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**GEOCHEMICAL CONSTRAINTS ON THE FUTURE OF
AGRICULTURE IN SRI LANKA**

by

Tara J. Tampoe

Department of Geology

**Submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy**

**Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
November 1988**

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ABSTRACT

In tropical Sri Lanka, agriculture has been and still is the mainstay of her economy. Cash crops earn approximately 43% of export trade. However, intense tropical rainfall leads to a paradoxical combination of lush vegetative growth and infertile soils where regeneration can only be ensured by maintaining a closed ecosystem, through rapid recycling of the litter layer, as in a rainforest. Economists depending on cash crops have not taken into account the totally contrasting conditions prevailing in plantations where essential plant nutrients are annually removed, as indicated by the increasing number of deficient nutrient element diagnoses.

Distinct geochemical and mineralogical differences exist between the intensely cultivated Wet Zone soils and the Dry Zone soils of Sri Lanka.

Compared to Amazon soils, Sri Lankan soils are reassuringly enriched in Na, Mg, Ca and K. However only ~10% of Wet Zone soils have Na, Mg and Ca levels comparable to the Earth's crust. Crustal levels obtain in 33% of samples for potassium (a major plant nutrient), 30-50% of samples for Sr and Ba and 50-80% for Rb, Mn and P. Corresponding values in the Dry Zone soils are Na(83%), Mg(14%) Ca(39%) and K(100%).

Mass balance calculations indicate that while K is slightly more resistant, less than 5% of Mg, Ca and Na remain from the original rock in a Wet Zone soil. T' vs. Zr plots are successfully used for the first time to discriminate between horizons derived from gneissic banding. Extensive physical removal of soil particulate matter is indicated in these plots (resulting from the severity of rainfall), a factor not sufficiently recognised hitherto. Groundwater percolation rates govern soil mineral formation and distribution. Groundwaters can only be saturated with oxyhydroxides and kaolin in this intense weathering regime where primary minerals are non-existent even within

the silt fraction. Hence oxyhydroxides can be the first and last minerals to form. Dry Zone soils with abundant primary minerals and smectitic clays are fertile. Kaolin-smectite interstratification previously not identified in Sri Lanka is common and substitutes for much of the mineral identified as smectite.

Wet Zone soils can provide potassium requirements for a maximum of 2 years from available exchangeable potassium compared to a 3-4 period from Dry Zone soils. If the total reserves of potassium were utilisable, Wet Zone soils have a 40-year supply compared to a 1000-2000 year supply for Dry Zone soils.

Logistical problems would arise if rock powder alone is substituted for fertiliser since an adequate 50 kg/ha supply of potassium, is equivalent to 34 tons of rock powder in terms of exchangeable potassium. However, when the poor nutritional status of Wet Zone soils and the emergence of nutrient deficiencies are considered in context with the new insight into tropical weathering, it becomes clear that applications of rock powder and smectite are essential for long term soil maintenance if these soils are to continue to support an agricultural economy.

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Chapter I

"Sri Lanka (until recently known as Ceylon) has always been an agricultural country. Hence, the parent earth was, and ever will be, the heart of Sri Lanka life."

Food and the People (Brohier, 1975).

1.1 Introduction

Agriculture has been, and still is, the mainstay of the economy of Sri Lanka, a tropical island, situated south of the Indian sub-continent. The island supports a population of 16.1 million, within its land extent of 64,000 sq. kms, giving a density of 6 persons per cultivated hectare which is above the average of 4.5, for Southeast Asia (Didal, 1987). The crucial importance of agriculture to her economy can be judged by the fact that it engages approximately 45% of the work force (Census, 1981), while contributing 27% to the Gross National Product of the country (Central Bank of Sri Lanka, Annual Report, 1986).¹

Economic dependence on agriculture would not in itself pose a problem for Sri Lanka, but for the implications of two socio-ecological factors.

