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Revised manuscript

Timescales and mechanisms of formation of amorphous silica coatings on fresh basalts at

Kilauea Volcano, Hawai'i

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Abstract

Young basalts from Kilauea Volcano, Hawai'i, frequently feature opaque surface coatings, 1–80 μm thick, composed of amorphous silica and Fe-Ti oxides. These coatings are the product of interaction of the basaltic surface with volcanically-derived acidic fluids. Previous workers have identified these coatings in a variety of contexts on Hawai'i, but the timescales of coating development, coating growth rates, and factors controlling lateral coating heterogeneity were largely unconstrained. We sampled and analyzed young lava flows (of varying ages, from hours to ~40 years) along Kilauea's southwest and east rift zones to characterize variation in silica coating properties across the landscape. Coating thickness varies as a function of flow age, flow surface type, and proximity to acid sources like local fissure vents and regional plumes

emitted from Kilauea Caldera and Pu'u O'o. Silica coatings that form in immediate proximity to acid sources are more chemically pure than those forming in higher pH environments, which contain significant Al and Fe. Incipient siliceous alteration was observed on basalt surfaces as young as 8 days old, but periods of a year or more are required to develop contiguous coatings with obvious opaque coloration. Inferred coating growth rates vary with environmental conditions but were typically 1-5 $\mu\text{m}/\text{year}$. Coatings form preferentially on flow surfaces with glassy outer layers, such as spatter ramparts, volcanic bombs and dense pahoehoe breakouts, due to glass strain weakening during cooling. Microtextural evidence suggests that the silica coatings form both by *in situ* dissolution-reprecipitation and by deposition of silica mobilized in solution. Thin films of water, acidified by contact with volcanic vapors, dissolved near-surface basalt, then precipitated amorphous silica in place, mobilizing more soluble cations. Additional silica was transported to and deposited on the surface by silica-bearing altering fluids derived from the basalt interior.

Keywords

chemical weathering; Hawaii; silica coatings; basalt

1. Introduction

Silica coatings form in numerous terrestrial settings as the product of chemical interaction between a rock substrate and fluids in its environment (Dorn, 1998). Hydrous amorphous silica is a common product of incongruent chemical weathering of basalt glass and basalt-associated minerals; thus, silica coatings are frequently observed in other basalt-dominated landscapes (Fulignati et al., 2006; Gordon and Dorn, 2005; Prinsloo et al., 2010). Silica coatings are also

frequently observed in both cold and warm desert settings (Perry et al., 2006; Weed and Ackert, 1986) and anthropogenically altered terrains (Durocher and Schindler, 2011; Mantha et al., 2012; Schindler et al., 2009) and have been suggested to occur on the surface of Mars (Kraft et al., 2003; Skok et al., 2010). Despite their small volume relative to their substrate, silica coatings may significantly impact the physical susceptibility and chemical reactivity of rock surfaces. Amorphous silica layers slow mineral dissolution rates by passivating the mineral surface (Daval et al., 2011; Gordon and Dorn, 2005). Silica mobilization and redeposition is an important contributor to the case hardening of some rock surfaces, which reduces chemical and physical weathering rates (Dorn et al., 2012). Thus, understanding the properties and formation mechanisms of silica coatings is critical for estimating weathering rates and fluxes in a variety of geologic settings.

Characterizing rates and mechanisms of coating formation also has implications for terrestrial and Mars-based remote sensing studies. The presence of silica coatings modifies the visual appearance and thermal infrared and visible/near-IR reflectance spectroscopic signatures of the basalt substrate (Kraft et al., 2003; Seelos et al., 2010). Along with physical weathering and other chemical reactions such as oxidation, the development of silica coatings produces a predictable spectral evolution of basalt surfaces that allows remote mapping and relative dating of lava flow fields (Abrams et al., 1991; Byrnes et al., 2004; Crisp et al., 1990; Kahle et al., 1988).

Young basaltic lava flows at Kilauea Volcano, Hawai'i, frequently feature white, yellow, blue, orange or red surface coatings composed primarily of amorphous silica (Chemtob et al., 2010; Curtiss et al., 1985; Farr and Adams, 1984; Minitti et al., 2007). These silica coatings are prominently visible at well-trafficked sites within Hawai'i Volcanoes National Park, including

along the Ka'u Desert, Crater Rim, and Mauna Ulu trails. Numerous formation mechanisms have been demonstrated and/or proposed for the formation of silica coatings and cements on young Hawaiian flows, including dissolution-precipitation of near surface glasses (Hellmann et al., 2013; Minitti et al., 2007), dissolution-precipitation of windblown particulates (Curtiss et al., 1985; Farr and Adams, 1984), and transport and deposition of externally derived Si in solution (Schiffman et al., 2006). However, the timing and rate of coating formation are poorly constrained. The dissolution rates of basaltic glass have been studied experimentally by many researchers (Gislason and Oelkers, 2003; Gudbrandsson et al., 2011; Hurowitz et al., 2005; Oelkers and Gislason, 2001; Tosca et al., 2004; Wolff-Boenisch et al., 2004); however, *in situ* weathering rates may be orders of magnitude lower than those measured experimentally (White and Brantley, 2003). Reports of rates of silica coating formation on fresh basalts vary widely. Just-erupted Pele's tears and hairs from Masaya Volcano, Nicaragua, featured siliceous alteration layers several μm thick, formed within hours from exposure to the plume (Moune et al., 2007). In an experiment in which basaltic glass spherules were exposed to the acid plume of Etna, Murano, Italy, chemical alteration was visible after just 4 hours and $\sim 10 \mu\text{m}$ Si-rich leached layers were present after 63 days (Spadaro et al., 2002). In contrast, Crisp et al. (1990) observed the remote spectral signature of amorphous silica coatings only on lava flows at least three years old. Also poorly understood is the physical and chemical evolution of the coatings post-formation.

In a previous study, we observed the chemistry, mineralogy and morphology of silica coatings from a single 1974 lava flow in the Ka'u Desert, along the Southwest Rift Zone (SWRZ) of Kilauea (Chemtob et al., 2010). Here we expand these observations to include field and laboratory descriptions of alteration products of basaltic samples from Kilauea locales of a

variety of ages. We document how the chemistry and morphology of these coatings vary as a function of age, proximity to acid sources, and surface properties. This information is used to assess the rates and mechanisms of coating formation and to understand the post-depositional history and present-day distribution of coatings across the Hawaiian landscape.

2. Geologic setting and sampling strategy

Modern activity at Kilauea volcano falls along one of two main rift systems: the less-active southwest rift zone (SWRZ) and the more-active east rift zone (ERZ). The Pu'u O'o – Kupaianaha eruption of Kilauea's ERZ began in 1983 and has continued uninterrupted for 30 years. An excellent summary of the recent history of this eruption is found in Koeppen et al. (2013).

