples were corrected for instrumental drift and offset, and sample size and  $\delta^{34}$ S linearity. The 1-sigma precision for duplicate analyses was better than 0.4 per mil. Standards run as unknowns yielded the following  $\delta^{34}\text{S}$  VCDT values: NBS 127 + 21.4  $\pm$  0.1 ‰, NIST 1577a + 7.7  $\pm$  0.4‰, and NIST 2710 + 1.75  $\pm$  0.03‰. Although not widely used as a sulfur isotope standard, a value of + 2.7  $\pm$  0.5‰ was measured for NIST 2710 (soil) in a previous study (Bern and Townsend, 2008).

The percent sulfur was calculated using a calibration curve constructed from the size series of NIST 1577B standards in terms of mg sulfur (mg sulfur vs mass spec. peak area). The percent sulfur in NIST 1577B is 0.79. The ratio of the weight of sulfur, calculated from the sample peak areas, to the sample weight times 100 yielded percent sulfur.

#### 2.5. Strontium isotopic analysis

The two samples of lichen from the 3500 mm rainfall site on the Pololu volcanics were analyzed for their strontium (Sr) isotopic composition. The  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of plants provides a particularly robust differentiation between basaltic and atmospheric sources of Sr and is used here to compare with the differentiation associated with sulfur. The samples were prepared and analyzed at the University of Colorado as described in Bern et al. (2005). A preparation of SRM-987 analyzed on the same day yielded a  ${}^{87}$ Sr/ ${}^{86}$ Sr ratio of 0.71032  $\pm$  0.00001 (2 $\sigma$ ).

### 3. Results

#### 3.1. Bulk deposition

The pH of bulk deposition at Oheo Gulch and West Wailuaiki ranged from 4.2 to 5.4 (Table 2, Fig. 2a). Bulk deposition from Kepuni Gulch had more variable pH ranging from 3.9 to 6.4. Distinctive patterns in pH were not apparent, except that all sites recorded their lowest or second lowest pH in samples collected in June 2009. Concentrations of major ions in bulk deposition at Oheo Gulch and West Wailuaiki were quite low, while Kepuni Gulch often had much higher concentrations (Table 2). Warm temperatures and low humidity at the site, in combination with similar cation ratios to the other two sites, suggest evaporation in and on the collector as a likely explanation. Bulk deposition data are included in an electronic supplement to this article.

Expected concentrations of  $\mathrm{SO}_4^{2-}$  in bulk deposition originating from sea-salt (C\_{SS}) were calculated from

$$C_{ss} = (C_{BK}/Ref_{BK}) \times Ref_{samp}$$
(2)

where  $C_{BK}$  is the concentration of  $SO_4^{2-}$  in bulk seawater and  $Ref_{BK}$  and  $Ref_{samp}$  are the concentrations of a reference species in bulk seawater (Holland, 1984) and a bulk deposition sample, respectively (Keene et al., 1986). The ions Na<sup>+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup> were tested as reference species. Non-sea-salt sulfate concentrations were calculated from  $C^* = C_T - C_{SS}$  where  $C_T$  is the total concentration of  $SO_4^{2-}$  in the sample. Non-sea-salt sulfate concentrations were lower, even negative, when Cl<sup>-</sup> was the reference species, possibly due to high Cl<sup>-</sup> concentration in volcanic emissions. Correlation of expected  $SO_4^{2-}$  concentrations between the reference species Na<sup>+</sup> and Mg<sup>2+</sup> was good (R<sup>2</sup> = 0.90) and results using Na<sup>+</sup> are presented. Sulfate excess, expressed as C<sup>\*</sup>/C<sub>T</sub>, ranged from 19 to 77%, and the maximum value for each site was recorded for the samples collected in June 2009 (Fig. 2b).

The  $\delta^{34}$ S of bulk deposition varied widely by sampling date (Fig. 2c) and ranged from +8.2 to +19.7‰ across the three sites (Table 2). Correlation of values between the Maui sites was not particularly apparent, with the exception of the samples collected in June 2009. The lowest  $\delta^{34}$ S for each site was recorded for those samples, corresponding with the maximum excess SO<sup>2</sup><sub>4</sub><sup>-</sup> and relatively low pH (Fig. 2a, b, c).

