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Microbial mediation of authigenic clays during hydrothermal alteration of basaltic tephra, Kilauea Volcano

Kurt O. Konhauser
Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E3

Peter Schiffman
Department of Geology, University of California, Davis, Davis, California 96516, USA (schiffman@geology.ucdavis.edu)

Quentin J. Fisher
School of Earth Sciences, University of Leeds, Leeds, England LS2 9JT

[1] Highly altered, glassy tephras within the active steam vents at Kilauea Volcano, Hawaii, contain subsurface bacteria characterized by small (<500 nm in diameter), epicellular grains attached directly to the cell walls. Compositionally, the grains were dominated by Si, Al, Fe, and K, in a stoichiometry similar to a dioctahedral smectite. The initial dissolution of glass, which may in part have been microbiologically mediated, served as the source for many of the elements sequestered into the biomineralized clays. Overlying the tephras are white crusts (silica and calcite) and green-colored biofilms. The biofilms comprise a filamentous, likely cyanobacterial, community coated with spherical (<100 nm in diameter) grains of amorphous silica directly attached to the sheaths. Individual precipitates can easily be resolved, but quite often they coalesce, forming a dense mineral matrix of amorphous silica. For both the clays and silica, the microbial surfaces are clearly sites for mineral nucleation and growth. These observations imply that microbial biomineralization may be a significant process in the overall alteration of primary basaltic glass in active steam vent systems.

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1. Introduction

[2] Recent studies have convincingly demonstrated that microorganisms reside in submarine basaltic glass, up to hundreds of metres deep within the Earth's crust [e.g., *Furnes et al.*, 2001a]. Although their metabolic processes are largely unknown, several points of evidence seem to suggest that these lithophiles promote dissolution of the rock substratum, and then grow within the micro-pitted surfaces [e.g., *Torsvik et al.*, 1998]. First, cell-sized, granular and tubular etch marks and bacteria

in-filling the pores have been identified in cores of fresh basaltic glass [*Furnes et al.*, 1996; *Fisk et al.*, 1998; *Furnes and Staudigel*, 1999], albeit near the interface with palagonitic or other secondary mineral precipitates [*Thorseth et al.*, 1992]. They are invariably connected to, or are directly rooted in, fractures in the glass [*Furnes et al.*, 2001a]. Second, some of the altered glass is enriched in bioessential elements, such as C, N, P and K, which suggests the presence of biological material [*Furnes et al.*, 1996; *Giovannoni et al.*, 1996; *Fisk et al.*, 1998]. Third, DNA is also present in altered basalts [*Thorseth et al.*, 1995a; *Giovannoni et al.*, 1996]. Fourth, carbon isotopes ($\delta^{13}C$) of carbonates from glassy basalts show fractionations characteristic of microbial activity [*Thorseth et al.*, 1995a; *Furnes et al.*, 2001b].

[3] The low-temperature alteration of glassy basalts commonly leads to the formation of fine-grained, geochemically heterogeneous material, including palagonite, silicate clays and (Fe, Al)-hydroxides. Several models have been developed to explain the mechanisms of such secondary mineral formation. One advocates that incongruent leaching of cations from the glass results in a silica-rich, porous material [e.g., *Berger et al.*, 1987]. Another model argues in favor of complete congruent dissolution of glass, followed by mineral precipitation [e.g., *Crovisier et al.*, 1987]. More recently, *Thorseth et al.* [1991] proposed a two-step process, with an initial loss of cations yielding a leached zone several micrometers thick in the glass, followed by a variable degree of congruent network dissolution of the silica-rich residue. The elements that suffer the greatest losses are Ti, Fe, Mg and Na, followed by Ca and Al. If the solution pH remains alkaline, then the residual siliceous material will continue to dissolve, leaving behind a distinctly porous structure. Iron, aluminium and silica may re-precipitate as hydroxide or silicate phases in the pores. In this regard, it has been suggested that the microbes growing on, or within, the basalts contribute to authigenic mineral formation. In experimental studies, dense colonies of bacteria develop rapidly on fresh glass surfaces when submerged in growth media, leading to preferential dissolution at points along fractures, and subsequently etching within weeks to months [e.g., *Staudigel et al.*, 1995; *Thorseth et al.*, 1995b]. The microbes then live within those pits, where they accumulate a range of elements, many derived from the glass (i.e., Al, Si), into their cell biomass. Often the concentration of elements leads to secondary mineral precipitation in the bioalteration zone [*Furnes et al.*, 1996]. There has, however, been little convincing evidence that microbial communities are actively mediating the precipitation of authigenic minerals (e.g., layer silicates). In this work we have therefore focused on providing unequivocal evidence that indigenous microbial communities can directly contribute to secondary mineral formation in steam vents, and most importantly, that biomineralization can be the main microbial role in the overall basaltic glass alteration process.

2. Geological Setting

[4] For the present study, we examined young basaltic tephras undergoing hydrothermal alteration within active steam vents at Kilauea Volcano, Hawaii. Tephra deposits of the Keanakako'i Ash Member of the Puna Basalt [*Easton*, 1987], exposed across the summit of Kilauea Volcano, were deposited from pyroclastic surges and related fall-out, initiated by phreatic and phreatomagmatic eruptions which originated from within Kilauea Caldera [*McPhie et al.*, 1990; *Mastin*, 1997]. The lower-most, vitric tephras were deposited between approximately 1500 and 1790 AD [*Swanson et al.*, 1998; Swanson et al., unpublished ^{14}C data, 2000]. Since their deposition, these vitric tephras have experienced differential weathering and hydrothermal alteration [*Hay and Jones*, 1972; *Schiffman et al.*, 2000] in response to varying environmental conditions (e.g., in pH, rainfall and temperature) across the summit of Kilauea. Hydrothermal alteration of these tephras is an active process within steam vents spatially related to the circumferential fault system which defines the boundaries of Kilauea caldera. On the northeast side of the caldera, steam vents in the Steaming Bluff region have been active for over 100 years [*Casadevall and Hazlett*, 1983].

