

Rare Earth Elements in Soils from Selected Areas on the Island of Hawaii¹

WÄLTHER M. BARNARD² and JOSEPH B. HALBIG³

ABSTRACT: Fifty soil samples from the wet, windward (east) side and dry, leeward (west) side of the Island of Hawaii were analyzed for La, Ce, Sm, Eu, Yb, and Lu by neutron activation/gamma-ray spectroscopic analysis. Data on concentrations in each sample are listed and analyzed statistically for soil samples collected from the western slope of Kohala Mountain, the western coastal plain of Mauna Kea, and the northeastern coastal plain of Mauna Loa.

Rare earth element (REE) concentrations are two to six times greater in soils from the western, dry side of the island, and good statistical correlation is exhibited among the samples for pairs of individual REEs. In the organic-rich soils of the east side, correlations are poor but are markedly improved when sample weights are adjusted for weight due to organic matter and water in soil colloids.

If the mean compositions of selected rock samples from the Hawaii Reference Suite are representative of the compositions of the parent materials, REEs in the soils are moderately enriched (up to two times, based on oven-dry weights). Rare earth element concentrations in the island's western soils are as much as two times greater than the mean REE values of common sedimentary rocks worldwide; however, they are well within the concentration ranges of soils of continental origin. The eastern soils tend to have less La and Ce, but similar amounts of the middle and heavy REEs.

IN THE FIFTY YEARS since Minami (1935) made the first rare earth element (REE) determinations in sedimentary rocks, several investigations have established the abundance of these elements in common sediments and sedimentary rocks, particularly in those formed from sediments of continental origin. The results of these studies have been applied to studies of the provenance of ancient sedimentary rocks. However, the REE content of

sediments derived from volcanic-dominated source terranes, especially those far from continental source areas, is still not well known, although Easton and Easton (1983) have contributed observations on the effects of weathering on trace and REE contents of some volcanic sediments (pyroclastics and sediments derived mainly from weathering of lava flows) on the Island of Hawaii.

The present study is part of an environmental baseline survey of soil geochemistry (Halbig et al. 1985) started in 1981 in three geographic areas on the Island of Hawaii (Figure 1). The purposes of this paper are (1) to present data and statistical analyses of concentrations of selected REEs (La, Ce, Sm, Eu, Yb, and Lu) in soils that have developed from volcanic parent materials under different climatic conditions; (2) to compare concentrations of REEs in each of the three areas by examination of seven distribution factors

¹This research was supported by grants from the Marine Affairs Coordinator, subsequently the Ocean Resources Office, State of Hawaii Department of Planning and Economic Development; from the County of Hawaii Department of Research and Development; and from the United States Department of Energy. Contribution no. 24 from the Ocean Resources Office, State of Hawaii Department of Planning and Economic Development. Manuscript accepted 2 January 1985.

²State University of New York College at Fredonia, Department of Geology, Fredonia, New York 14063.

³University of Hawaii at Hilo, Chemistry and Geology Discipline, Hilo, Hawaii 96720.

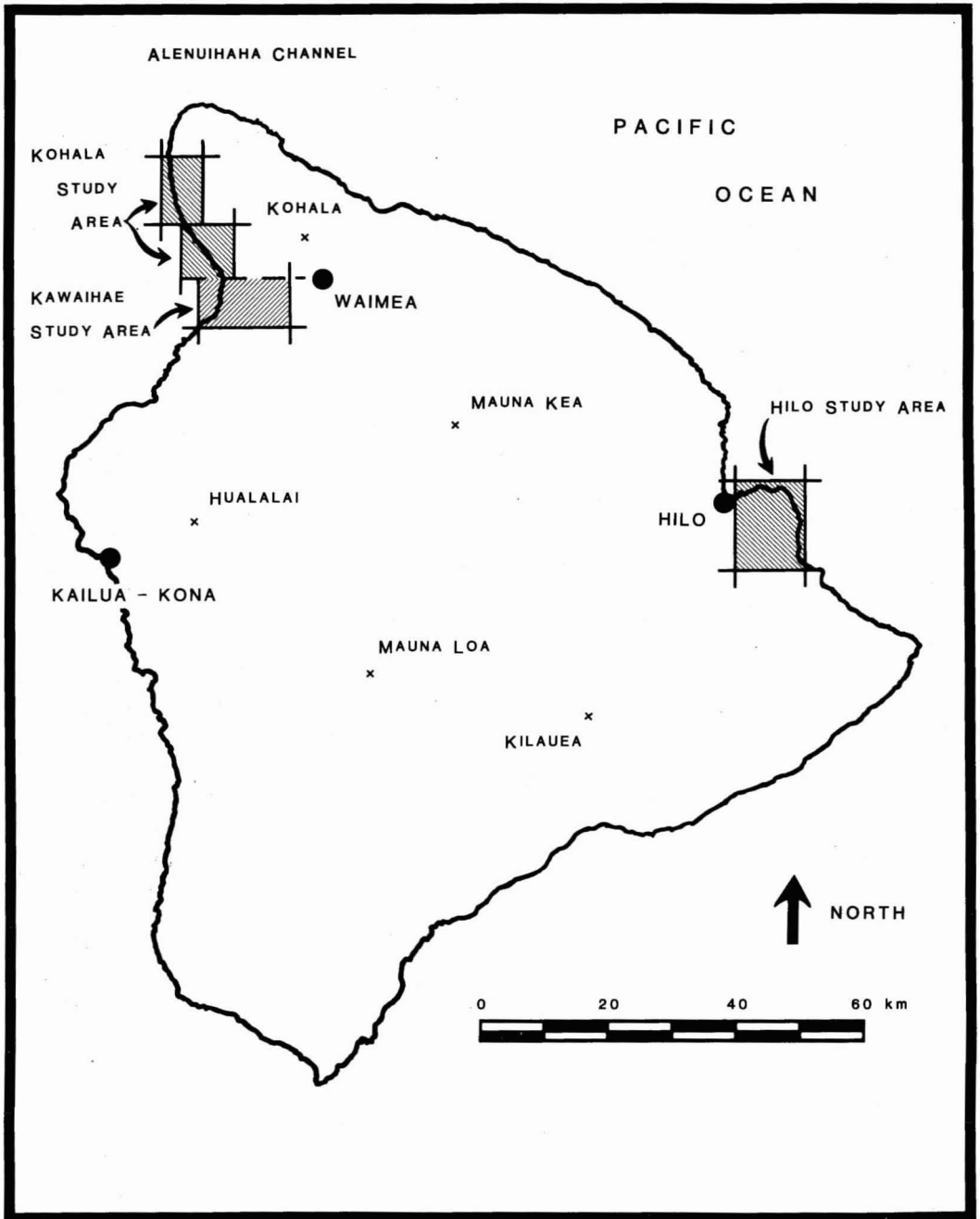


FIGURE 1. Location map of study areas on the Island of Hawaii.

(mean, median, trimmed mean, maximum, minimum, and first and third quartile values); (3) to establish correlations among the samples for pairs of individual REEs, for each REE and organic content, and for each REE and pH of soil; (4) to speculate on the role of REEs (retention and mobility) in the soil-forming processes in these areas; and (5) to compare the REE concentrations of the Hawaiian soils with those in common sediments and sedimentary rocks in other areas.

STUDY AREAS

The field areas are designated in Figure 1 as the Kohala and Kawaihae study areas, located on the northwestern coastline of the Island of Hawaii, and the Hilo study area, located immediately east and southeast of the city of Hilo on the island's east side. The Kohala study area encompasses about 68 km² on the west slope of Kohala Mountain; the Kawaihae study area, covering 42 km², is located on the western coastal plain of Mauna Kea Volcano; and the Hilo study area, containing about 85 km², is on the northeast coastal plain of Mauna Loa Volcano.

Geology

The geology of the Island of Hawaii was first described in some detail by Stearns and Macdonald (1946), and is summarized by Macdonald, Abbott, and Peterson (1983). The earlier study produced a reconnaissance map of the island that illustrates the distribution of lava flows and other volcanic products according to their age relationships and volcanic source. Except for a few quadrangles that have been mapped since that time, this early report remains as the authoritative source on the geology of the island, particularly for the Kohala and Mauna Kea shield volcanoes. The only other field geology study performed in the vicinity of the Kohala and Kawaihae study areas is the mapping and petrographic investigation of volcanic products in the Kawaihae 7.5' quadrangle by Malinowski (1977). Information on the geology of this

part of the northwestern coastline is therefore restricted mainly to the works of these investigators, which is summarized below.

Kohala Mountain is the oldest volcano on the island; most of the mountain was built above sea level in the last 400,000 yr, and it last erupted about 60,000 yr ago. The eruptive history of the volcano can be divided into two main events separated by a distinct hiatus. The hiatus is marked by an erosional unconformity and a red, ashy lateritic soil horizon, which in the Kawaihae quadrangle is up to 0.4 m thick.

The earlier flows that represent the main shield-building stage of Kohala are assigned to the Pololu Formation; they consist of tholeiitic basalts and, in the upper part of the formation, alkalic olivine basalts. These flows are 'a'ā and pāhoehoe, and are generally layered, with smooth, rounded surfaces that define a low topography. The greatest areas of coverage by Pololu flows occur east of Kawaihae and north of Makeahua Gulch, and from Mahukona southward for approximately 4–5 km. The remaining part of the Kohala study area is capped by alkalic rocks of the Hawi Formation, which consists chiefly of mugearite with lesser amounts of hawaiiite, benmoreite, and trachyte. These lavas are mainly 'a'ā type, and often show autobrecciation with a trend toward block lava. They range in thickness from 0.6 m near the coast to over 40 m in the summit areas, and represent lavas more viscous than those of the Pololu Formation. As a result, the topography in areas covered by Hawi lavas tends to be very hilly.

