

Rock Varnish on Hualālai and Mauna Kea Volcanoes, Hawai‘i¹

R. I. DORN,² A. J. T. JULL,³ D. J. DONAHUE,³ T. W. LINICK,³ L. J. TOOLIN,³
R. B. MOORE,⁴ M. RUBIN,⁵ T. E. GILL,⁶ and T. A. CAHILL⁶

ABSTRACT: Tropical rock varnishes found on Hualālai and Mauna Kea Volcanoes, Hawai‘i, vary systematically with time and environment. Radiocarbon dating of encapsulated organic matter, $(K^+ + Ca^{2+})/Ti^{4+}$ ratios, and Zn, Cu, and Ni trace element concentrations in rock varnish are consistent with lava flow ages established by K-Ar and ¹⁴C dating, where samples are collected from arid microsites well away from the soil surface. However, inaccurate ages are obtained from rock varnish in subsurface locations and from sites with abundant lichens, cyanobacteria, and fungi that chemically erode varnish. In contrast with continental deserts, Hawaiian varnishes commonly interfinger with and are less common than rock coatings of amorphous silica. Laboratory experiments on Hawaiian rock varnishes indicate that K and Ca are preferentially leached relative to Ti over time and at higher temperatures. The location of in situ leaching has been identified in Hawaiian varnishes as porous textures without abundant detrital grains.

THE STEADY GROWTH AND IMPROVEMENT of stratigraphic dating methods have been fundamental components of Quaternary research during the past two decades. In contrast, surface exposure dating (SED) methods have been a weak sister; they attempt to measure the time since a land surface formed. Even though erosion of landforms is an ongoing process, SED methods utilize fossil remnants of “original surfaces” to date the landform (e.g., patches of glacial polish). Radiometric dating of lava flows and other stratigraphic units can offer valuable insights into rates of earth-surface processes (e.g., Dohrenwend et al. 1987). However, datable materials that provide surface exposure dates have a limited

distribution—that is, until the recent revolution in SED methods.

SED methods can be classified as biological, cosmogenic, and weathering. Biological SED methods rely on the growth of trees or lichens to constrain the age of the underlying deposits. Cosmogenic SED methods measure the time-dependent buildup of stable and unstable isotopes that occur in situ in minerals because of nuclear reactions caused by cosmic rays. Weathering SED methods, in contrast, measure the time-dependent decomposition and diagenesis of minerals in terrestrial weathering environments.

Originally proposed by Lal and Peters (1967), the measurement of in situ cosmogenic isotopes was not possible before the advent of accelerator mass spectrometry (AMS) (Brown 1984, Elmore and Phillips 1987). Helium-3 is the stable cosmogenic isotope that has received the most attention (Cerling 1990, Kurz et al. 1990). Chlorine-36 (Phillips et al. 1990), ¹⁰Be and ²⁶Al (Brown 1987, Nishiizumi et al. 1989), ¹⁴C (Jull et al. 1989), and ¹²⁹I (Fabryka-Martin et al. 1985) have seen the widest application of a large suite of radioactive cosmogenic isotopes. Other in situ cosmogenic isotopes that are being actively studied include ⁴¹Ca and ²¹Ne (Elmore and Phillips 1987, Lal 1988).

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²Department of Geography, Arizona State University, Tempe, Arizona 85287-0104.

³Regional Facility for Radioisotope Analysis, University of Arizona, Tucson, Arizona 85721.

⁴U.S. Geological Survey, Federal Center, MS-903, Denver, Colorado 80225.

⁵U.S. Geological Survey, 971 National Center, Reston, Virginia 22092.

⁶Crocker Nuclear Laboratory, University of California, Davis, California 95616.

The rate of chemical weathering is a function of the mechanisms that break the bond between the atoms of a crystal. Even though the kinetics of these processes continue to elude detailed study, many scientists have demonstrated an empirical time-dependence to weathering systems, including soils, weathering rinds, boulder decay, hornblende etching, quartz decrystallization, and other post-depositional modifications (Colman 1982, Birkeland 1984). Some have calibrated indices of weathering and soil development using established numerical ages (Switzer et al. 1988). One of the major difficulties in obtaining calibrated dates with weathering SED methods is the influence of environment. Unlike cosmogenic isotopes, weathering SED methods are dependent on pH, Eh, temperature, moisture, organic compounds, and other environmental variables.

An area destined to become a classic for testing SED weathering methods and assessing the influence of environment is the island of Hawai'i (Peterson and Moore 1987, Moore and Clague in press, Wolfe et al. in press). The radiocarbon dating of charcoal beneath lava flows (Rubin et al. 1987) and ^{40}K - ^{40}Ar dating of lava flows (Porter 1979*a,b*, 1986, Wolfe et al. in press) has already provided numerical age control to assess hydrous silica rock coatings (Farr and Adams 1984, Curtiss et al. 1985), paleomagnetic secular variations (Holcomb et al. 1986), radar roughness (Gaddis et al. 1989), and the in situ buildup of ^3He (Kurz et al. 1990). We concur with Farr and Adams (1984: 1077) when they write that Hawai'i "provides a unique opportunity to study, side by side, rocks of similar composition that have been exposed to subaerial weathering for vastly different lengths of time. . . . Furthermore, the wide variations in topography and rainfall make it possible to assess how these factors affect rock weathering."

The purpose of this study is to examine time-dependent and environment-dependent signals of one low-temperature weathering system, rock varnish, on Hualālai and Mauna Kea volcanoes, Hawai'i. Weathering is not simply the decay of minerals, but also includes diagenesis of mineral material into low-tem-

perature weathering products such as rock varnish. Rock varnish is a dark accretion of clay minerals, manganese and iron oxides, and over 30 other minor and trace elements (Dorn and Oberlander 1982, Whalley 1983). Three time-dependent chemical signals in rock varnish are discussed here for Hawai'i: radiocarbon content of organic matter encapsulated by rock varnish; $(\text{K}^+ + \text{Ca}^{2+})/\text{Ti}^{4+}$ ratios; and the scavenging of trace metals Ni, Cu, and Zn by Mn-Fe oxides.

Study Sites

The island of Hawai'i is composed of five major volcanoes, the highest of which is Mauna Kea, which reaches 9–10 km above the Hawaiian Deep (Figure 1; Chase et al. 1980). Basaltic lavas exposed at the surface range in age from about 450,000 yr at Kohala (McDougall and Swanson 1972), to the Holocene lava flows of Mauna Kea (Porter 1979*a, b*, 1986, Wolfe et al. in press), to the historic flows of Mauna Loa, Hualālai, and Kīlauea (Stearns and MacDonald 1946, Moore et al. 1987). These lava flows usually lose their initial glassy surface within a few years of extrusion (Farr and Adams 1984), but some glassy surfaces last as long as 3000 yr (R. B. Moore, unpubl. observations). Parts of pahoehoe and aa flows retain vesicular constructive surfaces for 10^4 yr on the drier parts of Hawai'i (Dorn et al. 1989, Kurz et al. 1990).

Farr and Adams (1984: 1081) first observed Hawaiian rock varnish on the very dry western slope of Kohala, noting that it is similar to "...varnish coatings found in deserts throughout the world." Manganese-rich and Mn-poor (iron-rich) rock varnishes have a rich history of study in tropical settings [e.g., von Humboldt (1799–1804) published 1907:243–247, Boussingault 1882, Darwin 1897:12–13, Francis 1921, Lukashev 1970, Alexandre and Lequarré 1978, Potter and Rossman 1979*b*, Chukrov et al. 1983].

Hawaiian varnishes have bulk chemistries of the major varnish elements (Al, Si, Mn, Fe) roughly similar to those of other rock varnishes (Table 1) and express a similar degree of micrometer-scale chemical variability (Table 2). Hawaiian varnishes have textures

