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OLIVINE DOES NOT NECESSARILY WEATHER FIRST

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The study of weathering of minerals and rocks is a starting point for a number of disciplines that interface with tropical geography, including soil science, paleoecology, geomorphology, surficial geology, and climatic change. Chemical weathering is very active in a tropical setting and there is a need to better understand the rates and processes that take place in the weathering sequences. A better understanding of the rates and processes will provide a critical step in the interpretation of prevailing geomorphic processes and ultimately the evolution of tropical landforms.

The longest standing paradigm of weathering is Goldich's (1938) half-century old sequence of mineral susceptibility that is the reverse of Bowen's (1922) reaction sequence. 'It is generally agreed that olivine yields readily to weathering and that the rate of attack of this mineral exceeds that of any of the other common ferromagnesian silicates' (Goldich, 1938: 55). The majority of research papers and textbooks in weathering have either assumed that olivine weathers first (Pettijohn, 1957; Boul *et al.*, 1973; Press & Siever, 1974; Ritter, 1978; Marsh & Dozier, 1981; Colman & Dethier, 1986) or affirmed this conclusion (Pettijohn, 1941; Reiche, 1943; Jackson *et al.*, 1948; Stevens & Carron, 1948; Marel, 1949; Sindowski, 1949; Gruner, 1950; Sherman & Uehara, 1956; Craig & Loughnan, 1964; Füchtbauer and Müller, 1970; Colman, 1982). We report here the initial results of a study of relative stability of forsteritic and fayalitic olivine in weathering rinds in Hawaii, where age and environment of the parent lava flows are controlled in a natural setting.

OBSERVATIONS OF OLIVINE WEATHERING ON HAWAIIAN LAVA FLOWS

Hawaii provides an ideal site to study rates of weathering. The island of Hawaii, at the northern extent of the tropics, is composed of five major volcanoes. Samples were collected from Hualalai and Mauna Kea volcanoes where surface olivine basalt lava flows range in age from about 450,000 years to historic (Fig. 1). Numerical age is determined by historic observations, radiocarbon and K-Ar dating (Rubin *et al.*, 1987; Wolfe *et al.*, in press). Lithologies are as similar as possible for a natural chronosequence (Moore *et al.*, 1987; Moore & Clague, 1991; Wolfe *et al.*, in press), and the same lava flows traverse climates and flora that range from rainforest to desert (Giambelluca *et al.*, 1986).

Sample age ranges from 190 years to 153,000 years (Fig. 1). All but two samples were collected from the constructional surfaces of lava flows in a wide variety of environments. Three of the flows span a range in environment from desert (lower elevation) to savanna (upper elevation). The 15,000-year old site near the summit of Mauna Kea is from glacial polish in a periglacial environment (Dorn *et al.*, 1991; Dorn *et al.*, 1992) and the oldest sample at 153,000-years old was collected from the b-horizon of an oxisol soil.

After being embedded in epoxy and polished, weathering rinds were examined by light microscopy and scanning electron microscopy using backscatter (BSE) and secondary electron detectors. Plates 1-3 display representative BSE images of the Hawaiian weathering rinds sampled from sites in Figure 1. Plates 1 and 2 display weathered (porous and etched) minerals from millimeter-scale weathering rinds. Plate 3 provides a view of unweathered (non-porous, non-etched) minerals found beneath weathering rinds and coatings of amorphous silica.

Electron microprobe measurements were made with a JEOL Superprobe using the wavelength dispersive mode. BSE was found to be a particularly effective method for studying weathering because texture and