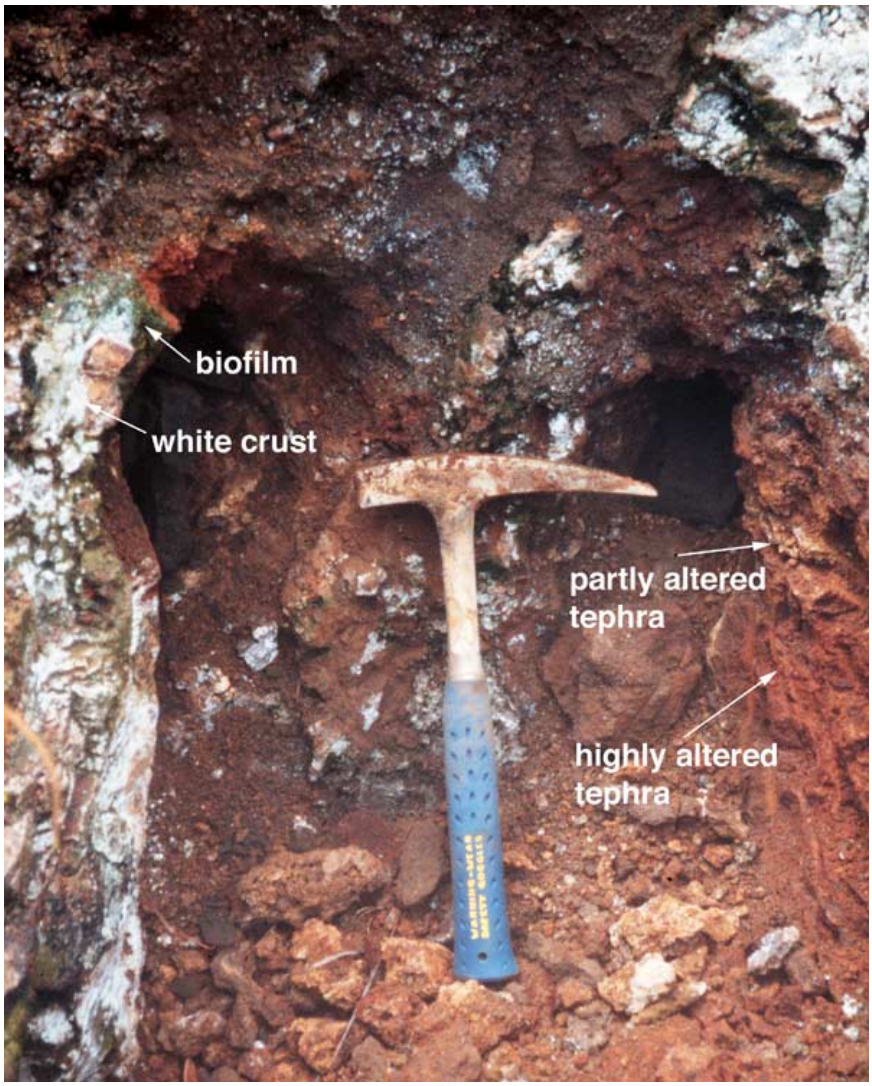

Figure 1. Soil pit dug in an 80°C steam vent within the Steaming Bluffs on the summit of Kilauea Volcano. The original bedding in the tephra deposits is best seen in the right side of the image. The superposition of the crusts and biofilms above the tephra deposits (white over green over red) is best seen in the upper left corner.

[5] Monitoring of selected steam vents within the northwest portion of the Steaming Bluff field over the past 3 years indicates that temperatures have remained close to a maximum of 80°C and that new authigenic crusts on the surface of vents can develop within several months. Figure 1 is a photograph of a soil pit within a steam vent originally dug in September 1999. The thinly-bedded nature of the vitric tephras can be seen along the right hand margin of the figure. The photograph was taken in September, 2000, when tephra samples were collected for this study. The surficial white crusts and green biofilms seen in the photograph developed between September, 1999 and September, 2000. The spatial relationships amongst the alteration layers are best seen in the upper-left hand corner of Figure 1. The outermost layer is a thin (<1 cm), white, porous crust. A thinner (ca. 1–2 mm), less continuous, green microbial layer lies beneath. The highly altered tephra layers beneath both the green biofilm and white crust are characterized by reddish hues. Samples collected from all three layers at the steam vent shown in Figure 1 were immediately placed in 15 mL sealed plastic vials containing aqueous glutaraldehyde (a fixative) for electron

microscopy. Partially altered tephra layers within the same steam vent were also sampled for mineralogical and textural investigations, specifically for signs of the microbial mediation of glass dissolution.

3. Methodology

3.1. X-Ray Diffraction

[6] The mineralogy of the crust and altered tephra samples was determined by X-ray diffraction (XRD), using a Rigaku Miniflex diffractometer. The samples were sonically disaggregated using a Branson 450 Sonifer, and the fine suspensions were poured through a Millipore filtration system, which collected the solids onto 0.45 μm filter papers. The samples were subsequently saturated with 0.1 M $MgCl_2$ solutions. The wet films were transferred onto glass slides for XRD analysis. Some samples were also solvated with ethylene gylcol overnight in a closed desiccator at 60°C.