#### 3.2. Soil and vegetation

Along the age gradient of sites receiving approximately 2500 mm of annual precipitation, soil  $\delta^{34}$ S ranged from + 0.0 to + 19.3‰ (Fig. 3). Values increased with substrate age and varied little with depth relative to the variation along the age gradient. Sulfur concentrations in soil ranged from 0.02 to 0.22 wt.%. Values of  $\delta^{34}$ S in leaves from *M. polymorpha* were similar to soil at the site where they were collected,

Means and ranges for the sulfur isotopic composition and concentrations of selected elements in bulk deposition samples. Data for individual samples are included in a supplementary table included with the electronic version of the paper.										
	δ <sup>34</sup> S VCDT	pН	$SO_4^{2-}$	Cl <sup>-</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Sr <sup>2+</sup>	$SO_4^2^-$ excess

		$\delta^{34}$ S VCDT (‰)	рН	SO4 <sup>2-</sup> (ppm)	Cl <sup>_</sup> (ppm)	Mg <sup>2+</sup> (ppm)	Ca <sup>2+</sup> (ppm)	Na <sup>+</sup> (ppm)	K <sup>+</sup> (ppm)	Sr <sup>2+</sup> (ppb)	$SO_4^{2-}$ excess ( $C^*/C_T$ )
Kepuni Gulch	Mean	14.3	5.2	13.5	51.6	3.7	1.6	28.2	5.0	21.0	45%
	Range	8.2–16.4	3.9–6.4	0.5–48.5	1.4–205.4	0.1–14.9	0.2–5.4	0.7–115	0.03–40.8	0.7–82.0	23–77%
Oheo Gulch	Mean	15.0	4.8	1.3	5.5	0.3	0.2	2.6	0.2	2.4	47%
	Range	10.6–18.5	4.4–5.4	0.6–3.4	2.6–8.4	0.1–0.7	0.1–0.3	0.9–4.1	0.1–0.3	0.6–5.1	27–72%
West Wailuaiki	Mean	16.1	4.9	0.9	4.5	0.3	0.2	2.1	0.1	1.7	37%
	Range	10.5–19.7	4.2–5.3	0.3–1.7	1.3–6.7	0.1–0.5	0.1–0.2	0.6–3.9	0.03–0.2	0.8–2.7	19–77%

although there is greater variance for the two oldest sites (Fig. 3). Soil data are included in an electronic supplement to this article.

On the island of Hawaii, soil derived from the 150–170 ka Hawi volcanics had  $\delta^{34}$ S values that ranged from + 8.1 to + 15.1‰ (Fig. 4),



Fig. 2. Time series of chemical and isotopic parameters in bulk deposition samples collected on the island of Maui: (a) pH (b) SO<sub>4</sub><sup>2-</sup> excess calculated relative to Na<sup>+</sup>; (c)  $\delta^{34}$ S VCDT.

and sulfur concentrations that ranged from 0.03 to 0.17 wt.% (Supplementary Fig. 1). The  $\delta^{34}$ S values of soil derived from the 350 ka Pololu volcanics ranged from + 13.9 to + 18.1‰ and sulfur concentrations ranged from 0.04 to 0.15 wt.%. Sulfur concentrations generally increased with increasing elevation, distance to the coast, and rainfall (Supplementary Fig. 1) mimicking trends in soil carbon (Vitousek et al., 2004) and suggesting predominance of organic sulfur forms. Correlations of  $\delta^{34}$ S with environmental variables were more obvious when data from the two parent material ages were combined. Values of  $\delta^{34}$ S generally decreased with increasing elevation and distance to the coast (Fig. 4a, c), but showed less correlation with annual rainfall (Fig. 4e).

The two samples of B horizon material from the 3500 mm rainfall site on the 350 ka Pololu volcanics had  $\delta^{34}$ S values of + 11.5 and + 12.6‰ (Fig. 4 a, c, e) and sulfur concentrations of 0.14 and 0.20 wt.%, respectively. In contrast, the two samples of lichen from the same site had  $\delta^{34}$ S values of + 4.3 and + 6.4‰, and sulfur concentrations of 0.06 and 0.16 wt.%, respectively. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios measured in the two lichens were 0.70825 and 0.70819.