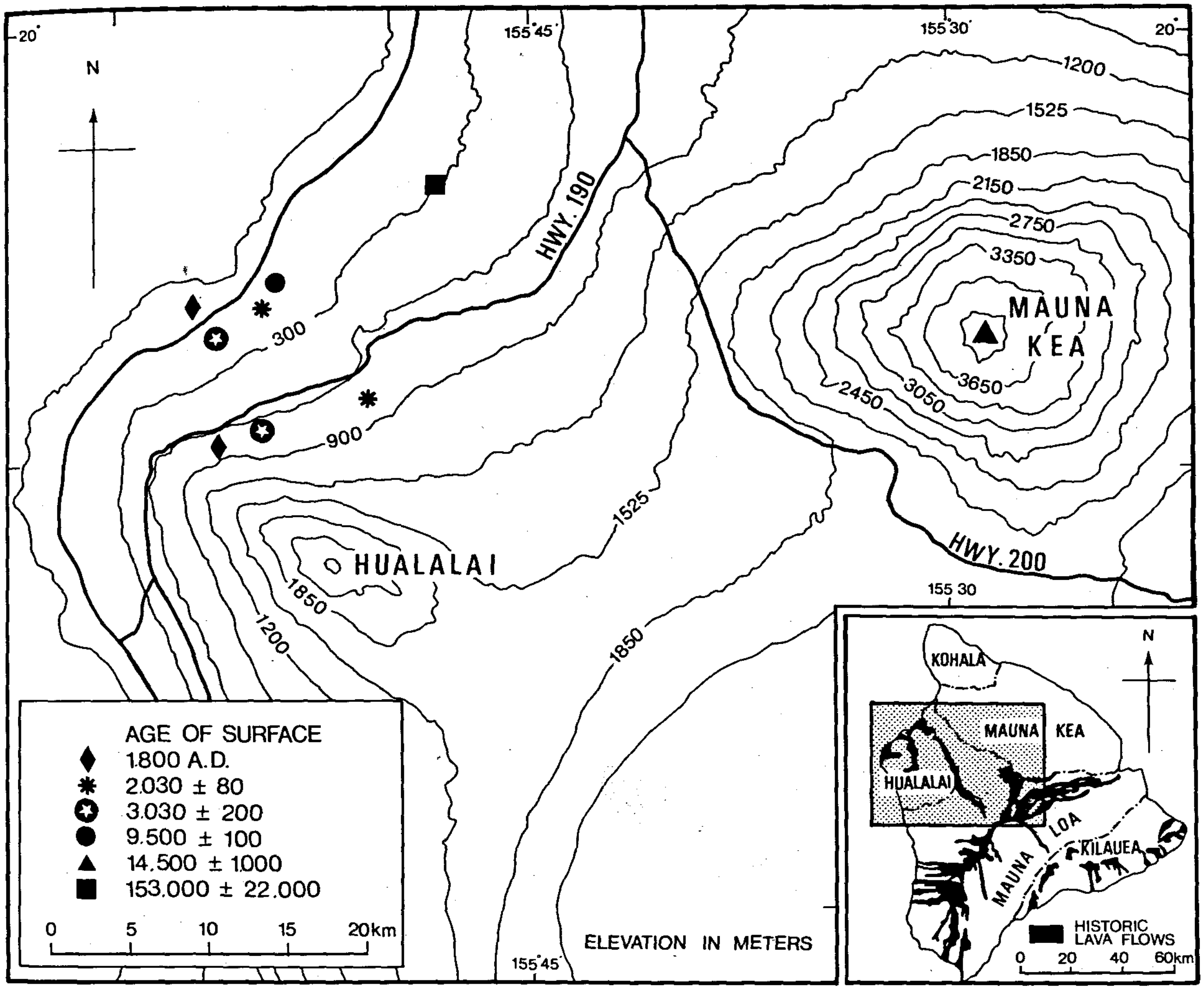

Fig. 1. Collection sites. The 1800 AD flow is a historic flow. The 2,030 and 3,030 flows were radiocarbon dated by Rubin et al. (1987). The 9,500 and 14,500 flows were radio carbon dates using rock varnish (Dorn et al., 1991). The 153,000 flow was dated by Wolfe et al. (in press) using K-Ar dating.

chemistry can be imaged simultaneously (Krinsley & Manley, 1989). Electron microprobe analyses in Table 1 correspond with the numbers in Plates 1-3. Throughout this paper, probe analysis numbers in Table 1 are abbreviated 'PA'; for example, probe analysis 2 in Plate 1A is PA2.