Specimens were collected from locations on the SWRZ and ERZ in March 2010, July 2010, and March 2012. Sampling sites are mapped in Figure 1 and described in Table 1. Sites were selected for a range of flow ages (hours to ~40 years), flow surface types, and proximity to source vents and major gas plumes. Samples of older lavas (1969-1974) were collected from the Ka'u Desert (SWRZ) and from the flow field and summit region of Mauna Ulu (ERZ). We exerted a particular focus on sampling the on-rift region of the ERZ between Napau Crater and the Pu'u O'o cone, which featured all of the youngest lavas analyzed in this study. Flows from Episodes 55 and 58 (erupted in 1998 and 2007, respectively) were collected from near the rim of Pu'u O'o in July 2010) (**Fig. 1c**). Those collection sites were buried by new lavas during the March 2011 Episode 63 eruption that extended from the flank of Pu'u O'o to the edge of the Kamoamoia fissures 2 km west (**Fig. 1d**). We sampled the Episode 63 lavas in March 2012, one year after eruption; additionally, we received a suite of Episode 63 spatter samples collected 1 to 8 days after eruption by personnel of the Hawai'i Volcano Observatory (HVO-USGS).

3. Analytical methods

Micro-images of coatings on collected samples were acquired by scanning electron microscopy (SEM), using a LEO 1550 VP field emission SEM at Caltech. Both cross-sectional thick sections and natural surfaces of basalts were analyzed. Thick sections were prepared using Burnham Petropoxy resin and curing agent and were polished to 0.3 μm using diamond and alumina polishing papers. Backscattered electron (BSE) and secondary electron (SE) images were acquired at a 9 to 12 mm working distances and at a range of magnifications, using 10 kV accelerating voltage. $\text{K}\alpha$ X-ray intensity maps of Si, Mg, Al, Ca, Fe, Ti, Na, F, and/or K were collected using an Oxford X-Max SDD energy-dispersive spectrometer (EDS) system. Coating thicknesses were determined by direct measurement from cross-sectional thick sections; for samples in which natural surfaces were analyzed, coating thicknesses were estimated by measuring the length of exposed coating edges near vesicles.

Major and minor element compositions of silica coatings and basalts were acquired by electron probe microanalysis (EPMA) using Caltech's JEOL JXA-8200. Phase identification was achieved by Raman spectroscopy using a Renishaw M1000 micro-Raman spectrometer with a 100x objective and a 514.5 nm green laser.

4. Results and discussion

4.1. Sample descriptions

Detailed descriptions and field and micro-scale imagery of the sites and samples investigated in this study can be found in the Supplemental Information. These results are summarized in Table 2 and discussed below.

4.2. General field observations

Siliceous alteration layers were present on portions of lava flow surfaces at nearly every field site visited in this study. The coatings are often brightly colored, but incipient or very thin coatings may be colorless and/ or invisible upon macroscopic inspection. The coatings display a variety of textures, either appearing as a matte, opaque surface glaze or as a powdery white material. Surfaces with brightly colored coatings frequently appear dark along surface cracks (**Fig. 2a,b**).

The occurrence and visual prominence of brightly colored coatings is frequently heterogeneous over short spatial scales. Coating distribution appears to be dependent on lava surface properties. Wilmoth and Walker (1993) distinguish two main types of Hawaiian pahoehoe lava: S-type (spongy) pahoehoe, the most abundant type, which has abundant vesicles and tends to spall its glassy surface layer, and P-type (pipe vesicle-bearing) pahoehoe, which is dense, vesicle-poor and may display a silvery blue color when fresh (Oze and Winter, 2005). Brightly colored coatings tend to form prominently on P-type pahoehoe breakouts and other lava surfaces with smooth, glassy exteriors such as spatter ramparts (**Fig. 2a**), spatter adhering to lava trees and lava molds, and dense volcanic ejecta like Pele's tears and breadcrust bombs (**Fig. 2c**). Coatings may form on the undersides of hollow pahoehoe shells and spatter chunks. Coatings may be present on less smooth ropery pahoehoe or sheet pahoehoe surfaces, but tend to be sparser in their surface coverage (**Fig. 2d**). Brightly colored coatings are rare on a'a and on S-type pahoehoe surfaces that have spalled their outer glassy layer (**Fig. 2d**). Heterogeneities related to lava surface properties are apparently the result of surface-selective alteration; that is, lavas with

smooth, glassy rinds are especially susceptible to the type of alteration that produces opaque silica coatings.

Other observed heterogeneities in coating coverage appear to be related to surface geometry and post-formational physical abrasion. Coating distribution is frequently sensitive to surface topography at a number of length scales. At the cm-to-m scale, coatings may be absent immediately adjacent to topographic barriers like pahoehoe flow fronts and underneath lava "awnings" (**Fig. 2e**). At smaller scales, coatings were often observed to be absent or actively eroding on surfaces with ~0.1–5 mm roughness. Bright coatings on older flows were observed to be eroding and oxidizing concentrically away from topographic nubs (**Fig. 2f**)

4.3. Coating microtextures and chemistry

Basalts collected from Kilauea for this study were glassy, highly vesicular and tholeiitic in composition (Table 3). The outer glassy rind of the basalt, on which silica coatings most frequently formed, is composed largely of glass with no more than 10% phenocrysts (primarily plagioclase (An₇₁) and pyroxene, with rare olivine). In some cases, interior basalt contained up to 60% dendritic phenocrysts. No obvious secondary alteration of the basalt interior was observed.

BSE images of polished cross sections of coated basalt indicate that the coatings consist of a layer of amorphous silica, 1–80 µm thick, capped in some cases by a ~1 µm layer of Fe-Ti oxide (**Fig. 3a**). Based on its distribution, the Fe-Ti oxide layer appears to be responsible for the bright colors and opaque pigmentation observed on coated basalts in the field. In samples from the Ka'u Desert and Pu'u O'o sampling regions, the silica coating layer is nearly pure SiO₂, with variable sulfur enrichment (**Table 3**), and has a high Si-OH content as determined by ²⁹Si NMR and IR methods (5.4 wt% as H₂O in the PU-009 coating) (Chemtob et al., 2012). In contrast,

silica coatings at Mauna Ulu are less chemically pure, being notably enriched in Al_2O_3 and FeO^* . Fe-Ti coatings on samples from the Ka'u Desert have ~78% TiO_2 , ~20% FeO^* (total Fe expressed as ferrous iron oxide) and percent-level enrichment of sulfur and phosphorus (Chemtob et al., 2010). The Fe/Ti ratio in the coatings at other sites is higher and more variable. The mineralogy of the Fe/Ti coatings in the Ka'u Desert is dominated by anatase and rutile; pseudobrookite, hematite and lepidocrocite have also been identified (Chemtob et al., 2010).

The contact of the siliceous layer with underlying basalt is undulating but chemically sharp (**Fig. 3a**). Basaltic glass immediately adjacent to the coating is visually unaltered and chemically identical to far-interior basalt. The silica layer is frequently dissected by cracks, attributable either to volume changes during a replacement reaction (Ruiz-Agudo et al., 2014) or to desiccation after coating formation or within the SEM. The silica coatings frequently display textures consistent with a residual formation mechanism. A silica layer may bridge a near-surface vesicle with no underlying basalt substrate (**Fig. 3b**). This observed geometry implies *in situ* incongruent dissolution of basalt, since a depositional mechanism would require a substrate to deposit upon. Small basaltic glass protrusions may be thinned on all sides by silica material, again implying a replacement process. Siliceous alteration may also penetrate the basalt substrate along near-surface cracks.

