

Manganiferous Soil Concretions from Hawaii¹

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ABSTRACT: Manganiferous soil concretions have been located in pineapple and sugar cane plantations of the Schofield Plateau, Oahu, and black manganiferous coatings on the surface of soils have been observed on the crests of embankments next to pineapple plantations on Oahu, Molokai, and Lanai. The concretions and coatings are found in oxisols derived from volcanic parent material. The moisture regime of the soils is characterized by alternate wet and dry periods. This alternation facilitates remobilization and reprecipitation of manganese and to a much lesser extent iron and associated trace metals in the soils. Optimum conditions for manganiferous soil concretion development are encountered on the Schofield Plateau, where mean annual rainfall exceeds 1000 mm/year but where there is a net evaporation loss from the soils during the dry period (May through October). Remobilization of manganese is less pronounced in the oxisols of Molokai and Lanai, where mean annual rainfall is lower. Thin manganiferous coatings rather than concretions therefore form in these islands.

The contents of Mn, Fe, Cu, and Ni of the soils on which Hawaiian concretions form are higher than those of New Zealand soils in which manganese soil concretions are found. This is reflected by the much redder color of the Hawaiian concretion-bearing soils compared with their New Zealand counterparts. Rare earths show an enrichment sequence: parent rock → soil → soil concretion. A small positive Ce anomaly is noted in the soil and is more marked in the concretions. This may be due to the increasing oxidation of Ce in the concretions relative to the soil, although contamination of the soil by concretionary material may also play a role. The parent rock shows no Ce anomaly. Barium and Pb are enriched in concretions relative to the surrounding soil, whereas U, Th, Hf, Nb, Zr, and As are present in similar or higher concentrations in the soil relative to the concretions. Arsenic may follow Fe in the soils. Todorokite is the predominant manganese mineral in the Hawaiian soil concretions, not pyrolusite as previously reported. Scanning electron microscope studies show the crystalline nature of the manganese oxide minerals in the concretions.

CONCRETIONS ENRICHED IN iron and manganese with respect to surrounding soil material are relatively common in soils throughout

the world (Bryan 1952; Childs 1975; Childs and Leslie 1977; Norrish and Pickering 1977; Ross, Franzmeier, and Roth 1976; Sindhu et al. 1977), and the occurrence of manganiferous and ferruginous concretions in Hawaiian soils has previously been reported by Patterson (1963, 1971); Sherman (1959); Sherman and Kanehiro (1954); Sherman, Ikawa, and Matsusaka (1969); Sherman, Tom, and Fujimoto (1949); and Walker (1964). Manganiferous soil concretions have been located in pineapple and sugar cane plantations of the Schofield Plateau, Oahu.

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In addition, black coatings of manganese oxides are seen on the surface of soils on the tops of embankments and on the surfaces of volcanic pebbles exposed above the soils associated with the pineapple plantations. Manganiferous and ferruginous deposits have also been reported in other regions of the Hawaiian Islands. Sherman, Tom, and Fujimoto (1949:120), for example, have reported a thin layer of MnO_2 around shrub roots in Lanai, and ferruginous concretions have been reported in certain soils from various localities on Kauai and Oahu (Sherman and Kanehiro 1954, Walker 1964). Black manganese coatings (1 mm or more in thickness) on weathered basalt and displaying botryoidal surface textures have also been noted in a 4-m embankment in Kahaluu, Oahu (S. V. Margolis, personal communication).

From the soil, geological, topographic, and rainfall maps of the islands of Oahu, Molokai, and Lanai (College of Tropical Agriculture 1971, McCall 1973), it is apparent that the pineapple plantations of these three islands have been established in oxisols (derived from volcanic rock) in areas of gentle slope. In the Oahu plantations, the soil is Wahaiwa Series; in Molokai, Molokai Series; and in Lanai, mainly Molokai and to a lesser extent Lahaina Series (Ruhe et al. 1965, United States Department of Agriculture Soil Conservation Service 1972). The parent rock from which these soils are derived is the Koolau volcanic series on Oahu and the West Molokai volcanic series on Molokai and Lanai. The plantations are generally at an altitude of 150 to 300 m, extending up to 600 m in Lanai. Rainfall in the region is variable due to the influence of the mountain ranges on a maritime climate, but in the region of the pineapple plantations the mean annual rainfall is of the order of 1000 mm/year on Oahu, 750 mm/year on Molokai, and 500 to 700 mm/year on Lanai. This compares with a value of 6000 mm/year in the Koolau Range, Oahu, overlooking the Schofield Plateau. The dry season for these islands is May to October, and monthly rainfall values in the plantations would be of the order 25 mm on Oahu, 12 mm on Molokai,

and 6 to 18 mm on Lanai in the dry season. This would increase to monthly average values of 125, 100, and 50 to 100 mm, respectively, for the rest of the year. The reasons for the lack of manganiferous concretions in the soils of the pineapple plantations of Molokai and Lanai are not known but may be related to the nature of the parent material (i.e., lithology, Mn and Fe contents, redox and pH characteristics) or, more importantly, the hydrological balance (and therefore the leaching and evaporation characteristics) in the regions in which these soils occur. In this paper we report on the geochemistry, mineralogy, and mode of formation of manganiferous soil concretions from the central plateau of Oahu, Hawaii.