The contact between Late Pleistocene flows from Mauna Kea Volcano and Pololu and Hawi flows from Kohala Volcano follows approximately the course of Makeahua Gulch on the southwest flank of Kohala Mountain. The Mauna Kea flows of the Hamakua Formation that cover the Kawaihae study area consist mainly of alkali basalts and alkali olivine basalts. They are of the 'a'ā type, and form a distinctive hummocky topography. These Hamakua lavas probably represent the upper part of the section of the main shield-building stage of Mauna Kea.

The topography in these two study areas is almost entirely the result of constructional landforms that represent the original land surface built by the volcanoes. Erosional features, consisting of low, noncontinuous sea cliffs (less than 15 m in height) and stream gullies, are all in a youthful stage of development. The difference in slope between the Kohala study area (approx. 218 m/km) and the Kawaihae study area (approx. 106 m/km) is due mainly to differences in viscosity of the flows.

Except for one relatively young Hawi flow on Kohala Volcano (i.e., the Puu Loa flow), much of the region is covered by varying thicknesses of Pahala ash. In the part of the Kohala study area covered by the Kawaihae quadrangle, the ash deposit ranges from 1.2 to 1.5 m in thickness and is the source material for soil formation (Macdonald, Abbott, and Peterson 1983; Malinowski 1977; Stearns and Macdonald 1946).

The geology of the region within the Hilo study area has not been investigated previously in any great detail, but is presently being mapped by Jane Banks of the U.S. Geological Survey. The bedrock consists of Mauna Loa flows of the Prehistoric Member of the Ka'u Formation, and probably originated within the Late Pleistocene to Holocene Epochs. One major flow in the Panaewa area has been radiocarbon dated at approx. 2900 yr B.P. (J. Lockwood, personal communication). Most probably, the flows are typical tholeiitic basalts of the 'a'a type in the western and central parts of the study area and of the pāhoehoe type along the northern and eastern coastlines. The soil map of the area (Figure 4, shown below in the section on *Soils*) broadly reflects the distribution of these lava types. Rock quarries developed in the central part of the study area within a few kilometers south of the airport show that the underlying bedrock consists predominantly of 'a'a flows up to 6 m thick. The dense interiors of the thicker flows are being quarried and crushed for use as aggregate material. The surface topography of this study area has a 0–5% slope, and the coastlines are characterized by the occurrence of small embayments (e.g., at Ha'enokalela and Papa'i) and the absence of sea cliffs.

Climate and Vegetation

Marked differences in climate exist between the windward and leeward sides of the island. The climatic conditions on Hawaii are discussed in the inventory on water resources published by the State of Hawaii (1970), which also provides extensive records of climatological data.

The island lies in the path of the northeasterly tradewinds. Most of the rainfall on the island's eastern side results from the cooling of the moist tradewinds as they rise to higher elevations on the flanks of the mountains. The leeward (Kona) side of the island is in the rain shadow formed by the high mountains, and is considerably drier. Tropical storms during the winter are a major source of rainfall for the leeward side, although thermal convection cells do provide anomalously higher rainfall regions on the leeward flanks of Mauna Loa and, to a lesser degree, Hualalai Volcano (State of Hawaii 1970).

The Kohala and Kawaihae study areas have mean annual temperatures between 21 and 24°C (70 and 76°F), with lower temperatures occurring at the higher elevations inland. Mean annual rainfall ranges from less than 25 cm to 50 cm (less than 10 in. to 20 in.), except in the northeast corner of the Kawaihae area, where it is as much as 127 cm (50 in.). The Koeppen climate classifications are BWh (hot desert) near the coastline and BSh (hot semidesert) inland (Jenkins et al. 1981:170).

The small amount of vegetation in the Kohala and Kawaihae study areas conforms with the prevailing dry climate. Kiawe is by far the dominant tree, and ground cover consists of sparsely scattered small shrubs and grasses such as 'ilima, lantana, bermudagrass, piggrass, and fingergrass.

The Hilo study area experiences mean annual temperatures between 22 and 23°C (72 and 74°F). Mean annual precipitation is estimated to vary between 230 and 380 cm (90 and 150 in.), increasing inland and upslope (State of Hawaii 1970). The Koeppen climate classification is Af (tropical and continuously wet) (Jenkins et al. 1981: 170).

The moderately dense vegetation in the

Hilo study area is reflective of the warm, moist conditions of the windward side of the island. Plant types are highly variable; typical species include ohia, guava, sword ferns (kupukupu and pamoho), false staghorn (uluhe), and, in coastal areas, hala and hau.

Soils

The soils on the Island of Hawaii have been described and classified by Sato et al. (1973) according to the Soil Taxonomy System, which was adopted by the United States government in 1970. Five of the ten orders of the system are represented on the island. The great variety of soils results from wide differences in climate, vegetation, relief, drainage, and age and type of parent material.

Soil maps for each of the study areas are presented as Figures 2, 3, and 4 (after Sato et al. 1973). Table 1 lists the main soil types in these areas and gives a brief description of each. The table does not include other soil types present in minor amounts in the study areas. Soils are here identified only according to series; reference may be made to Sato et al. (1973) for a more definitive classification.

METHODS

Collection and Initial Preparation of Soil Samples

Soil sampling stations were established at the corners of a 1.6-km-square (1.0-mi-square) grid system with axes oriented north-south and east-west (Figures 2, 3, 4). This plan provided for unbiased sampling and achieved coverage of the three study areas with a reasonable number of samples. Where the grid points fell very near roadways or in highly developed residential or industrial areas, sampling sites were not established; and in some instances in the Hilo study area, stations were offset from the grid pattern because of field inaccessibility due to thick vegetation and rough terrain. The stations were located in the field with the use of a Brunton compass and altimeter and with the aid of aerial photographs.

Soil samples were collected at each station by means of a small garden trowel. Most samples were taken from the surface to a depth of approx. 10–15 cm within a 250-cm² area. However, the depth of soil sampling was limited to just a few centimeters at some locations (particularly in the Hilo area) due to shallow soil development. Chunks of rocks and mats of vegetation were excluded as much as possible at the time of collection. Two samples (one for archival storage), each about 400 cm³ in volume, were collected at each site and placed in cloth bags for transport to the laboratory.

At the laboratory, the soil samples were spread out on plastic wrapping material, covered with porous tissue paper, and allowed to air-dry overnight. The exposure resulted in slight weight changes of less than 2% for the Kohala and Kawaihae soils, but for some of the high-moisture, organic-rich soils from the Hilo area, weight losses were estimated to be greater than 10%. The soils were then placed in 1-liter plastic containers and mechanically mixed by shaking in order to break apart and homogenize clotted masses. The mixed soils were fractionated by sieving through 2-mm plastic mesh. The <2-mm size fraction was used in all the analytical determinations. The coarser fraction, which was discarded, consisted of less than 20% by weight of the total sample in all cases; in the great majority of the Kohala and Kawaihae soils, the coarser fraction was less than 5% of the total sample weight. The sieved fractions were stored for analysis in airtight plastic containers.

Determination of Oven-Dry Weight, Loss on Ignition, and pH

The procedures for determination of oven-dry weight, loss on ignition, and pH closely followed those outlined by McKeague (1978). Approximately 2 g of soil, weighed to the nearest 0.1 mg, was placed in a porcelain evaporating dish and heated in an oven at 90–95°C for a minimum of 16 hr. This drying temperature, which is lower than the normally recommended 105–110°C, was used in order to reduce possible error caused by the decomposition (oxidation) of organic material. After