The cash crops, tea, rubber and coconut, which constitute the mainstay of the island's modern export-import economy are those which can only flourish under wet, humid conditions - a fact recognised and taken advantage of, since colonial times. Unfortunately, the very intensity of rainfall that promotes the existence of such lush vegetation and ensures the profitability of these crops, is extremely

1. In comparison, less than 3% of the work force is engaged in agriculture in the United Kingdom (Britain, 1986) a modern developed country. It has a population density similar to that of Sri Lanka (231 persons/sq km), corresponding to 4.7 persons per cultivated hectare; however combined Agriculture, Fishing and Forestry contribute - 2% to the GDP (United Kingdom, 1986).

harsh on the soils that are called upon to sustain such growth; it leaches out most nutrients from the soil leaving behind a very infertile soil of which much is demanded. This is an instance of the type of paradox that characterises the working of many of Nature's systems - abundance of rainfall promoting lush tropical vegetation which at the same time adversely affects the soil that sustains such growth.

The sustainability of agriculture depends on the recognition of how vulnerable the soils are, under these tropical conditions and the adoption of long-term measures to nurture and conserve this all important resource. An apparent upperhand over Nature seemingly exists, forged by the artificial maintenance of soil fertility, through the use of chemical fertiliser. Scant attention has hitherto been paid to the maintenance of its long term fertility. However the ever increasing amounts of chemical fertiliser required to maintain soil fertility bears testimony to the magnitude of the problem and is likely to place an even larger burden on the country's economy in the years to come, unless the situation is reassessed and remedial action taken. For example, Mg had already reached deficiency levels for coconut in the south and southwestern regions of the wet zone in the fifties and has extended alarmingly to other areas as well, according to Jeganathan and Dias (Handbook of Fertiliser Recommendations, 1985-1986). Applications of dolomite (and Keiserite in the more affected areas) have been recommended.

The intricate links between the ecological and economic ramifications of Sri Lanka's problems are becoming apparent as the impact of soil degradation manifests itself in economic terms. In 1986, agricultural exports constituted 46.3 % of the total export volume. The Annual Report of the Central Bank of Sri Lanka for 1986 states "unfavourable trends continued to be present in the external trade sector in 1986, for the second consecutive year. Largely owing to a sharp drop in the prices of agricultural exports, the total value

of exports declined by 21 per cent during the year" and "Owing to reduced fertiliser application consequent on depressed prices and unfavourable weather conditions, particularly in the high and mid-country areas, tea production fell marginally by 1 per cent to 211.3 million kgs in 1986". Increasing quantities of chemical fertiliser will be required to maintain soil fertility as present trends indicate (fig. 1.1). The difficulty of doing this under adverse economic conditions will place an even larger burden on the country's economy unless fresh thinking is addressed to the entire issue.

Problems are further compounded by a staggering imbalance in the distribution of population which has been the natural outcome of a cash crop oriented economy, by causing landuse pressure on available arable land in the wet zone where the cash crops grow. According to the 1981 census, 57% of the population was concentrated in the south west quadrant which comprises the wet zone, demarcated as such because it receives more than 2500 mm annual rainfall. The remaining 43% of the population is scattered inhomogenously throughout the dry zone areas that receive less than 1875 mm of annual rainfall during a few months of the year.

1.1.1 Statement of Problem

Modern fertiliser strategy using NPK soluble fertiliser, employed in Sri Lanka was developed for the fertile soils of the northern hemisphere, where, as a result of a less intense rainfall regime, leaching rates are not as severe as in tropical areas (Kronberg et al., 1985). Garrels and Christ (1965) popularised the currently well accepted concept of the control leaching rates play, in soil mineral formation and preservation. Low leaching rates in the northern hemisphere have been responsible for the formation and preservation of soil minerals such as the smectite group that have, as a result of their structure, high retention powers of bio-essential nutrient elements such as the base cations K, Mg, and Ca. In the