Other observed morphologies imply silica mobilization and deposition. One sample (PU-009) featured amorphous silica filling and mantling the edges of a surface vesicle, preserving concentric microstratigraphy (**Fig. 3c**). Infilled silica extends above the height of the basalt edge and displays a coarse, blocky and porous texture. This morphology cannot form by *in situ* alteration alone, instead requiring either precipitation of silica from solution or clastic remobilization of previously deposited silica. In another instance, a silica coating with the blocky

depositional texture mantled a silica layer apparently formed by replacement (**Fig. 3d**). Thus, silica coatings form both by *in situ* replacement of near surface basalt and by external deposition from silica-saturated fluids. There are no obvious compositional differences as measured by EPMA between silica coatings of the two morphologies.

Microtextures of unpolished natural surfaces further constrain the alteration processes. Fresh, unaltered spatter surfaces frequently display linear crenulations with 3-5 μm spacing and pockmarks, 1-25 μm in diameter (**Fig. 4a**). These textures are interpreted as primary deformation features, formed as the lava cools while the interior is still partially molten. Even as silica coatings develop and cover the majority of a lava surface, primary deformation textures are in some cases still visible. Well-developed silica coatings may appear either as smooth, continuous glazes (**Fig. 4b**) or as a porous, highly irregular "popcorn" textured material (**Fig. 4c**). On heterogeneously altered surfaces, regions with silica coatings were frequently topographically low-lying or deflated relative to neighboring regions with no alteration material (**Fig. S3f**).

Well-developed Fe-Ti oxide coatings occur in irregular patches across the surface. In places, the Fe-Ti coating displays fine internal lineations similar in scale to primary lineations observed on fresh surfaces; elsewhere, the Fe-Ti oxides appear massive and amorphous (**Fig. 4c**). Fe-Ti coatings on one Ka'u Desert sample was shown to be composed of microspheroids, ~100 nm in diameter (Chemtob et al., 2010). Very young (days old) lava surfaces may also display Fe-rich crystallites, occurring as dendritic bundles, polygonal tiles or amorphous masses (**Fig. 4d**). Such Fe-rich precipitates are likely primary features formed by oxidation of the basalt surface during cooling (Evans et al., 1982). Whether these initial Fe-rich deposits are precursors to Fe-Ti coatings on surfaces that have also developed silica coatings is unclear.

4.4. Timescales and rates of coating formation

Many parameters may affect the formation rate and properties of silica coatings, including proximity to acid sources, lava surface type, and environmental conditions. To assess the timescale of coating formation and estimate coating growth rates, we focus our interpretation of coating growth rate on sample sequences from near-identical collection locations with different ages: spatter collected in 2011 and 2012 from the Episode 63 Kamoamoa eruption, and lavas emplaced in 1997, 1998 and 2007 and collected in 2010 from other nearby ERZ locales.

4.4.1. Kamoamoa eruption

Fresh spatter samples (collected days after emplacement) from the Kamoamoa eruption site are not visibly discolored but display progressive incipient alteration observable by microanalytical techniques. The surfaces of samples KE59-2941 and KE59-2952, collected several hours and one day after emplacement, respectively, both displayed primary deformation textures (pockmarks, linear crenulations and microfolds) but no chemical alteration on their surfaces (**Fig. 4a**). The surfaces of samples KE59-2970 and KE59-2980, each collected 5 days after their eruption, featured dendritic Fe-rich precipitates identified by electron backscatter diffraction as magnetite and ilmenite (**Fig. S9**), but no apparent silica-rich alteration material (**Fig. 4d**). Sample KE59-2979, collected 8 days after the eruption, displayed localized spots of amorphous silica alteration, sometimes directly associated with patches of Fe-rich precipitate (**Fig. 5**). Silica alteration developed specifically along linear crenulations and at the centers of pockmarks, presumably reflecting portions of the surface that experienced maximum strain during cooling. This series of samples indicates that initial incipient silica coating formation occurs over a period of days, considerably longer than the characteristic timescale for pahoehoe

cooling (Jones, 1993). The observation of siliceous alteration layers on the surface of Pele's tears forming seconds or minutes after eruption at Masaya volcano, Nicaragua (Moune et al., 2007) are not replicated at this field site. Fe-rich precipitates appear to both pre-date and post-date the siliceous alteration.

Samples collected at the Episode 63 Kamoamo eruption site one year after eruption have a considerably different surface morphology. Although many lava surfaces appeared dark and unaltered one year after eruption, some spatter and volcanic bomb samples (NC-11-010 and NC-11-015) collected from the same locale as the KE59 fresh spatter suite displayed obvious discoloration. SEM-EDS images of these samples indicate silica coatings over wide swaths of their surfaces (**Fig. 6**), estimated from coating edges on the natural surface to be 3-4 μm thick. Primary surface deformation lineations appear to be preserved within the amorphous silica alteration texture, suggesting silica layer formation replacement rather than by external deposition (**Fig. 6b**). The coating thicknesses on these year-old samples suggest a silica alteration layer growth rate of a few $\mu\text{m}/\text{year}$.

4.4.2 Other East Rift Zone lavas

It is instructive to compare the suite of altered basalts from the Kamoamo eruption with samples from the 1997 Episode 54 fissure eruption, collected ~1 km away in the center of Napau Crater. Coatings on spatter ramparts from that eruption (sample NC-97-11b) had a maximum thickness of 3 μm , approximately equal to coating thicknesses from the recent eruption (**Table 2; Fig. S5**). These two sites illustrate that coating growth rate varies widely with time and location. The Kamoamo and Napau sites receive similar amounts of rainfall annually (Giambelluca et al., 2013) so climatic effects cannot explain the apparent differences in coating growth rate. Instead, the lower average coating growth rate at Napau Crater is presumably attributable to lower input

of acidic vapors from regional plumes and local fissure emissions. (The relative importance of each of these acid sources is discussed in the following section.)

Samples collected in the vicinity of the summit of Pu'u O'o have experienced intense and sustained exposure to a regional acidic plume, and as a result display accelerated coating growth rates. Sample PU-010, collected from 1998 overflow lavas ~10 m from the cone rim, and sample PU-011, collected from 2007 spatter ramparts ~100 m northeast of the cone, both feature powdery white silica coatings. The maximum coating thicknesses observed for samples PU-010 and PU-011 are 80 μm and 14 μm , respectively (**Table 2**). These thicknesses imply average coating growth rates of 5-6 $\mu\text{m}/\text{year}$. The maximum coating growth rate achieved at any time since the lavas' emplacement is unknown, but the basalt surfaces likely experienced enhanced exposure to acids during major eruptive periods.

4.5. Origin of acidity

Although silica-rich coatings may form on basalt over long time periods in neutral pH conditions (Dorn, 2012), the rapid alteration rates and *in situ* alteration textures (**Fig. 3**) suggest that the coatings in this study formed by interaction with acidic fluids and vapors. Specifically, the high sulfur content of Kilauean silica coatings, primarily present as jarosite (Chemtob et al., 2010; Minitti et al., 2007) indicate that SO_2 is the primary volcanically-derived acid source involved in coating formation. Here we assess the relative importance of possible primary sources of volcanically-derived acids, including local fissure vents, regional plumes, and volatiles degassed from the lava itself.

