The elemental content of Niue Island soils as an indicator of their origin

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Abstract The major and trace element contents of 241 Niue Island lateritic soils were determined, mainly by X-ray fluorescence, to deduce soil origins. The analyses showed very low SiO_2 content, and a high content of Mg, P, V, Cr, Sr, Y, Hg, and α-counts, compared with other laterites worldwide. The distribution patterns are consistent with derivation by weathering from calcite and dolomite rather than from deposited volcanic ash. Weathering is a particularly novel explanation for the origin of the relatively high content of P in these soils. The soils contain a negative Ce anomaly, consistent with an origin from seawater or coral, but not volcanic ash. If recent results showing in situ formation of magnetite in soils are applicable, the soil mineralogy is wholly consistent with an origin from calcite/dolomite. An origin from calcite is also consistent with the relative lack of volcanic ash on the seabed nearby, and very low deposition of aeolian dust. The radioactivity content is consistent neither with calcite/dolomite weathering, nor volcanic ash origin, but may have originated, like a few of the stable elements, from rising hydrothermal solutions.

Keywords Niue Island; weathering; cerium; phosphate; chromium; yttrium; mercury; soils

INTRODUCTION

The aim of this study was to determine the origin of the lateritic soils of Niue Island by analysis of the stable element and radioactive content.

Niue Island is a raised atoll to the east of the Tonga Group and situated at about 19°S. The island consists of porous coral and dolomite, and there are no surface streams. No surface rocks other than aragonite, dolomite, and calcite have been found, and drilling has not yet reached basement volcanic rock.

The soils are unusually radioactive (Marsden et al. 1958), and the radioactivity has been shown to be due to ^{230}Th and ^{231}Pa and their daughters (Whitehead et al. 1992), the parent radionuclides being almost absent. The Hg content is surprisingly high (Whitehead et al. 1990).

A survey was initiated more than a decade ago by the Soil Bureau of the New Zealand Department of Scientific and Industrial Research (now Landcare Research New Zealand Limited), partly to shed light on the origin of the soils and partly to assist in understanding the particular problems of fertility. The major element analyses formed the basis of the previous internal reports of Blakemore et al. (1979), Leslie (1986a), and the soil map of Leslie (1986b). All analysis results including trace element values are now available in an internal report (Whitehead et al. 1991).

The interior of the island carries thin lateritic soils classified (Blakemore et al. 1979) as inceptisols, mollisols, or oxisols. The inceptisols fell into the subgroups typic ustropept and oxic (ruptic-lithic) ustropept. The oxisols were typic eutrostox and tropeptic eustrostox. The mollisols were typic haplustoll, lithic haplustoll, ruptic-lithic haplustoll, and entic haplustoll. The mineral content consists mainly of gibbsite, goethite, crandallite, and boehmite, and the soils cover an irregular surface of weathered, pinnacled coral and dolomite.

In this paper we present some details of the analyses, an overview of the element distribution, and some deductions about the soil origins.

There is much debate about the origin of lateritic soils found on island limestones. The following hypotheses are typical: (1) soil washed in from nearby (Ahmad et al. 1966); (2) simple erosion (Sinclair 1967; Bosch et al. 1982); (3) weathering of volcanic ash (Comer et al. 1980); (4) weathering of aeolian dust (Land et al. 1967; Blackburn & Taylor 1969, 1970; Bricker & Mackenzie 1970; Macleod 1980; Rapp 1983; Muhs et al. 1987, 1990).

Extensive Pacific island soil studies have been carried out by the French ORSTOM centres in Tahiti and New Caledonia. In summary, they show that extreme weathering of volcanic rock can produce soils remarkably low in silica, and the authors believe volcanic ash is the origin of most of these soils, even when an origin from weathering of coral would seem more obvious.

Most mature soils formed on volcanic rocks still contain much more silica than alumina and a substantial clay content (Tercinier 1965; Tercinier & Quantin 1968). This is not similar to Niue Island soils. However, the most extremely weathered soils contain very little silica, and TiO_2 increases to 8–18%, probably associated with the magnetite (Tercinier 1974). Various authors (Latham 1980–81, 1983; Jamet 1986; Jamet & Trichet 1987a; Jamet et al. 1990), re-surveying what was known about soil development on volcanic ash in Pacific islands, showed that if the rainfall was >2000 mm/yr, clay formation was prevented because silica was almost completely leached away. An environment rich in Ca and Mg also prevented clay formation. This was demonstrated from

Tahiti, Fiji, Vanuatu, Reunion, Rennell, and Jamaica. Niue Island was also claimed as an extreme example. Phosphate in these soils was mainly immobilised by iron. Remnant minerals from the volcanic rock were mainly titanomagnetite, with occasional anatase and augite. There were significant quantities of goethite, gibbsite, and hematite.

The authors argued that even on coral surfaces, the main origin of soils was deposited volcanic ash, or pumice (e.g., the Loyalty Islands (Tercinier 1971b, 1972) which contain pumice on lower terraces).

Various authors (Tercinier 1969; Tercinier & Latham 1980–83; Jamet & Trichet 1987b), and particularly Tercinier (1971a) in a detailed review article, examined Pacific island soil development on coral rather than volcanic rock. There is low silica, alumina, and iron oxide in young coral-derived soils, but high phosphate. Mature soils develop to a composition hard to differentiate from that supposed to originate on volcanic ash. Silica is usually absent. Aluminium is much more concentrated and present as boehmite, but sometimes as gibbsite. The phosphate is in the form of crandallite or hydroxyapatite, depending on the presence or absence of Al, respectively. For many islands, an improbable 400 m of coral would have to be weathered to produce the soils, which was unlikely since the surfaces are geomorphically young. They rule out dust or basaltic ash input, but argue without presenting details that trace mineral composition indicates a pumice or dacitic ash input. One difference from volcanic rock soils is that the latter often contain augite and usually TiO_2 as anatase.

In contrast, this study presents evidence that revives the possibility of a major contribution from weathering of calcite/dolomite to soil formation.

METHODS

Samples were collected in 1978. Because of difficulties in penetrating the scrub, they were taken near roads, but all soil types were surveyed. Ninety-nine sites were selected for detailed soil analysis, and samples were taken of all horizons above the underlying rock.

Samples were analysed for their radioactivity by measuring the α and β emissions in a Beckman Widebeta II proportional gas flow counter. A constant thickness of soil was placed in stainless steel planchets and counted for 1000 min. Appropriate filters and circuitry gave results both for β-counts and α-counts. Several samples were analysed several times as a check on internal consistency, which was generally good (i.e. the results were the same within uncertainties derived from counting statistics).