On the island of Maui, soils from the 53 ka Hana volcanics had  $\delta^{34}$ S values that ranged from + 13.7 to + 18.2‰ (Fig. 4b, d, f), and sulfur concentrations that ranged from 0.08 to 0.17 wt.%. Soils derived from the 226 ka Kula volcanics had  $\delta^{34}$ S values that ranged from - 8.6 to + 20.3‰, and sulfur concentrations that ranged from 0.04 to 0.12 wt.%. Sulfur concentrations were not well correlated with elevation, distance from the coast, or annual rainfall (Supplementary Fig. 1). Trends of decreasing  $\delta^{34}$ S values with increasing elevation and distance from the coast were apparent when data for both parent material ages were combined (Fig. 4b, d). Any trends with annual rainfall were less clear, again possibly due to its restricted range (Fig. 4f).



Fig. 3. Sulfur isotopic composition of soil and vegetation along the age gradient. Soil is denoted by solid symbols and plotted by depth. Vegetation (*Metrosideros polymorpha*) is denoted by open symbols plotted at an arbitrary height above soil. For reference, substrate ages are printed below soil profiles and the isotopic compositions of basalt parent material, volcanic emissions, marine biogenic, and sea-salt sulfur are marked by dashed lines.





Fig. 4. Sulfur isotopic composition of shallow (generally 0-30 cm) soil plotted versus elevation for Hawaii (a) and Maui and Kauai (b), plotted versus distance to the coast for Hawaii (c) and Maui and Kauai (d), and plotted versus annual rainfall for Hawaii (e) and Maui and Kauai (f). Legends describe the island and name and age of the volcanic suite associated with each transect. For reference, the isotopic compositions of basalt parent material, volcanic emissions, marine biogenic, and sea-salt sulfur are marked by dashed lines.

On the island of Kauai, soils on the Na'Pali volcanics had  $\delta^{34}$ S values that ranged from + 15.4 to + 16.8‰, and sulfur concentrations ranged from 0.04 to 0.15 wt.%. Although weak trends of decreasing  $\delta^{34}$ S values with increasing elevation, rainfall and distance from the coast were detected (Fig. 4b, d, f), the small number of sampling locations suggests caution in interpreting the trends.

а

#### 4. Discussion

#### 4.1. Hawaiian sulfur sources and isotopic compositions

On the Hawaiian Islands, the parent material for most soils is mantle-derived basaltic volcanic rock or tephra, with a  $\delta^{34}$ S value of  $-0.8 \pm 0.2\%$  (Sakai et al., 1982). Marine sources strongly influence atmospheric deposition in Hawaii. Marine sulfur in atmospheric deposition has two components: sea-salt and sulfur of biogenic origin, including dimethyl sulfide  $((CH_3)_2S)$  and its oxidation products of SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. Sea-salt has a  $\delta^{34}$ S value around +21.1‰. Although  $\delta^{34}$ S values ranging from +15 to +22% have been suggested for marine biogenic sulfur (Li and Barrie, 1993; McArdle and Liss, 1995; Norman et al., 1999), here we use the value of  $+15.6 \pm 3.1\%$  that has been measured over the remote Pacific Ocean (Calhoun et al., 1991). Another significant component of atmospheric sulfur in Hawaii is emissions from the active volcano, Kilauea, which have a  $\delta^{34}$ S value around +0.85‰ (Sakai et al., 1982). On average, Kilauea Volcano emitted  $8.6 \times 10^4$  and  $5.9 \times 10^5$  tons/year of SO<sub>2</sub> from the summit crater and the East Rift Zone, respectively for the years 1992-2010 (Elias and Sutton, 2012). Resulting volcanic aerosols are fine ( $\leq 0.3 \,\mu m$ ) and consist of both H<sub>2</sub>SO<sub>4</sub> emitted by the volcano and SO<sub>2</sub> rapidly oxidized to H<sub>2</sub>SO<sub>4</sub>. While the dominant northeasterly trade wind direction would seem to carry volcanic emissions out to sea (Fig. 1), diurnal heating generates daytime upslope and nighttime downslope surface airflow components over much of the island of Hawaii, and the pattern dominates on the leeward side of the island (Chen and Nash, 1994). Breaks in the northeasterly trade wind pattern occur roughly 74 to 155 days per year (Garza et al., 2012), and those breaks can allow reverse air flow to carry volcanic emissions northwest along the archipelago to a degree that causes noticeable declines in air quality.