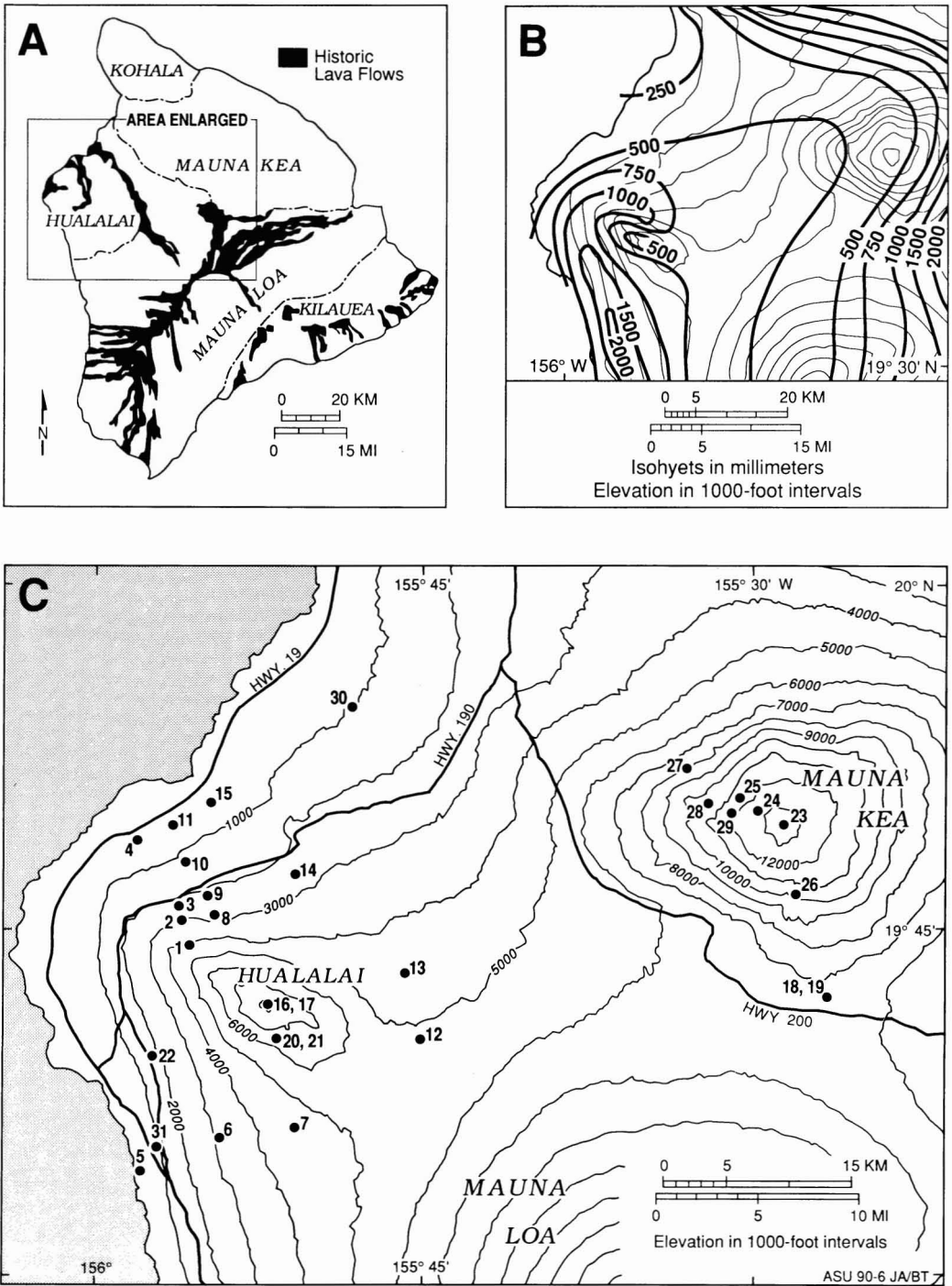


FIGURE 1. A, Volcanoes of Hawai'i (from Stearns and MacDonald 1946, Peterson and Moore 1987); B, generalized isohyets of Hawai'i (from Giambellu et al. 1986); C, study sites on Hualālai and Mauna Kea volcanoes (numbers correspond to sites in Table 3).

TABLE 1

ELEMENTAL WEIGHT PERCENTAGE OF ROCK VARNISH FROM HAWAII, COMPARED WITH CONTINENTAL LOCATIONS (MEASUREMENTS BY PIXE, NORMALIZED TO 100%)

AREA	SITE	ENVIRONMENT	Na	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Rb	Sr	Zr	Ba	Pb	
Hawaii above 3000 m	Mākanaka Till (25)*	>1 m above soil	0.25	0.98	21.58	31.72	0.44	bld	2.47	3.49	0.91	18.11	20.05	bld	bld	bld	bld	bld	bld	na	bld	
	Mākanaka Till (25)	With silica skin	0.62	1.98	21.13	29.77	0.69	0.20	3.30	4.89	0.73	13.60	21.13	bld	0.33	0.49	bld	bld	bld	bld	0.16	0.98
	Mākanaka Outwash (26)	>1 m above soil	0.59	2.37	21.20	32.50	0.97	0.21	3.27	2.09	0.87	18.37	16.28	0.14	0.52	bld	bld	bld	bld	bld	0.12	0.50
	Top of 33 ka flow (29)	>1 m above soil	na**	na	15.63	21.70	bld	bld	4.41	1.56	1.04	26.86	27.82	bld	0.04	0.19	0.37	0.38	bld	na	bld	
	Top of 33 ka flow (29)	Many lichens	na	na	10.28	15.60	2.82	0.23	2.47	5.10	2.89	26.65	33.25	bld	bld	0.10	bld	0.19	0.13	na	0.29	
Hawaii below 3000 m	On glacial polish (24)	>1 m above soil	0.34	2.14	20.53	34.66	0.34	bld	3.05	2.77	0.85	12.59	22.15	bld	bld	bld	bld	bld	bld	na	0.58	
	Pu'u Wa'awa'a Ranch (10)	>1 m above soil	3.33	2.81	18.73	26.01	2.08	0.52	3.95	4.89	1.14	12.49	20.60	bld	0.21	bld	bld	bld	bld	0.52	1.66	1.04
	Pu'u Wa'awa'a Ranch (10)	With silica skin	0.64	1.54	19.74	27.61	0.66	bld	6.49	4.51	1.06	21.34	15.68	bld	bld	bld	bld	bld	bld	bld	0.12	0.61
	Keōpū Ahupua'a (22)	>1 m above soil	3.19	1.55	22.12	39.58	0.50	bld	3.27	3.60	1.19	10.96	11.29	0.16	0.24	0.16	0.16	0.16	0.00	0.87	0.99	
	Keōpū Ahupua'a (22)	Many lichens	2.70	0.82	24.00	31.53	1.17	0.62	1.90	2.00	0.94	19.15	12.10	bld	0.30	0.30	bld	bld	bld	bld	2.10	0.37
	Puu Neneakolu (20)	>1 m above soil	2.58	1.84	18.40	26.98	0.98	0.64	3.80	3.43	1.03	24.65	11.77	0.18	0.27	bld	0.80	0.29	0.38	1.51	0.45	
	Puu Neneakolu (21)	Many lichens	2.76	1.42	15.65	32.69	0.88	0.88	2.98	2.38	1.13	23.24	12.65	bld	0.39	0.21	bld	bld	bld	bld	2.00	0.75
	Unnamed flow (13)	From rock crack	3.07	1.90	23.26	44.82	bld	0.71	5.34	6.32	0.98	0.39	11.53	bld	bld	bld	bld	bld	bld	bld	1.69	bld
	Flow MKH-4 (30)	From rock crack	1.54	2.58	19.50	27.28	0.84	0.94	4.41	4.09	1.26	18.67	16.47	bld	0.27	0.15	bld	bld	bld	0.73	1.26	bld
	Pu'u Anahulu (15)	>1 m above soil	5.31	1.87	19.97	33.71	0.70	0.95	2.76	3.11	0.66	11.75	15.50	bld	bld	bld	0.43	0.68	bld	2.18	0.43	
Continental arid	Pu'u Anahulu (14)	>1 m above soil	3.12	1.51	20.80	31.29	0.31	0.51	2.69	3.30	0.70	18.23	15.29	bld	0.20	0.40	bld	bld	bld	1.21	0.43	
	Sinai Peninsula, Egypt	>1 m above soil	0.28	1.50	22.94	32.81	bld	bld	2.42	2.91	0.68	11.97	22.94	bld	0.25	0.42	bld	0.42	bld	0.18	0.27	
	Petroglyph, S. Australia	>1 m above soil	0.17	1.21	22.81	33.34	0.53	bld	2.79	2.18	0.65	21.70	13.26	bld	0.44	0.44	bld	bld	bld	0.14	0.34	
	Trail fan, Death Valley	Former rock crack	bld***	0.14	23.74	39.09	0.49	0.70	3.45	4.87	1.52	10.87	13.47	0.13	0.12	0.27	bld	bld	bld	0.29	0.85	bld
	Ingenio, Peru desert	At soil surface	na	2.11	20.45	45.88	0.53	1.13	2.91	6.22	0.85	4.94	12.03	bld	0.04	0.16	bld	0.11	bld	2.42	0.22	
	Ayers Rock, Australia	From rock crack	na	1.58	28.77	35.69	bld	bld	2.11	1.45	1.19	11.91	16.57	bld	bld	bld	bld	bld	bld	0.73	bld	

* Number in parentheses refers to sites identified in Figure 1 and Table 3.