3.2. Electron Microprobe

[7] Samples of both highly and partially altered tephras were mounted in a high vacuum epoxy resin and polished for subsequent examination in a Cameca SX-50 electron microprobe, possessing both wavelength dispersive (WDS) and energy dispersive (EDS) spectrometers, as well as high speed back-scattered electron (BSE) imaging capabilities. Quantitative analyses by WDS were conducted at 15 kV and 5 nA (beam current), with an electron beam which was rastered across the surface of the sample at a magnification of approximately 20,000 times. Such low currents and large spot sizes are necessary to ensure that highly hydrous materials are not damaged during electron beam analysis [*Schiffman and Day*, 1999]. Net analyte intensities in the unknowns were ratioed to those in silicate and oxide calibration standards and then converted to concentrations through application of ZAF correction factors.

3.3. Electron Microscopy

[8] Samples of highly altered tephras, surficial white crusts and green biofilms were prepared for thin-sectioning by scraping unexposed surfaces with a sterile scalpel, and then washing the fine-grained material/biomass in solutions of 0.05 M N-2-hydroxyethylpiperazine-N′-2-ethane-sulfonic acid (HEPES) buffer at pH 7.2 to remove excess glutaraldehyde. The samples were then post fixed in osmium tetroxide for 2 hours, washed again with HEPES buffer and then dehydrated through a graded alcohol series and embedded in resin. Thin sections, approximately 60 nm in thickness, were obtained using a Reichert-Jung Ultracut E ultramicrotome, and mounted on Formvar and carbon-coated copper grids. Some thin sections were stained with uranyl acetate and lead citrate to increase the electron contrast of cytoplasmic material inside intact cells.

[9] Specimens were examined using a Philips CM20 transmission electron microscope, fitted with a LaB_6 emitter, which was operated at 200 kV with an emission current of ~10 mA and a condenser aperture of ~100 μm diameter. The TEM is equipped with a model LZ-5 light element detector positioned to give a X-ray take-off angle of ~20°. Specimens were rotated a further 20° toward the detector to give increased X-ray counts. Energy dispersive X-ray spectroscopic (EDS) analyses were made by focusing the electron beam into a 100 nm probe, which was positioned onto isolated grains associated with cell surfaces. Data were collected using a Link exL multichannel analyser; 800 to 2000 counts per second were obtained for a live-time of 50 seconds. The background was automatically subtracted from the spectra.

[10] The elemental compositions of grains were calculated by correcting the characteristic element X-ray intensities using the 'k-value' procedure described by *Cliff and Lorimer* [1975]. A fundamental requirement of this correction procedure is that specimens must be sufficiently thin that X-ray fluorescence and X-ray absorption are negligible; such specimens are said to adhere to thin-film criterion. K-values were determined by the use of muscovite, biotite and paragonite standards of known composition. The validity of assuming thin-film criterion was checked by analysing a large number of biotite grains with a constant composition, but different thickness. The X-ray

Table 1. K-Values and Their Standard Deviations Used to Calculate Mineralogical Compositions From X-Ray Analysis Data

	K-value	sd
Mg	1.8	0.30
Al	1.4	0.09
K	1.2	0.11
Ti	1.2	0.10
Fe	1.0	0.07

intensity of an element with a low atomic number (Mg) was then plotted against the X-ray intensity of an element with a high atomic number (Fe); the resulting linear relationship indicated that X-ray absorption and fluorescence were not significant over the range of thickness/count-rates used for analysis. To monitor instrumental drift, approximately 20 analyses of standards were conducted prior to sample examination. The mean K-values for the elements Mg, Al, K, Ti and Fe, and their standard deviation (sd) are given in Table 1.

4. Results

4.1. Mineralogy and Geochemistry of Tephra and Secondary Crusts

[11] Within the steam vents, the extent of glass dissolution varies considerably, although all samples examined for this study showed some evidence of alteration. In partially altered tephra layers which retain relict glass, the ash-sized, vitric pyroclasts are coated with thin, ''palagonitic'' alteration rinds similar to those described from fossil steam vents at Kilauea [see *Schiffman et al.*, 2000, Figure 2c]. We have thus far found evidence of pitting and tubing within glass in only one Kilauea tephra sample. This sample was collected from within the steam vent, stratigraphically 15 cm above the highly altered tephra sample shown on the right side in Figure 1. In it, some vitric pyroclasts display small pits or tubules immediately adjacent to the alteration rinds, which may indicate that the glass dissolution, was at least in part, biologically mediated.

[12] The highly altered tephra deposits within the steam vents have experienced profound mineralogical and chemical alteration. XRD analysis of the reddish tephra indicates that the crystalline material is dominantly smectite, although the observed, broad basal reflections suggest a very fine crystallite size. BSE imaging of the same samples (Figure 2a) reveals that much of the original vitric ash has undergone extensive dissolution and reorganization. The cores of most vitric clasts have dissolved, whereas the rinds have developed a banded texture. A detailed observation (Figure 2b) of an individual clast indicates that the banding was produced by extreme chemical leaching of the tephra. Relative to fresh glass described previously from localized deposits of the Keanakako'i Ash Member [e.g., *Schiffman et al.*, 2000], the altered vitric ash shards in the reddish tephra deposits from the Steaming Bluff vent are severely depleted in Na and Ca, moderately depleted in Si and Mg, and enriched in Ti and Fe (Table 2).