4.5.1. Local fissure vents

Fissure eruptions are typically accompanied by short but intense periods of enhanced gas emissions. Sulfur dioxide emissions during the single-day Episode 54 fissure eruption at Napau Crater were measured as 260 metric tons/day (mt/d) and fell to 80 mt/d the following day (Elias et al., 1998). Similarly, the SO₂ emission rates of the 2011 Kamoamoa eruption (Lundgren et al., 2013) peaked at ~10,000 mt/d at the height of the eruption (March 7-8) but had fallen to ~400 mt/d by March 11 (M. Poland, pers. comm.). In some cases, emissions from these fissures may continue at low levels long after the end of lava emplacement. Variations in syneruptional gas emission rates appear to correlate with coating growth rates (see subsequent section). Coatings on spatter ramparts adjacent to the SWRZ fissure vents are more contiguous than those on neighboring pahoehoe flows. This difference in coating coverage is apparent in aerial visible-near-IR false color imagery (Seelos et al., 2010).

In a previous study (Chemtob et al., 2010) we hypothesized that the fissure vents themselves may be the dominant source of acidity for coating formation. To test the hypothesis that fissure vent emissions influence coating formation, we collected samples from the Ka'u Desert July 1974 flow along a traverse perpendicular to the trace of the SWRZ. Silica-coated lava samples were collected from the surface of the rift-associated spatter rampart and 10 and 40 m to each side of the rampart. If fissure vents were important contributors of acidity for basalt alteration, gradients in coating thickness away from the spatter rampart should be observed. The maximum coating thicknesses at distances from the spatter rampart of 0, 10, and 40 m were 13, 16, and 7 μm , respectively (**Table 2**). This modest gradient in coating thickness away from the fissure vent suggests that those local vents may be a significant source of acidity. This gradient could reflect early coating formation during the eruptive period of enhanced emissions, or it

could indicate that low-level emissions continued after the eruption. Alternately, the thickness gradient could reflect increased kinetic rates of alteration due to higher local temperatures in the vicinity of fissure vents.

4.5.2. Regional plumes

Field observations indicate that regional acidic plumes are a dominant contributor of acidity leading to silica coating formation. Between 2008 and 2010, typical average SO₂ emission rates varied between 500 and 1000 mt/d at Kilauea summit and between 500 and 2000 mt/d at the ERZ (Elias and Sutton, 2012). Low regional rainwater pH (3-4) at the Kilauea summit has been attributed to the influence of volcanic plume emissions (Harding and Miller, 1982); lavas in close proximity to plume sources likely experienced even more acidic conditions. The lavas with the thickest coatings observed in the study (~80 µm), on the rim of Pu'u O'o, have undergone constant exposure to the ERZ acidic plume. Prevailing trade winds carry acidic vapors and condensates from Kilauea towards the southwest over the Ka'u Desert, where they may linger and interact with surface rocks (Schiffman et al., 2006). On days of Kona winds, transport of acidic fluids to the southwest is weakened, and acids may interact with local lava surfaces in all directions. We assess the effect of regional plumes on coating development by comparing three sites of similar age: a location on the 1974 flow near the SWRZ (sample KD-003g; waypoint 1), the distal toe of that same flow (sample KD-004; waypoint 2), and the 1973 Keanakakoi Crater spatter rampart (waypoint 3) (**Fig. 1b**). The maximum silica coating thicknesses measured at those sites (not including the region immediately adjacent to the spatter rampart) were 7, 4, and 3.5 µm, respectively (**Table 2**). Despite being closer to Kilauea Caldera, the Keanakakoi Crater lavas display thinner silica coatings, presumably because they are outside the typical path of plume transport and were thus less intensely exposed to acidic vapors. The

1974 flow distal toe was apparently sufficiently far southeast of the main trace of the plume to not develop thick coatings. This gradient and the thick Pu'u O'o coatings indicate that exposure to regional plumes is an important predictor of coating thickness.

4.5.3. *Auto-alteration*

A final potential source of acidity for alteration of a basalt surface is volatiles degassing from that basalt as it erupts and cools. White and Hochella (1992) observed surface depletion of Si, Fe and Al and enrichment in F on freshly emplaced distal basalt flows, which they attributed to mobilization of fluoride complexes facilitated by degassing. Such “auto-alteration” is a potentially attractive mechanism for explaining coating formation on distal flow fields (e.g. Mauna Ulu). However, we do not favor a general auto-alteration hypothesis for silica coating formation for several reasons. First, volatile fluxes from degassing flows on distal flow fields should be far lower than those observed at fissure vents and regional plumes. P-type pahoehoe surfaces that feature the most prominent coatings on distal flow fields are thought to have lost most of their volatile content before eruption (Wilmoth and Walker, 1993). Second, flow degassing ceases within hours of lava emplacement, and samples collected from the Kamoamoa eruption within that period do not feature siliceous alteration (see subsequent section). Volatiles from degassing do not linger on flow surfaces for the period of years required to produce thick silica coatings; White and Hochella (1992) observed no F enrichment on basalt surfaces 200 days after emplacement. Instead of auto-alteration, we attribute distal flow alteration primarily to exposure to the diluted regional plume and acidified rainwater. Alternatively, thin silica coatings have been shown experimentally to form on basalt on timescales of decades, solely through water vapor action (Dorn, 2012). Thus, P-type pahoehoe surfaces prone to alteration may alter with minimal input from acidic plumes, but over longer timescales.

4.6. Origin of coating coverage heterogeneity

The distribution of silica coatings across the Hawaiian landscape is not uniform. Heterogeneities in silica coating coverage are observable between eruption sites, between different flow surfaces at the same eruption site, and at a microscopic scale on an individual hand sample. Here we discuss three processes—surface-selective formation, erosion, and microenvironmental variability—that demonstrably contribute to the observed heterogeneities.

4.6.1. Surface-selective formation

Silica coatings do not form on all surface types with equal regularity. Coatings were observed to be most prominent on lava with smooth, glassy surfaces, including P-type pahoehoe breakouts, spatter and spatter ramparts, lava trees, and volcanic bombs. The consistency with which these surfaces feature more prominent coatings relative to their surroundings suggests that the glassy surface layers themselves are particularly susceptible to form silica alteration layers (**Fig. 2c**). One factor contributing to this susceptibility is the difference in crystallinity between the interior and flow surface. The interiors of basalt flows contain a higher proportion of phenocrysts than the quenched outer layer. At $\text{pH} < 2.5$, the measured dissolution rate of basaltic glass is higher than that of forsterite, diopside, and plagioclase (Hausrath et al., 2008); thus, in the presence of volcanically-derived sulfuric acid, glassy surfaces may alter faster than more crystalline material.