A primary observation is that plagioclase and clinopyroxene weathered before adjacent olivine, regardless of the age of the sample and of whether the sample was forsterite or fayalite olivine. For example, the phenocryst of olivine in Plate 1A is virtually fresh with only a few weathered fractures. In contrast, the adjacent plagioclase phenocryst (Plate 1A/PA1) is undergoing diagenetic changes to clay (close-up in Plate 1B). Clinopyroxene grains almost always weather by etching before adjacent olivines. (Plate 1C/PA4,5; Plate 1D/PA9; Plate 1E/PA10,13; Plate 1F/

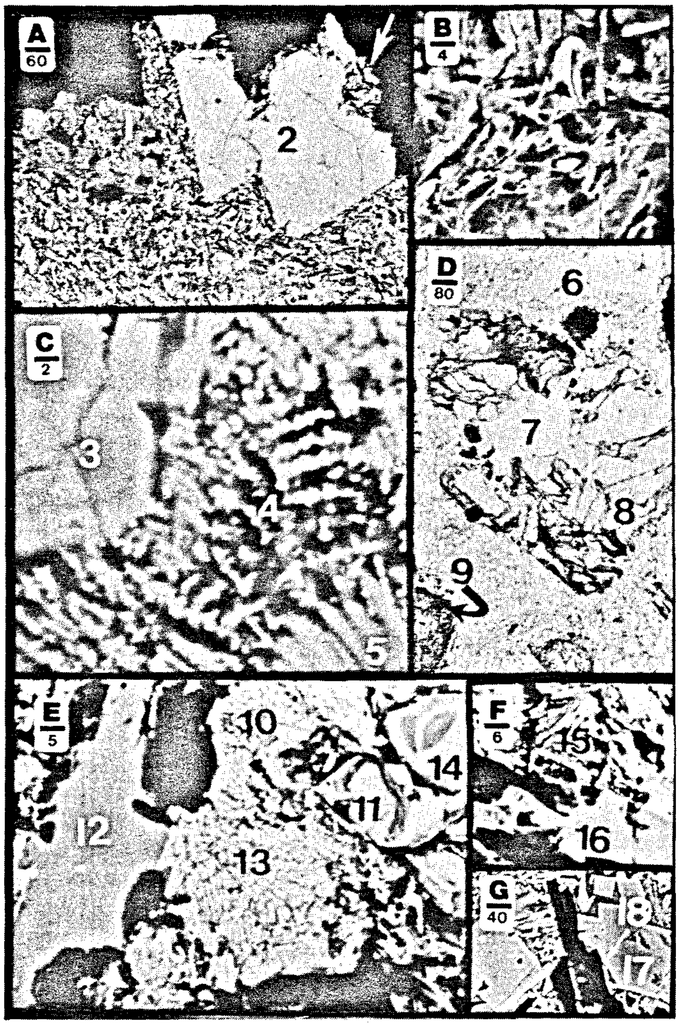

Plate 1. Backscatter (BSE) electron microscope images of Hawaiian weathering rinds. Scale bars in microns. Numbers identify electron microprobe analyses (PA) in Table 1. In BSE, brightness correlates with net atomic number (Krinsley and Manley, 1989). All images are of weathering rinds except 2G, which shows an interior position.

A. From the B-horizon of an oxisol on a 153,000-yr lava flow on Fig. 1. The arrow in the upper right hand corner points to ground mass that is protected from spalling by the relative stability of the olivine underneath.

B. Close-up of the weathered plagioclase grain, at the location of #1 in Fig. 2A.

C. From the 3,000-yr Puu Waawaa Ranch flow at the upper elevation site on Fig. 1. As the clinopyroxene weathers, a distinctive etching pattern evolves from position PA5 to PA4, with bright beads iron-oxides deposited in the etched areas of clinopyroxene.

D. From 15,000-yr glacial polish on top of Mauna Kea (Dorn et al., 1991) (Fig. 1). The more stable forsteritic olivine (PA6) and fayalitic olivine (PA7) contrast with plagioclases (PA8) and clinopyroxene (PA9) phenocrysts that are more weathered.

E. From the 3,000-yr Puu Waawaa Ranch flow at the upper elevation site on Fig. 1, olivine remains relatively fresh (PA11, 14) while plagioclase (PA12) appears to hollow and clinopyroxene becomes etched (PA10, 13).

F. From the 3,000-yr Puu Waawaa Ranch flow at the lower elevation site on Fig. 1, olivine (PA16) appears less weathered than the etched clinopyroxene (PA15).

G. The darker plagioclase, abundant clinopyroxene, and olivine (PA17) all appear fairly fresh in the interior of the rock away from the weathering rind of the 2,000-yr Puu Anahulu flow at the lower elevation site on Fig. 1. The arrow identifies the location of PA18, what may be a rim of iddingsite.