[13] The outer portions of the rinds on the altered shards have compositions closely approximating Fe-rich saponite (e.g., points 1–3 on Table 2). The inner-portions of the rinds, which appear brighter in the BSE images (Figure 2b), have compositions that indicate a greater degree of Si and Mg loss, with a concomitant increase in Ti and Fe accumulation. Mineralogically, these portions of the altered rind can not be composed solely of saponite, but rather a complex, nanophase mixture of Fe- and Ti-oxides, as well as layered silicates.

[14] The mineral crusts overlying the reddish tephra have a very different texture and mineralogy. They consist of very finely intergrown calcite and amorphous silica (the latter as indicated by EDS analysis of material that produces no coherent diffraction pattern).

4.2. Biomineralization

[15] TEM analyses of the white surface crusts and underlying, highly altered tephras reveal that the indigenous microorganisms are ubiquitously encrusted in fine-grained inorganic phases. The surface populations are associated with small (<100 nm in diameter) grains attached to the sheaths of filamentous microorganisms (Figure 3), which based on their green pigmentation, their large cell size (several micrometers in diameter), the presence of

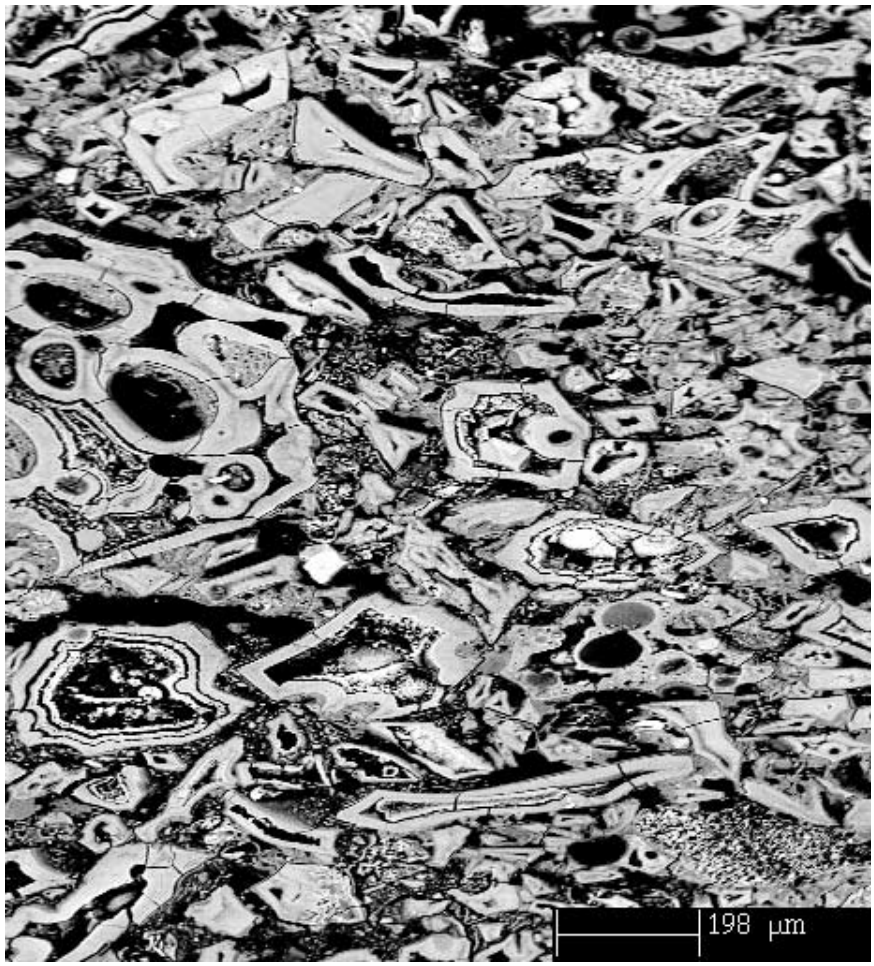

Figure 2. Backscattered electron microprobe images of highly altered tephra: (a) Low magnification image depicting relict vesicular glassy shards with banded alteration features; (b) Close-up of an individual, banded altered glass shard. The core of the shard is nearly completely dissolved. The numbers in the lower left and bottom margins of the shard refer to compositional analyses (i.e., p1–p5) presented in Table 2.

intracellular membranes and the lack of obvious chlorosomes (as in green bacteria), are likely a cyanobacterial species. Individual precipitates can easily be resolved, but quite often, they coalesce, forming a dense mineral matrix. Those grains found in the interstices between cells either formed on the sheath surface and were subsequently dislodged during sample preparation or they formed directly on the extracellular polysaccharides, which hold the microbial community together in a biofilm. EDS analyses of the grains indicates that the precipitates are predominantly Si-rich, with minor amounts of aluminium, while selected area electron diffraction (SAED) specifies that the grains have an amorphous structure. No calcite was evident in direct association with the bacterial populations.