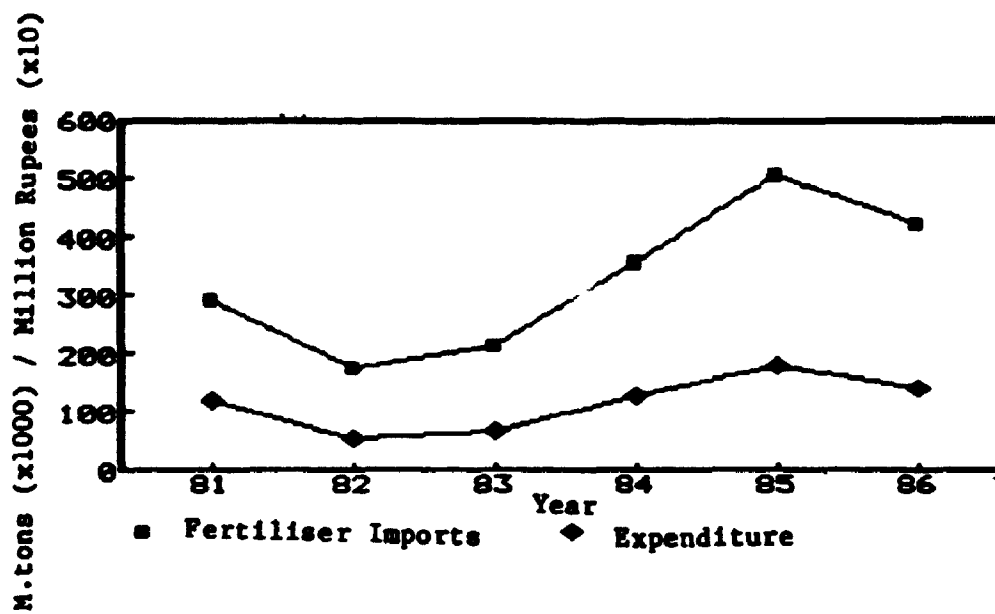


Fig. 1.1. Fertiliser import volume and import expenditure during the period 1981 - 1986 in Sri Lanka (Review of Fertiliser, 1985 - 1986).

tropics however, soils are dominated by the kaolin group of minerals and resistant oxyhydroxides of Al and Fe, that can survive the intense leaching environment. However these minerals, as a result of their structures, have very low retention capabilities of bio-essential elements. Leonardos et al., (1986) point out that had fertiliser technology been originally developed in the tropics, present day fertilisers might have been quite different. A concept that is rapidly gaining acceptance resulting from the work done on tropical soils, as set out by Leonardos et al., (1986) and Kronberg et al., (1985), is that, in the tropics where intense leaching results in a soil mineralogy incapable of retaining or buffering the array of essential nutrient elements required to maintain soil fertility, continued addition of conventional highly soluble fertiliser, is not a cost effective method of maintaining soil fertility.

The need has arisen to look at soils in these regions as geochemical entities with reserves that need total replenishment, instead of addition in parts. The long term objective is to restore and maintain a nutritatively balanced environment such as is found in naturally fertile soils. This is embodied in the concept of rock-fertiliser (Fyfe et al., 1983), currently being developed in Brazil.

A similar attempt at improving soil fertility, presently being developed (Imasuen, 1987), is that of converting kaolin type minerals to smectite, chemically. Conversion has proved successful at temperatures above 150°C so far.

In a country such as Sri Lanka, whose economy is highly vulnerable to the continued maintenance of soil fertility, it becomes doubly important in the light of this knowledge, to characterise her soils geochemically, and understand their weathering dynamics. This will enable assessment of the issues involved in incorporating appropriate fertiliser strategy into current day agricultural practice.

1.2 Review of Previous Work

Most of the soil research carried out in Sri Lanka reflects the deeply entrenched conventional western concept of soil fertility, as embodied in the Handbook of Fertiliser Recommendations (1985-1986). For example, even though it is recognised that rice plants require N (nitrogen), P (phosphorus) and K (potassium) as primary nutrients, calcium, magnesium and sulphur as secondary nutrients and iron, copper, zinc, manganese, boron, molybdenum and chlorine as micronutrients, the recommendations essentially imply that fertility can be maintained by N, P and K. A note of complacency exists regarding the overall soil fertility of Sri Lankan soils. As stated by Nagarajah (Handbook of Fertiliser Recommendations, 1985-1986), excepting for N, P and K "at present most rice soils in Sri Lanka can supply the other nutrients required by the rice plant". Hence, soil research has been oriented towards determining a wide spectrum of agriculturally important soil properties such as cation exchange capacity, base saturation and available P, N, and C contents. However, sufficient literature exists that shows such complacency to be misleading to agronomists especially since coconut and rice growing soils are interchangeable. For example, Mg deficiency once thought to be confined to certain types of coconut growing soils is now found to be widespread (Jeganathan and Dias, in Handbook of Fertiliser Recommendations, 1985-1986). In addition, increased yields have been obtained with applications of inorganic elements directly or inadvertently, e.g. it has been shown that silica applications increase rice yields and it has been postulated that enhanced availability of both silica and molybdenum during liming were responsible for increased yields in rice grown on lateritic soils (Puvananasivam and Kalpage, 1973).