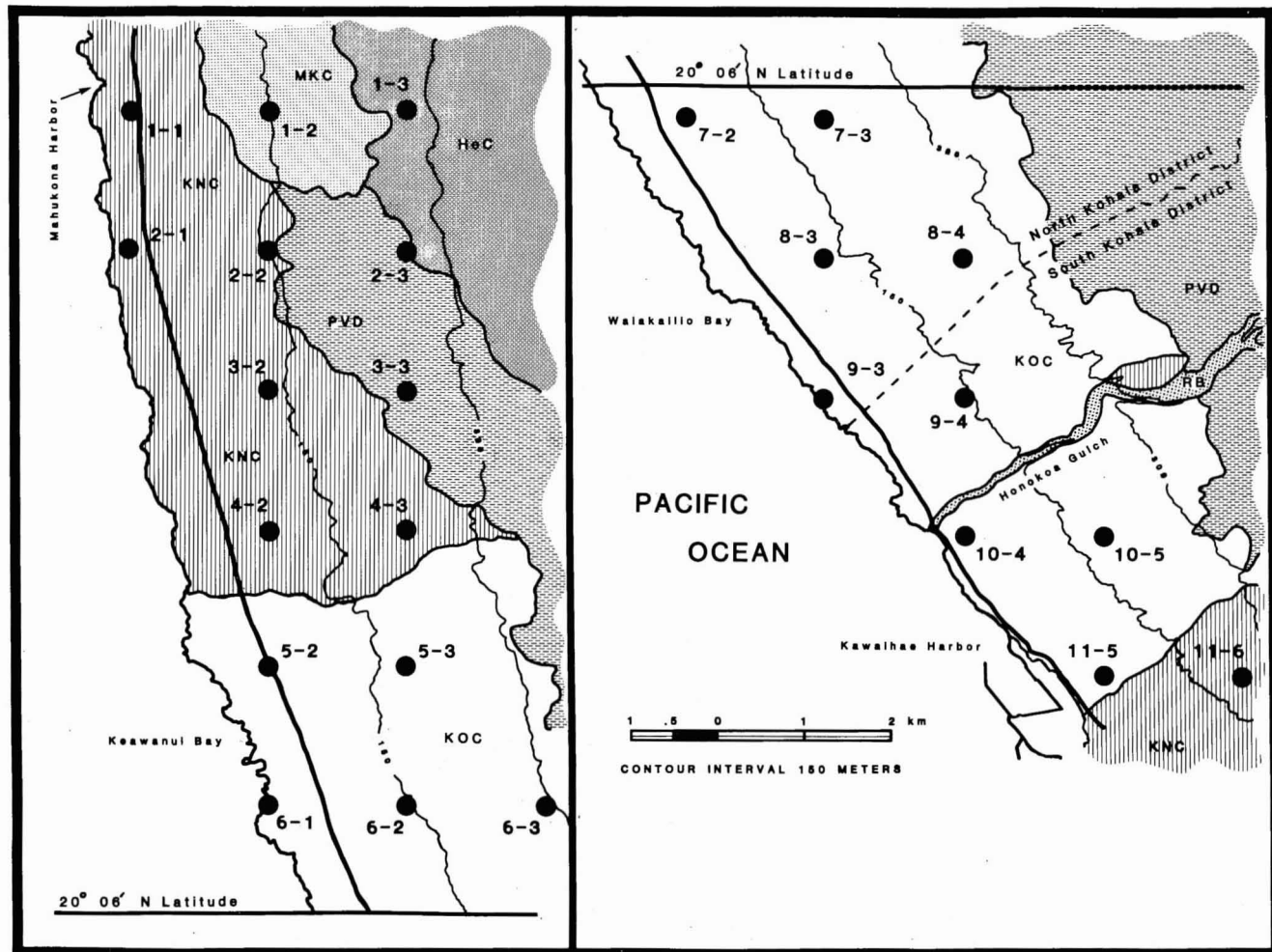


FIGURE 2. Sample locations and soil map of the Kohala study area (after Sato et al. 1973).

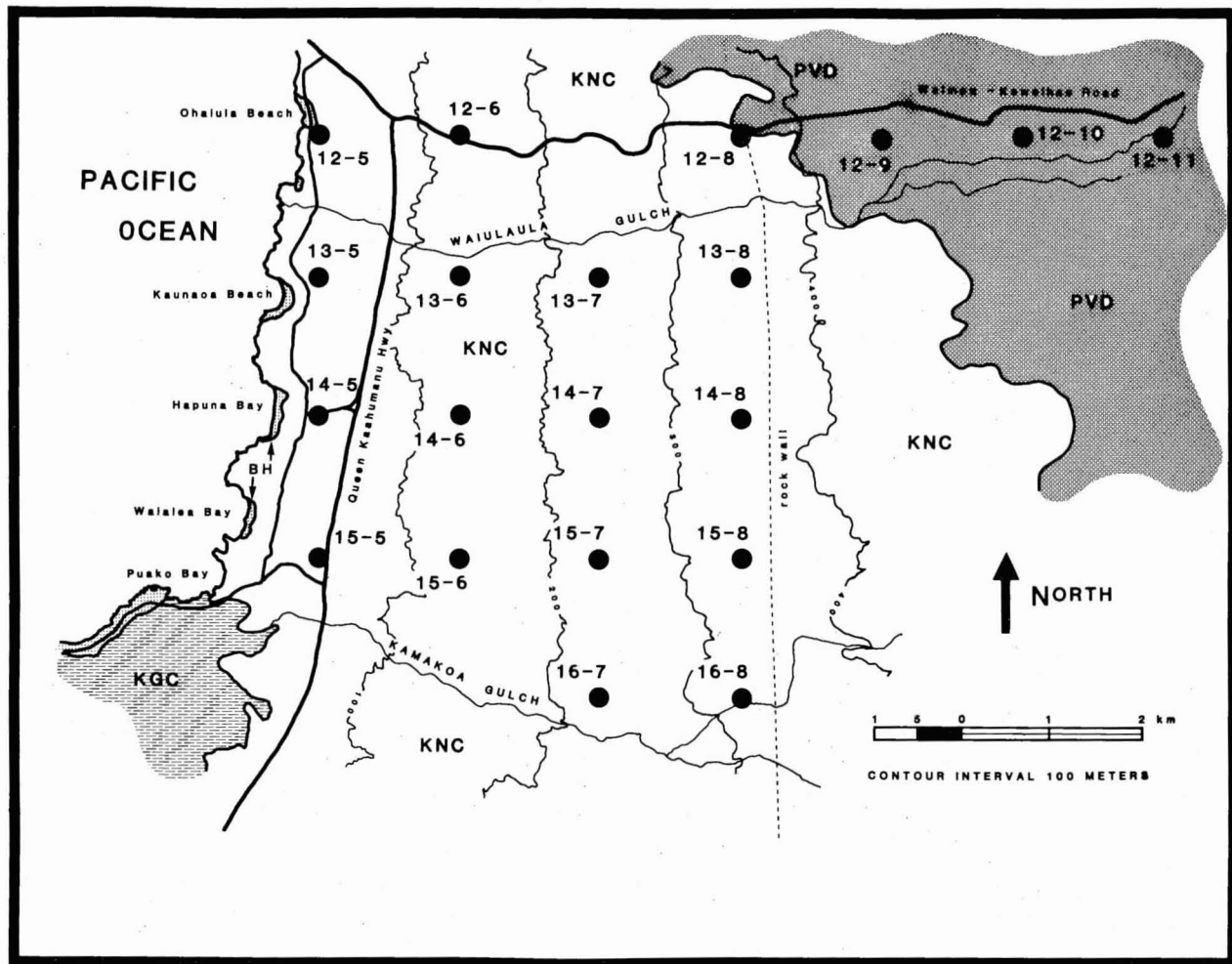


FIGURE 3. Sample locations and soil map of the Kawaihae study area (after Sato et al. 1973).

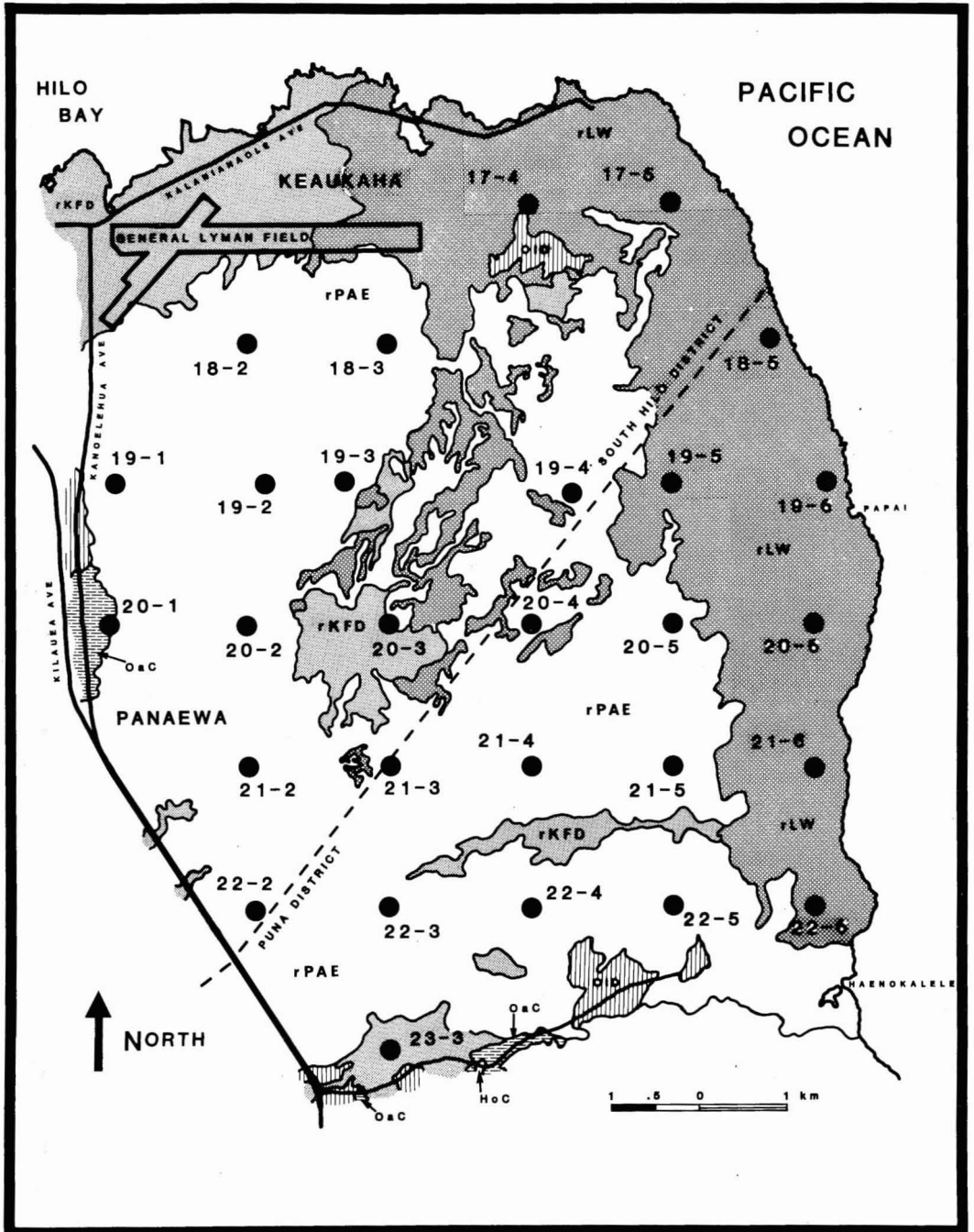


FIGURE 4. Sample locations and soil map of the Hilo study area (after Sato et al. 1973).