** Not available.

*** Below limit of detection.

TABLE 2

MICROCHEMICAL VARIABILITY IN SELECTED HAWAIIAN, WESTERN U.S., AND PERU ROCK VARNISHES

SITE	DEPTH (μm)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	FeO	NiO	CuO	ZnO	BaO
Mākanaka till, Mauna Kea, Hawai'i (site 25 in Table 3 and Figure 1)	Surface	1.25	2.41	16.19	20.70	na*	1.19	1.22	0.59	12.25	11.39	0.04	0.00	0.02	0.05
	4	1.35	1.23	15.57	19.85	na	1.06	1.04	0.33	14.57	13.36	0.00	0.09	0.04	0.13
	8	1.01	1.53	14.73	19.82	na	1.26	1.29	0.41	14.68	13.26	0.02	0.10	0.06	0.18
	12	1.22	1.41	16.67	17.64	na	1.36	0.95	0.57	16.77	15.06	0.06	0.13	0.00	0.10
	16	0.94	2.50	15.38	20.32	na	1.42	0.82	0.69	17.84	12.72	0.12	0.14	0.00	0.25
	20	0.28	1.44	16.85	20.88	na	1.23	1.33	0.44	13.88	14.23	0.00	0.16	0.10	0.33
	24	0.19	2.18	15.07	20.34	na	1.04	1.89	0.49	12.91	14.54	0.12	0.05	0.12	0.28
	28	0.13	2.41	18.18	19.71	na	1.10	1.21	0.52	16.99	13.64	0.02	0.20	0.20	0.20
	Just above rock	0.17	2.81	17.36	19.01	na	1.15	1.33	0.63	12.96	13.15	0.20	0.22	0.16	0.16
	Lathrop Wells cinder cone, southern Nevada	Surface	0.07	0.17	4.40	2.10	na	0.22	0.53	0.27	2.05	1.60	0.04	0.04	0.00
4		0.00	2.30	22.11	27.04	na	0.86	0.67	0.75	4.40	21.99	0.00	0.00	0.04	0.13
8		0.09	3.76	21.60	24.80	na	1.08	0.71	0.55	2.70	25.86	0.04	0.10	0.00	0.15
12		0.08	2.69	18.65	25.61	na	1.05	0.80	0.73	4.27	26.82	0.09	0.06	0.00	0.11
16		0.09	1.72	19.41	23.30	na	1.40	0.76	0.60	6.21	24.37	0.09	0.00	0.00	0.22
20		0.13	1.48	20.52	19.98	na	0.96	0.88	0.52	11.11	19.80	0.00	0.11	0.05	0.45
24		0.11	1.77	21.69	22.98	na	1.04	0.83	0.55	11.93	16.89	0.03	0.09	0.04	0.35
28		0.11	1.89	22.64	25.95	na	1.16	0.83	0.50	10.46	15.99	0.00	0.10	0.00	0.33
32		0.11	1.49	20.61	23.28	na	1.05	1.08	0.68	9.61	19.89	0.03	0.13	0.01	0.40
36		0.08	1.08	13.21	56.50	na	0.80	0.46	0.32	2.91	10.21	0.00	0.15	0.00	0.08
40		0.09	1.41	20.50	20.67	na	0.88	0.94	0.68	11.13	19.49	0.04	0.14	0.00	0.33
44		0.19	1.38	20.46	20.35	na	0.89	1.04	0.62	11.36	18.83	0.00	0.00	0.00	0.49
48		0.00	1.48	19.35	21.41	na	1.00	1.02	0.50	22.64	8.41	0.01	0.10	0.02	0.21
52		0.11	1.46	17.27	20.84	na	0.94	1.13	0.60	29.72	11.85	0.00	0.03	0.10	0.25
Just above rock	0.11	1.51	17.78	21.31	na	0.77	1.15	0.53	19.82	12.94	0.00	0.08	0.19	0.80	
Desert pavement, terrace of Rio Ingenio, north of Nazca, Peru	Surface	na	1.89	19.93	26.85	0.92	1.12	1.12	0.37	12.74	14.68	0.00	0.00	0.20	0.21
	4	na	2.02	18.71	28.65	1.26	2.22	0.88	0.63	9.25	14.58	0.09	0.01	0.06	1.21
	8	na	1.58	19.14	24.20	1.08	1.48	1.19	0.43	10.50	19.14	0.00	0.00	0.11	1.50
	12	na	1.67	15.78	19.70	1.08	1.59	1.41	0.70	9.53	24.24	0.09	0.00	0.08	2.17
	16	na	1.49	16.23	18.76	1.67	1.41	1.33	0.55	12.12	24.82	0.05	0.00	0.05	1.82
	20	na	1.76	16.55	21.67	1.40	1.78	1.23	0.58	10.67	24.59	0.03	0.00	0.04	1.84
	24	na	2.16	16.33	20.90	1.24	1.71	1.26	0.47	8.34	24.26	0.04	0.16	0.00	2.21
	28	na	1.24	14.40	16.41	0.89	1.64	1.12	0.58	9.17	22.77	0.11	0.11	0.00	1.98
	32	na	1.64	16.55	20.24	1.17	1.51	1.16	0.58	10.48	26.93	0.10	0.00	0.00	1.84
	Just above rock	na	1.49	15.49	17.97	1.33	1.48	1.09	0.63	12.47	22.69	0.00	0.08	0.00	2.05

*Not analyzed.

NOTE: Each sequence is a profile of electron microprobe analyses (wavelength dispersive mode) from top to bottom in a cross section. In each case, the texture is lamellate, and the microenvironment avoids microcolonial fungi and lichens. The Mākanaka sample was collected > 1 m above soil. Others collected < 10 cm above soil. All are from subaerial sites, not formerly in cracks.

(Figure 2) similar to those of continental varnishes (Krinsley et al. 1990). However, Hawaiian varnishes at lower altitudes (below trade wind inversion) have higher sodium, barium, and sulfur contents than continental varnishes in similar environmental settings (Table 1), perhaps because of their proximity to marine-generated sodium and barite at lower elevations (cf. Bishop 1988). The distribution of Hawaiian varnish is similar to what one would find in the pinyon-juniper woodlands of the western United States or in semi-arid central Australia: patchy with areas of intense development in neutral to alkaline microenvironments.

The major difference between Hawaiian varnishes and those in continental drylands is the relative abundance of coatings of hydrous silica, termed silica skins (Watchman 1985). Silica skins are common on rocks on the drylands of Hawai'i (Figure 2g; Farr and Adams 1984, Curtiss et al. 1985). Silica skins were first observed in deserts (Willet 1901, Fisk 1971), where they interlayer with varnishes (Butzer et al. 1979, Smith and Whalley 1988; Figure 2g). However, skins of amorphous silica dominate the basaltic surfaces of Hawai'i (Farr and Adams 1984, Curtiss et al. 1985) just as rock varnish dominates the rocks of continental drylands (Dorn and Oberlander 1982, Whalley 1983). This may result from the greater dominance of dew in Hawai'i (Blumenstock and Price 1978, Curtiss et al. 1985), perhaps aided by freezing temperatures (cf. Wada and Nagasato 1983) at the higher elevations on Hualālai, Mauna Kea, and Mauna Loa (Blumenstock and Price 1978).

MATERIALS AND METHODS

Over thirty sites on Mauna Kea and Hualālai volcanoes were sampled to test changes in varnish chemistry over time and in different environments at sites that have numerical age control (Figure 1C; Table 3). These locales experience mean annual precipitation from less than 250 mm to over 1800 mm (Figure 1B). The vegetation cover at these sites ranges from sparse (aerial cover less than 10%), to grassland (aerial cover of grasses and with a shrub cover greater than 10%), to woodland (mixture of *Metrosideros polymorpha* and grasses, where canopy is less than 50%), to forest (*M. polymorpha* canopy cover greater than 50%).

The details of sampling and sample preparation for radiocarbon and cation-ratio (CR) dating are provided elsewhere (Dorn 1989, Dorn et al. 1989, 1990). In brief, samples were collected from multiple outcrops, from at least 15 different rock surfaces per site. In addition to sampling from microsites without lichens, mosses, and other agencies known to erode varnish (Dragovich 1987, Dorn 1989), varnishes adjacent to lichens and other acid-producing organisms were collected to test the influence of these biogeochemical agents in Hawai'i (Table 3; Figures 2f–2h). The varnishes sampled for dating in this study are not interdigitated with silica skins more than the first author has observed in the deserts of North America, Israel, the Sinai Peninsula, Peru, and Australia. Avoidance of silica skins is to facilitate a more accurate comparison of Hawaiian varnishes with continental dryland varnishes.

FIGURE 2. Scanning electron microscope images of Hawaiian rock varnishes. Length of scale bar (below letter) in μm . Micrographs *a–e* are polished cross sections imaged by backscatter, where brightness corresponds to atomic number (Krinsley and Manley 1989). Images *f–h* are secondary electron micrographs where relief is portrayed. *a–b*, varnish sections on Mākanaka till of Mauna Kea (site 25 in Table 3); *c–d*, varnish on lava flow of Mauna Kea (site 30 in Table 3) (In *a–c*, arrows to the lower left and lower right of white numbers identify paired areas of dissimilar textures, where hollow arrows identify a porous, leached texture and solid arrows identify a layered, unleached texture. In *d*, letters locate paired areas of layered textures [solid arrows] and hollows filled in with loose detritus [hollow arrows]. The paired textures in *a–d* were analyzed by electron microprobe, and results for these sites are given in Table 4); *e*, organic matter trapped in rock depression and buried by the brighter rock varnish (site 30 in Table 3); *f*, fungal filaments associated with Mn-rich varnish in an environment too acidic for varnish dating (site 2 in Table 3); *g*, amorphous silica skins (arrows) interstratified with varnish (site 26 in Table 3); *h*, titanium-rich detritus on the surface of varnish from the Kipahe'e flow (see Table 5).