SAMPLES

The concretions and surrounding soil sample were collected from a roadside site on route 99 on the Schofield Plateau, Oahu (Figure 1; cf. Macdonald and Kyselka 1967), at an elevation of approximately 280 m. The region is one of extensive pineapple and sugar cane plantations situated between the Koolau and Waianae ranges (cf. Macdonald and Abbott 1970).

The soil in which these concretions occur is dark red (2.5YR 3/6) and this constitutes the upper 2 cm of the soil profile. Below this, the soil is very dusky red (10R 2.5/2). The concretions are typically in the range 4 to 9 mm in maximum diameter, ellipsoidal to spheroidal with smooth surface texture, and found on or near the surface of the soils. Internally, the concretions are massive to vaguely concentrically laminated with no apparent nuclei. Surface densities of concretions larger than 5 mm diameter were estimated to be up to 600/m². For analytical purposes the two concretion samples are composites of concretions from the same site.

The concretions are observed in the soils of both the pineapple and sugar cane plantations, but are not distributed throughout the entire Schofield Plateau. Mulch paper (asphalt tarred paper) used to be laid just beneath the surface of the soil in the pineapple

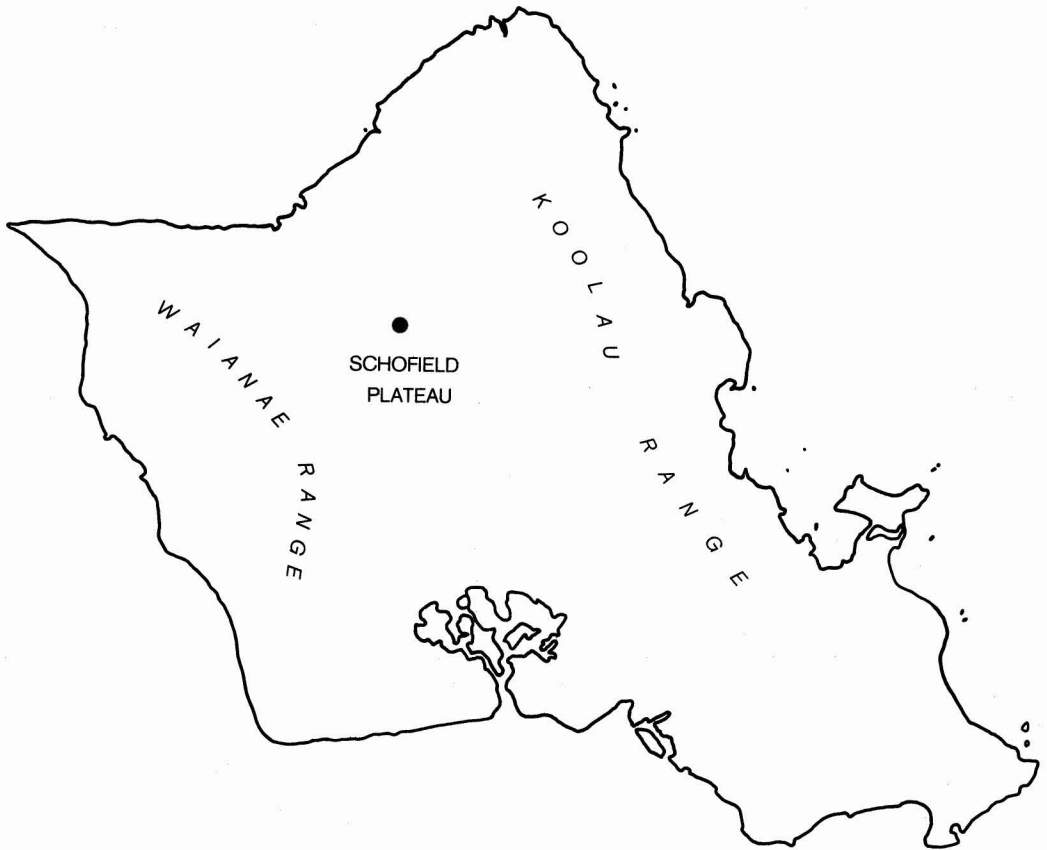


FIGURE 1. Schematic diagram showing location of soil concretions on the Schofield Plateau, Oahu, Hawaii

plantations to reduce soil moisture loss and to control weeds, although nowadays black polythene sheets are used. This sheeting marks the boundary between the two soil colors noted above.

ANALYTICAL METHODS

Scanning Electron Microscopy

The procedures used were those described in Margolis and Glasby (1973) on a fractured, unpolished surface of a concretion.