[16] The subsurface populations, within the highly altered tephras described above, are characterized by variable levels of mineralization, ranging from a few epicellular grains attached directly to the cell wall, to a very high density of clayey materials extending up to 1 μm from the cell wall (Figure 4). The grains around the highly encrusted cells are typically smaller than 500 nm in diameter, and have a random orientation, but clearly nucleate and grow outwards from the cell surface. EDS and SAED patterns were taken from twenty grains associated with a number of cells (Table 3). All of these grains proved to be amorphous to poorly ordered, with chemical compositions dominated by Si, Al, Fe and K. Based on the average compositions of the grains, the clay material appears to be

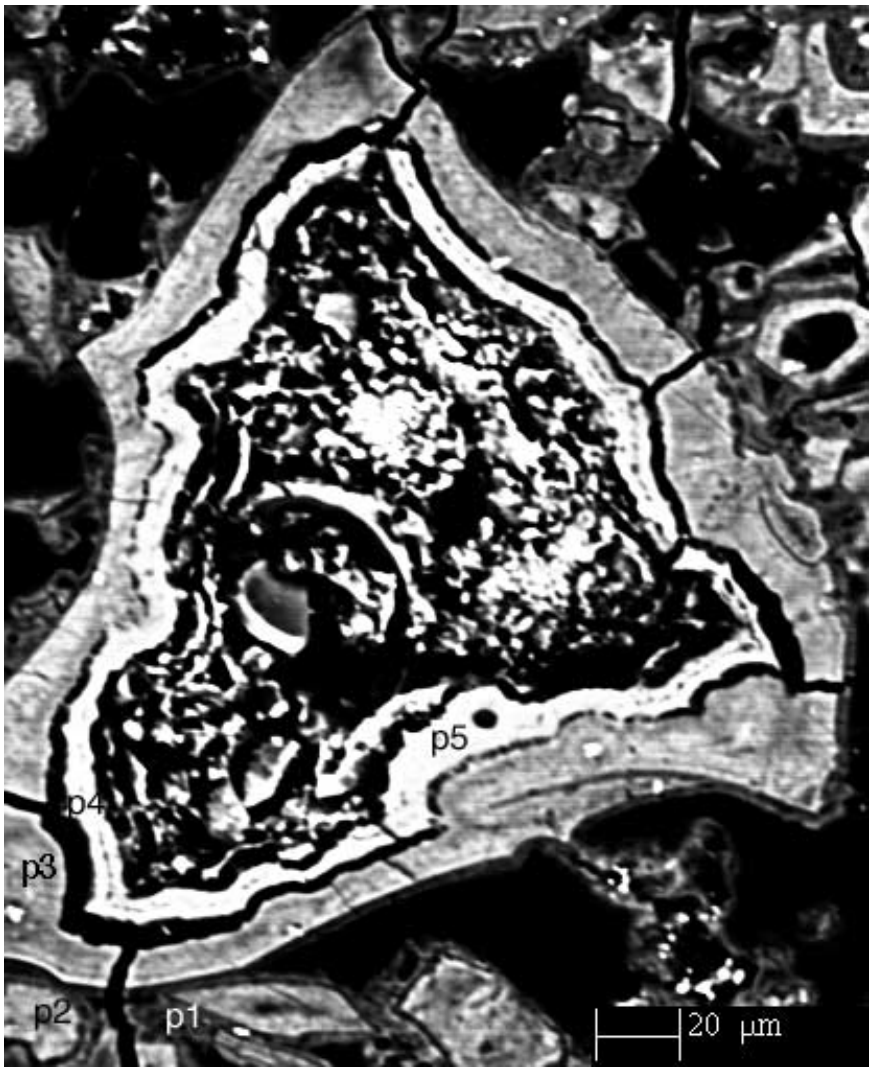

Figure 2. (continued)

close to a dioctahedral smectite with a $Al_{1.6}Fe_{0.36}$ ratio for the octahedral site and $Si_{3.8}Al_{0.2}$ for the tetrahedral site.

5. Discussion

[17] Previous studies on the role of microbial communities harboured on, or within, submarine basaltic glass suggest that the rock surface serves as a solid substratum for bacterial colonization, growth, and possibly metabolism. The impact of such a microbial population would be to enhance silicate mineral dissolution rates through the production of organic and inorganic compounds [*Ullman et al.*, 1996]. Experimental data have shown that the rate of glass dissolution by microbes may be on the order of 1 μm annually [*Thorseth et al.*, 1995b]. Such rates are commonly several orders of magnitude faster than that of inorganic processes [*Staudigel et al.*, 1995], although these experimentally determined rates are clearly dependent on factors including the media used, the type of microbial community and the chemical composition of the solution.

[18] Microbially enhanced dissolution can occur by at least four different mechanisms. First, the photosynthetic growth of microbes, such as cyanobacteria and algae, causes locally elevated pH which enhances glass dissolution rates [*Thorseth et al.*, 1992]. Second, fermentation and respiration pro-

Table 2. Electron Microprobe Analyses (in Weight %) of Fresh Glass and Altered Tephra From Steaming Bluff

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	sum
fresh glass	2.16	9.23	12.83	50.10	0.33	0.38	10.33	2.23	0.20	11.26	99.05
pt 1	0.20	2.54	27.92	41.09	0.19	0.14	0.85	1.96	0.13	10.63	85.64
pt 2	0.21	3.56	22.48	41.90	0.13	0.25	1.16	2.55	0.14	16.34	88.73
pt 3	0.14	3.96	20.39	39.80	0.09	0.15	1.21	3.65	0.22	20.92	90.51
pt 4	0.14	1.16	16.37	23.78	0.34	0.14	1.23	5.02	0.25	24.91	73.35
pt 5	0.07	0.56	8.63	17.49	0.36	0.12	0.94	7.72	0.08	38.33	74.30
	Na	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe	sum/22
pt 1	0.06	0.56	4.86	6.07	0.02	0.03	0.13	0.22	0.02	1.31	13.28
pt 2	0.06	0.79	3.93	6.21	0.02	0.05	0.18	0.28	0.02	2.03	13.57
pt 3	0.04	0.89	3.61	5.98	0.01	0.03	0.19	0.41	0.03	2.63	13.82
pt 4	0.06	0.35	3.89	4.79	0.06	0.04	0.27	0.76	0.04	4.20	14.46
pt 5	0.03	0.19	2.31	3.98	0.07	0.04	0.23	1.32	0.02	7.29	15.47