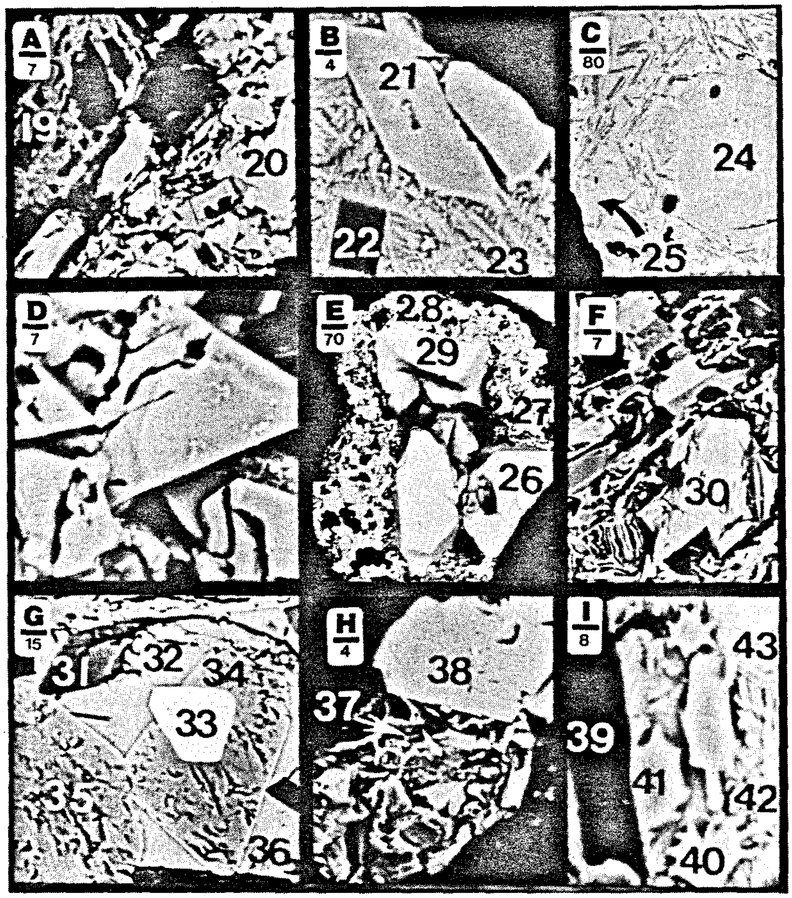

Plate 2. Backscatter (BSE) electron microscope images of Hawaiian weathering rinds.

A. Comparison of plagioclase (PA19) and olivine (PA20), collected from the San Francisco volcanic field, in northern Arizona.

B. From the 3,000-yr Puu Waawaa Ranch flow at the upper elevation site on Fig. 1, fresh olivine (PA21) and relatively fresh plagioclase (PA22) contrasts with etched clinopyroxene (PA23).

C. From the 1800 A.D. Kaupulehu flow at the lower elevation site on Fig. 1, showing no discernable weathering. PA24 highlights an olivine and the arrow for PA25 identifies a clinopyroxene grain.

D. From the 3,000-yr Puu Waawaa Ranch flow at the upper elevation site on Fig. 1, a three-dimensional BSE image of forsteritic olivine (based on energy dispersive X-ray analysis), illustrating the relationship between surface 'etch pits' and internally weathered fractures seen in cross-section.

E. A grain of sand collected from the black sand beach at South Point, Hawaii. Note how the clinopyroxene (PA27, 28) is thoroughly weathered, while the olivine (PA26, 29) is extremely fresh.

F. From the 9,500-yr lava flow on Fig. 1. The grain identified by PA30 is a relatively fresh mineral of olivine, surrounded by weathered plagioclase (darker laths) and clinopyroxene crystals.

G. From 15,000 yr glacial polish on Mauna Kea. In this part of the weathering rind, the forsteritic olivine (PA35) and fayalitic olivine (PA34) are much more weathered than adjacent clinopyroxene (PA32, 36), plagioclase (PA31), and magnetite (PA33) grains. Note how the clinopyroxene is starting to etch near PA36.

H. From the 1800 A.D. Kaupulehu flow at upper elevation site on Figure 1, some weathering is evident underneath lichens. Here, clinopyroxene (PA37) weathers faster than olivine (PA38), and the olivine acts as a pedestal in preserving the more weathered material underneath.