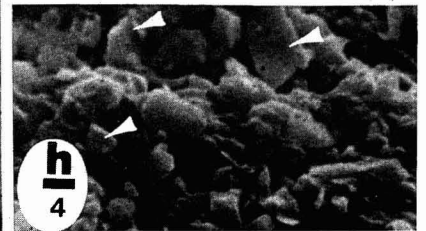
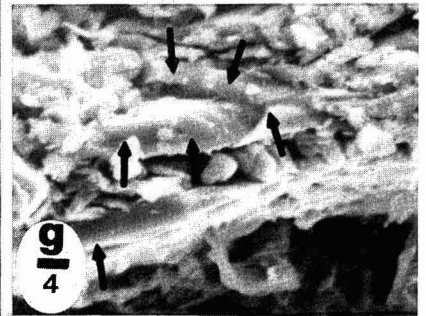
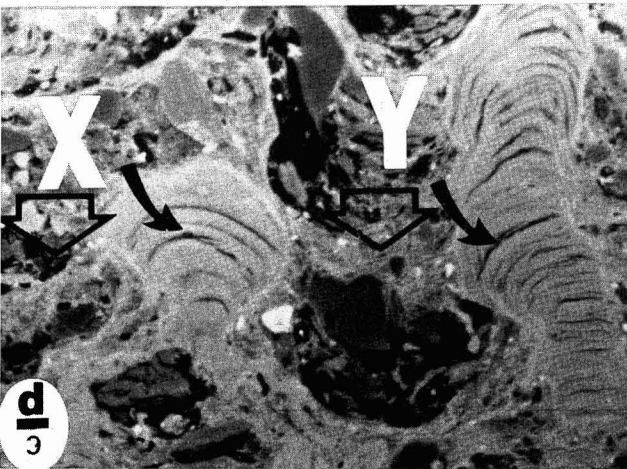
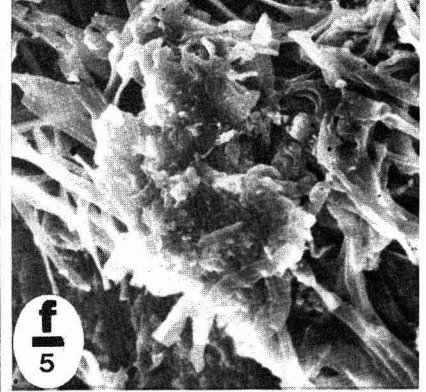
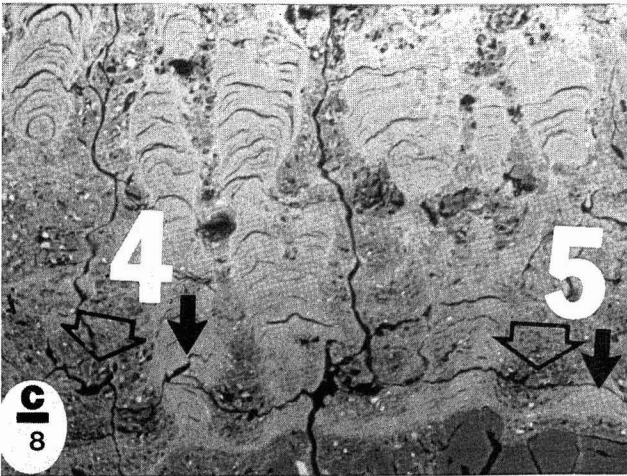
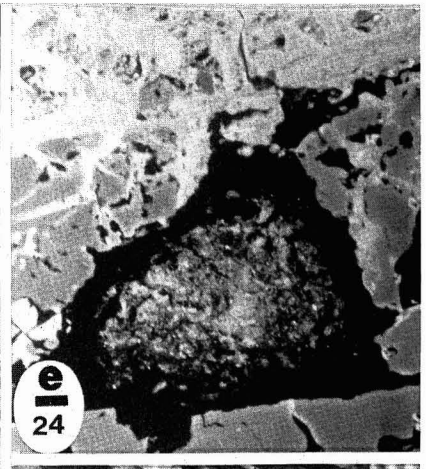
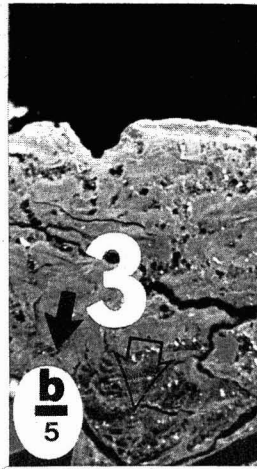
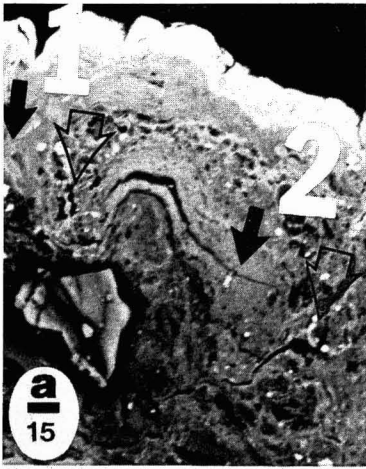


TABLE 3

VARNISH CATION RATIOS AT HAWAIIAN SITES WITH NUMERICAL AGE CONTROL

SITE (Numbers correspond to locations in Figure 1C)	NUMERICAL AGE CONTROL BY C-14 AND K-Ar	CATION RATIO (K + Ca)/Ti (± 1 sigma)	VARNISH C-14 AGE (± 1 sigma)	ELEVATION (m) (ASPECT)	VEGETATION
Xeric, subaerial environments					
3 @ Historic 1800 Ka'ūpūlehu flow c. xenolith site	185	12.60 \pm 2.00		61 (N)	Woodland
4 @ Historic 1800 Ka'ūpūlehu flow d. low road	185	12.20 \pm 1.40		1,113 (NW)	Sparse
5 + Wahapele flow (W5531) a. low site	710 \pm 150	10.22 \pm 0.12	605 \pm 70	1,512 (W)	Grassland
12 + Flow (W5491)	900 \pm 110	9.84 \pm 0.13		1,935 (S)	Sparse
13 + Flow (W5522) a. spatter cone	1,180 \pm 200	9.66 \pm 0.17		1,783 (S)	Sparse
13 + Flow (W5522) b. flow	1,180 \pm 200	9.62 \pm 0.13		1,980 (S)	Sparse
14 + Pu'u Anahulu (W4171) a. upper site	2,030 \pm 80	8.82 \pm 0.19		1,978 (NW)	Grassland
15 + Pu'u Anahulu (W4171) b. lower site	2,030 \pm 80	8.63 \pm 0.17	1,910 \pm 50 1,955 \pm 90 1,895 \pm 50	393 (NW)	Sparse
16 + Flow of 8001' cone (W5076)	2,670 \pm 80	8.40 \pm 0.16	2,470 \pm 65 2,450 \pm 100	2,377 (N)	Grassland
9 + Pu'u Wa'awa'a Ranch (W5559) b. upper middle	3,030 \pm 200	8.03 \pm 0.11		1,539 (N)	Grassland
10 + Pu'u Wa'awa'a Ranch (W5559) c. lower middle	3,030 \pm 200	7.95 \pm 0.17	2,550 \pm 80	975 (N)	Woodland
17 + Hainoa flow (W5132)	3,990 \pm 70	7.76 \pm 0.12		198 (NW)	Woodland
18 + Pu'u Kalaieha (W5541) a. cone	5,630 \pm 200	7.38 \pm 0.09		488 (S)	Grassland
19 + Pu'u Kalaieha (W5541) b. flow	5,630 \pm 200	7.43 \pm 0.09		1,006 (SE)	Grassland
20 + Pu'u Neneakolu (W5297) a. few lichens	6,360 \pm 100	7.00 \pm 0.19	5,220 \pm 80	762 (SW)	Woodland
22 + Keōpū Ahupua'a (W5056)	12,950 \pm 150	5.58 \pm 0.18	11,755 \pm 295	91 (W)	Woodland
23 * Glacially abraded bedrock	*15,900 \pm 1600	6.96 \pm 0.14	14,435 \pm 125	4,054 (SW)	Sparse
24 * Glacially abraded bedrock	*18,300 \pm 1900	6.77 \pm 0.16	16,600 \pm 170	3,962 (NW)	Sparse
25 * Mākanaka glacial till	*20,200 \pm 2100	6.55 \pm 0.17	18,325 \pm 190	3,536 (NW)	Sparse
26 * Mākanaka glacial outwash	*23,900 \pm 2500	6.17 \pm 0.18	21,690 \pm 300	3,158 (S)	Sparse
27 # Toe of K-Ar dated flow	33,000 \pm 12,000	4.60 \pm 0.20		2,316 (NW)	Woodland
28 # Middle of K-Ar dated flow	33,000 \pm 12,000	5.57 \pm 0.19		3,170 (NW)	Grassland
29 # Top of K-Ar dated flow	33,000 \pm 12,000	5.82 \pm 0.13		3,505 (NW)	Sparse
30 # K-Ar sample MKH-4	153,000 \pm 22,000	1.61 \pm 0.11		320 (W)	Grassland

Mesic, acidic environments

1 Historic 1800 Ka'ūpūlehu flow a. top	185	9.20 ± 3.30	2,042 (NW)	Grassland
2 Historic 1800 Ka'ūpūlehu flow b. nr radio tower	185	8.30 ± 4.90	2,042 (W)	Forest
6 + Wahapele flow (W5531) b. rainforest	710 ± 150	6.98 ± 0.39	1,935 (W)	Forest
7 + Wahapele flow (W5531) c. grassland	710 ± 150	7.35 ± 1.60	1,935 (SW)	Woodland
8 + Pu'u Wa'awa'a Ranch (W5550) a. rainforest	3,030 ± 200	4.07 ± 1.55	1,859 (N)	Forest
11 + Pu'u Wa'awa'a Ranch (W5559) d. many lichens	3,030 ± 200	7.92 ± 0.20	61 (N)	Sparse
21 + Pu'u Neneakolu (W5297) b. many lichens	6,360 ± 100	4.94 ± 0.34	290 (SW)	Woodland
31 + KAM III-Kuakini (W4391)	10,370 ± 150	4.07 ± 1.56	335 (W)	Forest
From rock cracks				
13 + Flow (W5522) c. orange varnish	1,180 ± 200	11.50 ± 0.52	1,978 (S)	Sparse
20 + Pu'u Neneakolu (W5297) c. orange varnish	6,360 ± 100	8.44 ± 0.30	73 (SW)	Woodland

@ Cation ratio average of 40 wavelength dispersive electron microprobe transects from cross sections with 5- μ m spot size.

+ Radiocarbon laboratory number from Rubin et al. (1987), where site location is provided.

* The radiocarbon date is corrected for the offset between surface exposure and the accumulation of a thick enough basal layer to date (see text).

K-Ar dates from Wolfe et al. (in press).