Seabird guano is another potential source of sulfur to Hawaiian ecosystems, though this source has declined precipitously. Populations and species diversity of seabirds were much greater prior to Polynesian colonization around 1400 years BP and subsequent European colonization (Brandt et al., 1995; Olson and James, 1982). Guano from birds feeding on marine foods should have  $\delta^{34}$ S near the sea-salt value of +21.1%.

Anthropogenic emissions do not seem to be a significant complicating factor in using isotopes to trace sources of sulfur except possibly in the vicinity of power plants. In 2005, the oil-fired power plants in Hawaii emitted  $2.1 \times 10^4$  tons of SO<sub>2</sub> (Commission for Environmental Cooperation, 2011) making their combined emissions  $30 \times$  smaller than the volcanic source. Long-range transport from dust or anthropogenic sources in Asia could contribute to sulfur in Hawaii (e.g., Yi-Balan et al., 2014) but inputs should be small relative to more local sources.

#### 4.2. Sulfur sources in bulk deposition

Chemical parameters provide relatively little insight into the contributions of sea-salt, marine biogenic emissions and volcanic emissions to sulfur in bulk deposition. Influence of volcanic emissions on bulk deposition chemistry at the Maui collection sites should be small based on distances from the major source (161-180 km) and prevailing winds carrying emissions to the southwest (Fig. 1). The low pH and high  $SO_4^{2-}$  excess in the June 2009 samples (Fig. 2a, b) are suggestive of H<sub>2</sub>SO<sub>4</sub> of volcanic emission origins decreasing the pH of deposition, but no broad correlations were observed between excess  $SO_4^{2-}$  (or Cl<sup>-</sup>) and pH across the sample set. Volcanic H<sub>2</sub>SO<sub>4</sub> has been linked to acidity in rainfall around Kilauea's summit (Harding and Miller, 1982) and high excess  $SO_4^{2-}$  has been detected in rainfall around the vent at Kilauea (Scholl and Ingebritson, 1995). Excess  $SO_4^{2-}$  and low pH are not definitive links to volcanic emissions though. Similar ranges of pH have been recorded both upwind (4.0-5.6) and downwind (4.1–5.6), with non-SO $_4^2$  sources contributing to the upwind acidity (Nachbar-Hapai et al., 1989; Siegel et al., 1990). Concentrations of major ions, including  $SO_4^{2-}$ , in the Maui bulk deposition are similar to those measured at the northern end of the island chain on Kauai (Carrillo et al., 2002), with the exception of the evaporated Kepuni Gulch samples. Even the spike in excess  $SO_4^2$  must be viewed skeptically, as excess  $SO_4^2$  can be 30% even on remote islands (Galloway et al., 1982).

Better insight into the influence of volcanic emissions can be achieved by examining the sulfur isotopic composition of bulk deposition. Excess  $SO_4^{2-}$  in bulk deposition is plotted versus  $\delta^{34}S$  in Fig. 5. Three likely

contributors to sulfate in bulk deposition are also plotted to define a mixing domain. These are +0.85% for volcanic emissions (Sakai et al., 1982), +21.1% for sea-salt (Rees et al., 1978) and +15.6% for marine biogenic emissions (Calhoun et al., 1991). A two-step series of calculations explored the relative contribution of these sources to sulfate in bulk deposition. The first step was based upon a classic two-endmember isotopic mixing equation, using the concentrations of SO<sub>4</sub><sup>2-</sup> in different components defined above and  $\delta_{samp}$ ,  $\delta_{SS}$  and  $\delta^*$  to represent the  $\delta^{34}$ S values of bulk deposition samples, sea-salt and the non-sea-salt fraction, respectively:

$$\delta_{samp} = \frac{(\delta^* C^*) + (\delta_{SS} C_{SS})}{C^* + C_{SS}}.$$
(3)

That equation can be rearranged to solve for the  $\delta^{34}S$  value of the non-sea-salt fraction by

$$\delta^{*} = \frac{\delta_{samp}(C^{*} + C_{SS}) - (\delta_{SS}C_{SS})}{C^{*}}.$$
(4)

Calculated  $\delta^{34}$ S values of non-sea-salt fractions of bulk deposition ( $\delta^*$ ) ranged from + 0.3 to + 16.2‰.