duce a variety of degradation products which are substantially more effective in dissolving some silicates than inorganic acids at the same pH [*Welch and Ullman*, 1996]. Third, many microbes produce high molecular weight compounds, such as extracellular polymers, that can enhance mineral dissolution by providing protons and complexing with ions in solution, thereby lowering solution saturation states [*Welch et al.*, 1999]. Fourth, other microorganisms release low molecular weight organic ligands, e.g., siderophores, which are produced specifically for scavenging iron and other nutrients [*Liermann et al.*, 2000]. These processes would initiate rapid dissolution at sites of high surface energy such as cracks, edges, point defects and dislocations. With time, this invariably leads to the partial or total breakdown of the primary mineral structure, mobilization and redistribution of the elements initially comprising the tephra, and ultimately the reprecipitation of layered silicates and other secondary mineral forms. Although a number of experiments have shown that biofilm formation increases the flux of most elements out of the primary glass, silica can often be retained in close vicinity of the weathering site through various biologically mediated processes [e.g., *Staudigel et al.*, 1998].

[19] This, and other studies of both fresh and altered tephras from the steam vents at Kilauea, however, have found relatively little evidence that microbes are actively involved in glass dissolution [see *Schiffman et al.*, 2000]. Specifically, in most samples containing relict fresh glass, which were analysed petrographically (aside from the one steam vent sample previously described), we have found no widespread textural evidence of pitting, tubing etc. within the glass. Furthermore, there were no biofilms, or obvious visual microbial remains found directly on the glass surfaces. The lack of more widespread textural evidence for biotic alteration within the Kilauea tephra samples is puzzling, especially as microbially mediated alteration textures have become increasingly documented in submarine glassy basaltic rocks (e.g., in the 3-km deep drill core from the Hawaiian Scientific Drilling Project [*Fisk et al.*, 2001]; in pillow lavas dredged from modern oceanic ridges [*Thorseth et al.*, 2001]). One explanation is that temperatures within the Kilauea steam vents are at the upper limits of those in which glass dissolving microbes effectively operate, at least within the oceanic crust [*Furnes and Staudigel*, 1999; *Furnes et al.*, 2001a]. Another possibility is that conditions above the water table are in some way not as conducive to microbial weathering as those in subaqueous environments. Although we cannot completely rule out the possibility that microbes may have played a significant role in glass dissolution in the Kilauea steam vents, their importance to the overall alteration process at Kilauea seems to be related to authigenic mineral formation. This observation corresponds closely to work by *Cochran and Berner* [1996] who showed that the rates of chemical dissolution of surficial Hawaiian basalts beneath lichens was minimal, more closely