Varnish scrapings were analyzed by proton-induced X-ray emission (PIXE) at Crocker Nuclear Laboratory, University of California at Davis (Cahill 1986). PIXE provides precise concentrations for all elements heavier than Ne on nanogram to milligram quantities of particulates. Important for this study are CRs of $(K^+ + Ca^{2+})/Ti^{4+}$ and concentrations of Ni, Cu, and Zn relative to Mn and Fe. The statistical approach used to develop a calibration of CR and time (called a cation-leaching curve) is described in detail in Dorn et al. (1990). In brief, a cation-leaching curve is a least-squares regression of CR and the log transform of age. Of note, CRs measured by PIXE have been found to be virtually identical to CRs measured by inductively coupled plasma (ICP) and wavelength dispersive electron microprobe on the same material (Dorn 1989, Dorn et al. 1990). Organic matter extracted from the bottom $\leq 10\%$ of the varnish was analyzed by AMS radiocarbon dating (Jull et al. 1986, Linick et al. 1989). Solutions from leaching experiments were analyzed by ICP. Varnish cross sections were viewed by secondary and backscatter electron microscopy, and analyzed by electron microprobe with wavelength dispersive mode.

Two experiments were conducted to examine cation-leaching in rock varnish. First, the electron microprobe (wavelength dispersive mode) was used with a $10\text{-}\mu\text{m}$ spot size to assess the chemistry of different textures in Hawaiian varnishes (Figure 2a-d). Ninety pairs of layered and porous textures were analyzed from the Hawaiian sites (Table 3). Second, rock varnish was mechanically scraped from the Pu'u Wa'awa'a Ranch lava flow of Hualālai, sampled from site 10 (Figure 1, Table 3). The sample was cleaned of rock contaminants as described by Dorn et al. (1990) and divided into 12 even portions of 20 mg each. Two hundred ml of deionized water was added to the varnish. The water was maintained at a pH of 5.5 throughout the experiment, with minor addition of HCl, to simulate the pH of rainfall. Four subsamples were kept at 5°C , four at 25°C , and four at 40°C . Subsamples within each temperature group were agitated, end over end by hand, five times a day for 5 days, 20 days, 50 days,

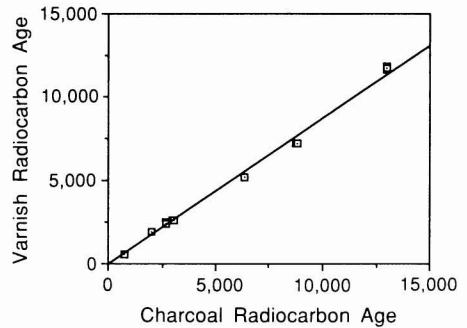


FIGURE 3. Conventional radiocarbon dating of charcoal, compared with accelerator mass spectrometry analyses of organic matter in the basal layer of rock varnishes. Note that the varnish dates are consistently slightly younger than the control ages.

and 100 days. At the end of each period, the varnish was centrifuged and the water decanted and analyzed by ICP.

RESULTS AND DISCUSSION

The Varnish Radiocarbon System on Hawai'i

By selectively scraping the bottom $\leq 10\%$ of layered varnish, and by chemically extracting stable organic matter, a minimum age is placed on the exposure of the underlying rock by accelerator ^{14}C dating (Dorn et al. 1989). A variety of tests was performed to assess sources of contamination and the accuracy of the method. Figure 3 summarizes the results from Hualālai, using the varnish radiocarbon dates in Table 3. Varnish radiocarbon dates are consistently younger than the conventional radiocarbon dates of Rubin et al. (1987).

The most conservative interpretation of a varnish radiocarbon date is that it is a minimum age for the exposure of the underlying rock, analogous to any other stratigraphic deposit formed on a formerly exposed geomorphic surface. As long as contamination of organic carbon from the underlying rock is avoided and carbonate dust is removed with HCl (Dorn et al. 1989), other sources of error would make the varnish date younger than the surface exposure.

For Hawai'i, an adjustment can be made

for the time between surface exposure and the ^{14}C age of a bottom layer of varnish, based on empirical observations on the difference between the varnish ^{14}C age and the control ^{14}C age for charcoal. We caution, however, that these empirical corrections should not be extrapolated beyond Hawai'i.

At xeric microsites on Hualālai Volcano (sites 5, 15, and 16 in Table 3), the sample radiocarbon dates were younger than the mean control dates by 105, 125, and 210 radiocarbon years, respectively. Site 5 was possible to date, despite the very young age, because two pockets of a few milligrams of organic matter were found trapped beneath the varnish. Without these deposits, it would have been possible to date only the entire varnish, rather than the basal layer. The three varnish dates for site 15 in Table 3 are tests of collection and sample preparation described in Dorn et al. (1989), as are the two measurements for site 16. At these few semiarid sites, the differences between measured ^{14}C in varnish and ^{14}C in subflow charcoal (not evaluating the counting errors) are between 6% and 17%, with an average of ca. 10%.

Extreme changes in the moisture content of soils can occur over a few meters in Hawai'i (Nullet et al. 1990). Similarly, extreme changes between xeric and acidic microsites on rock outcrops can occur over a few meters. At acidic Hualālai sites with abundant lichens, woodland, and forest flora (sites 10, 20, 22, and 11 in Table 3), varnish ^{14}C ages were 18, 22, 10, and 18% younger than the control. At these more mesic sites, the empirical corrections are between 10 and 22%, with an average of ca. 17%.

An example of how to estimate the surface exposure age of a land surface, based on a ^{14}C age of 2250 ± 105 yr B.P. (1 sigma, counting error only), is provided by a lava flow informally named "Sheep Station flow" at 1890 m on Hualālai Volcano ($19^\circ 42' 38''$ N, $155^\circ 54' 16''$ W). The vegetation is woodland with a sparse understory of shrubs. No charcoal has been found under this flow. The latest this flow could have erupted is about 1935 yr B.P. (subtracting 3 sigma counting error). Given that the environment is most similar to the humid control sites, a correction of 17% yields 2630

yr B.P. We estimate an error by combining the 1 sigma counting error (105 yr) and the difference between the extreme corrections for humid sites with age control (22% to 10%, or 270 yr). The "best" estimate at this time for the age of the Sheep Station flow is about 2600 ± 400 yr B.P., not accounting for the tree-ring calibration. This varnish ^{14}C age is consistent with new paleomagnetic measurements and the stratigraphic context (Moore and Clague in press).

Another example of a correction is varnish on glacially abraded bedrock near the summit of Mauna Kea (site 23 in Table 3). The AMS measurement on the basal layer of varnish is $14,435 \pm 125$. The latest the glacier could have receded from this site was 14,060 yr B.P. Using the semiarid sites with an average correction of 10%, the best estimate is about 15,900 yr B.P. Adding the counting error and the range of deviations for semiarid sites of from 17% to 6% yields an uncertainty of about 1600 yr. The best estimate for the recession of the Mākanaka glacier from this site is listed in Table 3 as $15,900 \pm 1600$ yr B.P.

Varnish Cation-Ratio System

CR dating started with empirical observations that the ratio of $(\text{K}^+ + \text{Ca}^{2+})/\text{Ti}^{4+}$ decreases over time in rock varnishes sampled from a chronosequence of landforms (Dorn and Oberlander 1981). This has been replicated in numerous subsequent studies of rock varnish (Dorn 1983, 1989, Glazovskiy 1985, Harrington and Whitney 1987, Pineda et al. 1988, Liu and Zhang 1990). When calibrated by numerical dates, CR decreases arithmetically as age increases logarithmically. However, this relationship is not a simple function of time. Like other weathering systems, environment plays a role, and over two dozen distinct environmental variables can influence varnish CRs other than time (Dorn 1989, Dorn et al. 1990, Krinsley et al. 1990).

Dorn (1983) proposed that cation leaching explains this empirical relationship, because Ca and K are much more mobile than Ti in the slightly acidic to strongly alkaline weathering environments where rock varnishes occur (cf. Colman 1982), and that the

major constituents of rock varnish (clays, Mn-Fe oxides) serve as cation-exchange (CE) complexes. An anonymous reviewer also suggested that it is likely that the organic matter in rock varnish acts as a CE complex.

The mineralogy of rock varnish is dominated by clay minerals: illite, montmorillonite, mixed-layer illite-montmorillonite, kaolinite (usually a minor constituent, but in some cases a major one), and some chlorite (Potter and Rossman 1977, 1979*a,b,c*). These minerals serve as CE complexes (Talibudeen 1981, Tucker 1983), and Potter (1979:146) determined that the CE capacity of varnish clays at three sites in the Mojave Desert of California was similar to CE capacities of mixed-layer illite-montmorillonite clays in soils. Manganese and iron oxides are the other major constituents of rock varnish, typically reaching a combined abundance of ~30% in subaerial varnishes (Tables 1 and 2). Potter and Rossman (1979*a,b*) identified birnessite as the dominant manganese mineral in black varnish, and hematite as a major iron oxide in both black and orange varnish. Jenne (1968) and Giovanoli and Brutsch (1979) noted that Mn- and Fe-oxides serve as CE complexes.

EXPERIMENTS ON CATION EXCHANGE IN HAWAIIAN VARNISHES. Although the above lays a theoretical foundation to explain empirical

observations, tests of the greater mobility of K and Ca in varnish, relative to Ti, have been lacking until now. A critical and previously unexplored control on rates of CE reactions in rock varnish is the texture of varnish.

When polished cross sections are viewed by backscatter electron microscopy (Krinsley and Manley 1989), Hawaiian varnishes have three dominant textures: (1) layered textures with low porosity; (2) porous varnishes with abundant pieces of large, angular detritus; and (3) porous varnishes without large pieces of detritus (Figure 2*a-d*). Layered Hawaiian varnishes can occur in columns that appear like stromatolites; these textures have also been found in the arid western United States (Krinsley et al. 1990) and arid Peru (Jones 1991). When viewed from above, the micro-morphology of these columns is botryoidal (Dorn and Oberlander 1982). Pieces of rock detritus and organic matter fall into these hollows at the surface; as columns continue to grow, the detritus is trapped (Figure 2*d*). The porous varnish without abundant detritus occurs adjacent to layered varnish, and there is usually a gradient of porosity, suggesting some sort of change between layered and porous varnish (Figure 2*a-c*).