The second step used assumed  $\delta^{34}$ S values for sulfate from biogenic emissions ( $\delta_{biogenic}$ ) and volcanic emissions ( $\delta_{volc}$ ) to determine the contribution of volcanic emissions to the non-sea-salt fraction by

$$\frac{C_{\text{volc}}}{C_{\text{volc}} + C_{\text{biogenic}}} = \frac{\delta^* - \delta_{\text{biogenic}}}{\delta_{\text{volc}} - \delta_{\text{biogenic}}}.$$
(5)

The calculation assumes that non-sea-salt sulfate comprises only sulfate from those two sources. Volcanic contributions to bulk deposition  $SO_4^{2-}$  ( $C_{volc}/C_T$ ) ranged from -2 to 58%, with a median value of 24%. The negative values resulted from samples falling outside the mixing domain (Fig. 5) therefore violating assumptions of the calculations. The concentration of  $SO_4^{2-}$  in bulk deposition from marine biogenic contributions was calculated as  $C_{biogenic} = C^* - C_{volc}$ . Marine biogenic contributions to bulk deposition  $SO_4^{2-}$  ( $C_{biogenic}/C_T$ ) ranged from -1 to 53% with a median value of 18%.

Several variables underlie such determinations, including both the isotopic composition of the contributing sources and error in the measurements made for the study. However, it is clear that each source can contribute substantially to sulfur in bulk deposition. The magnitude



**Fig. 5.** Sulfur isotopic composition ( $\delta^{34}$ S VCDT) of bulk deposition samples from the island of Maui plotted versus SO<sub>4</sub><sup>2-</sup> excess calculated relative to Na<sup>+</sup>. For reference, the endmember contributors to bulk deposition sulfate (sea-salt, marine biogenic emissions and volcanic emissions) are plotted to outline a three-component mixing domain.

of the volcanic emissions component is a bit unexpected and suggests that breaks in the trade wind pattern (Garza et al., 2012), along with complex diurnal shifts in leeward wind patterns from island heating and cooling (Chen and Nash, 1994), result in substantial transport of volcanic aerosols in directions perpendicular to the trade winds. Peak volcanic contributions in June 2009 correspond to a time of heightened emissions (Elias and Sutton, 2012) and more frequent breaks in the trade wind pattern (Garza et al., 2012). Additional insight into the geographic influence of volcanic emissions comes from the two lichen samples from the northern end of the island of Hawaii (Fig. 1). The lichens had Sr isotopic compositions much more similar to sea-salt (0.7092), than generally measured in Hawaiian basalt (0.7035; Kennedy et al., 1998), confirming their dependence on atmospheric contributions for nutrients. However,  $\delta^{34}$ S values of + 4.3 and + 6.4‰ indicate that the lichens contain substantial amounts of sulfur from volcanic emissions. Sorption of SO<sub>2</sub> on the surfaces of the lichens, followed by oxidation and uptake, may have enhanced their volcanic emissions signature over that of bulk deposition in the area. Nevertheless, the apparent magnitude of the volcanic emissions component is surprising considering the location is generally considered free of volcanic emission influence during normal trade wind patterns (Longo et al., 2005).

#### 4.3. Sulfur sources in terrestrial ecosystems

Sulfur isotopes can be reliable tracers of terrestrial ecosystem sulfur sources (Krouse et al., 1991). Fractionations associated with biological cycling of sulfur and sulfate sorption/desorption are on the order of 2‰ or less (Norman et al., 2002; Novák et al., 2001; Trust and Fry, 1992; van Stempvoort et al., 1990). Fractionations resulting from dissimilatory sulfate reduction can be large (Brunner and Bernasconi, 2005), but proportionately large net fractionations have not been found in well-drained upland soils. An intensive study of Puerto Rican soils found net fractionations of generally 3‰ or less resulting from plant uptake, oxidation of reduced sulfur by microbial mineralization, and dissimilatory sulfate reduction (Yi-Balan et al., 2014). There, in a pattern most generally attributable to plant uptake discrimination against <sup>34</sup>S, plants and near-surface soil were depleted in <sup>34</sup>S relative to average atmospheric deposition and deeper soils were enriched, but all values were generally within 2‰ of average atmospheric deposition that varied from 10.7‰ to 20.5‰ (Yi-Balan et al., 2014).