X-ray Fluorescence Analysis

Major elements in the soil concretions and surrounding soil sample were determined using the method of Norrish and Hutton

(1969) on a Siemens wavelength dispersive XRF. An Fe-mica standard (Flanagan 1973), a G-2 standard (Flanagan 1973), and a synthetic mixture (composition similar to manganiferous concretions) of three standards [BCS 176/1 (Mn ore), BCS 303 (Fe ore sinter), and BCS 269 (firebrick)] were used to assess the accuracy of the analyses as better than 3.5 percent for the major elements.

Spark-Source Mass Spectrometry

The samples were prepared as follows: They were ground with an agate mortar and pestle to pass a 50- μ m nylon sieve, added to an equal quantity of ultrapure graphite containing 500 ppm Lu_2O_3 internal standard, and thoroughly mixed in a polythene vial. Electrodes were formed using a polyethylene die and hydraulic press (Taylor 1965). The

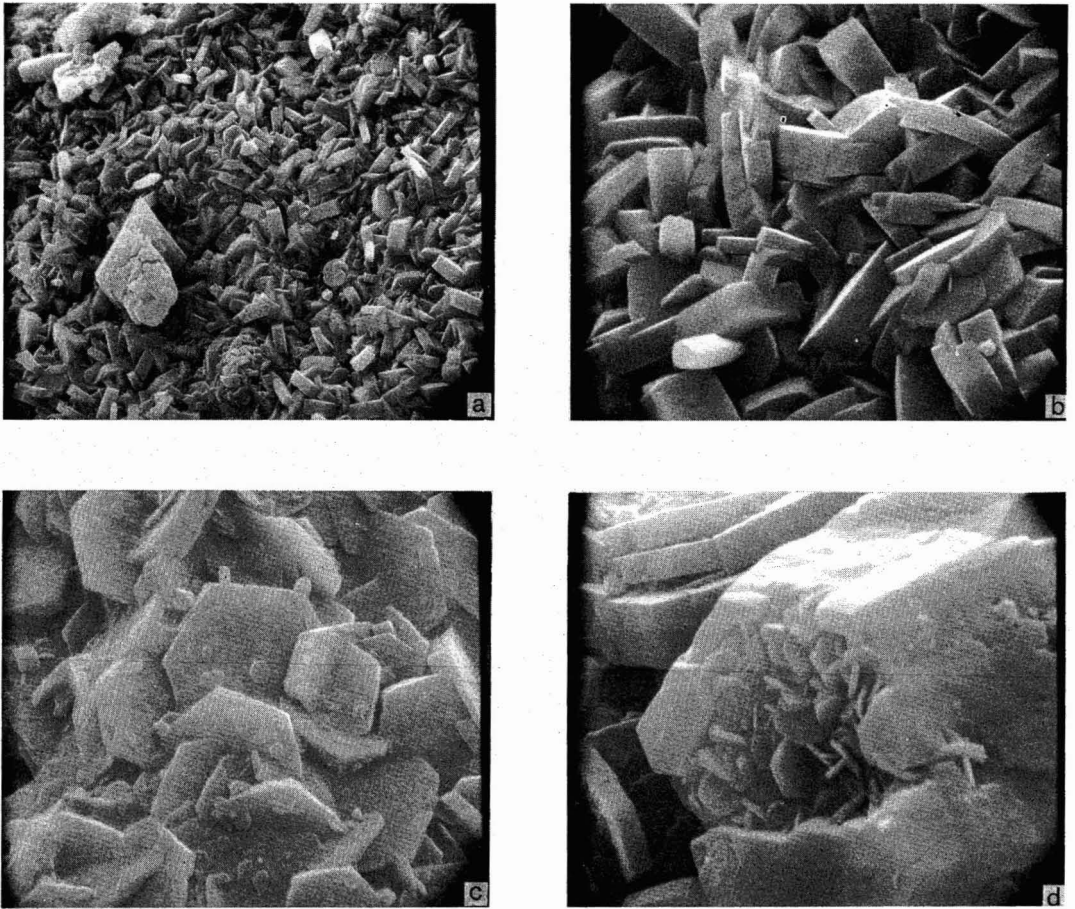


FIGURE 2. Scanning electron microscope photograph of fractured internal surface of Hawaiian soil concretion: *a*, mass of prismatic and tabular crystals (1440 \times); *b*, prismatic and tabular crystals (7500 \times); *c*, hexagonal platelets (3660 \times); *d*, hexagonal platelets on surface of larger prismatic hexagonal crystal (7200 \times).

electrodes were mounted in an AEI MS702 mass spectrograph, and sparked with a radio-frequency voltage of 20 kV at 100 pulses/sec with a 200 μ S pulse length. Standard Q-2 photoplates were used to detect the dispersed ion beam. Optical densities of the line images of selected isotopes on the photoplate were measured with a Zeiss densitometer. Isotopes of Hf, Yb, Er, Nd, and Ba were used to determine the Q-2 emulsion response curve (Taylor 1971). After determination of the average isotope to internal standard ratio from individual exposures, the element concentrations were obtained from standard curves derived from the analysis of United States Geological Survey, Japanese, and South African rock standards.