Results of the electron microprobe investigation into the chemistry of different varnish textures are presented in Table 4 for seven

TABLE 4

WAVELENGTH DISPERSIVE ELECTRON MICROPROBE ANALYSES OF DIFFERENT TEXTURES OF HAWAIIAN ROCK VARNISHES

AREA ANALYZED	TEXTURE	(K + Ca)/Ti	MnO%	Fe ₂ O ₃ %
1 (a)*	Layered	7.9 ± 0.8**	18.4 ± 2.7	14.3 ± 2.0
1 (a)	Porous, leached	5.3 ± 1.1	9.4 ± 1.4	10.3 ± 1.5
2 (a)	Layered	6.8 ± 0.5	20.1 ± 3.8	16.2 ± 0.3
2 (a)	Porous, leached	5.7 ± 0.9	8.0 ± 0.7	8.3 ± 1.1
3 (b)	Layered	8.2 ± 0.7	15.4 ± 5.4	16.0 ± 2.1
3 (b)	Porous, leached	4.2 ± 1.0	9.3 ± 1.3	11.7 ± 1.5
4 (c)	Layered	2.4 ± 0.3	19.5 ± 0.9	11.3 ± 3.0
4 (c)	Porous, leached	1.1 ± 0.4	10.4 ± 2.3	7.4 ± 0.9
5 (c)	Layered	3.0 ± 0.5	15.3 ± 0.5	17.3 ± 2.5
5 (c)	Porous, leached	0.8 ± 0.3	12.4 ± 2.2	14.6 ± 0.8
X (d)	Layered	2.3 ± 0.5	16.0 ± 3.0	14.0 ± 1.3
X (d)	Infilled hollow	2.9 ± 0.8	15.3 ± 1.1	16.9 ± 6.0
Y (d)	Layered	2.8 ± 0.6	17.3 ± 1.7	15.4 ± 2.0
Y (d)	Infilled hollow	3.9 ± 1.6	14.9 ± 2.0	17.2 ± 8.4

*Numbers and letters refer to locations identified in Figure 2*a-d*.

**The average and 1 SE of five different analyses with a 10- μ m spot size are reported.

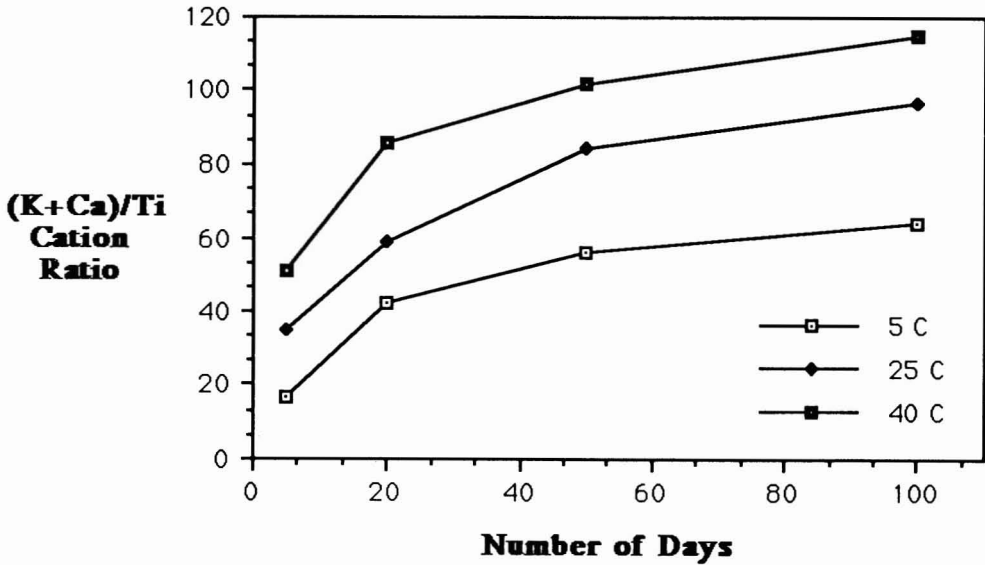


FIGURE 4. Laboratory leaching experiments, where splits of Hawaiian rock varnish were subjected to leaching at different temperatures and over different time periods in deionized water with a pH of 5.5. Results analyzed in text.

representative pairs in Figure 2a–d. In each pair, the layered texture is indicated by a solid arrow, and the porous or detritus texture is indicated by a hollow arrow. The porous textures in Figure 2a–c had lower concentrations of MnO and Fe₂O₃ and lower CRs, compared with adjacent layered textures. In contrast, the infilled hollows had a noisier geochemical signature of slightly higher CRs and MnO and Fe₂O₃ concentrations similar to those of the layered varnish.

The microprobe analyses in Table 4 suggest that porous textures without detritus have had some of the Mn-Fe oxides leached, as well as K and Ca, relative to Ti. We find no clear indication of enhanced leaching associated with a texture of hollows infilled with a mixture of detritus and varnish. Such a signal, however, could be masked by the geochemical noise associated with abundant detritus.

The simplest model is that the layered texture undergoes a diagenesis to a more porous condition, in response to spatially disjunct leaching concentrated in areas of capillary water flow. Prior data on the geochemistry of different textures in varnishes from continental deserts indicate that capillary water flow in

rock varnish is concentrated in fractures and tubes, mobilizing elements in rock varnish (Krinsley et al. 1990, O'Hara et al. 1990). Such fractures and tubes are typically associated with porous, leached textures in our Hawaiian samples. These porous, leached zones are quite different from infilled hollows, because they are caused by postdepositional diagenesis. It is only when hollows occur at the surface that detritus is encapsulated (Figure 2d). Detritus is lacking in the leached zones, because the textural change from layered to porous occurred in the subsurface.

Figure 4 presents results of an experiment on the treatment of varnish scrapings to water at different temperatures, described in the Materials and Methods section. This experiment reveals that: (1) leaching of K and Ca from varnish scrapings occurs at a faster rate than leaching of Ti over time; and (2) leaching rates of K and Ca are faster at higher temperatures.

EMPIRICAL CATION-RATIO RESULTS IN HAWAII. The tremendous range of environment on surfaces of known age permits us to learn more of the role of environment on varnish

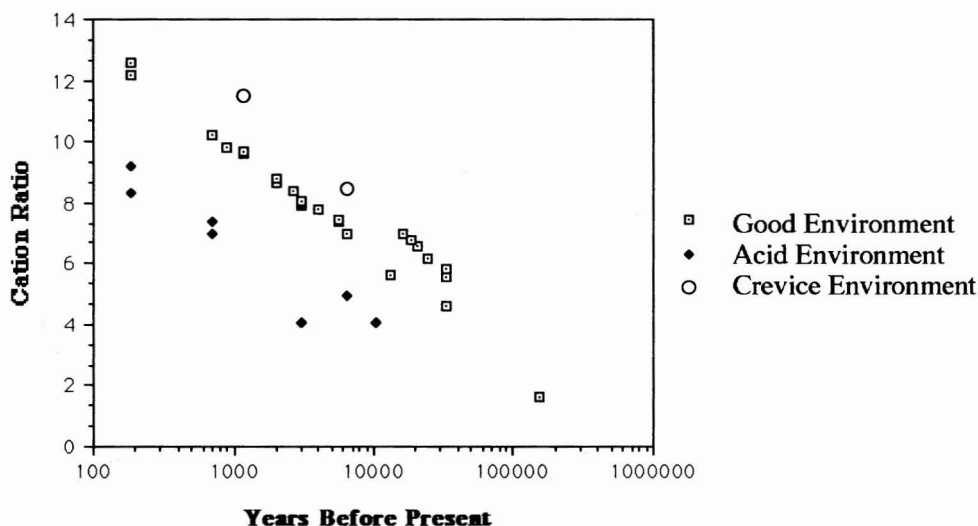


FIGURE 5. Comparison of numerical age and varnish cation ratios for sites in Table 3. Note that organic-rich, humid acidic sites plot lower than nonacidic sites, probably because of the importance of organic acids in cation exchange. Protected environments, like crevices, tend to have higher ratios. In contrast, the “good environments” are those appropriate for cation-ratio dating; these are xeric sites (see Table 3) that are not occupied by acid-producing organisms and are exposed only to the atmosphere.

CRs. Table 3 presents varnish CRs from sites on Hualālai and Mauna Kea, where conventional radiocarbon and K-Ar dates are available. The Hualālai sites are also located by Rubin et al. (1987). The Mākanaka glacial till sites are those of Porter (1979*a, b*, 1986). In Table 3, the xeric, subaerial microenvironments are sites where rock varnishes are not influenced by environmental factors known to alter CRs (Dorn 1989, Dorn et al. 1990, Kinsley et al. 1990). The “mesic, acidic” microenvironments in Table 3 are those locales where lichens, fungi, cyanobacteria, mosses, and plant litter exert an acidic influence, but varnish is still present. The “less leaching” environments are crack varnishes formed in crevices not open to subaerial conditions before sampling.

Figure 5 illustrates that acidic conditions in Hawai'i produce lower CRs, and our limited data suggest that protected crevice environments generate higher CRs, as compared to xeric subaerial sites. Elevation is also important. Above ca. 3000 m, varnish CRs form a separate cation-leaching curve (Figure 6). Both the high- and low-altitude semilog least-squares regressions in Figure 6 are significant

at $P < .01$. The lower-altitude curve is summarized by:

$$CR = 20.6 - 3.60 \log_{10} \text{Age} \quad (1)$$

The higher-altitude curve is summarized by:

$$CR = 24.4 - 4.14 \log_{10} \text{Age} \quad (2)$$

A semilog relationship is similar to other cation-leaching curves (Dorn 1989), and similar semilog functions have been observed in rock weathering (Colman 1982) and soil (Switzer et al. 1988) studies.