At the sites along the age gradient studied here reasonable matches are seen between the  $\delta^{34}$ S values of *M. polymorpha* leaves and soils, and generally small  $\delta^{34}$ S variations with depth (Fig. 3). The pattern of lower  $\delta^{34}$ S values near the surface and greater values at depth in some profiles matches patterns in soils from the Puerto Rico study (Yi-Balan et al., 2014). Similar to Puerto Rico, it appears ecosystem cycling integrates the temporal variability in sulfur sources such as that detected in Hawaiian bulk atmospheric deposition. The pattern of  $\delta^{34}$ S values becoming increasingly similar to marine sources, particularly sea-salt, could be interpreted as a straightforward, age-driven transition from rock-derived to atmospherically derived sources for sulfur (Fig. 3). Several points caution against that simple interpretation. First, subaerial basalts in Hawaii have low sulfur contents around 150  $\pm$  50 mg/kg due to outgassing of volatile components (Sakai et al., 1982). Low concentrations make parent material sulfur vulnerable to dilution by external inputs. Second, the variation of  $\delta^{34}$ S in bulk deposition (Fig. 2c) indicates uncertainty with regard to  $\delta^{34}$ S values expected for an ecosystem dominated by atmospheric sulfur deposition. Third, sulfur deposition rates can be high relative to ecosystem stocks. The age gradient sites shown in Fig. 3 contain 1900 to 3400 kg S/ha in the top 50 cm of soil, with the 150 and 1400 ka sites at the lower end of the range. On the island of Kauai, far from modern volcanic emissions, atmospheric deposition can provide 12 kg S/ha annually (Carrillo et al., 2002). Such a rate would supply enough sulfur to equal the stocks in the top 50 cm of age gradient soils in 150 to 300 years, indicating potentially high turnover rates and flow-through of sulfur. Incidentally, such high deposition

rates would limit the influence of sulfur inputs from modern or precolonization seabird guano. Finally, spatial variation in the patterns of  $\delta^{34}$ S values in soils of common age and narrow variation in annual rainfall on Maui indicates that factors other than degree of weathering are at play (Fig. 4).

Soil  $\delta^{34}$ S values that seem to decrease with increasing annual rainfall along the transects are notable (Fig. 4), because, other factors being equal, greater annual rainfall should drive more extensive depletion of rock-derived sulfur (Chadwick et al., 2003). That greater annual rainfall does not cause soil  $\delta^{34}$ S values to shift away from the basaltic parent material signature suggests that degree of weathering is not significant in determining ecosystem sulfur sources at these sites. Declines in  $\delta^{34}$ S values with both increasing elevation and distance from the coast are the clearest trends observed on the soil transects on Hawaii and Maui (Fig. 4). Spatial variations in the magnitude of marine sulfur inputs provide the best explanation based on the observed patterns. That explanation has been invoked for similar declines in  $\delta^{34}$ S of rainfall and soil sulfate with distance from the coast in Israel and Japan, respectively (Mizota and Sasaki, 1996; Wakshal and Nielson, 1982). The major element load of Hawaiian rainfall is dominated by sea-salt and salt content decreases with distance from the coast (Eriksson, 1957). Examining sulfur specifically, concentrations in rainwater decreased by half from near the coast to 2 km inland on the islands of Kauai and Oahu, far from active volcanic emissions (Hue et al., 1990). Sulfur concentrations also showed an approximately linear decrease with increasing annual rainfall (Hue et al., 1990). A major factor driving those patterns is that concentrations of sea-salt in the atmosphere can decline by about half in the interval from 10 to 30 m above sea level over open ocean, and decline more gradually above that (Blanchard et al., 1984). However, sea-salt aerosol deposition rates can decline by almost an order of magnitude within a few kilometers of a coastline even without great changes in land elevation (Nyaga et al., 2013). Thus, spatial variation in the intensity of marine aerosol deposition explains the increasing soil  $\delta^{34}$ S values with decreasing elevation and proximity to the coast.