I. From the 2,000-yr Puu Anahulu flow at the upper elevation site on Fig. 1, olivine (PA40,41) displays different crystal forms, all of which weather more slowly than adjacent clinopyroxene (PA42, 43) and at about the same pace here as adjacent plagioclase (PA39). Note how the clinopyroxene at PA43 is starting to evolve from an unweathered smooth crystal above PA43 to an etched crystal below PA43.

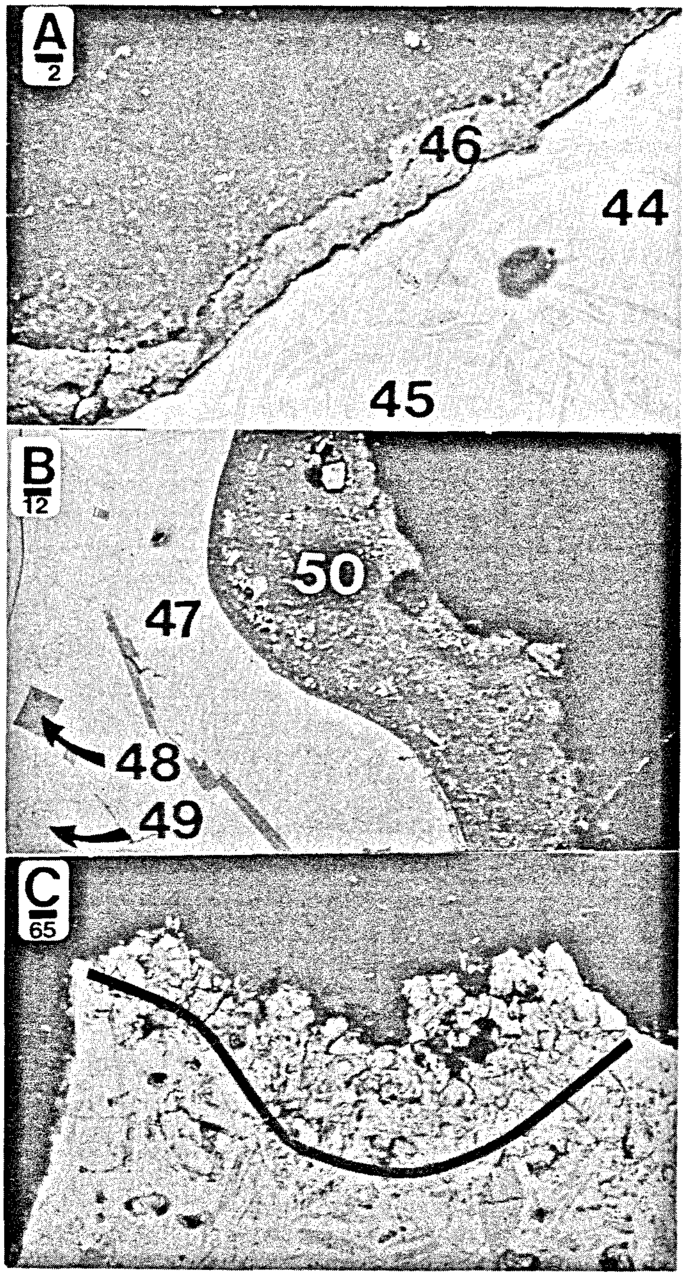

Plate 3. Backscatter (BSE) electron microscope images of unweathered minerals from Hawaiian lava flows.

A. From the 1800 A.D. Kaupulehu flow at upper elevation site on Fig. 1, showing fresh (unweathered, unetched) samples of clinopyroxene (PA44) and olivine (PA45). Amorphous silica (PA46) coats many of the surfaces of the Hawaiian lava flows (Curtis et al., 1985).

B. From the 9,500-yr lava flow on Figure 1. Unweathered clinopyroxene (PA47), olivine (PA48) and plagioclase (PA49) below a silica skin (PA50). Note how these unweathered minerals are not etched or porous.

C. From the 3,000-yr Puu Waawaa Ranch flow at the upper elevation site on Figure 1. The line separates the weathering rind from the fresh minerals below.

PA15; Plate 2B/PA23; Plate 2H/PA37; Plate 2I/PA42,43). Note that probe analyses on the more porous, weathered zones have lower totals in Table 1, and that the iron and magnesium concentrations in the olivines do not appear to affect its relative lack of porosity or etching.