An outstanding work in soil research is that by Herath and Grimshaw (1971) who divided the island into clay mineralogical provinces, though this was based only on alluvial soils. Geochemical studies have focused on restricted areas as revealed by the review

of limited literature on the micronutrient status of agricultural soils (Puvananasivam and Kalpage, 1973). These authors review reports of the occurrence of manganese deficiency in some tea and rubber growing soils, iron and molybdenum deficiency mostly in tea growing soils, boron deficiency in tea growing soils especially those derived from quartzitic rocks poor in accessory minerals, and zinc deficiencies increasingly common in tea, coffee and cocoa growing soils. Major oxide determinations of limited batches of soil have been presented (Panabokke, 1959). In the compilation of characteristics determined during the classification of soils in Sri Lanka, (Handbook of the Soils of Sri Lanka, 1973), Al_2O_3 and SiO_2 determinations are given for a number of soil profiles. However studies on a broader basis comparable to Herath and Grimshaws' (1971) mineralogical studies, that characterise the soils of Sri Lanka geochemically, do not exist.

1.3 Scope of Present Thesis

A research plan was designed:

1. To ascertain the geochemical attributes of the soils in the three different climatic zones of Sri Lanka, using major oxides.
2. To relate geochemical characteristics to current understanding of weathering phenomena, in order to explain their existence and to gauge the relative intensities of nutrient element loss within the climatic zones of Sri Lanka.
3. To attempt to quantify the loss of such elements in the process of weathering and examine the concept of applying rock fertiliser designed to maintain soil fertility, in terms of these results.

Chapter Two details the geochemical characteristics of a wide range of soils sampled during a reconnaissance survey designed to take in the regional factors described therein, that are widely considered to be responsible for soil type differentiation. This was followed by detailed pedological study of representative samples from the three main climatic zones of Sri Lanka, to establish links (a) between geochemical characteristics and soil properties such as cation exchange capacity and pH, that are considered important in agriculture, and (b) between soils in the present study and those in available literature, by characterising soils both according to the USDA and Sri Lankan soil classifications.

In Chapter Three, available literature on Sri Lankan soil mineralogy is reviewed. Subsequently, results of a mineralogical study are presented, carried out to verify if the soils of the present study fall into the established clay mineralogical provinces albeit, based solely on alluvial soils. This is followed by a discussion of the current understanding of weathering both from a pedological and geochemical perspective. Based on current geochemical understanding of weathering phenomena, an explanation is provided to understand the weathering processes that have been operative in the different climatic zones, that in turn has led to such geochemical differentiation between the soils as observed from preliminary studies. The explanation is tested using available hydrogeochemical data and observations from electron microscopy.

In Chapter Four Sri Lankan soils are compared to the composition of the Earth's Crust and Amazon soils. In the second part of this Chapter, quantitative changes due to weathering are tabulated. The significance of the results is discussed in terms of weathering processes in the tropics and extended to the concept of applying rock fertiliser for the purpose of maintaining soil fertility.

Chapter Five discusses the significance of the results obtained

from this study, within the context of Sri Lanka's predominantly agricultural economy and suggests temporary measures to sustain long term fertility of the wet zone soils, until technology provides superior methods to maintain and or improve soils in wet humid tropical regions.