Relatively low soil  $\delta^{34}$ S values at sites higher in elevation and farther inland could be the result of retained parent material sulfur or proportionately greater volcanic emissions in deposition. The transition to atmospheric dependence could be slower at inland locations, as Hue et al. (1990) found annual atmospheric sulfur deposition rates declining from 24 kg/ha at the coast to 1 kg/ha at 24 km inland on Kauai and Oahu. However, even at the lower end of those deposition rates, parent material ages on the transects suggest cumulative atmospheric sulfur inputs sufficient to easily dominate soil stocks. Therefore, the lower  $\delta^{34}$ S values on the Hawaii and Maui soil transects point to a substantial volcanic emissions contribution. Bulk deposition collected as part of this study sheds little light on deposition compositions for inland transect sites, as even the West Wailuaiki collection site was only 3 km from the coast and at 472 m asl. Even so,  $\delta^{34}$ S and pH values in some bulk deposition samples detect a volcanic emissions influence, detections that are more notable considering that samples integrate roughly two months of deposition. Values of  $\delta^{34}$ S of 4.3 and 6.4‰ in the lichens from the 3500 mm rainfall site in the interior of Kohala also suggest volcanic emissions inputs can be quite important to inland ecosystems far from, and not immediately downwind from, the active vents. A study of volcanic aerosols around the island of Hawaii found that their concentrations increased with altitude below the 1800 m temperature inversion (Longo et al., 2005). Thus, the absolute magnitude of volcanic emission inputs to ecosystems might also increase with elevation. Eq. (5) can be used to estimate the fraction of volcanic emissions sulfur in soils from the transects, with the 15.6% value for marine biogenic emissions providing a more conservative estimate than the  $\delta^{34}$ S value of sea-salt. By this means, it is estimated that volcanic emissions may account for as much as 30% and 48% of the sulfur in some of the Hawaii and Maui transect soils, respectively. Such percentages indicate a surprising level of volcanic influence, particularly for Maui considering its distance and position relative to the active volcano (Fig. 1). It is likely

that such high proportions may reflect the paucity of marine inputs at high elevations as much as the magnitude of volcanic emissions inputs.

As mass balance favors rapid transitions to dominance of ecosystem sulfur by atmospheric sources, it may be asked whether any site examined retains significant proportions of parent material sulfur. Of the age gradient sites, the 20 ka site may be the most likely (Fig. 3). Its location on the windward side of Hawaii with topographic shielding by Mauna Kea reduces the potential for contributions from volcanic emissions. The age of the site may be unfavorable from the mass-balance perspective, but the soil contains a buried A horizon indicating input of parent material sulfur via tephra more recently than the site age would indicate (Kennedy et al., 1998; Ziegler et al., 2005). Low  $\delta^{34}$ S values at the 0.3 ka age gradient site (Fig. 3) cannot be interpreted with any confidence because it receives 32 kg S/ha annually in rainfall and an additional 220 kg S/ha from fog deposition (Carrillo et al., 2002) due to its proximity to the East Rift Zone (Fig. 1). Intermediate  $\delta^{34}$ S values at the 150 ka site cannot be interpreted as indicating residual parent material sulfur as the lichens collected at a similar elevation and just 5.5 km away were dominated by volcanic emissions sulfur. The site on Hawi volcanics (150 ka) receiving only 180 mm annual rainfall (Fig. 4a, c, e) has low  $\delta^{34} S$  values that are difficult to interpret. Its low elevation and close proximity to the ocean suggest marine aerosol deposition should be significant. However, low rainfall and sparse vegetation may limit washout or surface capture of marine aerosols and the low  $\delta^{34}$ S values could indicate parent material sulfur not entirely diluted by marine inputs. Alternatively, some aspect of the site's location along the leeward Kohala Coast might cause it to receive greater than expected deposition of volcanic emissions and the low  $\delta^{34}$ S values could still be atmospheric. Retention of parent material sulfur seems unlikely considering the measurable silicate weathering and losses of rock-derived elements from the site (Chadwick et al., 2003). Thus, only the 20 ka age gradient site (Fig. 3) can be confidently said to contain a substantial fraction of parent material sulfur.