Most of the analyses for major and trace elements were carried out by X-ray fluorescence analysis using a minor modification of the tetraborate-sample fusion technique (Norrish & Hutton 1969). The instrument used was a Siemens SRS–1 sequential X-ray fluorescence spectrometer fitted with a chromium target tube and 10 position sample changer. The spectrometer was interfaced to a PDP–11/05 computer and ASR–33 teleprinter.

Element concentrations were obtained by comparing the ratios of counts obtained from the sample and a precalibrated multi-element standard. For both major and trace elements, extensive correction for matrix effects was carried out using the computer. Suitable corrections were made for background.

Seven soil samples from Niue Island (sites N1 (a and c), N2, N3, N4, N5, 106b; Fig. 1) and one each from Atiu and
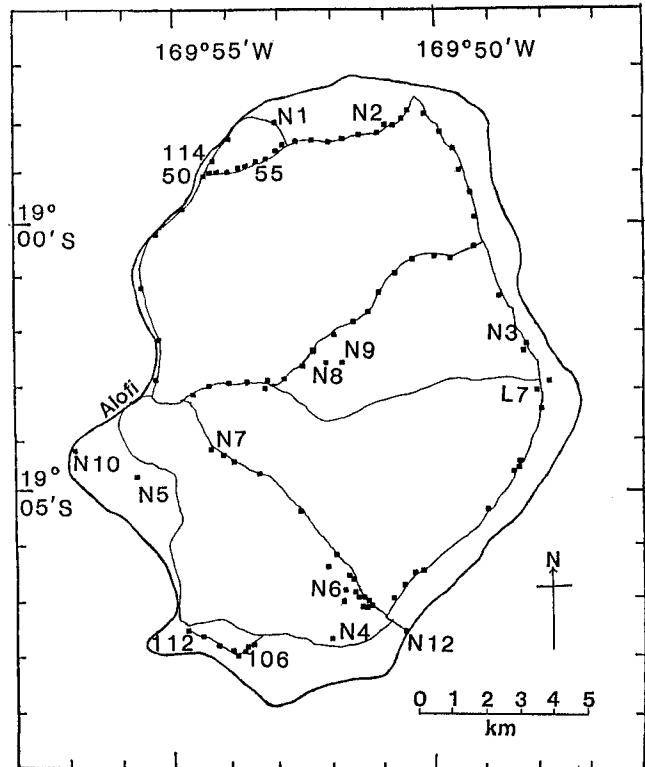

Fig. 1 Locations of sampling points on Niue Island named in the text. Other points marked are the remainder of the sampling network. Tafalomahina soils are near point N8 and a few sampling points immediately to the north.

Aitutaki (Cook Islands; Soil Bureau sample sites 9554 and 9045B, respectively) were analysed by spark-source mass spectrometry, mainly for the rare earth elements. Samples ground to <50 μm were combined with ultrapure graphite and Lu_2O_3, and mixed to form an electrode which was sparked in an AEI MS702 spark-source mass spectrometer. Isotopes of Hf, Yb, Er, Nd, and Ba were used to determine the Q2 photographic emulsion response, and concentrations were determined by comparison with analysis of USGS standard rocks (for further details see Rankin & Childs 1976).

RESULTS

The full results are available in a technical report (Whitehead et al. 1991) in which details of all analyses for each site are given. Here, we present only summary statistics with fuller discussion and interpretation.