These observations, contrary to Goldich's weathering sequence, hold true for minerals in weathering rinds (Plate 3C) regardless of whether they are phenocrysts or groundmass, olivine crystals of different compositions, or different olivine crystal morphologies (Donaldson, 1976). In contrast, crystals not in weathering rinds (Plates 3A & 3B) do not display the etched or porous features found in weathering rinds (Plates 1 & 2). Olivine is so resistant that it can act as a 'pedestal' to inhibit granular erosion of a weathering rind (Plates 1A & 2H).

Sand from a 'black sand' beach at Southpoint on Hawaii is composed of minerals that have weathered in a lava flow. It has been transported by slope and fluvial processes and exposed in a beach environment. The olivine here appears fresh, and more stable than clinopyroxene when they co-exist in the same sand grain (Plate 2E). Preliminary evaluation of weathering rinds in the San Francisco Volcanic Field, Arizona, indicates that olivine is more stable than clinopyroxene or plagioclase (e.g. Plate 2A).

This is not to say that olivine does not weather in Hawaii rinds. It does, and in a fashion predicted by studies on the rates and mechanisms of olivine weathering (Baker & Haggerty, 1967; Boland, 1976; Grandstaff, 1978; Delvigne *et al.*, 1979; Colman, 1982; Nahon *et al.*, 1982; Schott & Berner, 1985; Eggeleton, 1986; Wogelius & Walther, 1991). Microstructural weaknesses perhaps associated with surface etch pits (Plate 2D) are first accentuated (e.g. Plate 1A). Where these microcracks intersect, hollows grow (e.g. Plates 1G & 2G). A few of the olivine phenocrysts have rims of material, perhaps iddingsite (Eggleton, 1984), that may protect the rest of the olivine from weathering (e.g. Plate 2G/PA18), but this occurs only occasionally in our samples and cannot explain olivine's relative stability. In a few circumstances, olivine did appear to weather before clinopyroxene or plagioclase (Plate 2G); no systematic explanation could be discerned for these cases.

Microcracking may explain why plagioclase weathers before olivine. Microcracking is one of the dominant mechanisms by which plagioclase feldspars deform and weathering gains a foothold. The cleavage of plagioclase lends itself readily to the onset and continuation of microcracking (Tullis, 1983). The plagioclase in the Hawaiian basalts develop microcracks more readily than the olivine (Plate 1D/PA8). The fractures provide more surface area along which weathering can take place, successively increasing fracture area to volume ratios.

The relative stability of olivine in relation to plagioclase and clinopyroxene was not an anticipated outcome of our study, but it is consistent with other observations. Olivines are found to be resistant in black sand beaches (Plate 2E). Olivines are a good trap for cosmogenic He-3, suggesting stability of the crystal structure (Kurz *et al.*, 1990; Cerling, 1990). Organic-rich soil environments are known to produce anomalies in the order of feldspar weathering (Hinkley, manuscript in review). Concomitantly, we speculate that the extremely xeric microenvironments associated with weathering rinds exposed to the atmosphere may favour the relative stability of olivine. There is a need to conduct more research on the island of Hawaii from environments that have an abundance of organic matter, lichen and other rock-surface organisms to examine and compare the weathering found in these different environmental settings.

CONCLUSION

The findings from this study have shown that Goldich's mineral susceptibility sequence may not be applicable in all environmental settings. The sequence that was observed in the present study shows that under xeric conditions, such as those found in the rainshadow on Hawaii, olivine is more resistant to weathering. The examination of weathering rinds on Hawaiian lava flows with backscatter electron microscopy and electron microprobe revealed that olivine weathered more slowly than clinopyroxene and plagioclase minerals, regardless of lava flow age, crystal size, crystal morphology, or olivine composition. This conclusion is seemingly in line with what has been proposed by Curtiss *et al.* (1985) who believed that the aridity found in Hawaii limits the influence of organic acids and indirectly supports silica coatings on the lava flows.

Goldich (1938) did not claim that the mineral susceptibility series was absolute; on the contrary, he

TABLE 1. ELECTRON MICROPROBE ANALYSES THAT CORRESPOND WITH NUMBER IN PLATES 1-3. WAVELENGTH DISPERSIVE MODE USED WITH-2 MICRON SPOT SIZE. LOW TOTALS ARE ASSOCIATED WITH WEATHERED AREAS.