TABLE 1

IDENTIFICATION AND DESCRIPTION OF THE SOILS OF CHIEF IMPORTANCE IN THE THREE STUDY AREAS*

SOIL SERIES	SOIL TYPE/PHASE	DESCRIPTION/PROPERTIES
Hawi	(HeC): Extremely stony, silty clay; 6–12% slope	Well-drained silty clay with 3–15% stone cover; 1.2–1.8-m depth to weathered bedrock, with a silty clay surface layer 0–38 cm; 1.6–5-cm/hr permeability, moderate shrink–swell potential, medium runoff, moderate erosion hazard
Kawaihae	(KNC): Extremely stony, very fine sandy loam; 6–12% slope	Somewhat excessively drained, extremely stony soil formed in volcanic ash; 0.5–1.1-m depth to bedrock, with a 0–5-cm surface layer of fine sandy loam; 1.6–5-cm/hr permeability, low shrink–swell potential, medium runoff, moderate erosion hazard
Mahukona	(KOC): Very rocky, very fine sandy loam; 6–12% slope	Same as (KNC), except that rock outcrops occupy 10–20% of the surface
	(MKC): Very stony, silty clay loam; 6–12% slope	Well-drained silty clay loam formed in volcanic ash and basalt residuum; 0–15-cm, very stony, silty clay loam surface layer, with a subsoil of approx. 76 cm; 1.6–5-cm/hr permeability, low shrink–swell potential, medium runoff, moderate erosion hazard
Puu Pa	(PVD): Extremely stony, very fine sandy loam; 6–20% slope	Well-drained stony, very fine sandy loam formed in volcanic ash; 0–15-cm, extremely stony, very fine sandy loam surface layer, with a subsoil of approx. 86 cm overlying 'a'ā lava; 5–16-cm/hr permeability, low shrink potential when dried, medium runoff, moderate erosion hazard
Olaa	(OaC): Silty clay loam; slope generally less than 10%	Well-drained silty clay loam formed in volcanic ash; 0–41-cm surface layer of silty clay loam, with a subsoil approx. 23 cm thick overlying 'a'ā lava; 16–51-cm/hr permeability, high shrink potential when dried, slow runoff, slight erosion hazard
Keaukaha	(rKFD): Extremely rocky muck; 6–20% slope	Well-drained, thin organic soil overlying pāhoehoe lava; 0–20-cm surface layer of extremely rocky muck containing abundant roots; 16–51-cm/hr permeability, high shrink potential when dried, medium runoff, slight erosion hazard
Lava flows, pāhoehoe	(rLW)	Miscellaneous land type generally lacking soil development; however, in the Hilo study area the age of the flows and thick vegetation has allowed for a thin accumulation of organic-rich material which may thicken to several tens of centimeters in depressions in the flows
Papai	(rPAE): Extremely stony muck; 3–25% slope	Well-drained, thin, 0–20 cm of extremely stony organic muck overlying 'a'ā lava; contains abundant roots; 16–51-cm/hr permeability, high shrink potential when dried, slow runoff, slight erosion hazard

* Adapted from Sato et al. (1973).

the samples were allowed to cool in a desiccator, they were reweighed to determine oven-dry weight and then reheated to determine weight loss on ignition (LOI). The samples were ignited in a muffle furnace at 420°C for 2 hr and again weighed after cooling in a desiccator; the resulting weight loss can be taken as an estimate of the original content of organic matter. To a lesser extent, water loss from soil colloids may be a contributing factor in the LOI determinations; at the ignition temperature used, carbonate decomposition and

structural water loss is probably insignificant (McKeague 1978:149). The LOI was calculated on the basis of weight percentage of the soil weight after drying (i.e., the oven-dry weight). In order to achieve an indication of the reliability of the determinative methods involving drying and ignition, several duplicate samples were processed and some samples were subjected to longer periods of heat treatment. In all cases, the results showed a variation of less than 1% between different samples of the same soil.

Soil samples were prepared for pH determination (McKeague 1978:67) by mixing 20 g of soil with 20 ml of deionized water (pH = 5.9) in a 50-ml beaker. For samples with a high content of organic matter, a soil/water ratio of 1:2 was required. The suspensions were stirred several times over a 10-min period and allowed to stand for 30 min before the glass and calomel electrodes were placed in the supernatant solutions for pH readings. Prior to taking pH readings of the soil suspensions, the pH meter was temperature adjusted and calibrated with buffers having pH of 5 and 10. Several duplicate soil samples were run in order to check the reliability of the technique; in all cases, replications were within ± 0.2 pH unit.

Neutron Activation/Gamma-Ray Spectroscopic Analysis

The soil samples were analyzed for REEs at the Nuclear Science and Technology Facility of the State University of New York at Buffalo. Preweighed quantities of the soils, contained in 2/5-dram polyethylene vials, were submitted for analysis.

The samples, together with appropriate Canadian Soil Reference Standards (Bowman et al. 1979) and National Bureau of Standards SRM fly ash and coal, were subjected to 4-hr irradiations near the core of the 2-MW reactor at a neutron flux of approx. 3×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$. The samples were then allowed to decay to a reasonable activity level for 7–8 days before gamma-ray analyses were performed.

Prior to analysis of the soil samples, the gamma-ray spectroscopy system, a Canberra 1024-channel Model No. 8100 multichannel pulse height analyzer, was calibrated with New England Nuclear gamma-ray rod reference sources (^{22}Na , ^{60}Co , ^{133}Ba , ^{109}Cd , and ^{137}Cs). All the sealed $\frac{2}{5}$ -dram poly vials containing irradiated soil samples were then transferred to clean 2-dram counting vials. Each counting vial was in turn placed on its longitudinal axis 24 cm above a Ge(Li) semiconductor photopeak detector enclosed in a $60 \times 65 \times 60$ cm lead cave lined with cadmium and copper metals, and counted for 10 min.

Gamma-ray spectral lines were segregated into discrete channels of the multichannel analyzer and subsequently recorded in hard-copy format by means of a terminal line printer. Concentrations of each selected radionuclide in the samples were determined by comparison of activity per unit weight with the standards, using corrections for Compton scattering and decay.

Statistical Analysis

Statistical analysis of data was performed on-line with the Burroughs 6800 computer at State University of New York College at Fredonia, using the statistical package Minitab, a computing system of Minitab, Inc., State College, Pennsylvania.

RESULTS AND DISCUSSION

REE Concentrations and Statistical Analyses

Table 2 lists the concentrations of La, Ce, Sm, Eu, Yb, and Lu in 21, 15, and 14 soil samples from the Kohala, Kawaihae, and Hilo study areas, respectively. Concentrations are calculated to express their values in oven-dry weights of the soils. In addition, the table lists the mean, median, trimmed mean (TMEAN), standard deviation (STDEV), standard error of the mean (SEMEAN), maximum (MAX), minimum (MIN), third quartile (Q3), and first quartile (Q1) values. TMEAN is a 5% trimmed mean; the smallest 5% (rounded to the nearest integer) and the largest 5% of the values are trimmed, and the middle 90% are averaged. STDEV is the square root of $(x - \bar{x})^2 / (N - 1)$. SEMEAN is calculated as STDEV / N . Quartiles 1 and 3 are the positions at $(N + 1)/4$ and $3(N + 1)/4$, respectively, in a list of data ordered from smallest to largest; if the position is not an integer, interpolation is used.

The elements Lu and Yb are not reported in many samples. Quantification of these elements, present in very low concentrations, was adversely affected by an analytical problem (an observed spectral line shift in a region of high Compton scattering).