The results are shown in the form of histograms in Fig. 2. They show that major and trace elements tend to be approximately normally and log-normally distributed, respectively. They are given for A, B, and C horizons only, there being only four analyses of the underlying rocks, tabulated separately in Table 1. The results were close to the detection limits for some of the elements. The extreme example is Rb for which most of the results are at the detection limit of 2 mg/kg; hence the upper and lower quartiles are also 2 mg/kg. The data sets for K_2O and SO_2 also contain many points near the detection limit, which is 0.01% for both elements. In some cases, the ranges in the distributions are unusually wide, particularly for MgO, Zn, and Ni, in which there are a small number of very
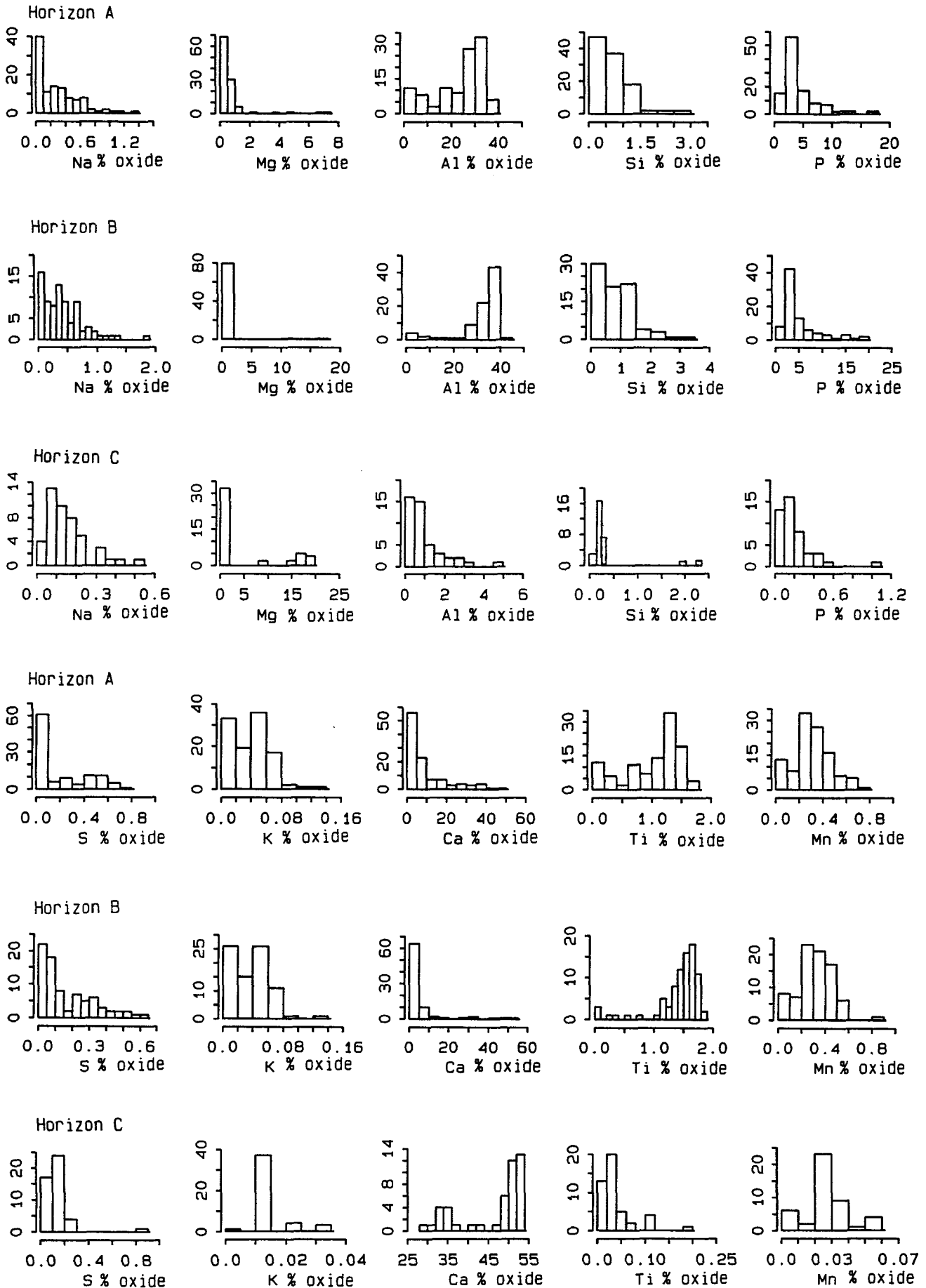
Fig. 2   Histograms of elemental values in Niue Island soils. "c/m" for the α and β counts means counts per minute.   (*continued*)
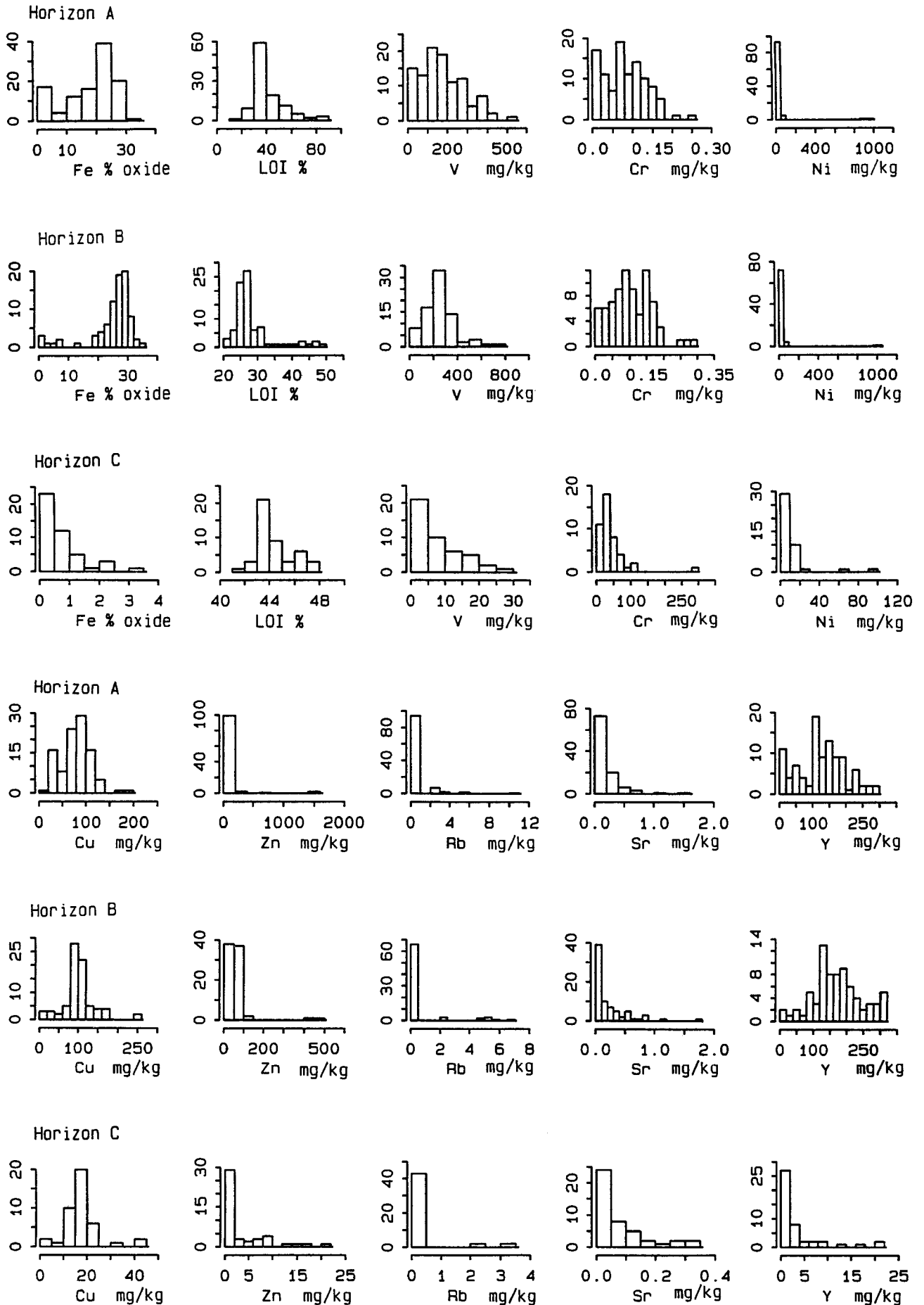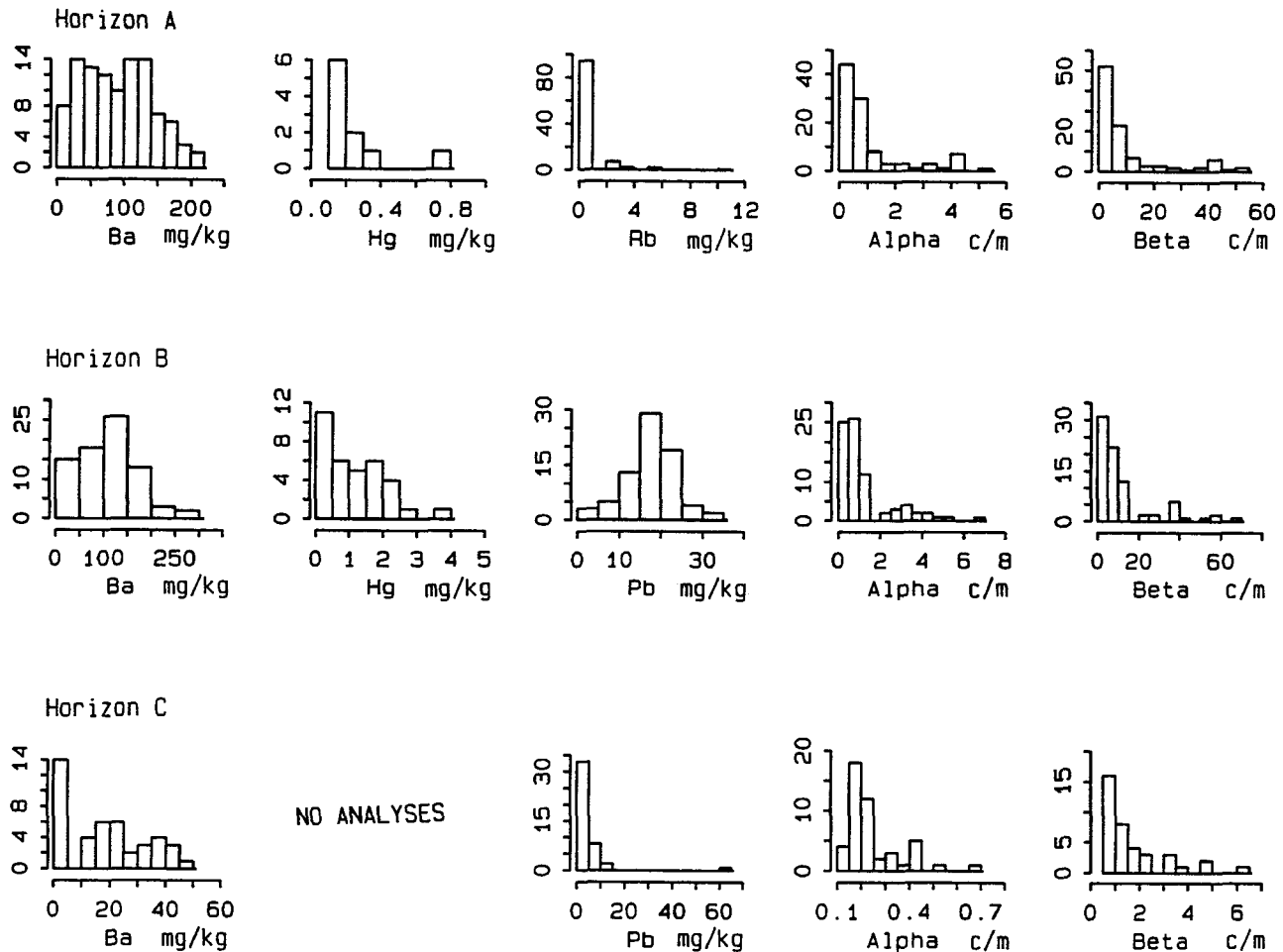
Horizon A