The predominance of atmospherically sourced ecosystem sulfur documented for Hawaii is not unusual, but it contrasts with other nutrient elements like calcium and phosphorus. Under annual rainfall of ~2500 mm/yr, the shift to predominance of atmospheric calcium at negligibly eroding sites happens between 20 and 150 kyr, driven by feldspar weathering and sea-salt deposition rates (Chadwick et al., 1999). For phosphorus the transition happens between 1.4 and 4.1 my, due to slower leaching losses and smaller atmospheric inputs via dust (Chadwick et al., 1999). Soil erosion can also rejuvenate the weathering-derived nutrient stocks of calcium and phosphorus (Vitousek et al., 2003), but it does not substantially influence sulfur in the same way (Bern et al., 2007). Settings do exist where parent material sulfur is detectable in ecosystems (Bern and Townsend, 2008) or even alters the broad geochemistry of soil (Fanning, 2006), but more frequently atmospheric deposition exerts the ultimate control over sulfur sources and availability.

The steep gradients in atmospheric and ecosystem sulfur sources and isotopic composition documented along relatively small (~10 km) spatial scales (Fig. 4) are striking. A number of sulfur isotope studies have found relatively little variation over large expanses of ocean (Calhoun et al., 1991) or continental interiors (Novák et al., 1996; Valenzuela et al., 2011). Others have found greater variation, but anthropogenic inputs often play a large role (Case and Krouse, 1980; Stack and Rock, 2011; Wadleigh, 2003). Gradients in natural sources of sulfur have only rarely been traced. In Israel, greater  $\delta^{34} S$  values were found in rainwater 0.5 km from the coast compared to sites 10-60 km inland (Wakshal and Nielson, 1982). A study in Japan documented a trend in  $\delta^{34}$ S relative to distance to the coast similar to that for Hawaii (Fig. 4c, d), although documentation of such patterns was not the primary goal of the research (Mizota and Sasaki, 1996). The pattern in Hawaii is explained by a combination of sources with wide isotopic separation (volcanic vs. marine) and a strong gradient in deposition rate from one particular source (marine aerosols from waves hitting shore). The existence of such steep gradients in sulfur sources and isotopic compositions has several implications. First, such coastal effects should be considered as the mapping of isotopic spatial patterns progresses in Hawaii and elsewhere (Bowen, 2010; Rodrigues et al., 2011; Stack and Rock, 2011). Second, steep coastal gradients likely also exist for other sea-salt derived nutrient elements, such as calcium. Finally, inputs of the often-limiting nutrient phosphorus from volcanic emissions are calculated to be  $11 \times$  greater than dust at sites close to the volcanic source in Hawaii (Vitousek, 2004). Volcanic sulfur influence at the distances documented here suggests volcanic phosphorus influence may extend farther from sources than is commonly appreciated.

### 5. Conclusions

Bulk deposition in Hawaii contains a temporally variable mixture of sulfur from sea-salt, marine biogenic, and volcanic emissions sources. Low sulfur content in basaltic parent material and relatively large atmospheric inputs favor ecosystem reliance on atmospheric sulfur. Of the sites examined, only one could be confidently interpreted as having retained substantial proportions of parent material sulfur. Dependence on atmospheric inputs indicates that soils can serve as proxies integrating variable atmospheric sulfur sources over time. Values of  $\delta^{34}$ S from soil transects on the islands of Hawaii and Maui indicate that the relative importance of sea-salt and marine biogenic sources of sulfur to atmospheric deposition decline across elevations from 0 to 2000 m and distances of 0 to 12 km to the coast while volcanic emissions sources increase. Although ecosystems close to the coast may derive up to 100% of their sulfur from marine sources, relatively high-elevation ecosystems on Hawaii and Maui may derive up to 30% and 48%, respectively, of their sulfur from volcanic emissions. It is likely that the proportion of volcanic emissions contributions increase with elevation, but the shift in magnitude is governed as much by a decline in marine sources as by an increase in volcanic sources. Where ecosystems rely on atmospheric deposition of sulfur or other nutrients, gradients in the sources and magnitude of atmospheric inputs are reflected in those ecosystems. Coastal environments across the globe could be generally expected to exhibit steep gradients in sulfur sources like those documented for Hawaii.

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