TABLE 2

CONCENTRATIONS, LOSS ON IGNITION, AND SOIL pH WITH STATISTICAL ANALYSES FOR SOILS FROM THE KOHALA, KAWAIHAE, AND HILO STUDY AREAS, ISLAND OF HAWAII

SAMPLE	A. KOHALA STUDY AREA							LOI (wt %)	pH
	La (mg/kg)	Ce (mg/kg)	Sm (mg/kg)	Eu (mg/kg)	Yb (mg/kg)	Lu (mg/kg)			
1-1	34.3	54.4	8.37	2.68	—	—	13.7	6.7	
1-2	73.0	156	15.2	3.85	—	—	17.5	5.9	
1-3	52.6	153	10.4	3.66	—	—	14.9	7.8	
2-1	34.0	129	11.6	3.43	—	—	6.3	7.1	
2-2	31.8	58.4	9.98	2.24	3.98	0.66	12.8	7.2	
2-3	40.7	134	8.98	3.08	—	—	14.3	7.0	
3-2	59.7	151	14.6	3.92	—	—	10.2	7.1	
3-3	50.8	158	11.8	4.23	—	—	14.2	6.1	
4-2	57.6	146	17.1	4.90	—	—	11.7	6.8	
4-3	58.5	178	16.8	5.63	—	—	17.1	7.9	
5-2	31.6	127	10.5	3.02	—	—	6.6	8.8	
5-3	52.6	150	13.6	4.95	—	—	7.5	7.1	
6-1	65.4	199	20.6	5.75	—	—	15.2	7.3	
6-2	82.0	197	22.6	7.10	—	—	7.1	7.1	
6-3	76.5	164	20.3	6.95	—	—	14.9	8.1	
7-2	56.3	166	15.8	4.49	—	—	7.7	7.2	
7-3	70.1	132	16.0	7.66	5.05	—	9.2	7.6	
8-4	89.7	225	21.2	5.14	—	—	5.6	7.2	
9-3	37.9	64.5	9.69	2.83	—	—	38.3	6.2 (1:2)	
10-4	48.0	147	12.9	3.05	—	—	4.8	8.0	
11-5	57.3	178	13.9	3.83	—	—	9.7	6.3	
N	21	21	21	21	2	1	21	20	
NMISS	0	0	0	0	19	20	0	1	
MEAN	55.3	146.1	14.38	4.40	4.515	—	12.35	7.22	
MEDIAN	56.3	151.0	13.90	3.92	4.515	—	11.70	7.15	
TMEAN	54.7	146.7	14.26	4.34	4.515	—	11.38	7.20	
STDEV	16.8	43.8	4.25	1.53	0.757	0	7.14	0.70	
SEMEAN	3.7	9.6	0.93	0.33	0.535	0	1.56	0.16	
MAX	89.7	225.0	22.60	7.66	5.050	—	38.30	8.80	
MIN	31.6	54.4	8.37	2.24	3.980	—	4.80	5.90	
Q3	67.8	172.0	16.95	5.39	—	—	14.90	7.75	
Q1	39.3	130.5	10.45	3.07	—	—	7.30	6.85	
B. KAWAIHAE STUDY AREA									
12-5	47.8	126	13.8	3.80	3.99	0.58	11.4	7.3	
12-6	36.2	113	10.6	3.76	—	—	10.0	7.3	
12-9	36.7	64.0	7.83	2.92	—	—	20.2	6.9	
12-11	51.8	105	9.28	4.27	3.49	—	19.7	6.8	
13-5	35.8	109	9.05	2.50	4.16	0.53	7.0	7.2	
13-6	78.8	139	8.45	3.88	7.48	0.86	12.7	7.6	
13-8	40.4	115	11.6	3.38	2.75	0.41	16.6	7.3	
14-5	51.9	132	13.2	3.14	5.82	0.61	11.5	7.9	
14-6	45.8	98.1	10.9	2.53	4.17	0.65	8.7	7.5	
14-7	41.3	93.2	8.95	4.52	4.02	—	13.9	7.1	
14-8	47.6	103	12.0	4.32	6.31	—	14.4	6.4	
15-5	79.8	111	15.1	7.53	7.08	—	10.2	7.5	
15-6	54.2	106	12.0	4.96	5.75	—	8.3	7.6	
15-8	50.8	119	15.3	4.27	3.56	—	15.8	6.2	
16-7	46.1	49.5	13.9	3.87	4.87	—	12.8	6.4	

TABLE 2 (continued)

SAMPLE	La (mg/kg)	Ce (mg/kg)	Sm (mg/kg)	Eu (mg/kg)	Yb (mg/kg)	Lu (mg/kg)	LOI (wt %)	pH
N	15	15	15	15	13	6	15	15
NMISS	0	0	0	0	2	9	0	0
MEAN	49.7	105.5	11.46	3.98	4.88	0.607	12.88	7.13
MEDIAN	47.6	109.0	11.60	3.87	4.17	0.595	12.70	7.30
TMEAN	48.4	107.3	11.45	3.82	4.84	0.607	12.77	7.15
STDEV	13.4	23.4	2.44	1.22	1.47	0.149	3.95	0.50
SEMEAN	3.5	6.1	0.63	0.31	0.41	0.061	1.02	0.13
MAX	79.8	139.0	15.30	7.53	7.48	0.860	20.20	7.90
MIN	35.8	49.5	7.83	2.50	2.75	0.410	7.00	6.20
Q3	51.9	119.0	13.80	4.32	6.07	0.702	15.80	7.70
Q1	40.4	98.1	9.05	3.14	3.78	0.500	10.00	6.80
C. HILO STUDY AREA								
17-4	9.40	31.1	4.58	2.03	2.30	—	16.7	5.2
18-2	11.4	33.4	5.01	1.80	1.91	—	2.3	5.5
18-5	4.64	58.6	6.85	2.97	1.78	—	64.5	6.1
19-1	6.64	35.9	5.12	1.09	1.35	0.30	63.7	—
19-6	6.38	49.6	7.35	1.76	1.87	—	66.0	5.6 (1:2)
20-1	10.4	56.9	5.05	2.06	1.16	—	23.4	6.3
21-2	8.61	41.2	7.46	1.98	1.21	—	11.5	6.1
21-3	8.58	33.8	6.35	0.99	1.24	—	2.2	7.2
21-5	16.2	39.8	6.18	2.81	2.84	—	8.7	6.8
22-2	5.19	35.2	3.71	1.25	0.88	—	45.5	—
22-3	9.71	44.9	4.46	1.72	3.08	—	3.8	6.8
22-5	15.4	34.6	6.10	1.45	3.68	0.39	5.3	6.8
22-6	6.24	47.6	6.42	2.61	3.28	—	35.9	5.6
23-3	9.96	49.9	4.83	2.05	1.62	0.13	48.1	—
N	14	14	14	14	14	3	14	10
NMISS	0	0	0	0	0	11	0	4
MEAN	9.20	42.32	5.68	1.898	2.014	0.273	28.4	6.24
MEDIAN	9.01	40.50	5.61	1.890	1.825	0.300	20.1	6.20
TMEAN	8.99	41.90	5.69	1.884	1.970	0.273	27.5	6.25
STDEV	3.46	9.03	1.15	0.603	0.887	0.132	24.9	0.66
SEMEAN	0.92	2.41	0.31	0.161	0.237	0.076	6.6	0.21
MAX	16.20	58.60	7.46	2.970	3.680	0.390	66.0	7.20
MIN	4.64	31.10	3.71	0.990	0.880	0.130	2.2	5.20
Q3	10.65	49.68	6.53	2.197	2.900	0.390	52.0	6.80
Q1	6.35	34.40	4.77	1.400	1.233	0.130	4.9	5.58

Several soil samples identified on the sample location maps (Figures 2, 3, 4) were not analyzed for REEs. These include 8-3, 9-4, 10-5, and 11-6 in the Kohala study area; 12-8, 12-10, 13-7, 15-7, and 16-8 in the Kawaihae area; and 19-2, 19-3, 19-4, 19-5, 20-2, 20-3, 20-4, 20-5, 20-6, 21-4, 21-6, and 22-4 in the Hilo area. These samples were analyzed for other major, minor, and trace constituents, as reported in Halbig et al. (1985).

Table 2 also lists the loss on ignition (LOI) for each soil sample, expressed as percentage of oven-dry weight, and soil pH resulting from a 1:1 soil/deionized water mixture (unless otherwise noted; McKeague 1978). The statistical analyses for the pH determinations do not include the values for the 1:2 soil/water mixtures (one each for the Kohala and Hilo area soils) nor three missing values for the Hilo area soils.

Geochemical Distribution of REE Concentrations

The REEs, comprising the 15 elements from La to Lu (atomic numbers 57–71), are usually present in terrestrial materials in no more than trace amounts. The following two general rules have been observed: (1) REEs of even atomic number are more abundant than their odd-numbered neighbors; and (2) abundance tends to decrease with increasing atomic number for even-numbered and odd-numbered sequences.

The analytical data for the Hawaiian soil samples conform rigidly to these general rules. The data include determinations of six REEs, three pairs of even/odd neighbors at the beginning (Ce/La), near the middle (Sm/Eu), and at the end (Yb/Lu) of the series. For all 50 soil samples, Ce exceeds La and Sm exceeds Eu. Only 10 samples were analyzed for both Yb and Lu, but in each the former exceeds the latter.

The decrease in abundance with increasing atomic number is evident in both even-numbered and odd-numbered sequences. In all 50 samples, Ce ($Z = 58$) concentrations exceed Sm ($Z = 62$); and in the 29 samples analyzed for three even-numbered REEs, Sm exceeds Yb ($Z = 70$). Similarly, in all 50 samples, La ($Z = 57$) concentrations exceed those of Eu ($Z = 63$), and in the 10 samples also analyzed for Lu ($Z = 71$), Eu exceeds Lu.

Because the determinations of these selected REEs in the Hawaiian soil samples do conform to the general observations of trends, the probable range of concentrations of other REEs not determined in this study can be predicted. In each soil sample, the concentration of Nd should be between those of Ce and Sm; and the concentrations of Gd, Dy, and Er should be between those of Sm and Yb. Similarly, the concentration of Pr should be between those of La and Eu; and for Tb, Ho, and Tm, the concentrations in each sample should be between those of Eu and Lu.

Comparisons of REE Concentrations in the Three Study Areas

Probably the most commonly used distribution factor for comparing concentrations in

different materials is the mean. Thus, the mean concentrations of the REEs are plotted relative to atomic number in Figure 5. In addition to providing a visual comparison of mean REE concentrations in soils from the three areas, Figure 5 illustrates that the means, like the individual determinations, conform to the two general rules regarding abundance noted above.