Another, potentially more important factor in determining surface susceptibility is the degree to which outer glassy layers have undergone strain weakening during lava cooling. We attribute observed lineations, crenulations, and pockmarks on the surfaces of fresh glassy lava to

primary deformation of a solidifying surface over a partially molten interior (Crispini et al., 2006). Deformed silicate surfaces have a higher density of defects, and silica glass hydrolysis may proceed 100,000 times faster at defect sites than on unstrained Si-O bonds (Bunker, 1994). Evidence in our sample suite for strain-based surface-selective alteration is apparent at both microscopic and macroscopic spatial scales. In the suite of days-old Kamoamo spatter samples, the microscopic primary deformation texture defines a compositional heterogeneity in which certain parts of the strained surface preferentially developed siliceous alteration (**Fig. 5**). At the macroscopic scale, the morphology of ropey pahoehoe was shown to affect coating coverage. On the Mauna Ulu flow field, bright coatings appeared only along the flow axis of a well-formed set of pahoehoe ropes, the region that experienced the most deformational strain (**Fig. S4a**).

4.6.2. Erosion and preservation bias

Post-formational erosion and removal also contributes to the heterogeneity of coating coverage. The outermost surface of fresh S-type pahoehoe is highly vesicular and therefore less resistant to physical weathering than P-type lavas. The upper portion of the glassy crust of S-type pahoehoe frequently spalls away during or immediately following emplacement (Wilmoth and Walker, 1993); P-type lavas may also spall their glassy crust as a result of wind and water abrasion over longer time scales. Coating growth or regrowth on spalled surfaces is rare, so the rate of spallation of outer glassy layers exerts a strong control on coating distribution.

Silica coatings may also be removed from basalt substrates by abrasion without the complete removal of the glassy layer by spallation. Physical abrasion induces coating coverage heterogeneity in cases where neighboring basalt flow surfaces feature different primary surface roughness. Lava surfaces with more roughness are more susceptible to physical and chemical weathering (Compton et al., 1986; Jiang and Arnell, 2000); areas with minimal roughness tend to

retain their coatings. At Mauna Ulu, we observed concentric coating oxidation and removal around mm-scale topographic nubs (**Fig. 2f**). The centers of these nubs bore no amorphous silica coating detectable by Raman spectroscopy. These protruding features were particularly susceptible to wind and water abrasion; continued physical weathering of this surface might result in complete removal of surface coatings without spallation of the glassy crust.

4.6.3. Microenvironmental variability

Localized heterogeneities in coating coverage may result from varying microenvironmental conditions, such as fluid availability and exposure to acid sources. Coatings were occasionally observed to be absent on flow surfaces beneath other basalt obstructions (**Fig. S4b**). Those surfaces may have been exposed to less rainwater than neighboring surfaces, remaining minimally altered. The degree of alteration of surfaces at the Kamoamo site one year after eruption (described in section 4.4.1) was heterogeneous. Some of this heterogeneity can be attributed to surface-selective alteration; dense P-type lavas and volcanic bombs tended to display more opaque surface alteration. However, cases in which lavas of similar surface type displayed different extents of alteration are potentially attributable to heterogeneous exposure to the degassing SO₂ plume during eruption.

4.7. Origin of coating chemical heterogeneity

EPMA analyses of silica coating layers from all sampling sites identified two primary chemical classes: nearly chemically pure layers with >95 wt% SiO₂ (water-free, after normalization), and layers with 80-85 wt% SiO₂ with considerable enrichments in Al₂O₃ content (**Table 3**). Chemically pure alteration layers were observed on the 1974 flow in the Ka'u Desert

and on flows near Pu'u O'o; Al-rich alteration layers were associated with flows at Napau Crater, Keanakako'i Crater, and the Mauna Ulu near-summit and distal sampling areas. Al-rich coatings are commonly less thick ($\leq 5 \mu\text{m}$) than chemically pure silica coatings.

Variation of basalt Al content is subdued across sampling sites and is therefore not the cause of the coating chemical heterogeneity. We attribute variation in alteration product chemistry to variable pH during alteration. Sites featuring Si-rich alteration materials are associated with intense and continuous exposure to regional acidic plumes, and therefore experience low pH conditions. Sites with more Al-rich coatings are more removed from these plume sources. Additionally, the Mauna Ulu and Napau Crater sites receive more rainfall than the Ka'u Desert sites (Giambelluca et al., 2013), indicating that weathering in these environments is therefore characterized by a diluted plume source, higher fluid-rock ratios, and higher pH. Numerous experimental aqueous basalt glass alteration studies show increasing effluent Al/Si ratios, implying increased Al release, with decreasing pH (Chemtob et al., 2014; Gislason and Oelkers, 2003; Hurowitz et al., 2005; Knauss et al., 1989). Similarly, the Al content of basalt alteration products at the Krysuvik geothermal site in Iceland increased with decreasing intensity of acidic input (Markusson and Stefansson, 2011). Those authors attributed the drop in Al mobility with increasing pH to increasing stability of Al-bearing secondary phases like kaolinite and montmorillonite. No crystalline phases were detected in silica coatings in this study, but Al partitioning into amorphous silicate phases may follow a similar trend with pH.

4.8. Preferred formation mechanism

In our previous study (Chemtob et al., 2010), we laid out two potential primary mechanisms for formation of the silica coating: deposition of externally derived silica, and *in situ* dissolution of near-surface basalt coupled with precipitation of silica. In that study, we favored the latter explanation. Our new observations suggest that although surface-selective alteration morphologies at the outcrop scale imply predominantly local reaction (**Fig. 2c**), both residual and depositional textures occur, sometimes on the same sample (as described in section 4.3). Thus, although coatings are primarily residual in character, silica must be at least partially mobile in this system.

Since other cations associated with basalt (Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , Ti^{4+}) are absent or strongly depleted in the silica coatings, they must have been mobilized and removed from the system. This mobilization must be facilitated by liquid water; although acids may interact with basalt surfaces both as vapors and liquids, even proposed vapor-phase alteration processes require surface condensation and liquid-substrate interaction (Schiffman et al., 2006; Tosca et al., 2004). Likely sources of liquid water include condensed water vapor from plume gases and rainwater. There were rain showers every day of the Kamoamo 2011 eruption (Tim Orr, pers. comm.), indicating that there was no shortage of liquid water for removal of leachates. With the exception of the Fe-Ti oxide layer, there are no secondary phases associated with the silica layer containing basalt-associated monovalent, divalent and trivalent cations, implying efficient transport and removal of those cations by runoff.

In coatings with residual morphologies, replacement of the near-surface basalt by amorphous silica is not an isovolumetric process; deflation of the surface occurs during coating

formation. We employ a chemical mass balance to determine the thickness of the silica coating (t_{coating}) produced by dissolving 1 μm of basalt:

$$t_{\text{coating}} / t_{\text{basalt}} = (X_{\text{Si,basalt}} / X_{\text{Si,coating}}) (\rho_{\text{basalt}} / \rho_{\text{coating}})$$

($\rho_{\text{basalt}} = 2.7 \text{ g/cm}^3$; $X_{\text{Si,basalt}} = 0.517$, $X_{\text{Si,coating}} = 0.91$; Chemtob et al., 2012). We estimate an effective density of the silica coatings of $\rho_{\text{coating}} = 1.84 \text{ g/cm}^3$. Hydrous gem opals have densities around $\rho_{\text{opal}} = 2.17 \text{ g/cm}^3$ (Graetsch, 1994), but low oxide totals from EPMA analyses suggest up to 15% porosity within the coatings.