SITE (AGE AND POSITION)	PLATE (NO)	MINERAL	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO	TOTAL
Analyses corresponding with numbers in Plate 1												
153±22 ka*	1 A (1)	Plagioclase	2.40	0.18	24.64	37.20	0.10	13.32	0.07	0.00	0.83	78.74
153±22 ka*	1 A (2)	Olivine	0.03	28.08	0.04	39.13	0.00	0.29	0.02	0.26	31.32	99.17
3030±200# (upper)	1 C (3)	Olivine	0.00	39.26	0.04	37.27	0.00	0.52	0.08	0.28	19.48	96.93
3030±200# (upper)	1 C (4)	Clinopyroxene	0.27	11.55	5.83	40.55	0.08	12.22	1.51	0.11	14.87	86.99
3030±200# (upper)	1 C (5)	Clinopyroxene	0.32	14.55	3.9	45.03	0.00	19.97	1.45	0.25	9.91	95.47
~15 ka**	1 D (6)	Olivine	0.03	39.98	0.02	39.19	0.02	0.31	0.05	0.26	21.20	101.06
~15 ka**	1 D (7)	Olivine	0.01	26.01	0.04	37.15	0.00	0.29	0.00	0.36	35.11	98.97
~15 ka**	1 D (8)	Plagioclase	2.83	0.18	28.30	44.22	0.13	13.21	0.10	0.05	1.14	90.16
~15 ka**	1 D (9)	Clinopyroxene	0.23	6.44	8.19	41.63	0.01	18.12	2.03	0.10	10.19	86.94
3030±200# (upper)	1 E (10)	Clinopyroxene	0.61	10.60	7.49	43.17	1.31	20.75	3.95	0.22	11.17	99.27
3030±200# (upper)	1 E (11)	Olivine	0.03	40.57	0.26	42.36	0.00	0.57	0.12	0.31	19.53	103.75
3030±200# (upper)	1 E (12)	Plagioclase	3.26	0.20	28.23	48.11	0.22	14.20	0.15	0.00	0.78	95.15
3030±200# (upper)	1 E (13)	Clinopyroxene	3.06	1.77	13.30	47.26	3.05	3.95	2.25	0.17	13.51	88.32
3030±200# (upper)	1 E (14)	Olivine	0.08	39.50	0.36	38.40	0.01	0.57	0.12	0.31	21.55	100.90
3030±200# (lower)	1 F (15)	Clinopyroxene	0.30	12.99	3.97	44.15	0.00	19.38	1.43	0.15	7.58	89.95
3030±200# (lower)	1 F (16)	Olivine	0.01	38.19	0.06	39.41	0.00	0.28	0.03	0.32	21.78	100.08
2030±80# (lower)	1 G (17)	Olivine	0.00	39.61	0.04	37.46	0.00	0.28	0.02	0.25	19.88	97.54
2030±80# (lower)	1 G (18)	Iddingsite	0.55	23.31	4.30	37.11	0.02	1.02	3.91	0.45	26.28	96.95
Analyses corresponding with numbers in Plate 2												
San Francisco Volc. Field	2 A (19)	Plagioclase	4.14	0.24	26.59	53.10	0.41	11.30	0.11	0.00	0.52	96.41
San Francisco Volc. Field	2 A (20)	Olivine	0.00	27.02	0.02	39.36	0.02	0.28	0.00	0.27	30.32	97.29
3030±200# (upper)	2 B (21)	Olivine	0.04	38.73	0.04	37.33	0.01	0.55	0.05	0.22	20.84	97.81
3030±200# (upper)	2 B (22)	Plagioclase	4.11	2.01	20.86	47.86	0.34	12.03	1.40	0.05	4.97	93.63
3030±200# (upper)	2 B (23)	Clinopyroxene	0.58	12.44	5.69	46.57	0.12	20.62	1.73	0.15	7.56	95.46
1800 A.D. (lower)	2 C (24)	Olivine	0.01	35.23	0.32	35.21	0.01	0.31	0.02	0.23	21.86	93.20
1800 A.D. (lower)	2 C (25)	Clinopyroxene	0.28	15.35	2.72	51.69	0.00	21.45	0.93	0.12	6.66	99.20
Beach Sand	2 E (26)	Olivine	0.09	32.27	0.30	38.34	0.01	0.35	0.07	0.19	28.09	99.71
Beach Sand	2 E (27)	Clinopyroxene	0.26	13.40	3.38	44.02	0.01	19.39	1.20	0.13	7.12	88.91