A more complete comparison of concentrations is made by examination of all seven distribution factors (mean, median, trimmed mean, maximum, minimum, and first and third quartile values) given in Table 2.

The greatest differences in concentrations of REEs occur between soils from the western and eastern sides of the island. For all distribution factors, the Kohala and Kawaihae soils have greater concentrations of REEs than do the Hilo soils (omitting consideration of Lu in Kohala soils because there is only one determination).

Kohala and Kawaihae soils are more similar to each other in REE content, but the former does have somewhat greater concentrations of Ce and Sm for all distribution factors and, except for the MIN and Q1 values, also shows greater values for La and Eu. There are too few Yb and Lu determinations in Kohala soils to make a valid comparison for these two elements.

Table 3 presents standard statistical one-way analyses of variance for the REE data of Table 2. The output gives (1) an analysis of variance table for each REE in the three areas; (2) the sample size, sample mean, and standard deviation corresponding to each population (or factor level); (3) the pooled estimate, $s_p = \sqrt{\text{mean square error}}$, of the common standard deviation; and (4) a display of individual 95% confidence intervals for each population mean. Each confidence interval is calculated from $\bar{x}_i - t^*s_p/\sqrt{n_i}$ to $\bar{x}_i + t^*s_p/\sqrt{n_i}$, where \bar{x}_i and n_i are the sample mean and sample size, respectively, corresponding to population i , and t^* is the value from a t table corresponding to 95% confidence and the degrees of freedom associated with the mean square error (Ryan, Joiner, and Ryan 1976).

The soils on the western side of the island

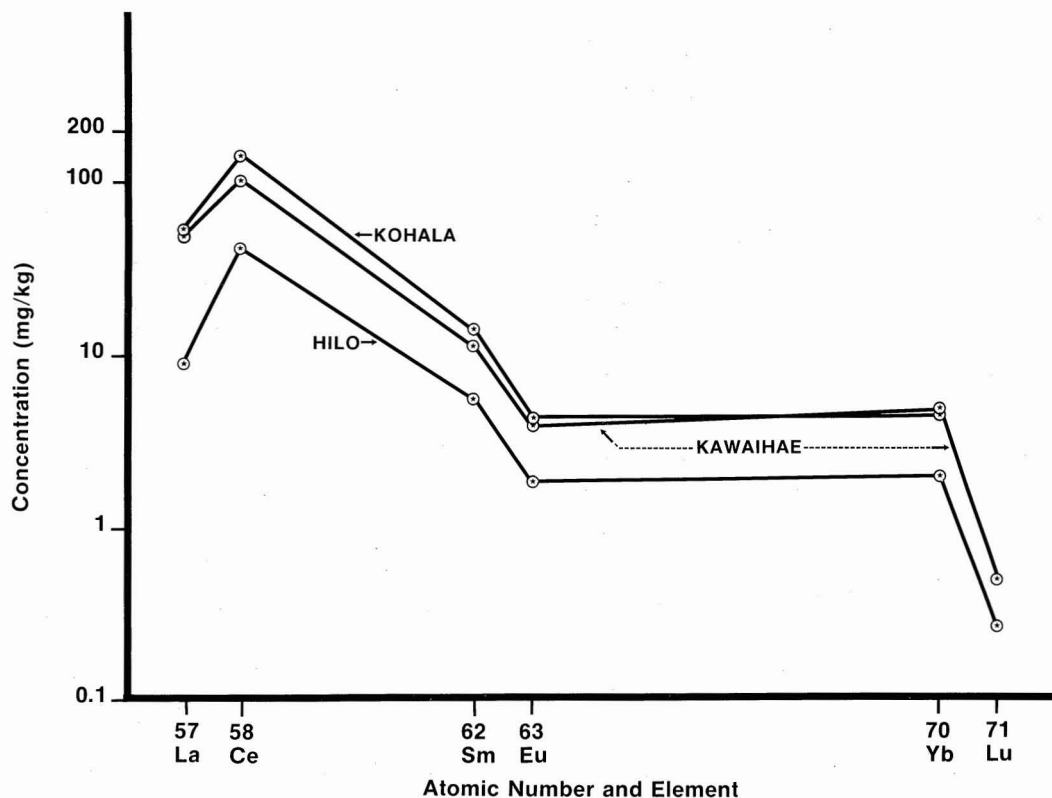


FIGURE 5. Mean concentrations of REEs in soils from three areas on the Island of Hawaii.

contain notably greater REE concentrations because of their association with alkalic rocks, less dilution by organic matter, and possibly differences in weathering (see the discussion below under the heading *REEs in Parent Material and Soil-Forming Processes*).

Statistical Correlations

Correlations were examined between pairs of individual REE concentrations based on oven-dry weights and based on weights adjusted to remove weight due to organic matter and water in soil colloids (calculated from LOI determinations; an adjusted concentration is calculated as the concentration based on the oven-dry weight divided by percent adjusted weight, which is 100% oven-dry weight minus percent LOI). Pearson product moment correlation coefficients were calculated for these relationships. The square of

the correlation coefficient (the coefficient of determination) multiplied by 100 gives the percent of variation in the second determination that can be predicted from the first determination using a straight-line prediction equation. Thus, the higher the coefficient of determination, the more useful one determination will be to predict the other (Ryan, Joiner, and Ryan 1976).

In general, a high degree of positive correlation can be expected between elements that are geochemically similar in both endogenic (e.g., magmatic, volcanic) and exogenic (e.g., weathering) processes. Thus, some of the strongest correlations are expected to exist, and actually do exist, among the geochemically similar REEs.

The 21 Kohala area soil samples exhibit a relatively high degree of positive correlation among La, Ce, Sm, and Eu; too few determinations of Yb and Lu prevent correlation with

TABLE 3

ONE-WAY ANALYSES OF VARIANCE FOR REE CONCENTRATIONS IN HAWAIIAN SOILS

ANALYSIS OF VARIANCE

SOURCE	DF	SS	MS	F
FACTOR	2	19551	9775	55.29
ERROR	47	8309	177	
TOTAL	49	27860		

INDIVIDUAL 95 PCT CI'S FOR MEAN
BASED ON POOLED STDEV

LEVEL	N	MEAN	STDEV
KOHA/LA	21	55.257	16.782
KAWA/LA	15	49.667	13.420
HILO/LA	14	9.196	3.458

POOLED STDEV = 1E+01

ANALYSIS OF VARIANCE

SOURCE	DF	SS	MS	F
FACTOR	2	90411	45206	45.01
ERROR	47	47201	1004	
TOTAL	49	137612		

INDIVIDUAL 95 PCT CI'S FOR MEAN
BASED ON POOLED STDEV

LEVEL	N	MEAN	STDEV
KOHA/CE	21	146.06	43.85
KAWA/CE	15	105.52	23.43
HILO/CE	14	42.32	9.03

POOLED STDEV = 31.69

ANALYSIS OF VARIANCE

SOURCE	DF	SS	MS	F
FACTOR	2	639.28	319.64	32.53
ERROR	47	461.79	9.83	
TOTAL	49	1101.07		

INDIVIDUAL 95 PCT CI'S FOR MEAN
BASED ON POOLED STDEV

LEVEL	N	MEAN	STDEV
KOHA/SM	21	14.377	4.251
KAWA/SM	15	11.464	2.438
HILO/SM	14	5.676	1.151

POOLED STDEV = 3.135

ANALYSIS OF VARIANCE

SOURCE	DF	SS	MS	F
FACTOR	2	56.08	28.04	18.24
ERROR	47	72.24	1.54	
TOTAL	49	128.32		

TABLE 3 (continued)

				INDIVIDUAL 95 PCT CI'S FOR MEAN BASED ON POOLED STDEV			
LEVEL	N	MEAN	STDEV	-----+-----+-----+-----			
KOHA/EU	21	4.400	1.530	(-----*-----)			
KAWA/EU	15	3.977	1.217	(-----*-----)			
HILO/EU	14	1.898	0.603	(-----*-----)			
POOLED STDEV = 1.240				2.4	3.6	4.8	
ANALYSIS OF VARIANCE							
SOURCE	DF	SS	MS	F			
FACTOR	2	57.72	28.86	20.37			
ERROR	26	36.85	1.42				
TOTAL	28	94.57					
				INDIVIDUAL 95 PCT CI'S FOR MEAN BASED ON POOLED STDEV			
LEVEL	N	MEAN	STDEV	-----+-----+-----+-----			
KOHA/YB	2	4.515	0.757	(-----*-----)			
KAWA/YB	13	4.881	1.473	(-----*-----)			
HILO/YB	14	2.014	0.887	(-----*-----)			
POOLED STDEV = 1.190				1.4	2.8	4.2	5.6

NOTE: There are insufficient data for an analysis of variance for Lu. In the analysis of variance tables, DF = degrees of freedom; SS = sum of squares broken down into two sources (FACTOR = variation due to differences among the three populations and ERROR = variation within each population); MS = mean square (due to the factor and due to error; each mean square is the corresponding SS/DF ratio); and F = the F ratio, i.e., (MS factor)/(MS error).

these elements. Correlations and corresponding coefficients based on oven-dry weights are La/Ce (0.779), La/Sm (0.892), La/Eu (0.786), Ce/Sm (0.781), Ce/Eu (0.604), and Sm/Eu (0.827). The coefficients are only slightly changed if concentrations are adjusted for weight by removing the weight of organic matter and water in soil colloids.