The mass spectrometric data are considered to have a precision of better than ± 15 percent. The accuracy of the data is related to the reliability of the standard rock data, and also to the presence of interfering ions in the mass spectra. Manganese soil concretions can have elevated levels of Ba, and complex ions of barium carbide can contribute significantly to the mass spectrum. The concentrations of elements such as Gd, Tb, and Dy could be anomalously high due to the presence of interfering ions. Such anomalies can be observed in the published data for two New Zealand soil concretions (Rankin and Childs 1976). The Arapohue and Waimatenui soil concretions have Ba concentrations of the order of 1 percent, and the interference

ions of barium carbide have produced anomalously high apparent concentrations for Gd, Tb, and Dy. The Hawaiian soil concretions studied here have a much lower Ba content (approximately 0.1 percent), and interference effects are much reduced.

RESULTS

Scanning electron microscope (SEM) studies of the concretions show that the surface is relatively featureless and almost smooth, although somewhat grainy. In cross section at high magnification, however, the fractured internal surface of the concretions is seen to consist of a mass of euhedral crystals and interpenetrating twins showing well-defined crystal planes in all directions. Typically, these crystals are 1.5μ long and 0.5μ in diameter (Figure 2a, b). Also present to a much lesser extent are hexagonal platelets (Figure 2c). These sometimes grow within a larger crystal (Figure 2d). Each side of these platelets is about 4μ long and the platelets are about 1μ thick. Smaller platelets with sides 0.5μ long are also observed. These crystal sizes are large considering the usual cryptocrystallinity of natural ferromanganese oxide minerals (Johnson and Glasby 1969) and are the same size range as laminations in deep-sea nodules [typically in the range 0.25 to 10μ according to Margolis and Glasby (1973)]. The appearance of masses of crystals at high magnification under SEM is totally different from the structure of deep-sea manganese nodules where well-developed crystals are rarely observed even on fracture surfaces, although some much poorer examples have been reported (Brown, Pabst, and Sawyer 1971; Fewkes 1976, p. 131, fig. 49, p. 132, fig. 51; Glasby 1978; Glover 1977; Xavier 1976). Although no definite assignment of mineralogy can be made, it is believed that the elongate crystals are todorokite, whereas the less abundant hexagonal platelets are birnessite (cf. Burns and Burns 1977). Woo (1973, p. 169, fig. 12), for example, has identified as birnessite hexagonal platelets that have identical dimensions to those described here. The interpretation of the SEM pictures may be complicated if

TABLE 1
X-RAY FLUORESCENCE ANALYSIS (%) OF ELEMENTS IN
HAWAIIAN SOIL CONCRETIONS AND ADJACENT SOIL

	CONCRETION 1	CONCRETION 2	SOIL
SiO ₂	19.07	18.89	31.84
Al ₂ O ₃	26.43	26.19	31.54
Fe ₂ O ₃ *	9.21	9.24	15.87
MgO	0.66	0.60	0.55
CaO	0.23	0.24	0.12
Na ₂ O	N.A.	N.A.	N.A.
K ₂ O	1.14	1.14	1.68
MnO	21.33	21.53	1.33
TiO ₂	1.49	1.51	2.72
P ₂ O ₅	0.02	0.02	0.09
L.O.I. [†]	17.33	17.50	14.23
Total	96.91	96.86	99.97
Cu [‡]	0.33	0.29	0.04
Ni [‡]	0.29	0.43	0.04

NOTE: N.A. = not analyzed.

* Total Fe as Fe₂O₃.

[†] L.O.I. weight loss following ignition to 1000°C for 1 hr; Cu and Ni were determined on dried sample without ignition.

[‡] Copper and Ni data obtained by EDAX X-ray fluorescence spectroscopy at the University of Hawaii (M. A. Meylan).

the elongate crystals are in fact only platelets on their side. The observations do, however, agree with the X-ray diffraction data, which show the dominant manganese mineral in the soil concretions to be todorokite. It should be noted, however, that Burns (quoted in Curtis 1977, p. 371) considers lithiophorite to be the dominant manganese mineral in these concretions. The reasons for the well-developed crystallinity of these concretions, compared with deep-sea nodules, is not understood at present but it may reflect the slow growth rate of these concretions compared with deep-sea nodules (about $3 \text{ mm}/10^6$ years) or, more probably, the low Fe/Mn ratio (of the order 0.4) of the concretions.