Horizon B

Horizon C

Horizon A

Horizon B

Horizon C

Fig. 2   (*continued*).

Horizon A

Horizon B

Horizon C

NO ANALYSES

Ba mg/kg   Hg mg/kg   Rb mg/kg   Alpha c/m   Beta c/m

Ba mg/kg   Hg mg/kg   Pb mg/kg   Alpha c/m   Beta c/m

Ba mg/kg   Pb mg/kg   Alpha c/m   Beta c/m

Fig. 2 (continued).

Table 1 Analyses of rocks underlying soils. For locations see Fig. 1.

	N7	N8	N10	N12
Na	0.1	0.18	0.19	0.32
Mg	17.88	4.11	1.12	1.45
Al	1.6	1.06	0.61	1.76
Si	0.2	0.23	0.23	0.24
P	0.16	0.13	0.21	0.93
S	0.15	0.11	0.19	0.18
K	0.01	0.02	0.01	0.02
Ca	32.36	48.29	51.94	49.37
Ti	0.06	0.03	0.01	0.05
Mn	0.02	0.02	0.02	0.02
Fe	1.29	0.92	0.4	1.28
LOI	46.42	44.34	43.75	43.03
V	37	<5	<5	<5
Cr	105	71	10	43
Ni	<6	9	<6	15
Cu	18	18	25	22
Zn	3	<3	4	5
Rb	<2.1	<2.1	N.A.	<2.1
Sr	283	207	N.A.	2553
Y	15.2	13	N.A.	10.9
Ba	<12	13	<12	29
Pb	4.3	<3.6	4.8	4.3
Alpha	523	N.A.	153	217
Beta	4833	N.A.	728	1159

Units: Elements Na-Fe % oxide; LOI (loss on ignition) %; V-Pb mg/kg; Alpha and beta counts are counts per 1000 minutes. N.A. indicates no analysis result available.

high results. The results for the major elements Al_2O_3 and Fe_2O_3 are skewed in the opposite way; there are a relatively small number of low results and most results are at the high end of the distribution.

Some statistical summaries of the results for major elements and trace elements appear in Tables 2 and 3, respectively. Included in Table 3 are results for Hg. These are taken from Barrie (1979), who used a gold film mercury analyser, and confirmed by a few analyses carried out at Chemistry Division, Department of Scientific and Industrial Research.

Results for the rare earth elements determined by spark-source mass spectrometry are given in Table 4, and the chondrite-normalised curves are shown in Fig. 3.

A contour map for P_2O_5 concentrations is given in Fig. 4 and for Cr in Fig 5. These two represent the two types of elemental distribution found (i.e. concentration in the centre or periphery of the island, respectively). The following showed some concentration in the centre: Mg, Al, Ti, V, Fe, Ni, Sr, Y, Hg, α-counts. The following showed some concentration at the periphery: P, Zn, Sr, Ba, Hg.

DISCUSSION

Elemental levels

In this discussion specific sites are sometimes referred to and their locations can be found in Fig. 1. Discussion refers to the A soil horizon unless otherwise indicated.

The results are compared with global means in Table 5. A good comparison with ranges is not possible since even the compilation of Schellmann (1986) does not include them. The values for the upper and lower quartiles for the Niue Island samples are unusually high for P_2O_5, Cr, Sr, Y, and Hg and unusually low for SiO_2, K_2O, Ni, Zr, and Ba. Most of the differences can be geochemically explained by the association with phosphate, or by intense weathering which has caused concentration of some elements and loss of others.

The values for Cr are high, but probably consistent with what can be expected from other Pacific laterites. Birrell et al. (1939) reported values of 1700 mg/kg in soils from Niue, and values of 1600 and 2400 mg/kg in soils from Western Samoa, with even higher values for soils from the Solomon Islands and Cuba.

The values for Hg are exceptionally high, closer to those expected of mineralised ground. This is considered by Whitehead et al. (1990) to be the result of the action of Hg-containing waters, though direct adsorption from seawater cannot be excluded.

The results for MgO include some high values which are consistent with the known dolomitisation of the interior of Niue Island.

Correlations

Figure 5 shows that Cr, in contrast to the P_2O_5 distribution, is concentrated in the centre of the island and is associated with the soils richest in bauxite. The α-counts, Fe_2O_3, TiO_2, and Y followed the same pattern of association.

The results for alphas and betas were highly correlated but showed no relationship to the K_2O content. The K_2O content was usually so low that it did not contribute significantly to the β-count, and the α and β counts were chiefly from [230]Th and its daughters.

Table 2 Results of major element analyses of Niue Island soils (A Horizon).