In the Kawaihae samples, the only correlations with coefficients above 0.7 for concentrations based on oven-dry weights are for La/Yb (0.775, 13 samples); La/Lu (0.898, 6 samples); and Yb/Lu (0.909, 6 samples). These same element pairs are also the only ones to exhibit correlation coefficients greater than 0.7 after sample weights are adjusted for the weight of organic matter and water in soil colloids, and the differences are less than 4% in all cases.

In contrast, in the organic-rich soils of the Hilo study area, coefficients are markedly improved if based on adjusted weights. If

relationships with less than 4 samples are eliminated, no coefficients above 0.6 are obtained for element/element correlations using concentrations based on oven-dry weights; after weights are adjusted for weight due to organic matter and water in soil colloids, several coefficients above 0.6 are obtained in all 14 soil samples: Ce/Sm (0.931), Ce/Eu (0.907), Ce/Yb (0.663), Sm/Eu (0.823), Sm/Yb (0.716), and Eu/Yb (0.695).

Correlations between individual REEs and LOI are generally weak; the only coefficients greater than ± 0.5 in any of the soils are for the Hilo samples, with La/LOI (-0.689) and Lu/LOI (-0.573).

Correlations between individual REEs and pH in a given area are also weak; the only coefficients greater than ± 0.5 (for more than two samples) are for the Kawaihae soils, with Ce/pH (0.504), based on oven-dry weight; and Lu/pH (0.508, 6 samples), based on weights adjusted for LOI weight.

REEs in Parent Material and Soil-Forming Processes

Comparison of REE concentrations in soils to their concentrations in parent material would permit speculation on the processes of soil formation. Unfortunately, chemical analyses of original parent material from the vicinity of the soil sampling locations of this study are almost nonexistent. However, a considerable amount of analytical data on compositions of Hawaiian rocks has been tabulated by the Basaltic Volcanism Study Project (1981), including whole-rock determinations of major and some minor elements in rock specimens from Kohala, Mauna Kea, and Mauna Loa volcanoes. Lava flows from each of these three volcanoes serve as parent material for the formation of residual soils in the Kohala, Kawaihae, and Hilo areas, respectively, although some soils in the southern part of the Kohala area and in the Kawaihae area are developed in a thin cover of pyroclastic material (Pahala ash) of uncertain origin. (Throughout most of its extent the once glassy ash has been weathered to a mixture of clay minerals and hydrated oxides of aluminum and iron, making it impossible to determine the original composition of the material or its exact source; Macdonald, Abbott, and Peterson 1983.) Therefore, comparisons between parent rock and soil chemistry in these two latter areas should be viewed with some caution.

Another problem involved in making meaningful judgments on the behavior of chemical retention and migration during weathering and soil formation is the dilution effect of humus in the organic-rich soils. Because all analytical data for the soils are on an oven-dry weight basis and the soils include organic matter that is not present in the parent rocks, the element compositions of the organic-rich soils of the Hilo area, in particular, are diluted to a smaller weight percentage fraction (i.e., dilution is greater).

Considering these problems, comparisons of soil REE concentrations with those in rock samples of the Hawaii Reference Suite reported by the Basaltic Volcanism Study Project (1981) should be made with caution.

For comparative purposes, seven tholeiitic basalts from the southwestern side of Mauna Loa (*HAW-4* through *HAW-10*) were selected to represent parent material for the Hilo area soils (REE data for Mauna Loa tholeiites in the Hilo area are not available). The rocks of the Kohala and Kawaihae study areas belong to the alkaline series basalts. (Alkalic olivine basalts, hawaiites, and ankaramites of the upper member of the Hamakua series dominate the Kawaihae study area, while those in the Kohala study area are alkalic olivine basalts of the upper part of the Pololu Formation and alkali rocks of the Hawi Formation; Macdonald, Abbott, and Peterson 1983.) Corresponding rocks in the Hawaii Reference Suite are *HAW-16* through *HAW-20*. However, Pahala ash of unknown original composition also serves as parent material for the soils from these western study areas.

In Table 4 the statistical summary REE data for the soils are juxtaposed with the REE data for the selected individual rock samples of the Hawaii Reference Suite. Comparison of mean concentrations of REEs in the soils with those of the corresponding rocks reveals that the soils are moderately enriched in REEs relative to the rocks. Based on oven-dry weights, enrichment of individual REEs ranges up to two times; for weights adjusted for LOI, enrichment is as much as 2.7 times (for Ce in the Hilo soils). Thus, if the mean compositions of the selected rock samples from the Hawaii Reference Suite are generally representative of the composition of parent materials, REEs in the soils are moderately enriched in the soil-forming processes. This conclusion concurs with conclusions made by Easton and Easton (1983), who state that mugearites and resultant soils and sands on Kohala Mountain have undergone intense chemical alteration resulting in enrichment of REEs and positive Ce anomalies, with the effects being most pronounced in mugearites from the wetter, east side of the mountain, which also has the more acidic ground water.

Leeman et al. (1980:798) tabulate the means and standard deviations for several major and trace element concentrations in tholeiites from six Hawaiian volcanoes. For 13 tholeiites from the summit, south, and northeast rifts, and the

TABLE 4
REEs IN SELECTED ROCKS IN THE HAWAII REFERENCE SUITE AND IN SOILS

REE	HAW-4	HAW-5	HAW-6	HAW-7	HAW-8	HAW-9	HAW-10	7 HAWS (Mean ± SD)	HILO SOILS (Mean ± SD)
La	9.38	6.16	7.58	8.54	8.75	8.81	8.52	8.25 ± 1.07	9.20 ± 3.46
Ce	25.0	16.4	21.0	22.8	23.0	23.3	22.5	22.0 ± 2.74	42.32 ± 9.03
Sm	4.80	3.30	4.40	4.95	4.98	4.97	4.85	4.61 ± 0.61	5.68 ± 1.15
Eu	1.70	1.10	1.60	1.68	1.67	1.64	1.55	1.53 ± 0.21	1.898 ± 0.603
Yb	2.00	1.35	1.98	2.08	2.08	2.07	2.00	1.94 ± 0.26	2.014 ± 0.887
Lu	0.29	0.20	0.29	0.31	0.32	0.30	0.29	0.29 ± 0.04	0.273 ± 0.132

REE	HAW-16	HAW-17	HAW-18	HAW-19	HAW-20	5 HAWS (Mean ± SD)	KAWAIHAE SOILS (Mean ± SD)	KOHALA SOILS (Mean ± SD)
La	51.2	17.4	68.4	20.4	38.0	39.1 ± 21.4	49.7 ± 13.4	55.3 ± 16.8
Ce	125	41.0	146	51.0	85	89.6 ± 45.6	105.5 ± 23.4	146.1 ± 43.8
Sm	15.2	6.15	14.4	7.40	11.8	11.0 ± 4.07	11.46 ± 2.44	14.38 ± 4.25
Eu	4.9	1.92	4.3	2.4	3.5	3.40 ± 1.25	3.98 ± 1.22	4.40 ± 1.53
Yb	3.60	1.75	3.80	2.25	3.08	2.90 ± 0.88	4.88 ± 1.47	4.515 ± 0.757
Lu	0.50	0.25	0.53	0.32	0.42	0.40 ± 0.12	0.607 ± 0.149	— —

NOTE: Data on rocks (HAWs) from Basaltic Volcanism Study Project (1981: 173); HAW-4 through HAW-10 are tholeiites from Mauna Loa Volcano; HAW-16, hawaiite, Mauna Kea Volcano; HAW-17, ankaramite, Mauna Kea Volcano; HAW-18, trachyte trending to mugearite, Kohala Volcano; HAW-19, hawaiite, Kohala Volcano; HAW-20, alkali olivine basalt, Kohala Volcano. Mean concentrations and standard deviations (SD) in soils are based on oven-dry weights. All concentrations are in milligrams per kilogram.

northwest slope of Mauna Loa, the data (in mg/kg) are 9.2 ± 0.8 La, 25 ± 2 Ce, 4.9 ± 0.2 Sm, 1.74 ± 0.05 Eu, 1.97 ± 0.06 Yb, and 0.27 ± 0.02 Lu. These values range from 2 to 14 percent greater (except for Lu, which is 7 percent less) than the means for the seven tholeiites in the Hawaii Reference Suite. Comparison of REEs in the Hilo soils with those in the 13 Mauna Loa tholeiites reveals identical mean concentrations of La and Lu and moderately greater concentrations of the other REEs in the soils (soil/rock ratios are Yb, 1.02; Eu, 1.09; Sm, 1.16; Ce, 1.69). These data corroborate, for the Hilo soils, the conclusion that REEs are moderately enriched (especially if weights are adjusted for LOI) and display a positive Ce anomaly.

Ronov, Balashov, and Migdisov (1967) studied the behavior of REEs in the sedimentary cycle. That study showed that the concentrations and ratios of REEs in weathering products depend on the mineralogical and chemical composition of the primary rocks and on the physiochemical conditions of the weathering environment. Under surface conditions, the geochemical behavior is determined by easy hydrolysis of REE compounds,

capacity of REEs to form complexes (including natural organic compounds), and changes in the oxidation states of some of the elements (especially Ce).