The major element composition of the two concretions and adjacent soil is given in Table 1. The Mn contents of the concretions are in general agreement with those previously reported by Sherman et al. (1949), and the soil concretions are seen to display a high Mn/Fe ratio (2.6) and to be enriched in Cu and Ni compared to the underlying soil. Iron is, however, higher in concentration in the soil than in the concretions. X-ray diffraction patterns indicate that the concretions contain, in order of apparent abun-

TABLE 2

SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSIS (PPM)
OF RARE EARTH AND TRACE ELEMENTS IN HAWAIIAN
SOIL CONCRETIONS AND ADJACENT SOIL

	CONCRETION 1	CONCRETION 2	SOIL
La	54	53 (73)	23
Ce	>200	>200 (1,460)	110
Pr	21	19	5.9
Nd	91	82 (119)	23
Sm	28	25 (34)	5.0
Eu	8.7	7.5 (11)	1.6
Gd	20	16 (20)	4.1
Tb	2.5	2.4 (3.1)	0.52
Dy	13	12	2.8
Ho	2.0	1.8	N.A.
Er	6.0	4.4	N.A.
Yb	4.6	3.5 (4.8)	1.9
U	2.9	2.9	2.9
Th	10	10 (10)	12
Pb	>100	>100	23
Hf	2.8	2.8 (4.5)	4.3
Ba	>1,000	>1,000	320
Nb	14	11	21
Zr	160	130	230
Y	37	33	19
As	20	20	>35

NOTE: N.A. = not analyzed. Data in parentheses obtained by P. J. Potts and M. Sarre (Open University, England) by neutron-activation analysis. See Figure 3 for graphical comparison of neutron-activation and mass spectrometric data.

dance, kaolinite, quartz, gibbsite, hematite, and todorokite, whereas the underlying soil contains quartz, kaolinite, gibbsite, and hematite. The concretions do not contain pyrolusite as previously reported by Sherman et al. (1949).

Table 2 lists the concentration of the rare earth elements (REE) in the two manganese soil concretions and their surrounding soil. It has become a standard practice to normalize REE concentrations in iron-manganese concretions with respect to a standard material such as shale (Piper 1974). Figure 3 shows the distribution of REE in the analyzed samples relative to the mean concentrations in shale (as given by Haskin and Schmitt 1967). Comparison of the rare earth data of the soils with those of Hawaiian basalts (Schilling and Winchester 1966) shows that the rare earths are enriched in the soil (with a positive Ce anomaly) relative to their source rocks. With the exception of the Arapohue soil concretions, the rare earth contents in

the Hawaii concretions and soil are higher than those of their New Zealand counterparts (Rankin and Childs 1976).

Figure 4 shows the variation of enrichment factors (concentration in concretion/concentration in surrounding soils) with atomic number. The pattern of REE enrichment is similar to that observed in the group 2 soil concretions studied by Rankin and Childs (1976).

Hawaiian soil concretion 2 was analyzed by neutron-activation analysis (P. J. Potts, personal communication). The data are plotted in Figure 3. Although the absolute REE concentrations differ from those obtained by mass spectrometry, the shale-normalized patterns are similar.

Table 2 also lists a number of other trace elements determined by spark-source mass spectrometry. Childs (1975) has previously shown that Ba and Pb are enriched in New Zealand soil concretions relative to the surrounding soil. Barium was shown to be largely associated with the Mn-rich phases of the concretions rather than the Fe-rich phases. The Hawaiian soil nodules are markedly enriched in Ba and Pb relative to the surrounding soil. Yttrium is also similarly enriched in the Hawaiian soil concretions. The pattern of enrichment of these trace elements in the Hawaiian concretions relative to underlying soils differs from those of New Zealand. The elements U, Th, Hf, Nb, and Zr are present in either similar or higher concentration in the soil relative to the concretions. The depletion of elements that are not chemically involved in concretion formation in the concretion relative to the soil is attributable to the dilution effect, in weight per weight terms, which occurs when Mn and Fe oxides precipitate in the pores among soil particles.

DISCUSSION

The formation of ferromanganese concretions in soil profiles is well known and is due to the ability of iron and manganese to change their oxidation states in response to Eh and pH changes in the associated naturally