Element (%)	N	Med.	Min.	Max.	SD	LQ	UQ
Na_2O	99	0.28	0.03	1.11	0.22	0.20	0.41
MgO	98	0.34	0.10	7.13	1.11	0.22	0.69
Al_2O_3	99	27.2	0.25	38.9	10.8	16.2	31.0
SiO_2	99	0.64	0.11	2.6	0.49	0.30	0.84
P_2O_5	99	3.11	0.20	16.4	3.04	2.33	4.91
SO_2	99	0.05	0.01	0.79	0.23	0.01	0.43
K_2O	99	0.04	0.01	0.13	0.023	0.01	0.05
CaO	99	4.68	1.34	46.6	10.7	2.85	13.8
TiO_2	99	1.38	0.03	1.69	0.48	0.66	1.36
MnO_2	99	0.30	0.01	0.79	0.16	0.21	0.40
Fe_2O_3	99	21.2	0.5	28.6	8.5	11.4	23.7
LOI	99	37.1	19.0	86.3	12.9	34.2	46.2
Alphas	91	570	120	5450	1170	375	1030
Betas	92	4950	751	53000	12400	3090	10500

N is the number of analyses. Med. is the median. The alpha and beta analyses are counts per 1000 minutes. SD is the standard deviation of the distribution. LQ and UQ are the Lower and Upper quartiles.

Table 3 Concentrations of trace elements in Niue Island soils determined by X-ray fluorescence (Hg values (B horizon) measured by gold film detector).

Element	N	Med.	Min.	Max.	SD	LQ	UQ
V	95	164	5	425	104	83	235
Cr	94	770	5	2080	495	300	1130
Ni	91	9.0	6	981	164	6	22
Cu	91	80	19	192	31.6	58	93
Zn	94	46	4	1580	222	34	62
Rb	97	2.1	2	3.4	0.24	2	2
Sr	95	820	131	14700	2390	363	2350
Y	91	130	1	260	69	65	167
Ba	93	92	12	219	53	44	129
Hg	25	0.99	0.14	3.68	0.91	0.37	1.56
Pb	79	15	2.5	31.5	6.4	13.2	21.4

Units in mg/kg. Other conventions as in Table 2.

Table 4 Concentrations of rare elements in Niue Island soils determined by spark-source mass spectrometry. Their major element composition is also given.

Element	N1a	N1c	N2a	N3a	N4a	N5a	106b	Chondrite
Zr	105	88	105	95	100	100	32	
La	34	9.7	41	18.5	22	44	4.1	0.31
Ce	53	16.5	65	24	37	60	6.6	0.82
Pr	10	2.8	10.5	5.1	6.4	11.5	1.1	0.12
Nd	51	14.1	60	26	31	63	6.4	0.59
Sm	12.5	4.9	15	7.2	8.2	15.5	N.A.	0.2
Eu	4.0	1.65	4.6	2.3	2.8	5.0	N.A.	0.073
Gd	15	6.0	18.5	9.6	11.5	19.5	2.1	0.29
Tb	2.6	1.1	2.9	1.65	1.95	3.3	N.A.	0.049
Dy	20	7.8	23	13	15	24	4.1	0.31
Ho	5.8	2.5	6.3	3.8	4.5	7.1	1.25	0.073
Er	15.5	6.5	16	10.5	12	20	2.7	0.21
Yb	12	6.8	13.5	9.5	9.5	16	3.5	0.21
Mg	0.47	0.32	0.28	0.22	0.16	0.24	0.86	
Al	16.61	34.60	33.6	29.61	22.99	26.9	11.45	
Si	0.76	2.05	0.46	1.16	<1.3	0.29	1.29	
P	2.61	3.96	4.4	8.28	3.14	3.98	2.67	
Ca	18.82	2.64	2.83	4.56	15.43	10.17	33.09	
Ti	0.66	1.49	1.38	1.26	0.93	1.10	0.51	
Fe	11.29	25.53	24.83	22.14	16.94	19.42	7.91	

Units in mg/kg except for major elements which are the % oxide. N.A. indicates no analysis result available. The chondrite figures used for normalisation are included.

Fig. 3 Chondrite-normalised rare earth curves, with negative Ce anomaly indicated. Sites are shown in Fig. 1.
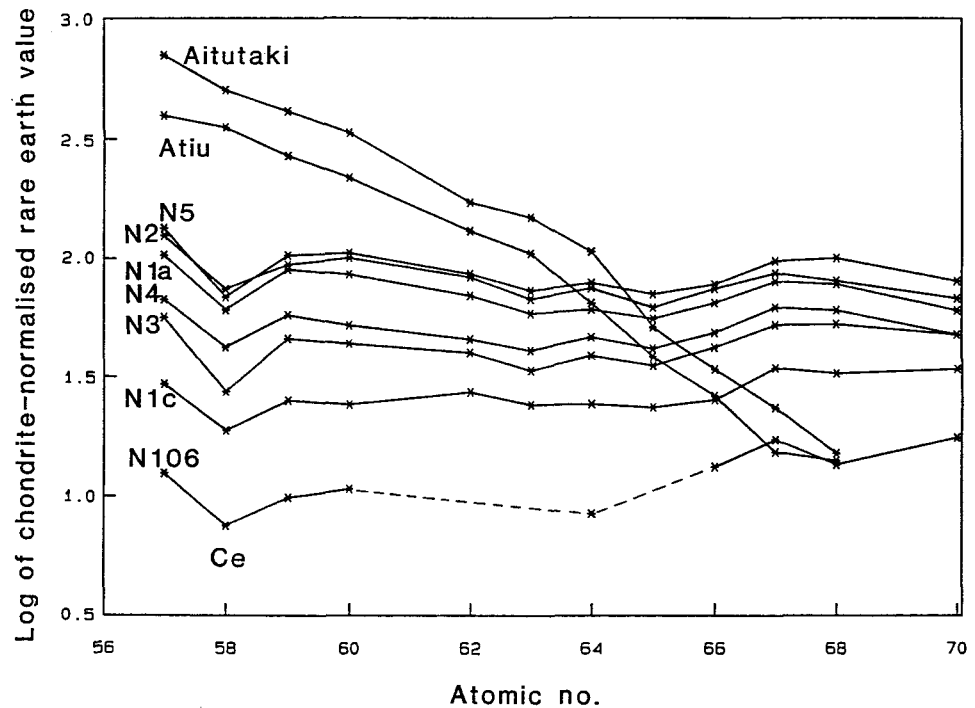
Figure 6 shows a correlation matrix for the elements. Correlations were often futile because of L-shaped relationships (like that in Fig. 7). There are, however, unequivocal correlations between Fe_2O_3, Al_2O_3, TiO_2, V, Cr, and Y in one group and between P_2O_5, Sr, Zn, and Cu in a second group.