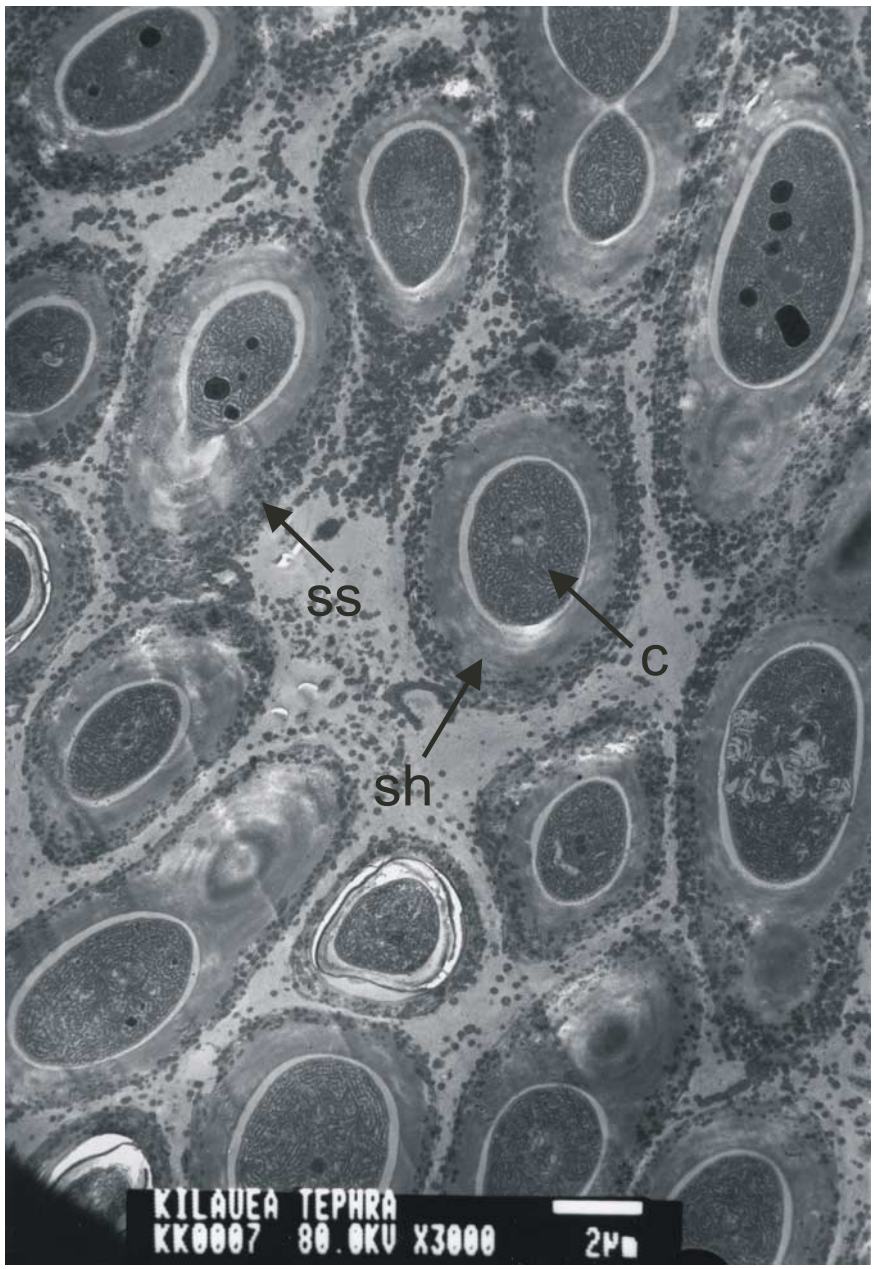

Figure 3. TEM cross-section of intact, likely filamentous, cyanobacterial cells (c) with small (<100 nm in diameter), amorphous silica spheres (ss) associated with the outer sheath (sh).

representing those found in the absence of vegetation than beneath higher plants. The only observable contribution by those microorganisms was the secondary precipitation of ferrihydrite.

[20] The dissolution of the tephra has presumably acted as a source for many of the elements sequestered into the biomineralized clays. Moreover, recrystallization of the tephra into secondary phases at the fresh glass interface has released Si and Ca, and much of these components have reprecipitated, first as insoluble, clayey phases in the subsurface, and then as amorphous silica and calcite to form the bulk of the white surface crusts on the steam vent walls. Although Al, Fe, and K are abundant in the alteration products of the tephras, their extreme porosity (c.f. Figure 2a) implies that there has also been a net loss in mass

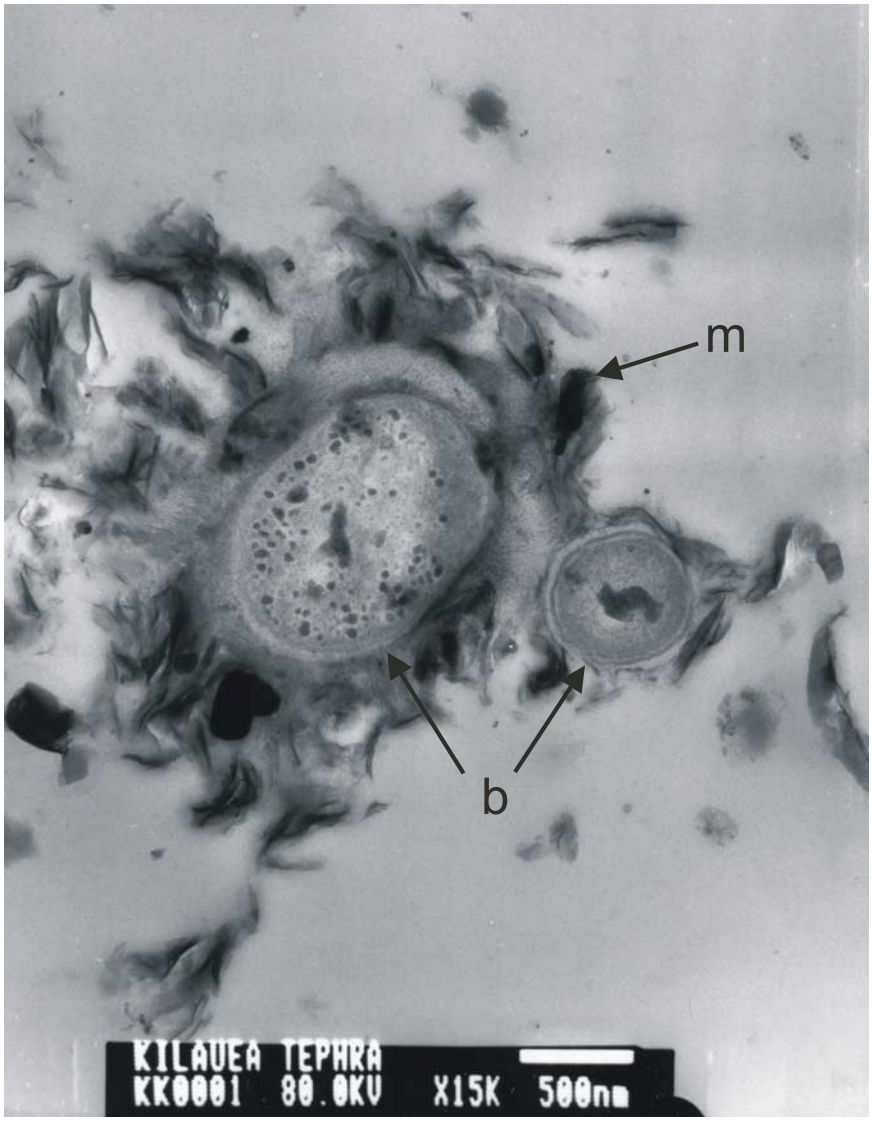

Figure 4. TEM image of two unidentified, intact bacterial cells (b) completely encrusted in fine-grained (<500 nm), amorphous, (Al, Fe)-silicate phases (m).

of these elements during the conversion from fresh glass to weathered residue. Interestingly, it is during the later stages of the overall alteration process that microbes appear most important. Specifically, biofilms can form a boundary layer that limits the diffusion of elements out of the system, thus causing them to concentrate, exceed mineral solubility and precipitate as secondary mineral phases [*Staudigel et al.*, 1995].