Beach Sand	2 E (28)	Clinopyroxene	0.28	12.65	2.72	43.49	0.00	18.77	1.05	0.10	7.66	86.72
Beach Sand	2 E (29)	Olivine	0.13	31.57	0.40	38.66	0.00	0.48	0.08	0.21	27.53	99.06
9500±100#	2 F (30)	Olivine	0.10	40.49	0.11	36.01	0.02	0.29	0.02	0.23	17.39	94.66
~15 ka**	2 G (31)	Plagioclase	4.67	0.28	27.04	49.42	0.20	13.61	0.22	0.00	1.19	96.63
~15 ka**	2 G (32)	Clinopyroxene	0.27	15.54	3.06	51.73	0.02	21.63	1.10	0.13	7.03	100.51
~15 ka**	2 G (33)	Magnetite	0.05	1.51	1.01	0.31	0.10	0.28	23.14	1.10	71.55	99.05
~15 ka**	2 G (34)	Olivine	0.03	20.85	0.25	36.64	0.01	0.27	0.02	0.19	27.83	86.09
~15 ka**	2 G (35)	Olivine	0.03	31.02	0.30	37.38	0.01	0.31	0.05	0.17	18.77	88.04
~15 ka**	2 G (36)	Clinopyroxene	0.30	15.52	3.57	51.32	0.00	21.59	1.15	0.10	6.73	100.28
1800 A.D. (upper)	2 H (37)	Clinopyroxene	0.30	13.81	5.91	47.84	0.01	20.02	1.32	0.12	7.02	96.35
1800 A.D. (upper)	2 H (38)	Olivine	0.05	23.89	0.16	38.87	0.30	2.14	0.62	0.25	29.80	96.08
2030±80# (lower)	2 I (39)	Plagioclase	5.02	0.88	27.10	48.63	0.17	13.17	0.08	0.03	1.36	96.44
2030±80# (lower)	2 I (40)	Olivine	0.04	28.49	0.35	40.58	0.41	4.03	1.03	0.26	24.63	99.82
2030±80# (lower)	2 I (41)	Olivine	0.06	41.77	0.26	38.79	0.00	0.42	0.03	0.27	18.90	100.50
2030±80# (lower)	2 I (42)	Clinopyroxene	0.34	10.08	3.82	43.49	0.00	21.66	1.08	0.12	6.56	87.15
2030±80# (lower)	2 I (43)	Clinopyroxene	0.65	14.41	8.91	50.81	0.73	9.67	1.83	0.10	11.54	98.65
Analyses corresponding with numbers in Plate 3												
1800 A.D. (upper)	3 A (44)	Clinopyroxene	0.19	16.62	4.11	48.57	0.19	21.77	1.14	0.31	7.05	99.95
1800 A.D. (upper)	3 A (45)	Olivine	0.05	54.11	0.13	37.27	0.00	0.49	0.19	0.58	7.09	99.91
1800 A.D. (upper)	3 A (46)	Silica Skin	0.74	0.95	13.21	65.34	0.72	1.75	1.23	0.03	5.35	89.32
9500±100#	3 B (47)	Clinopyroxene	0.19	9.44	8.57	44.27	0.97	22.07	2.04	0.47	10.55	98.57
9500±100#	3 B (48)	Olivine	0.00	47.18	0.34	39.05	0.00	0.27	1.55	0.41	10.86	99.66
9500±100#	3 B (49)	Plagioclase	5.07	0.34	26.42	29.47	0.29	15.09	0.11	0.00	2.10	98.89
9500±100#	3 B (50)	Silica Skin	0.82	1.34	11.88	67.2	1.04	1.53	0.78	0.03	5.45	90.02

* K–Ar age in Wolfe *et al.* (in press)

\# Radiocarbon age in Rubin et al. (1987).

** Radiocarbon and Chlorine–36 age in Dorn *et al.* (1991).

noted that exceptions could easily occur. It is by finding and explaining these exceptions, however, that a better understanding can be obtained on the importance of environmental variables on weathering. The next step will be to examine the weathering sequence that is found in more acidic environments. If a sequence similar to the one observed in our study persists, it means that some of our most basic assumptions in weathering will require re-examination.

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