Origin of phosphate

Figure 4 is the contour map of the P_2O_5 content. It shows that the highest values occurred mostly on the parts of the island nearest the sea (i.e. near the top of the uplifted ancient reef or on coastal ledges). The maximum value for P_2O_5 (18.56%, at site L7 in the B horizon, in the form of crandallite) was exceptionally high. The median was 3.11% (Table 2).

A closer examination of the data indicated high values for the Sr, Y, and Zn in the phosphate-rich soils, as also found by Altschuler (1980). Table 6 shows that the elemental signature for Niue Island soils, while typical of island phosphate, is not typical of marine phosphorite.

The origin of the phosphate concentrations on several Pacific islands has been somewhat controversial and the present work is very relevant to the debate. Hutchinson (1950) summarising the traditional view, strongly urged an origin from guano. More recently, Ayliffe et al. (1990) found that the oxygen isotopic composition of Nauru phosphate did not seem consistent with a guano origin. Many others such as Bourrouilh-Le Jan (1980) and Rodgers (1989) prefer a solutional-depositional hypothesis, and Rougerie & Wauthy (1989) prefer an endothermal upwelling hypothesis. The present results support, however, a new hypothesis— concentration during weathering of coral.

The content of phosphate in young soils directly on coral is typically low (0.03%; Tercinier & Latham 1980–83) but increases with maturity. Fieldes et al. (1960) and Jamet & Trichet (1987a), cite more mature atoll soils developed on beach rocks containing 6% (all the figures are in terms of P_2O_5). Other substrates produced soils with the following P

contents: dunes 14–20%; calcareous algae 6–17%; and marsh soils, up to 19%.

It is possible to compare the P elemental analysis results with a weathering index, which is used in later sections also. It might be thought that the most appropriate weathering index is $Ca/(Fe+Al)$ (all expressed as oxides), but extensive examination showed that the traditional weathering ratio $Si/(Fe+Al)$ gave similar but tighter relationships, and it was therefore preferred. The ratio is high if the material is relatively unweathered and low if it is highly weathered. This expresses the well-known observation that, during prolonged weathering, Si is leached away leaving Fe/Al-rich residues.

The P_2O_5 content plotted versus the weathering index (Fig. 7) is strongly L-shaped. The least weathered samples originate from material that is very low in P_2O_5; if $Si/(Fe+Al)$ > 0.4, then the mean P_2O_5 content is only 0.1%, and the highest value is 0.25%. This suggests that the soils originated from material relatively low in phosphate, not a phosphate deposit, for example.

When the weathering is advanced the phosphate is greatly enriched. This is because the form of the phosphate is crandallite, in which the phosphate is strongly bound (Borggnard et al. 1990). In most other soils, the opposite is true: as weathering proceeds, the phosphate content decreases (Smeck 1973; Kronberg et al. 1979; Jamet 1986).

We conclude that there is strong evidence the phosphate content of Niue Island soils results from weathering of parent calcite/dolomite. Whether that suggestion might be applicable to other Pacific islands would need to be examined on a case-by-case basis.

Correlation with dolomite

An examination of the α-count values >1500 counts/1000 min (as an indicator of high radioactivity levels) showed that of the 34 points 15 were on the soil type known as Tafalomahina (order oxisol, subgroup tropeptic eutrustox). A
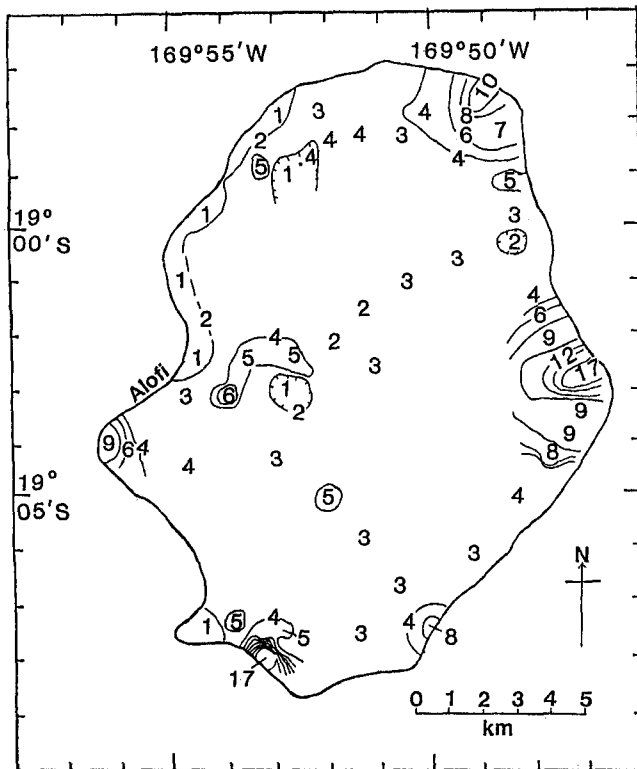
Fig 4 P$_2$O$_5$ in Niue Island soils. Contours were derived from consideration of 99 analyses but, for clarity, representative rounded values only are shown.
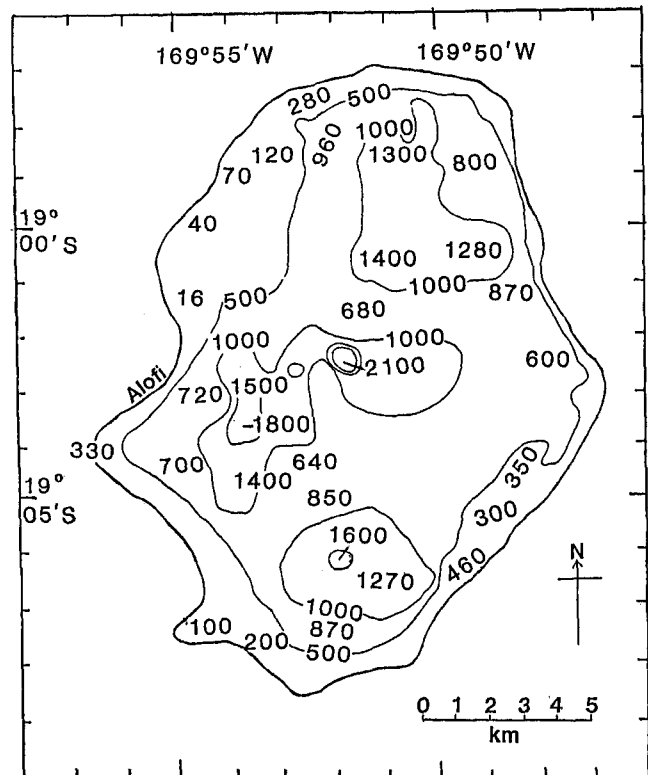

Fig. 5 Distribution of Cr in Niue Island soils. Contours were derived from consideration of 99 analyses but, for clarity, representative rounded values only are shown.

further four were on Palai soils (order mollisol, subgroup ruptic-lithic haplustoll). Both these develop on dolomite rather than calcite. The other points were fairly evenly distributed over all soil types. The association with dolomite is significant. Further examination showed that the Tafalo-

Table 5 Comparison of mean values for concentrations of some trace elements in Niue Island soils with literature values.