The generalized explanation for the decline in the rate of CR change at progressively older sites is that it becomes progressively harder to remove fewer and fewer Ca and K cations while Ti remains (Dorn 1989). This has been found in the leaching experiments (Figure 4). The behavior of Ti may also relate to this gradual slowing in natural systems. Morad and Aldahan (1986) reported that as detrital Fe-Ti oxides weather, Ti oxides replace the Fe-Ti phases. Titanium may be present as nonexchangeable clay-sized anatase (Bain 1976). Harden (1988) found a net influx of Ti into finer fractions with time; Akimoto et al. (1984) explained this by low-temperature oxi-

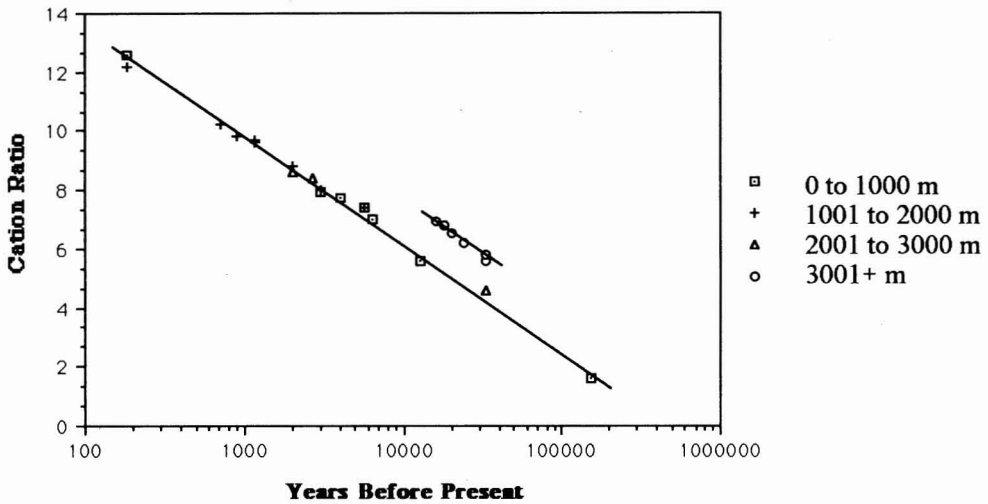


FIGURE 6. Least squares regressions of varnish CRs and numerical age, where the varnishes were sampled only from the xeric, subaerial sites in Table 3. The importance of altitude (and temperature) is illustrated. Sites less than 3000 m (highest 2377 m) fall on the same least-squares semilog regression (equation 1 in text). Sites higher than 3000 m rest on a different regression (equation 2 in text).

dation of titanomagnetites resulting in the depletion of mobile cations such as Mn^{2+} and the relative enrichment of the highly stable Ti^{4+} .

The different high- and low-altitude curves cannot be explained by differences in local chemistry, because the rock types have similar chemical compositions. Asian-derived dust, however, contributes to the soils of the Hawaiian Islands (Jackson et al. 1971, Shaw 1980, Parrington et al. 1983). Braaten and Cahill (1986) found that the majority of the transported dust is in the size range of 0.5 to 3.0 μm aerodynamic diameter, and is primarily composed of Si, Al, K, Ca, Ti, and Fe; these are important components of rock varnish in Hawai'i (Tables 1, 2). The higher elevations above the trade wind inversion are dominated not by local surface winds, but more by general and mesoscale circulation (Miller 1981). It is possible that the quantity of airborne dust fallout at higher altitudes is substantially different from that at lower elevations. A more abundant supply of dust might increase the CRs and explain why the CRs are higher for the high-altitude sites. The CRs of Hawaiian varnishes are substantially higher than many of the CRs in western North

America (Dorn 1989), but are similar to those of western China (Liu and Zhang 1990). The higher CRs in Hawaiian varnishes could, therefore, relate to an Asian source for the dust.

An alternative explanation for the difference between high- and low-altitude CRs is that freezing temperatures are common in Hawai'i in the winter months above 2500 m (Blumenstock and Price 1978). The influence of colder temperatures would be to slow leaching, as found in Figure 4. This could explain why the CRs for a given time interval are higher for the high-altitude sites.

All of the Holocene sites are at lower elevations, where freezing temperatures are infrequent at present. The only low-elevation sites that are Pleistocene in age, and would have experienced a lowered snow line, are Keōpū Ahupua'a at 91 m and MKH-4 at 320 m (Table 3). It is probably not reasonable to expect the elevation at which abundant snowfall occurs to have dropped over 2000 m, as this would have brought the glaciers on Mauna Kea to much lower altitudes than found by Porter (1979a, b, 1986). A future test of importance of freezing on varnish CRs would be to examine late Pleistocene surfaces

just below where current freezing temperatures are found.

A number of other environmental variables were tested to assess their influence on CRs. Rainfall, exposure, and vegetation class did not show a statistically significant relationship with varnish CRs. Unfortunately, dew estimates are not available, but dew could be an important source of moisture in Hawai'i (Blumenstock and Price 1978) that might influence CRs.

USE OF CATION RATIOS TO ASSESS AGES OF LAVA FLOWS. Equation 1 is used to estimate the ages of lava flows on Hualālai where sub-flow charcoal has not been found. Multiple CR measurements were made of varnish on each of the undated flows. These were compared with equation 1, yielding CR ages presented in Table 5. These mean ages were averaged (and a standard error determined), representing the average ± 1 sigma CR age, also presented in Table 5. Because the calibration curve is tied to the charcoal ages that reflect the timing of flow emplacement, these CR ages should approximate the time of eruption.

Several Hualālai sites proved to be undatable by the CR method (Table 5). A review of these problems is useful, because it illustrates some of the limitations of CR dating of geomorphic surfaces. Sample A from the Hīnau flow was sampled from a site with abundant lichens, organic matter, and moss. Sample C from the Hīnau flow was from a crevice, not a subaerial environment. Varnish on the cinder cone at 1795 m (19° 39' 40" N, 155° 48' 24" W) was covered with tephra. Varnish on the Kīpahe'e flow had anomalous Ti values (Figure 2h), possibly because of a former tephra cover with abundant titanium. 'Umiāhu flow was sampled from an erosional surface and cannot be related to the charcoal age of the flow (6260 ± 100 yr B.P.; Moore and Clague in press). The Kealoha cone at 2119 m and the Māwae flow had abundant hollows created by past episodes of varnish erosion; this allowed the hollows to be filled with younger varnish.

Clearly, CR dating of rock varnish is not a panacea. Varnish chemistry is subject to a number of biogeochemical variables that

influence the CR signal other than time. However, there are geomorphic circumstances where rock varnish is the only tool available to obtain a time signal. The CR ages obtained from carefully selected sites (Table 5) illustrate the potential of varnish to assist in the dating of geomorphic surfaces in Hawai'i.

The Varnish Trace Metals System in Hawai'i

Manganese and iron oxides are excellent scavengers of a variety of elements, such as Cu, Co, Ni, Zn, Pb, Ba, and many other elements including radionuclides such as ^{10}Be and ^{26}Al . This has been recognized in the literature on soils and marine nodule, lake nodule, and ore deposits (Jenne 1968, Loganathan and Burau 1973, Shuman 1977, McKenzie 1977, Vuceta and Morgan 1978, Benjamin 1983, Hem et al. 1989).

Dorn and Oberlander (1982) examined a relative chronosequence of three varnishes and found that progressively older varnishes had higher relative concentrations of Ni and Cu. The hypothesis proposed by Dorn and Oberlander (1982) was that the relative abundances of these scavenged metals would provide an indication of time. This tool would be especially valuable if varnishes to be studied were buried, because the CR method is inappropriate for buried varnishes.

Figure 7 presents the abundance of Ni, Cu, and Zn at the sites of known age. The micro-environments sampled for this test were the xeric, subaerial sites in Table 3. These elements were selected because they are scavenged and are analyzed by PIXE. Because the abundance of Ni, Cu, and Zn is theoretically related to the scavenging properties of the Mn and Fe oxides, the abundance of these elements is normalized to the abundance of Mn and Fe. The elemental ratio of $(\text{Ni} + \text{Cu} + \text{Zn})/(\text{Mn} + \text{Fe})$ yielded the best statistical relationship with age. The line in Figure 7 is represented by the equation:

$$\text{"scavenging ratio"} = 0.0084 \log_{10} \text{Age} - 0.24$$

This relationship, statistically significant at $P < .05$, indicates that trace metals like Ni, Cu, and Zn are scavenged by Mn and Fe oxides over time.