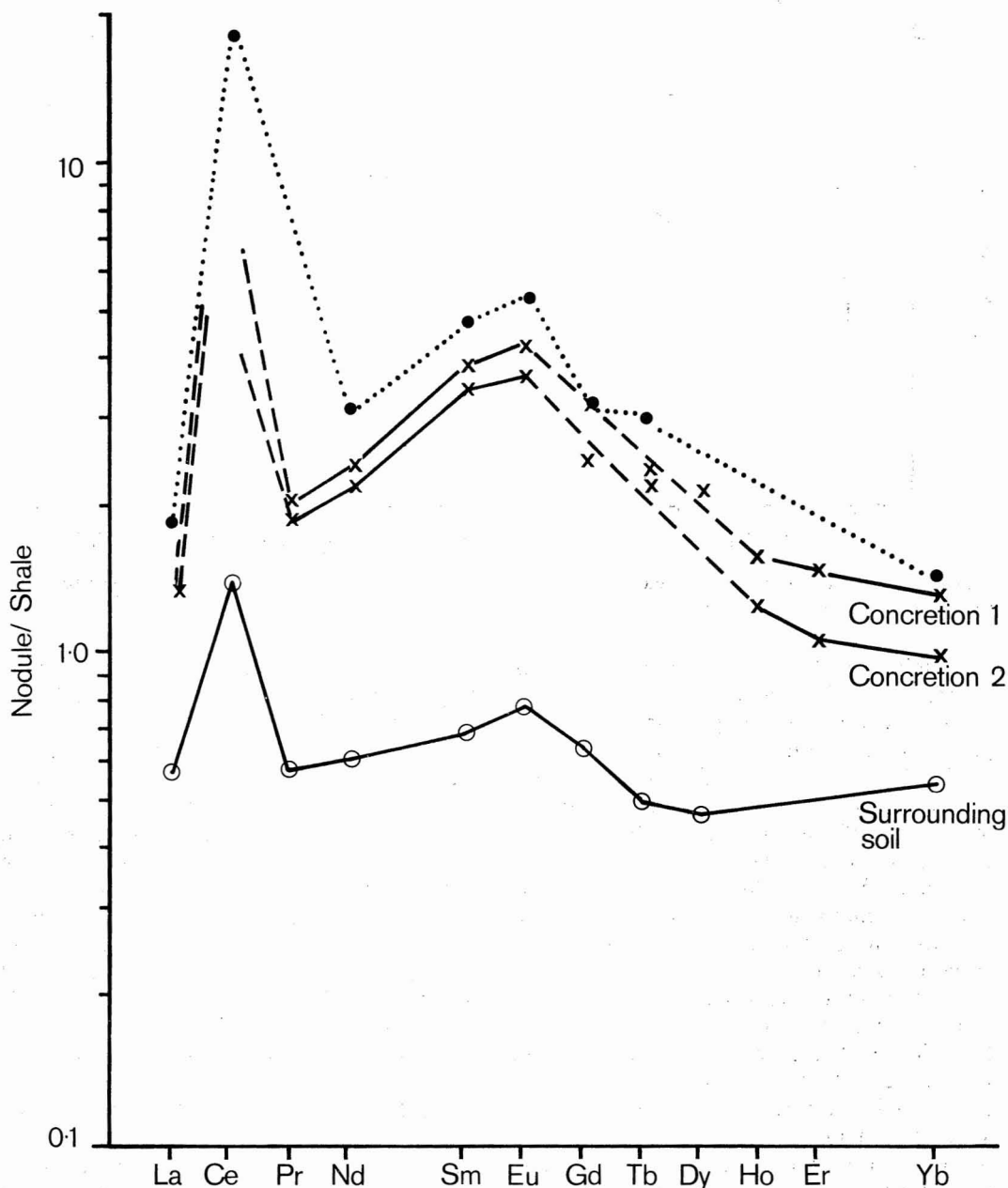


FIGURE 3. Shale-normalized rare earth concentrations for two Hawaiian soil concretions and their surrounding soil. Dotted line refers to neutron-activation analysis data obtained by P. J. Potts and M. Sarre.

occurring aqueous system (Childs 1975). In the case of the manganiferous concretions studied here, it seems probable that the formation of the deposits is related to leaching of manganese from the associated soils during

the wetter season of the year and precipitation as concretions or coatings during the drier seasons (i.e., conditions of intermediate annual rainfall). The more immobile Fe is left behind in the soil under these conditions.