Element	Mean	LQ	UQ	Global means	Basaltic laterite
SiO$_2$	0.62	0.1	0.88	71	24
K$_2$O	0.035	0.01	0.05	1.7	0.30
P$_2$O$_5$	4.11	2.38	4.99	0.096	0.32
V	161	83	235	90	682
Cr	756	300	1133	70	366
Ni	45.2	6	22	50	155
Cu	74.9	58	93	30	199
Zn	93.8	34	62	90	143
Sr	1810	363	2351	250	41
Y	118	65	167	40	9
Zr	82	95	100	460	232
Ba	91	44	129	500	472
La	26	18.5	41	40	38
Ce	38	24	60	50	134
Hg	1.06	0.37	1.56	0.05	0.205
Pb	16.9	13.2	21.4	35	11

Global soil means given in Martin & Whitfield (1983), except for the value for Hg taken from Stock & Cucuel (1934) and the value for Zr taken from Jones et al. (1987). Ranges taken from Bowen (1979). Values for lateritic soils taken from Schellmann (1986) except for the value for Hg taken from Flanagan et al. (1982). Units are in mg/kg. LQ is lower quartile and UQ is upper quartile. Units as in Table 4.

mahina soils contained the highest Cr and Hg values also. This is particularly significant, because the Tafalomahina soils are only a few percent of the total. Although such values occur on other soils, they occur more often on dolomite-based soils. Use of t-tests showed that Hg, Cr, and α-counts were significantly higher on dolomite compared to calcite. The actual means and standard deviations of the distributions are: Hg = 2170 ± 820 (dolomite), 1040 ± 740 (calcite); Cr = 1490 ± 680 (dolomite), 1160 ± 320 (calcite); α-counts = 3230 ± 1520 (dolomite), 1240 ± 1210 (calcite).

Concentration from source rocks

The phosphate content increases very rapidly after extreme weathering. Similar plots to Fig. 7 were obtained for Al$_2$O$_3$, TiO$_2$, V, Cr, Fe$_2$O$_3$, Y, Hg, and α-counts. The implication is that the relatively high analytical values obtained are also the result of concentration through weathering. Examination of changes of concentration with depth in the different soil horizons did not yield interpretable results for or against the hypothesis. However, if concentration has occurred, it may be calculated from comparing rock and soil values from Tables 1 and 5 that the highest concentration factors are for P$_2$O$_5$ (about 20) and for V (32). These are high (a typical lateritic concentration factor for most elements from source rocks is about 7) but not so high that we are forced to invoke other mechanisms to explain the high concentrations. It may be calculated that a reasonable 4.5 m of weathering would be required. However, for the radioactivity, it was shown in Whitehead et al. (1992) that a concentration factor of about 300 would be implied, and another mechanism is probably necessary; it was argued that concentration from seawater is possible during brief submergence. A similar mechanism
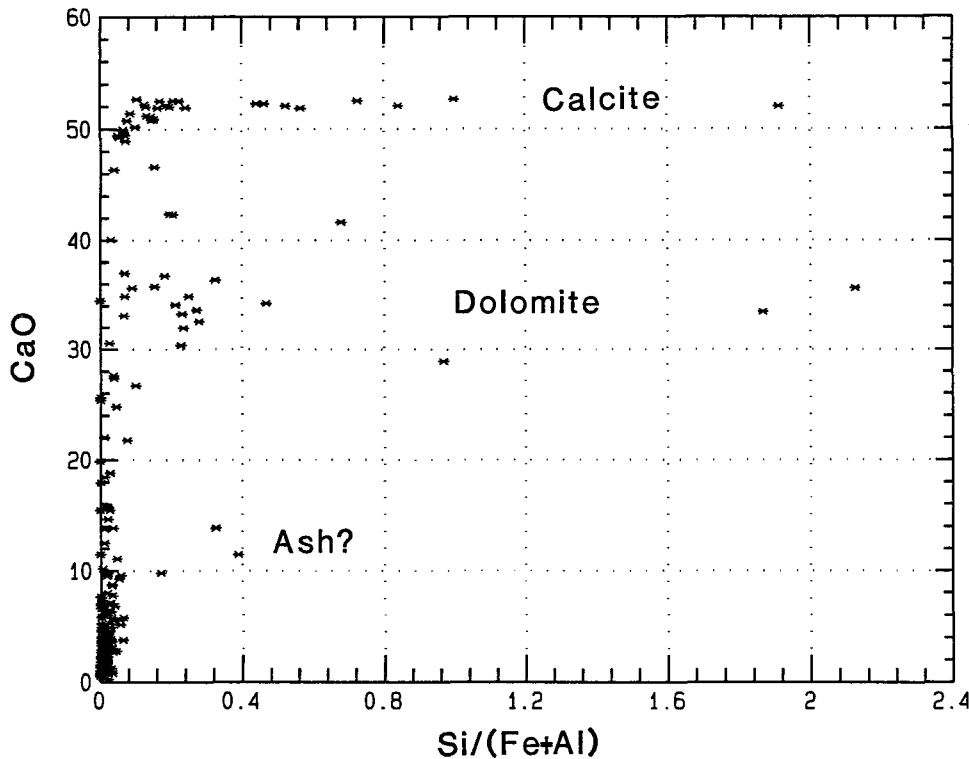
A horizon

Fig. 6 Correlation matrix for A horizon elements (those for B and C horizons were similar). The size of the dot indicates the value of the Spearman correlation coefficient. The filled-in dots represent positive coefficients, and the hollow circles represent negative correlations. If $P > 0.05$ no entry was made in a square. For cases in which the relationship was two orthogonal lines (as in Fig. 7), the square contains a diagonal line because correlation coefficients are extremely misleading.

may still apply to some of the stable elements in Niue Island soils.

An element which may be too concentrated to explain by a calcite/dolomite weathering process is Sb. Values as high as 1% have been found independently for Niue soils (J. Barrie pers. comm.). This element has not been routinely analysed for in lateritic soils but seems particularly interesting. The only other parallel analysis seems to be for Rennell Island soil (975

mg/kg Sb; Bourrouilh-Le Jan 1980), which also possesses a radioactive anomaly (De Weisse 1970; Taylor & Hughes 1975).