[21] The association of clays and amorphous silica with bacteria is unsurprising since their biogenic formation is well documented. Fine-grained (Fe, Al)-silicates in association with microorganisms have been described in metal-contaminated lake sediments [*Ferris et al.*, 1987], river sediment [*Konhauser et al.*, 1993, 1994, 1998] and geothermal environments [*Ferris et al.*, 1986; *Konhauser and Ferris*, 1996]. Their formation seems to follow a two-step model initially proposed by *Beveridge and Murray* [1976] to explain the copious amounts of metals observed on the cell walls of *Bacillus subtilis*. In the first step, iron is preferentially bound to the reactive functional groups belonging to the cell surface. This occurs because under circumneutral conditions any bacterium that produces

Table 3. Composition of Clay Phases Associated With Bacterial Cells Within Altered Tephra[a]

Al	Si	K	Fe
	weighted % oxides		
26.71	62.95	1.09	9.25
25.67	64.45	1.36	8.53
26.79	62.27	0.96	9.98
28.98	61.85	1.25	7.93
28.05	51.30	1.19	19.46
32.41	56.79	0.00	10.79
21.95	66.47	2.12	9.46
21.95	66.47	2.12	9.46
35.08	57.05	1.25	6.62
34.66	56.36	1.75	7.23
32.93	56.47	2.24	8.36
24.82	59.68	2.82	12.68
21.42	58.06	2.63	17.90
36.53	56.38	1.57	5.51
17.53	45.40	1.50	35.57
27.65	60.94	2.60	8.82
24.60	65.06	0.52	9.82
30.47	59.78	1.24	8.51
27.28	59.93	0.00	12.79
23.99	64.02	1.26	10.73
27.47	59.58	1.47	11.47

acidic, extracellular polymers will non-specifically adsorb cationic iron [*Ghiorse*, 1984]. The Fe-rich sites then serve as kinetically favourable sites for iron hydroxide growth [*Warren and Ferris*, 1998], and the potential formation of clay-like inorganic phases [*Konhauser and Urrutia*, 1999]. This clayey material presumably uses some fraction of the precursor surface as a template for its own growth, in effect circumventing the need for direct nucleation [e.g., *Steefel and van Cappellen*, 1990]. Once it begins to grow, the more stable clay phase increases its own surface area until it can control the composition of the proximal solution. When this happens, the saturation state of the solution moves below the solubility of the precursor, inhibiting further growth, or even dissolving the precursor. If the microbes are subject to sufficiently concentrated solutions (with SiO_2 and soluble aluminium), then the cells can become completely encrusted in clay-like material as abiological surface reactions accelerate the rate of mineral precipitation.

[22] Microbial silicification is ubiquitous in active geothermal settings. The mineralization associated with microorganisms occurs as spheroidal grains (ranging from 100s of nm to 2 μm in diameter) both extracellularly, on the sheaths of living cells, and intracellularly, within the cytoplasm, presumably after the cells have lysed. If silicification is sustained, the silica particles eventually coalesce until the individual precipitates are no longer distinguishable: entire colonies can become cemented together in a siliceous matrix several micrometers thick [*Ferris et al.*, 1986; *Schultze-Lam et al.*, 1995; *Konhauser and Ferris*, 1996; *Jones et al.*, 1998; *Konhauser et al.*, 2001]. The microbial role in silicification appears to be restricted to providing reactive interfaces for silica adsorption, thereby reducing the activation energy barriers to nucleation, and permitting surface chemical interactions that sorb more silica from solution to take place. In this way, the bacterium functions as a template for heterogeneous nucleation. If the weathering of tephra provides a sufficient supply of silica (in excess of mineral solubility), continued adsorption results in the surface sites becoming saturated, allowing particle nucleation to take place. After bacteria initiate silica precipitation, continued growth of the silica precipitates occurs autocatalytically and abiogenically, due to the increased surface area generated by the small silica phases.

[23] One of the unique findings in this work is that although calcite is precipitating at the surface as a crust, it is not directly associated with any of the bacterial cells analysed. On one hand this is surprising because in most modern carbonate deposits, i.e., tufas, travertines, stromatolites and thrombolites, calcite formation is intimately linked with growing microbial populations. Their role is generally attributed to photosynthesis, organic decay and/or the concentration of calcium to microbial exopolymers [e.g., *Krumbein*, 1979; *Pentecost and Riding*, 1986; *Thompson and Ferris*, 1990; *Chafetz and Buczynski*, 1992]. However, none of those studies have viewed the calcite-cell surface association via thin sections under the TEM, and as such convincing evidence to show that their surfaces actually nucleate it remains absent. In our opinion, the large size of the calcite crystal would likely preclude its formation on a bacterial surface, where the anionic organic ligands are closely spaced.

Thus, the microbial role may simply have been limited to the alkalinization of the local environment via photosynthesis, which ultimately led to calcium carbonate supersaturation.

6. Summary

[24] An electron probe and TEM study of tephras within the Kilauea steam vents has shown that microbial activity is integral in the overall alteration process. Although we can not rule out that biologically mediated glass dissolution has occurred in these vents, we have unequivocally demonstrated that microbes play an essential role in the subsequent precipitation of secondary silicate phases. Specifically, steam fluxing through glassy tephra is promoting the (apparent) abiotic dissolution and recrystallization into smectite and other alteration products. The soluble components of these alteration reactions – mainly Si and Ca – are transported in the steam to the surface of the vents where they are actively precipitating as crusts of silica and calcite. Within the surface crusts, microbes appear to be directly mediating the precipitation of amorphous silica, while below, they form clays. Thus the steam vents apparently support a synergistic and necessary integration of abiotic and biotic processes which collectively promote the alteration of basaltic glass.

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