Given the above values, if Si is completely immobile during weathering, then dissolving 1 μm of basalt would produce 0.83 μm of amorphous silica. Because silicon isotope fractionation between the silica coatings and their substrate require some Si loss from the system (Chemtob et al., 2014), this calculated degree of deflation is a minimum bound. Thus, the presence of a 10 μm silica coating on the surface of a basalt implies that at least 12 μm of basalt was consumed during formation of that coating. This calculation is consistent with the deflational morphology observed on some coated samples (**Fig. S3f**)

We present two hypotheses for the origin of the Fe-Ti oxide coating. In our previous study, we attributed the presence of the Fe-Ti oxide coating to the precipitation of relatively immobile dissolved Fe^{3+} and Ti^{4+} liberated from the basalt in formation of the silica layer (Chemtob et al., 2010). Hawaiian basalts typically have $\text{Fe}^{3+}/\text{Fe}_{\text{total}} = 0.2$ to 0.3 (Burkhard, 2001), but because subaerial alteration conditions are oxidizing, iron released during basalt dissolution is primarily Fe^{3+} (Hay and Jones, 1972; Morris et al., 2000). More mobile elements remain in solution after basalt dissolution and are removed from the system, but Fe^{3+} and Ti^{4+} precipitate out quickly. Fe^{3+} -bearing anatase is a common product of oxidative weathering of Ti-bearing

materials (Schroeder and Shiflet, 2000; Anand and Gilkes, 1984). Percent-level enrichment of phosphorus, another largely immobile element present in basalt glass, in the Fe-Ti layers supports the hypothesis that the layers are derived from dissolved basalt substrate. This model requires a mechanism to explain coating stratigraphy, i.e., the observation that Fe-Ti coatings typically cap the silica alteration layer. To form this capping morphology, Fe^{3+} and Ti^{4+} must be fluid-transported up to tens of μm from their source at the site of *in situ* dissolution-reprecipitation to the subaerial surface. The transport of iron and titanium from their release site in the basalt substrate to their deposition site at the surface could be facilitated by a sharp redox gradient. Iron released from the basalt as Fe^{2+} might remain stable in solution until full exposure to atmospheric oxygen, after which it would oxidize and precipitate as a Fe^{3+} -bearing phase. If solution transport is the mechanism for concentrating Fe-Ti oxides at the surface, one might expect the occurrence of intermediate distributions of Fe and Ti within the silica layers. Such intermediate distributions were rare but observable; sample PU-011 (emplaced 2007) displayed diffuse Fe and Ti enrichment within its silica layer and no discrete Fe-Ti coating (**Fig. S7**).

The presence of magnetite and ilmenite crystallites on 5-day old spatter samples (**Fig. 4d**) at Kamoamo suggests an alternate hypothesis: that Fe-Ti oxides crystallize during initial cooling of the basalt flow and are later altered along with the underlying glass. Subaerially cooling basalt may crystallize near-surface dendritic titanomagnetite crystals, up to 200 nm across, that produce thin film interference colors (C. Ma and G. Rossman, unpublished data). Perhaps the distribution of Fe-Ti coatings observed on coated flows today simply reflects the distribution of early-formed oxide crystallites. The Fe-Ti oxide layers are thin, discontinuous, and porous enough such that fluid transport to the underlying basalt substrate would not be impeded. This hypothesis would account for both the heterogeneity of Fe-Ti oxide distribution

and the capping morphology. However, the crystallites observed on young Kamoamoa spatter had a higher Fe/Ti ratio (~3–4) than the oxide coatings on silica coated basalts (Fe/Ti as low as ~0.25). Incongruent dissolution of Fe-Ti oxides mobilizes Fe relative to Ti (Temple, 1966), but even if Ti remains perfectly immobile such an elemental fractionation requires >90% Fe loss. The total volume of Kamoamoa crystallites is not sufficient to sustain this loss and produce observed volumes of Fe-Ti coatings as seen on older flows. Additionally, this mechanism fails to account for the fate of Fe, Ti and P released from the weathered glass layer. Thus, we do not favor a mechanism involving high-T crystallization and subsequent alteration as the sole source of Fe-Ti oxide coatings, but high-T crystallites may contribute in small proportions.

Our preferred coating formation mechanism is illustrated as a cartoon in **Figure 7**. Liquids on the surface of fresh, unaltered basalts are acidified by volcanically derived vapors. A portion of near-surface basalt is dissolved and replaced *in situ* by amorphous silica. Additional silica may be transported and deposited at the surface by fluids that partially dissolved interior basalt. Much of the dissolved load (Mg^{2+} , Ca^{2+} , Na^+ , Al^{3+} , etc.) remains soluble at low pH and is removed from the system as these fluids are washed away. Titanium and ferric iron have lower mobility and precipitate as Fe-Ti oxides. As acidic alteration of basalt surfaces continue over a period of years, the silica alteration layer grows thicker and Fe and Ti are remobilized by repeated episodes of dissolution-reprecipitation to form a contiguous layer at the surface.

5. Conclusions and implications

Silica coatings are ubiquitous on young lava flows at Kilauea. The coatings consist of a layer of amorphous silica, up to 80 μm thick, capped in some cases by a ~1 μm layer of opaque Fe-Ti oxide. The thickness of these coatings is dependent on the age of the flow, proximity to

acid sources, and climatic conditions. Siliceous alteration does not occur on lava flows during their emplacement or as they cool, but is observed to begin within days of emplacement. Inferred rates of silica layer formation were as high as several $\mu\text{m}/\text{year}$ but varied sharply through time and across the Hawaiian landscape. The coatings form by acidic dissolution of near-surface basalt, followed by *in situ* precipitation of amorphous silica. Coating formation is surface-selective, occurring most prominently on surfaces with glassy surface layers. Regional plumes are the most important source of acidity driving the breakdown of these glassy layers, but local fissure vents may in some cases be a short-lived but significant contributor.

The set of coatings described in this study are primarily an ephemeral phenomenon, because they are easily removed both by abrasion and by spallation of the glassy layer. However, the coatings described in this study, composed of relatively pure amorphous silica, are one endmember of a broader continuum of surface alteration products on Hawaiian basalts described in the literature (Curtiss et al., 1985; Farr and Adams, 1984; Hay and Jones, 1972). Coatings on lava flows 1,000–2,000 years old are thicker and more alumina-rich; these coatings on older flows typically incorporate wind-blown dust and basaltic ash as well as amorphous silica. Silica coatings on older flows may infill vesicles and case harden the surface, increasing the surface's resistance to physical and chemical weathering (Dorn et al., 2012; Gordon and Dorn, 2005). Sustained exposure of basalt to intense solfataric alteration may result in volumetric replacement of the basalt with opal (Macdonald, 1944).