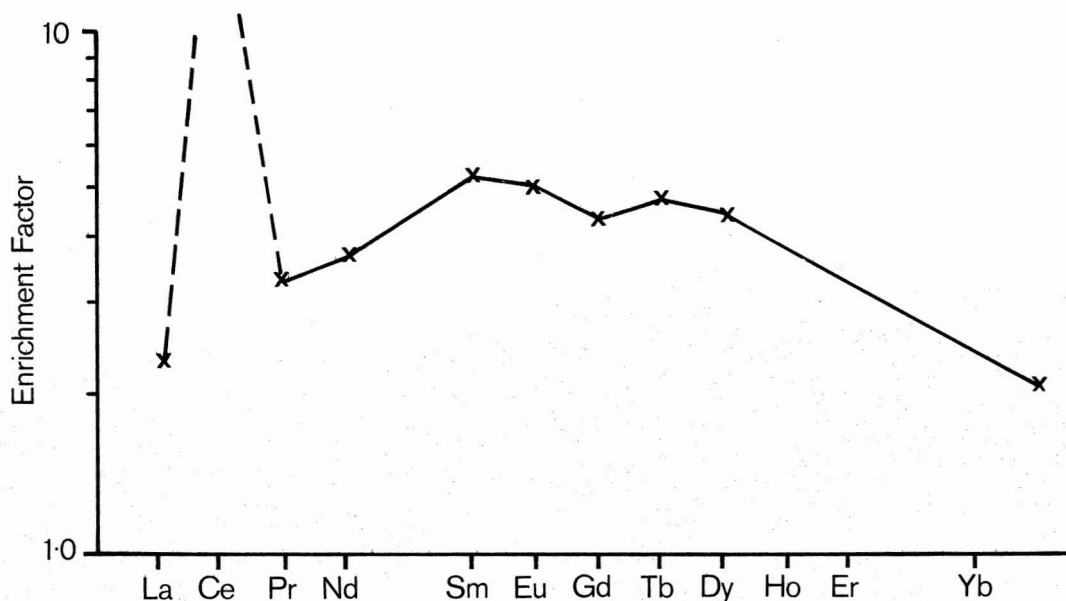


FIGURE 4. Rare earth enrichment factors (average concentration in soil concretions/concentration in surrounding soil) for Hawaiian soil concretions.

The higher Mn/Fe ratio of these concretions compared to the underlying soils therefore reflects the more facile migration of Mn compared to Fe in aqueous systems (Krauskopf 1957). By contrast, ferruginous concretions on the Hawaiian Islands are generally found in regions of higher rainfall than on the Schofield Plateau, Oahu [in excess of 2500 mm/year; Walker (1964)], when manganese would be completely leached from the soil and iron mobilized and precipitated. This situation is reflected in high Fe/Mn ratios of these ferruginous deposits.

The trace element data for the two Hawaiian soil nodules are comparable and they have a total REE concentration approximately six times that in the surrounding soil. Iron-manganese concretions are able to concentrate and control the distribution of metal ions in soils (Jenne 1968). Rankin and Childs (1976) have shown that REE are associated with Mn enrichment rather than Fe enrichment in New Zealand soil concretions.

The Hawaiian soil nodules exhibit the characteristic positive Ce anomaly found in soil and marine manganese nodules (Glasby

1973, Piper 1974, Rankin and Childs 1976). The stabilization of Ce in the 4+ oxidation state within the oxidizing environment of the concretions is thought to be the cause of the marked Ce enrichment with respect to the other REE. The small positive Ce anomaly exhibited by the surrounding soil is probably due to microconcretions in the soil or "skins" of iron-manganese deposits on the soil particles. Alternatively, it may reflect the increasing oxidation of Ce on passing from parent rock to soil to soil concretion. The parent rock shows no Ce anomaly (Schilling and Winchester 1966).

Arsenic has been shown to be associated with Fe^{3+} in soil horizons (Goldschmidt 1954). Rankin and Childs (1976) suggested a relationship between As and Fe in New Zealand iron-manganese soil concretions. This relationship is also apparent in the Hawaiian soil concretions and their surrounding soil. The As concentration in the surrounding soil is considerably greater than that in the concretions. Phosphorus, like As, occurs in anion form in soil solutions and can be seen (Table 1) to be enriched in the surrounding soil.

Sherman et al. [1949, quoting the data of Kelley (1912)], have suggested that alternating wet and dry conditions of the soil are essential to the development of concretions of "pyrolusite" and "ferruginous-pyrolusite" concretions since they provide the conditions for the solution, leaching, oxidation, and precipitation of the manganese which are necessary for the process. According to these authors, "pyrolusite" concretions are not found in soils that receive sufficient rainfall to keep the soil in a moist condition throughout the year.

From the data presented here, it is suggested that the distribution of concretions may be rationalized in terms of the hypothesis put forward by Sherman, Tom, and Fujimoto (1949). In this, maximum mobilization of manganese from the soil occurs in the Wahiawa soils of the Schofield Plateau where mean annual rainfall exceeds 1000 mm/year. This high rainfall leads to a lowering of the pH, which facilitates transport of manganese in the soil. The manganese is then deposited as soil concretions during the dry season (May to October) when there is a net moisture loss from the soil due to an excess of evaporation over rainfall. The process of mobilization of manganese is progressively less well developed in the oxisols of Molokai and Lanai where the annual rainfall is lower. Thin manganiferous coatings, rather than concretions, form in these soils. The changes in rainfall significantly influence the characteristics of the Wahiawa, Molokai, and Lahaina Series soils, and the moisture regimes of these oxisols are described as udic, ustic, or torric depending on precise conditions [see McCall (1973) for definition of terms]. The precise mechanism for water loss from these soils, and therefore concretion formation, may be complex because of the complex water-holding capacity of oxisols (Tsuji, Watanabe, and Sakai 1975). Significantly, the Paaloa Series soils, which are upland soils between the Schofield Plateau and Koolau Range at altitudes of 300 to 520 m and with an annual rainfall of 1750 to 2250 mm/year, do not contain manganiferous soil concretions, although perhaps minor amounts of manganese oxides occur in the