TABLE 5
ROCK VARNISH CATION RATIOS FOR HUALĀLAI LAVA FLOWS

HUALĀLAI SAMPLING SITE	CR AGE*	(K + Ca)/Ti*
Flow of 'Umiahu 2,103 m, 19° 40' 52", 155° 50' 58" Grass and sparse shrubs	Sampled from erosional surface that does not relate to age of lava flow	(8.60 ± 0.06) 8.60 8.70 8.55 8.62 8.59 8.51
Lalakaukole flow 2,073 m, 19° 40' 16", 155° 51' 35" Grass and some shrubs	(10,000 ± 1,000) 9,570 9,449 9,818 9,329 11,516 10,599	(6.21 ± 0.13) 6.28 6.30 6.24 6.32 5.99 6.12
Hīnau flow 1,756 m, 19° 40' 16", 155° 50' 21" Sample A. black varnish with abundant organic matter, lichens, moss (CR date rejected)	Sample cannot be dated because of acidic nature of rock surfaces at this site	(4.32 ± 0.76) 4.20 3.88 3.95 3.42 5.19 5.30
Hīnau flow 1,756 m, 19° 38' 44", 155° 50' 21" Sample B. black varnish from environment good for sampling (Dorn 1989)	(3,500 ± 300) 3,446 3,111 3,212 3,604 3,841 3,817	(7.86 ± 0.14) 7.88 8.04 7.99 7.81 7.71 7.72
Hīnau flow 1,756 m, 19° 38' 44", 155° 50' 21" Sample C. orange varnish from crevice (CR date rejected)	Crevice location sample is not appropriate for cation-ratio dating	(12.18 ± 2.14) 10.24 12.29 13.00 11.40 15.93 10.21
Māwae flow 1,780 m, 19° 38' 34", 155° 49' 51" Dwarf woodland	Sample cannot be dated because of abundance of paleoerosional depressions in the varnish	(6.23 ± 0.11) 6.22 6.17 6.29 6.38 6.05 6.26
Flow of cone at 1,811 m, 19° 39' 01", 155° 49' 37" Grass cover	(8,500 ± 950) 9,329 9,755 8,864 7,413 7,654 8,316	(6.46 ± 0.17) 6.32 6.25 6.40 6.68 6.63 6.50
Kipahe'e flow 2,271 m, 19° 41' 42", 155° 54' 16"	Sample cannot be dated because of very high Ti values (see Figure 2h)	(4.22 ± 0.18) 4.22 4.40 4.05

TABLE 5 (continued)

HUALĀLAI SAMPLING SITE	CR AGE*	(K + Ca)/Ti*
From cone at 1,795 m, 19° 39' 40", 155° 48' 24"	Sample cannot be dated because of burial in tephra	(9.20 ± 0.71) 9.23 10.37 9.59 8.61 9.02 8.40
Flow of cone at 1,804 m, 19° 39' 54", 155° 48' 26" Sparse vegetation cover	(7,600 ± 850) 7,802 6,780 6,823 7,089 8,808 8,316	(6.65 ± 0.17) 6.60 6.82 6.81 6.75 6.41 6.50
From Kealoha cone at 2,119 m, 19° 41' 09", 155° 49' 20" Grasses and isolated shrubs	Sample cannot be dated because of abundance of paleoerosional depressions in the varnish	(6.94 ± 0.13) 6.90 7.00 7.11 7.05 6.82 6.78
From flow of Kealoha cone 2,057 m, 19° 41' 17", 155° 49' 32" Sparse vegetation cover	(1,200 ± 150) 1,187 1,005 1,164 1,366 1,340 1,031	(9.57 ± 0.20) 9.55 9.81 9.58 9.33 9.36 9.77
Flow of Po'ikahi cone 2,143 m, 19° 41' 13", 155° 50' 23" Sparse vegetation cover	(2,400 ± 300) 2,335 1,965 2,162 2,473 2,602 2,687	(8.48 ± 0.19) 8.49 8.76 8.61 8.40 8.32 8.27
Flow of cone at 2,195 m, 19° 41' 18", 155° 50' 28" Grasses and sparse shrubs	(4,600 ± 600) 4,477 5,054 5,285 4,834 4,227 3,866	(7.43 ± 0.18) 7.47 7.28 7.21 7.35 7.56 7.70
Cone at 2,301 m, 19° 41' 35", 155° 50' 50" sampled from 4 bombs Grasses and sparse shrubs	(6,200 ± 600) 6,360 6,044 5,457 6,823	(6.97 ± 0.15) 6.92 7.00 7.16 6.81
Sheep Station flow 1,890 m Woodland Radiocarbon age on varnish 2,250 ± 105 19° 42' 38", 155° 54' 16"	(2,150 ± 325) 2,247 1,808 2,162 1,763 2,520 2,410	(8.63 ± 0.23) 8.55 8.89 8.61 8.93 8.37 8.44

* ± 1 sigma.

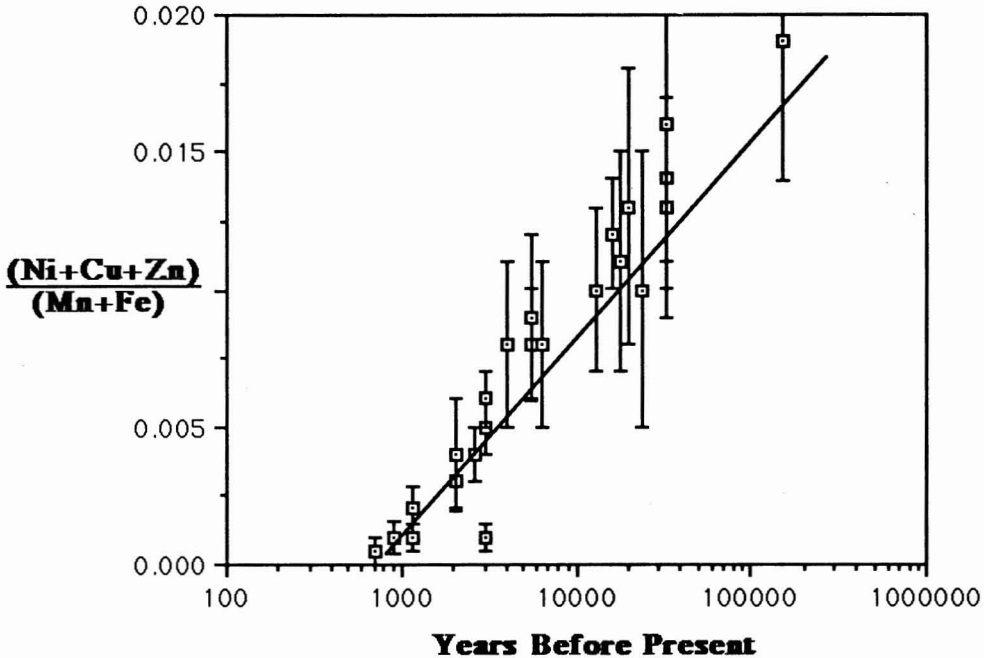


FIGURE 7. Semilog least-squares regression, where the abundance of trace metals that are scavenged by Mn and Fe oxides ($Ni + Cu + Zn$) is normalized by the concentration of Mn and Fe. Bars represent 1 sigma uncertainties for both the scavenging ratio and numerical age (uncertainty less than box width not shown).

This relationship appears to have more noise than the varnish CR of $(K + Ca)/Ti$. This greater uncertainty may involve the mineralogy of Mn and Fe oxides, and the structural relationship of these oxides to clay minerals in the varnish. It may also be related to the difficulty in making precise measurements of these elements at concentrations of 0.01 to 0.50%. Still, Figure 7 indicates that a "scavenging" method of dating rock varnish warrants further investigation.

The major conclusions of this study are as follows:

(1) The major elements of rock varnishes (Al, Si, Mn, Fe) on Hawai'i are similar in chemistry and structure to varnishes found in continental drylands. However, higher concentrations of sodium, barium, and sulfur at low elevations (<3000 m) probably reflect marine influences. The distribution of rock varnishes is restricted to sites without acid-producing organisms, similar to semiarid regions in the southwestern United States

and central Australia. Hawaiian varnishes are unique in the world in that they are less common on rocks than coatings of amorphous silica (Farr and Adams 1984).

(2) The first laboratory experiments on cation leaching in varnish are reported, and they indicate that K and Ca are leached preferentially to Ti over time and at higher temperatures.

(3) The location of leaching in natural Hawaiian varnishes has been identified, and tested with the electron microprobe, as areas of porous textures without abundant detritus.

(4) The varnish CR of $(K^+ + Ca^{2+})/Ti^{4+}$ of tropical varnish can be calibrated by numerical radiocarbon and K-Ar dates. Two separate cation-leaching curves are found at high and lower altitudes. The difference may be explained by the importance of temperature on the kinetics of cation exchange; it may also relate to the fallout of Asian dust at higher altitudes.

(5) The CRs at sites of abundant vegetation, mosses, lichens, fungi, and other acidic-

producing organisms were not systematic with respect to time. This emphasizes the need for appropriate site selection.

(6) Radiocarbon dating of rock varnish is the most precise and accurate method of providing minimum ages for the exposure of the rock underlying the varnish. Cation-ratio dating can provide age estimates for geomorphic surfaces in Hawai'i, but the method is subject to biogeochemical uncertainties that do not influence a radiocarbon analysis.

(7) Radiocarbon and CR dating of varnish is used to assign ages to lava flows of Hualālai Volcano, where no subflow charcoal has been found.

(8) Mn-Fe oxides in varnish scavenge trace metals. When the concentration of Ni, Cu, and Zn are compared to age, after the abundance of Mn-Fe oxides is controlled, a statistically significant semilog relationship is found. This "scavenging" method of dating varnish would be of most use where varnish has been buried and the site is beyond the limit of radiocarbon dating.

(9) The Hawaiian cation-leaching curves in Figure 6 (equations 1 and 2) have a much steeper slope (-3.6 , -4.1) than curves for western North America (from -1.7 to -2.4 in Dorn 1989). The steepest slopes of the established continental curves are from regions where abundant warm-season precipitation occurs, suggesting that temperature of the leaching solutions is very important, as was found for the laboratory experiment (Figure 4). The steeper slopes of the Hawaiian curves may also be from abundant dew that occurs in Hawai'i (Blumenstock and Price 1978). The higher CRs of the Hawai'i curves are similar to the western China curve (Liu and Zhang 1990), perhaps reflecting the Asian source of Hawaiian dust.

(10) Although rock varnish studies have been largely limited to continental deserts, there is great potential to use rock varnish in earth science studies in tropical regions.

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