Despite their ubiquity and impact on the appearance of the Hawaiian landscape, surficial alteration responsible for silica coating formation is a minor contributor to the overall dissolved cation flux entering the ocean due to chemical weathering. The geochemical signature of chemical weathering in Hawaiian waters is dominated by groundwater interaction and longer-

term breakdown of flows and basaltic soils (Schopka and Derry, 2012). Groundwater collected from wells near Kilauea is enriched in sulfate, chlorine and fluorine due to the input of magmatic volatiles; however, the dissolved chemistry implies a more complex subsurface mineral assemblage than that observed in this study, consisting of quartz, smectite, calcite and/or chlorite precipitated between 90° and 140° C (Hurwitz et al., 2003). Although siliceous surface alteration is apparently not representative of island-wide chemical weathering trends, it may indirectly influence element release by modifying basalt surface reactivity. Amorphous silica layers thinner than those observed in this study ($< 1 \mu\text{m}$) may greatly reduce mineral and glass dissolution rates (Daval et al., 2011). Thus, local element release rates associated with chemical weathering of newly emplaced flows may deviate from experimentally predicted rates within days of eruption.

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Figure Captions

Figure 1. Maps of Kilauea Volcano and research areas. Numbered field sites are indicated. a) Shaded relief map of Kilauea Volcano, with southwest (SWRZ) and east (ERZ) rift zones indicated. KC = Kilauea Caldera MU = Mauna Ulu, MP = Makaopuhi Crater, PU = Pu'u O'o, and ML = Mauna Loa. Inset shows island of Hawaii. b) SWRZ region of study, as indicated in (a), highlighting recently emplaced lava (since 1973). Broken lines indicate lava-producing fissure vents associated with the December 1974 flow. c) Lava flow map of ERZ region of study, as indicated in (a), as the region appeared in July 2010. d) Same region as (c), as it appeared in March 2012. Note that new activity covered some collection sites from previous season.

Figure 2. Coating field morphologies. a) Heavily coated spatter rampart proximal to SWRZ, Ka'u Desert 1974 flow. b) Coated surfaces at spatter rampart depicted in (a). c) Heavily coated volcanic bombs of unknown age deposited on a spalled, uncoated 1998 flow surface near the rim of Pu'u O'o. d) Sparser coating coverage on Ka'u Desert 1974 flow, ~40 m from spatter rampart depicted in (a). e) Local heterogeneities in coating coverage proximal to topographic barriers, Ka'u Desert. f) Oxidation and preferential removal of coating around small protrusions, 1969 flow, Mauna Ulu.

Figure 3. Cross sectional SEM images of coating microtextures. a) Silica coating, ~13 μm thick, capped by a 1 μm layer of Fe-Ti oxide, on the 1974 Ka'u Desert spatter rampart depicted in Fig. 2a. b) Coating on bomb sample PU-009 (depicted in Fig. 2b) displaying residual morphologies, including bridging a near-surface vesicle and altering both sides of a narrow glass

protrusion. c) Silica-infilled vesicle on a separate aliquot of sample PU-009, suggesting chemical deposition of silica or physical deposition of remobilized silica clasts. d) Silica with blocky texture associated with deposition overlying a silica layer with texture associated with *in situ* formation, sample PU-010. The white dotted line indicates the approximate position of the contact between silica layers.

Figure 4. Microtextures of natural basalt surfaces. a) Sample KE59-2941, hours old at time of collection, displays deformation texture but no chemical heterogeneity. b) Coated surface of sample KK. Bright material at left is Fe-Ti rich; glazed surface with particulate nubs at right is amorphous silica. c) Alternate coating morphology on sample KK, featuring lineated Fe-Ti coating capping silica with abundant desiccation cracks and "popcorn" texture. d) Fe-rich dendrites on surface of sample KE59-2970.

Figure 5. Incipient alteration on days-old spatter surface at Kamoamo. a) Backscattered electron image of pockmarked surface of sample KE59-2979 showing primary deformation lineation texture. b) Enlarged view of large pockmark at lower left of (a). Dark material with desiccation cracks in center is amorphous silica. Bright material between pockmarks is fine-grained Fe-rich crystallites. (c-e) EDS maps of Si (c), Al (d) and Fe (e) in the region indicated by the black box in (b). In each map, brightness corresponds relative concentration.

Figure 6. Alteration on year-old lava surfaces at Kamoamo. a) Backscattered electron image of the unpolished surface of sample NC-11-010. The material featured in the image is highly porous amorphous silica. b) Sample NC-11-015, spatter deposited away from the active fissure. Most of the spatter surface is covered by an amorphous silica alteration layer that preserves the

lineated primary surface deformation textures as seen in Figures 4a and 5a. The image also features a large vesicle (lower left) and an unaltered basaltic ash grain (upper right).

Figure 7. Schematic cartoon depicting silica coating formation. a) The surface of a fresh, unaltered basalt flow is wetted by rainwater or condensed water vapor in the presence of acidic vapors. b) Surface fluids (light gray) are acidified by the vapors. c) Acidic vapors dissolve a portion of the surface basalt and precipitate amorphous silica in place (striped). Fe and Ti have limited mobility. More soluble cations are removed away from the system. d) Silica-bearing fluids that interacted with subsurface basalt are transported to the surface. e) Subsurface-derived silica-bearing fluids evaporate, causing amorphous silica to supersaturate and precipitate in depositional morphology (crosses). f) Silica coatings accumulate over a period of years. Over that time, Fe-Ti oxides are mobilized and redeposited at the surface. Silica coatings may bridge near-surface vesicles. Surfaces may display deflationary morphology if $< 1 \mu\text{m}$ of silica is deposited for every $1 \mu\text{m}$ basalt dissolved (the dotted line represents the original, unaltered basalt surface).

Table 1. Sampling locations and samples discussed in this study. Waypoint coordinates are presented in Table S1.

Table 2. Summary of sampling site observations and sample properties.

Table 3. Representative electron microprobe chemical analyses of coatings analyzed in this study. ^aKa'u Desert 1974 flow, from Chemtob et al. (2010). ^bNormalized to unity on an anhydrous basis. ^cMauna Ulu analysis includes both surface alteration and underlying basaltic material. ^dMU-014 end-member silica-rich composition, calculated by subtracting basalt from EPMA analysis until a basalt-associated element (MgO) reaches zero.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1

Sampling Location/ Sample Name	Sample Description	Eruptive age	Collection Date	Age Upon Collection	Waypoint number
Ka'u Desert, Kilauea SWRZ					
KD-003a	Spatter rampart with contiguous white coatings	1974	2010	36 years	1
KD-003e	sheet pahoehoe, 10 m NW of rampart				2
KD-003g	sheet pahoehoe, 40 m NW of rampart				
KD-004	Coated pahoehoe at southeast edge of 1974 flow				
Keanakakoi Crater					
KK	Spatter ramparts near southeast rim of crater	1974	2012	38 years	4
Mauna Ulu, summit region					
MU-014	Pahoehoe slab from walls of near-summit lava channel	1969	2010	41 years	5
MU-017c	Shelly pahoehoe with coatings on shell underside	1969-73	2010	37-41 yrs.	6
Mauna Ulu, medial flow field					
MU-029	P-type pahoehoe breakouts with bright coatings	1969-73	2010	37-41 yrs.	7
Napau Crater, Episode 54 eruption					
NC-97-011b	Spatter rampart in center of Napau Crater	1997	2010	13 years	8
Pu'u O'o summit lavas, Episode 55					
PU-009	Volcanic bombs strewn on overflow lava surface	1998 ^a	2010	12 years ^a	9
PU-010	Doubly-coated shelly pahoehoe	1998	2010	12 years	
Pu'u O'o summit lavas, Episode 58					
PU-011	Spatter adjacent to fissure vent, initial Episode 58 activity	2007	2010	3 years	10
Kamoamo 2011 eruption					
KE59-2941 ^b	Spatter deposited on older tephra, collected while still hot	Mar. 6, 2011	Mar. 6, 2011	< 1 day	13
KE59-2952 ^b	Spatter deposited on older tephra	Mar. 5, 2011	Mar. 6, 2011	1 day	14
KE59-2970 ^b	Spatter deposited on older tephra	Mar. 5, 2011	Mar. 10, 2011	5 days	
KE59-2979 ^b	Spatter deposited on older tephra	Mar. 6, 2011	Mar. 14, 2011	8 days	15
KE59-2980 ^b	Spatter deposited on older tephra	Mar. 9, 2011	Mar. 14, 2011	5 days	16
NC-11-008	Iridescent lava from main spatter rampart	March 2011	March 2012	1 year	17
NC-11-010	Volcanic bomb adjacent to main spatter rampart				18
NC-11-015	Spatter deposited on older tephra				