Ronov, Balashov, and Migdisov (1967) concluded that accumulation of REEs, with preferential enrichment in light lanthanides, takes place in the weathering of pyroxenites, gabbro-anorthosites, and nepheline syenites; and that removal of REEs from clastics is more easily effected in humid rather than arid environments. The data of Table 4 are not in full accord with conclusions drawn by Ronov, Balashov, and Migdisov; however, the rocks and soils of the two studies are not similar. In the absence of additional data, further comparisons and conclusions are premature.

Comparison of REEs in Hawaiian Soils with Those in Common Sediments and Sedimentary Rocks

In Table 5, the mean values of individual REE concentrations in the Hawaiian soils are juxtaposed with those in composites of shales, graywackes, sandstones, limestones, and averages of sedimentary rock types as fractions of

TABLE 5

MEAN REE CONCENTRATIONS IN HAWAIIAN SOILS AND IN COMMON SEDIMENTS AND SEDIMENTARY ROCKS

REE	KOHALA	KAWAIHAE	HILO	A	B	C	D	E	F	G	SOILS*
La	55.3	49.7	9.2	45	34	33	17	4.1	29	40	41, 34, <30–200
Ce	146.1	105.5	42.3	91	67	62	33	6.5	57	80	86, 75, <150–300
Sm	14.4	11.5	5.68	7.2	6.9	5	3.7	1.4	6.0	6.4	—
Eu	4.40	3.98	1.90	1.4	1.4	1.3	0.7	—	1.2	1.3	—
Yb	4.52	4.88	2.01	3.6	2.6	3.0	1.2	0.3	2.2	3.3	4, 3, <1–50
Lu	—	0.61	0.27	0.7	—	0.5	—	—	0.4	0.6	—

NOTE: All concentrations are in milligrams per kilogram. A, composite of 36 European Paleozoic shales, average from analyses of Haskin and Haskin (1966), Herrmann and Wedepohl (1967), and Haskin, Frey, and Wildeman (1968), as presented by Herrmann (1970); B, 8616 shales from the Russian platform (Paleozoic, Mesozoic, Cenozoic), from Ronov, Balashov, and Migdisov (1967), as presented by Herrmann (1970); C, composite of 17 typical graywackes, as presented by Herrmann (1970); D, 6051 sandstones from the Russian platform, from Ronov, Balashov, and Migdisov (1967), as presented by Herrmann (1970); E, 11,205 limestones from the Russian platform, from Ronov, Balashov, and Migdisov (1967), as presented by Herrmann (1970); F, average of sedimentary rock types as fraction of sediment mass on the continents (77% shales, 15% sandstones, 8% limestones) using data of Ronov, Balashov, and Migdisov (1967; columns B, D, E), as presented by Herrmann (1970); G, average of sedimentary rock types as fraction of sediment mass on the continents (77% shales, 15% sandstones, 8% limestones) calculated on the basis of the composite of 36 European Paleozoic shales (77% for shales plus 1% shales instead of the clay residue of 8% limestones) and the composite of 17 typical graywackes, as presented by Herrmann (1970).

*The arithmetic mean, geometric mean, and range, respectively, from Shacklette et al. (1971; see text).

sediment mass on the continents, as summarized and tabulated by Herrmann (1970) from studies of several investigators. The table also lists the arithmetic mean, geometric mean, and range determined by Shacklette et al. (1971) for three of the REEs (La, Ce, Yb). These determinations were made from 863 samples of soils or other regolith, unaltered or very little altered from their natural conditions and supporting plant life, which were taken at a depth of approx. 20 cm (8 in.) from locations about 80 km (50 mi) apart throughout the conterminous United States.

In general, compared to the composites and averages of the common sedimentary rocks listed, the REE concentrations of the Kohala and Kawaihae soils exceed by as much as two times the mean concentrations of the former. However, the REE concentrations of these soils are well within the concentration ranges of soils of continental origin studied by Shacklette et al. (1971). Hilo area soils tend to have less La and Ce (except in limestones), but similar amounts of the heavy and middle REEs.

Inasmuch as the REE concentrations in these Hawaiian soils of volcanic origin are well within the concentration ranges of soils of continental origin, and presumably within the ranges of samples making up the composites

of the common sedimentary rock types (actual data on individual samples are not available), any attempt to interpret the provenance of ancient sedimentary rocks based on REE concentrations, especially in attempting to distinguish between sources of volcanic-dominated terranes far from continental sources and those of continental origin, must be approached with caution.

ACKNOWLEDGMENTS

The neutron activation/gamma-ray spectroscopic analyses were performed by Ronald H. Denk, Research Manager, Nuclear Science and Technology Facility, State University of New York at Buffalo.

The authors extend their thanks to Steven E. Johnston, Robert A. Butts, and Steven A. Bartlett, who assisted in the field and laboratory.

LITERATURE CITED

- BASALTIC VOLCANISM STUDY PROJECT. 1981. Oceanic intraplate volcanism. Pages 161–192 and Appendix A6 in *Basaltic volcanism on the terrestrial planets*. Pergamon Press, New York.

- BOWMAN, W. S., G. H. FAYE, R. SUTARNO, J. A. MCKEAGUE, and H. KODAMA. 1979. Soil samples SO-1, SO-2, SO-3 and SO-4—Certified reference materials. Canada Centre for Mineral and Energy Technology, Rept. 79-3. Energy, Mines and Resources Canada, Ottawa.
- EASTON, M. G., and R. M. EASTON. 1983. Effects of weathering on trace and rare-earth element contents of volcanic sediments, Island of Hawaii, U.S.A. Abstr. Joint Ann. Meet. Mineralog. Assoc. Can. and Can. Geophys. Union, May 11–13, 1983, Univ. Victoria 8:A19.
- HALBIG, J. B., W. M. BARNARD, S. E. JOHNSTON, R. A. BUTTS, and S. A. BARTLETT. 1985. A baseline study of soil geochemistry in selected areas on the Island of Hawaii. State of Hawaii Department of Planning and Economic Development, Honolulu.
- HASKIN, L. A., F. A. FREY, and T. R. WILDEMAN. 1968. Relative and absolute terrestrial abundances of the rare earths. Origin and distribution of the elements. Internat. Ser. Monogr. Earth Sci. 30:889–912.
- HASKIN, M. A., and L. A. HASKIN. 1966. Rare earths in European shales: A redetermination. Science 154:507–509.
- HERRMANN, A. G. 1970. Abundance [of yttrium and lanthanides] in common sediments and sedimentary rock types. Pages 39, 57-71-K-1 to 39, 57-71-K-6 in K. H. Wedepohl, ed. Handbook of geochemistry. Springer-Verlag, Berlin.
- HERRMANN, A. G., and K. H. WEDEPOHL. 1967. Die quantitative Bestimmung der Seltenen Erden (La–Lu) und des Yttriums in silicatischen Gesteinen. Zeit. Anal. Chem. 225:1–13.
- JENKINS, R. W., M. K. JUGEL, K. M. KEITH, and M. A. MEYLAN. 1981. The feasibility and potential impact of manganese nodule processing in the Puna and Kohala districts of Hawaii. Prepared by the State of Hawaii Department of Planning and Economic Development and the U.S. Office of Ocean Minerals and Energy. Department of Planning and Economic Development, Honolulu.
- LEEMAN, W. P., J. R. BUDAHN, D. C. GERLACH, D. R. SMITH, and B. N. POWELL. 1980. Origin of Hawaiian tholeiites: trace element constraints. Amer. Jour. Science 280-A:794–819.
- MACDONALD, G. A., A. T. ABBOTT, and F. L. PETERSON. 1983. Volcanoes in the sea; the geology of Hawaii. 2nd ed. University of Hawaii Press, Honolulu.
- MALINOWSKI, M. J. 1977. Geology of the Kawaihae quadrangle, Kohala Mountain, Island of Hawaii. M.S. Thesis, University of Hawaii, Honolulu.
- MCKEAGUE, J. A., ed. 1978. Manual on soil sampling and methods of analysis. 2nd ed. Canadian Society of Soil Science, Ottawa.
- MINAMI, E. 1935. Gehalte an seltenen Erden in europaischen und japanischen Ton-schiefern. Nachr. Ges. Wiss. Goettingen. Math.-Physik. Kl. Fachgruppe IV, 1(14):155–170.
- RONOV, A. B., Y. A. BALASHOV, and A. A. MIGDISOV. 1967. Geochemistry of the rare earths in the sedimentary cycle. Geochem. Internat. 4:1–17.
- RYAN, T. A., JR., B. L. JOINER, and B. F. RYAN. 1976. Minitab student handbook. Duxbury Press, North Scituate, Mass.
- SATO, H. H., W. IKEDA, R. PAETH, R. SMYTHE, and M. TAKEHIRO, JR. 1973. Soil survey of the Island of Hawaii, State of Hawaii. U.S. Government Printing Office, Washington, D.C.
- SHACKLETTE, H. T., J. C. HAMILTON, J. G. BOERNGEN, and J. M. BOWLES. 1971. Elemental composition of surficial materials in the conterminous United States. U.S. Geological Survey Prof. Pap. 574-D. U.S. Government Printing Office, Washington, D.C.
- STATE OF HAWAII. 1970. An inventory of basic water resources data: Island of Hawaii. State of Hawaii Department of Land and Natural Resources Division of Water and Land Development Rept. R34. Honolulu.
- STEARNS, H. T., and G. A. MACDONALD. 1946. Geology and ground-water resources of the Island of Hawaii. Hawaii Division of Hydrography Bull. 9. Honolulu.