The ratio Fe_2O_3/Al_2O_3 is usefully diagnostic because it is not supposed to change very much with weathering. It should be about 0.45 for an andesite (or 0.58 for a basalt), but from Niue calcites we obtained a ratio of 0.78 and for dolomite 0.77. For the specimens rich in phosphate we obtained a ratio of 0.75. There is no significant difference between the last three. For all Niue Island soils there is a mean of about 0.75, with a few samples yielding much lower ratios (0.48–0.55). They are mostly in the A horizons. There were three particularly interesting soils most likely to represent volcanic ash compositions—sites 55, 112, and 114 (all A horizons). CaO was 25.6, 9.81, and 13.87%. Silica was only 0, 0.64, and 0.64%, so if these soils originated from volcanic ash, they have lost most of their silica and are very highly weathered. It thus appears that no soils in this collection reflect a relatively unweathered state that clearly corresponds to volcanic ash. Almost all have CaO and SiO_2 contents corresponding to an origin from calcite and dolomite.

Confirming the above, when we take those samples that have $Si/(Fe+Al) > 0.4$ (i.e. least weathered; 17 samples), we find that six of them are clearly dolomite, and the remainder all have CaO content >45% and are calcite. Two have Fe_2O_3/Al_2O_3 ratios of 0.50 and 0.55, but the Fe_2O_3 and Al_2O_3 content is low, and both samples are dolomite.

Similarly, examination of a plot of CaO content versus weathering (Fig. 8) shows a top curve due to weathering of calcite, an intermediate line due to dolomite weathering, and only three isolated points near 10% CaO but quite weathered (sites 50, 112, and 114), which possibly correspond to volcanic ash. The latter two also had Fe_2O_3/Al_2O_3 ratios possibly corresponding to an andesitic origin.

There is therefore very little evidence of volcanic ash origin for these soils.

Fig. 7 Plot of phosphate content versus Si/(Fe+Al) (all expressed as oxides) for all horizons combined.

Fig. 8 Plot of Ca content versus Si/(Fe+Al) (all expressed as oxides) for all horizons combined.

Dust contribution

Could dust be a contributor to the soil formation on Niue Island, perhaps through being blown from Australia during dry and windy glacial periods? No. As previously noted (Arimoto et al. 1987), mineral aerosol concentrations in this region are among the lowest recorded anywhere, neither are the Niue Island soil silica levels consistent with substantial dust input. Other studies analysing sea sediments from the area do not find an ancient strong input of minerals that may be ascribed to dust (I. Graham et al. in prep. "Provenance of pelagic sediments"). Dust is therefore quite unlikely to be a major contributor to the soil formation on Niue Island.

Resistant minerals

Mineralogical examination of Niue Island soils (Fieldes et al. 1960) showed that goethite, crandallite, gibbsite, and hematite were present, as well as the somewhat rare mineral maghemite. Only two samples contained clearly detectable kaolinite. Significant quantities of magnetite were found in all the soils in varying proportions and identified by their

Table 6 Comparison of contents of a few trace elements in phosphates from various locations. Values in mg/kg.

	Zn	Sr	Cr	Hg	V
Niue Island[1]	666	14680	651	0.355	89
Christmas Island[2]	400	8800	185	–	–
Island phosphate[3]	590	–	–	0.36	21
Marine phosphorite[4]	190	750	75	0.055	70
Marine phosphorite[4]	240	–	–	0.08	80

[1]This work; Niue Island site L7 horizon A.
[2]Island phosphate (Dar'in & Zanin 1985).
[3](Weissberg & Singers 1982).
[4]Altschuler (1980).

magnetism, XRD pattern in the soils, and separation using heavy liquids. No other resistant minerals were found.

Augite and anatase were not found in Niue Island soils (Fieldes et al. 1960). This does not support an origin from weathering of volcanic rock. The median TiO_2 content of 1.38% is very low compared with the highly weathered volcanic-rock derived soils which contained 8–18% (Tercinier 1974). However, it might seem that magnetite could only originate from strong weathering of a volcanic rock. This is not correct and need not be invoked. Magnetite is now clearly known to form in situ in many soils (Smirnov 1978; Lowson et al. 1986; Maher & Taylor 1988; Machel & Burton 1992). Particularly relevantly, Hart & Fuller (1988) found this happened as a late stage of weathering of dolomite. If these results hold also for Niue Island soils, the resistant minerals in Niue Island soils are consistent with an origin from weathering of calcite/dolomite, and it is unnecessary to invoke an origin from volcanic ash.

Occurrence of negative Ce anomaly

The results from the rare earth analyses were normalised against chondritic values (Frey et al. 1968; Rankin & Childs 1976). All seven Niue Island samples showed a negative Ce anomaly in contrast to two control soil samples from Atiu and Aitutaki Islands which showed a quite different trend in the rare earth data (Fig. 3). It would be interesting to compare other compositional features of the Cook Island samples with those of Niue Island, but the analyses for the former are not immediately available. Negative Ce anomalies are symptomatic of a marine environment and are rare in terrestrial rocks. This suggests that the origin for the rare earths in the soils was not volcanic ash or rock, but seawater, directly or indirectly. Fleischer & Altschuler (1986) found a negative Ce anomaly in marine phosphorite, but as noted above, marine phosphorite is unlikely to be the origin of Niue Island soils. However, Rankin

& Childs (1976) noted negative Ce anomalies in limestone. It is possible the rare earth content of the soils originated in the coral, or dolomite.

Geomorphology

Against a hypothesis of soil formation by calcite/dolomite weathering, might seem the assertion that the surfaces are geomorphically young (i.e. relatively flat and not dissected into a forest of pinnacles). However, this is deceptive. The central Niue Island region actually consists of a pinnacled region filled in with soil. There has certainly been significant erosion, but this is concealed. This is also well known on Makatea and Nauru. Erosion can occur under soil as well as subaerially (Ford & Williams 1989), and this is suggested as the simplest explanation.

CONCLUSIONS

Niue Island is an interesting location for a study of this type. It has an atmosphere relatively free of the confounding effects of aeolian dust. The effects of volcanic ash are small, if present at all.

Most of the highest concentrations of the elements in soils are found on dolomite, and the data support a concentration mechanism from very strong weathering of dolomite/calcite.

The negative Ce anomaly is not consistent with a volcanic ash origin of the rare earths, and suggests an ultimate marine origin, possibly simply from strong weathering of coral.

Adsorption from seawater as proposed elsewhere for the radioactive components may be a factor in the genesis of these soils, but contrary to opinion in the literature, weathering of volcanic ash is not a major factor.

In some cases the evidence in this paper does not exclude some other origins, such as endothermal upwelling, or even extreme weathering of volcanic ash, but it seems that weathering of calcite/dolomite is a predominant factor in the genesis of the soils, and contributes strongly to the elemental concentrations and radioactive content.

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