upper few centimeters of some soils. The Mn content of the Paaloa soils is 0.06 percent on average (United States Department of Agriculture Soil Conservation Service 1972, p. 222, Table 6). Here, the annual rainfall is so high that sufficiently dry conditions never develop to facilitate deposition of leached manganese. In addition, the Wailua, Wai-pahu, and Ewa soils, which are alluvial material derived from the Schofield Plateau (Ruhe et al. 1965), contain manganiferous concretions to a depth of 17 m. Certainly, enrichment of manganese at such depths could not have taken place after deposition of the soils. These soils are middle to late Pleistocene. Interestingly, the Wahiawa soils of the Schofield Plateau display a color change from very dusky red above 30 cm in the soil profile to dark reddish-brown below that depth. This color change may reflect the fact that most of the manganese in the upper 30 cm is in the tetravalent state but is in the reduced form below that depth. Significantly, when this soil is tilled, the deeper soil rapidly assumes a darker color. This is compatible with the idea that manganese in the soil is being oxidized to the tetravalent state on exposure to air. The formation of manganiferous coatings on oxisols (as on embankments) is also dependent on the $pH_{z,p.c.}$ of the oxisol, which has been determined to be in the range 4 to 6 (Keng and Uehara 1973). Finally, it should be mentioned that two techniques of pineapple production are used in Hawaii. In the Dole plantations, the pineapple residue is left on the soil surface as mulch, whereas in the Del Monte plantations, the residue is burned off. Burning off would influence the amount of organic matter introduced into the soil and therefore the leaching characteristics of Mn and Fe in the soil. High organic content of the soil will facilitate movement of Mn and Fe by causing anaerobic conditions during water saturation.

Sherman and Alexander (1959) report that the oxisols studied here are similar to the "red earths" of Australia, Africa, and India and are very similar to the Terra Roxas of Brazil. An interesting test of the hypothesis presented here would be to identify the rela-

tionship between manganese soil concretion formation and rainfall characteristics in these other environments.

One interesting problem is the rate of accretion of these concretions. The oxisols on which these soil concretions form are generally found on remnants of old geologic surfaces (Keng and Uehara 1973), and on Kauai these surfaces have an age of about 1 million years (Beinroth, Uehara, and Ikawa 1974). However, based on the low content of eolian-derived quartz in the soils of the Schofield Plateau, Jackson et al. (1971) have suggested that considerable erosion and/or mass wasting of these soils has occurred since their formation in the mid-Pleistocene. The small size of the concretions therefore indicates either a very slow rate of accretion of these deposits (somewhat faster than deep-sea nodules) or, alternatively, periodic dissolution and reformation following tilling or periods of abnormally high rainfall. Agricultural practices in Hawaii are, however, too recent to affect significantly the overall mass balance of manganese in soils. Increased cold frontal rainfall in Hawaii during the last glaciation (P. C. Ekern, personal communication; Ruhe 1964; Selling 1948), for example, may have been sufficient to prevent concretion formation during this period and concretions may therefore post-date the end of the last glaciation.

Based on the data of Childs (1975), there appear to be several differences between the Hawaiian soil concretions studied here (Table 1) and New Zealand soil concretions. In particular, Hawaiian soil concretions are characterized by much higher contents of Mn, Cu, and Ni and lower contents of Fe than New Zealand soil concretions. The Mn/Fe ratio is also an order of magnitude higher in the Hawaiian concretions. The elements Mn, Fe, Cu, and Ni are all present in higher concentrations in the associated Hawaiian soils than in the associated New Zealand soils, but particularly notable is the higher concentration of Fe. These higher concentrations may be due in part to the higher contents of these elements in the parent rock from which the soils are derived, which in Hawaii is dominantly basalt and

in New Zealand loess, volcanic ash, andesite, or limestone (Childs 1975). There is considerable enrichment of elements during soil formation in Hawaii; the Mn and Fe contents of rocks from the Waianae ranges are on average 0.21 percent and 8.05 percent, respectively (Cross 1915, Macdonald 1940). From this, it is suggested that the parent material from which Hawaiian soil concretions is derived is generally much higher in the transition elements Mn, Fe, Cu, and Ni than in the New Zealand examples so far studied. In both cases, Mn, Cu, and Ni are enriched in the concretions relative to the soil, but in the Hawaiian situation Fe is depleted in the concretions relative to the soil and not enriched as in the New Zealand concretions. This suggests a more effective fractionation of Mn and Fe in the Hawaiian situation, possibly due to a more complex transport process involving a cycle of solubilization and precipitation of these elements during alternate periods of rainfall and aridity. The Mn and Fe contents in Hawaiian soils might suggest that Hawaiian soil concretions should be more prevalent than their New Zealand equivalents, although this would depend on rainfall and evaporation characteristics. Interestingly, soils from pineapple plantations are described as being iron-deficient (i.e., deficient in soluble iron) and ferrous sulfate is used as a fertilizer in this region. The extremely high Fe content (15.87 percent as Fe_2O_3) of the soil sample studied here suggests that at least part of the Fe may be derived from the application of fertilizers. The lower Fe content of the soil concretions (9.2 percent as Fe_2O_3), however, suggests that uptake of the iron from the fertilizer into the concretions has not taken place on any significant scale.

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