Table 2

Sampling Location/ Sample Name	Surface Appearance	Coating Coverage	Max Silica Thickness (μm)	Micro-morphology
Kau Desert, Kilauea SWRZ				
<i>KD-003a</i> , spatter rampart	White, yellow and blue opaque coatings	Contiguous on spatter rampart, appears sparser on adjacent pahoehoe; absent where spalled	13	Silica layer capped by well-developed Fe-Ti layer; silica penetrates substrate along cracks
<i>KD-003e</i> , 10 m NW of rampart			16	
<i>KD-003g</i> , 40 m NW of rampart			7	
<i>KD-Mar10-004</i>			4	
Keanakakoi Crater				
<i>KK</i>	Yellow and orange opaque coatings	Prominent and contiguous on rafted spatter and lava trees; not present on lava lake surfaces	3.5	Silica appears as glaze or as "popcorn" texture; Fe-Ti coverage is irregular
Mauna Ulu, summit region				
<i>MU-014</i>	Dull white, yellow and orange opaque coatings	Present on spatter rampart and smooth pahoehoe surfaces, undergoing oxidation and removal; absent where spalled	5	Fe-Ti coating occurs in 30-100 μm bands on surface Silica may preferentially replace glass over pyroxenes
<i>MU-017c</i>	Powdery white and yellow coatings	Contiguous on underside of shelly pahoehoe		
Mauna Ulu, medial flow field				
<i>MU-029</i>	Bright white, yellow and orange opaque coatings	Contiguous on dense breakout pahoehoe toes; spotty and surface dependent on spongy pahoehoe	6	Not investigated
Napau Crater, Episode 54 eruption				
<i>NC-97-011b</i>	Yellow and orange opaque coatings	Prominent and contiguous on spatter rampart; present but sparse on pahoehoe toes ~100 m away	3	Fe-Ti coating particulate rather than continuous; silica layer penetrates basalt along cracks
Pu'u O'o summit lavas, Episode 55				
<i>PU-009</i>	Thick, white powdery coatings; on underside, opaque white, yellow, or blue material, or colorless glazes	Contiguous and heavy coatings on volcanic bombs, most pahoehoe surfaces, and shell undersides; absent where spalled and on 1983- 86 rim lavas	26; up to 100 in depositional morphology	Silica layers bridge near-surface vesicles; apparent deposition within some surface vesicles
<i>PU-010</i>			80 (underside); 35 (outer surface)	Thin Fe-Ti coating present capping thick silica coatings

Pu'u O'o summit lavas, Episode 58				
PU-011	Translucent white coatings	Contiguous on spatter next to fissure vent; sparse but present on pahoehoe of same age	14	No discrete Fe-Ti layer observed; some Fe-Ti enrichment within silica layer
Kamoamoa, 2011 eruption (collected immediately after eruption)				
KE59-2941	black glassy spatter, no visually obvious alteration	not applicable; hand samples	0	primary lineation and crinkle texture Fe-rich dendritic precipitate on surface primary lineation and crinkle texture; Fe-rich material on surface; incipient amorphous silica alteration Fe-rich material in subequant polygonal pattern
KE59-2952				
KE59-2970			0	
KE59-2979	black glassy spatter, no visually obvious alteration	not applicable; hand samples	< 1	
KE59-2980			0	
Kamoamoa, 2011 eruption (collected 1 year later)				
NC-11-008	iridescent colors on spatter rampart	Heterogeneous; matte coatings on some surfaces but absent on most	< 2	Topographically smooth; no Fe-Ti Highly porous surface cut by shallow cracks primary lineation texture; surface covered in silica desiccation cracks; Fe-rich polygonal deposits
NC-11-010	dull white, yellow, blue opaque coatings		3	
NC-11-015	Dull opaque blue or brown surface coloration	Contiguous over spatter surface; not apparent on older underlying spatter	4	

Table 3

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MgO	CaO	Na ₂ O	K ₂ O	MnO	SO ₃	P ₂ O ₅	Totals
<i>Basalts</i>												
Pu'u O'o summit	52.32	2.44	13.48	10.77	6.90	10.99	2.05	0.41	0.17	0.05	0.25	99.81
Ka'u Desert '74 flow	51.87	2.48	13.30	10.59	7.44	11.02	2.71	0.47	0.17	0.05	0.25	100.41
<i>Coatings</i>												
KD-74-001 ^a	94.87	0.19	0.12	0.28	0.33	0.06	0.03	0.03	0.06	1.41	0.02	97.44
<i>Normalized^b</i>	97.36	0.19	0.12	0.29	0.36	0.06	0.03	0.03	0.06	1.45	0.02	100.00
PU-009	81.89	0.50	0.13	0.66	0.07	0.32	0.11	0.05	0.03	0.11	0.03	83.89
<i>Normalized^b</i>	97.60	0.59	0.15	0.79	0.08	0.38	0.13	0.06	0.03	0.14	0.04	100.00
PU-011	79.87	0.56	0.21	0.36	0.09	0.36	0.20	0.06	0.01	0.15	0.02	81.91
<i>Normalized^b</i>	97.51	0.69	0.25	0.44	0.11	0.44	0.24	0.07	0.01	0.18	0.02	100.00
MU-014 ^c	59.83	1.31	6.24	6.03	2.57	4.65	0.62	0.27	0.09	0.15	0.07	81.84
<i>Normalized^b</i>	73.09	1.60	7.63	7.37	3.14	5.68	0.76	0.33	0.11	0.18	0.08	100.00
<i>Model endmember^d</i>	86.85	0.98	4.54	5.33	0.00	1.64	0.50	0.30	0.08	0.15	0.12	100.00

Highlights

- Amorphous silica coatings are ubiquitous on fresh Kilauean basalts, 0 to 40 years old
- Silica coatings form by low-temperature alteration of near-surface basalt by volcanically-derived acidic fluids
- Microstructures indicate both *in situ* and depositional mechanisms of coating formation
- Lavas from the 2011 Kamoamoa fissure eruption displayed initial surface siliceous alteration within 8 days of emplacement