Chapter II

Regional Description, Preliminary Geochemical

Investigation and Sequence Characterisation

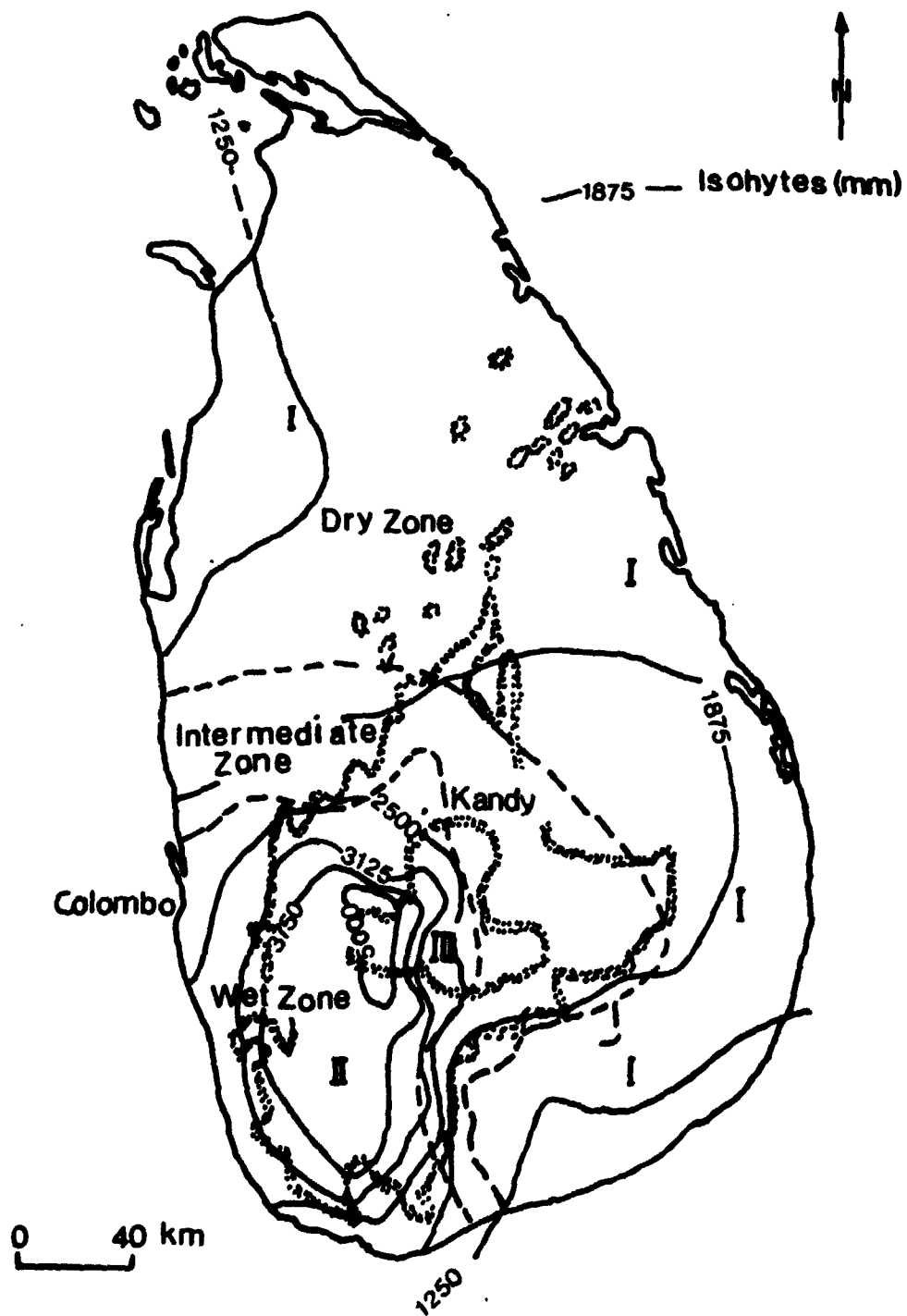
2.1 Introduction

Sri Lanka consists of diverse agro-ecological zones resulting from both a complex physiography and by its location in the monsoon belt in the tropics. In the first part of the chapter, the geology, physiography and its link to the island's rainfall distribution, is described prior to detailing the climate, the most likely dominant influence in the development and differentiation of soil types in Sri Lanka. In the second part of the chapter, results of preliminary geochemical and routine pedological investigations are presented prior to characterising representative soil sequences in the last part of the chapter.

2.2 Physiography

The landscape in central Sri Lanka is relatively youthful (in spite of having been geologically inactive since the breakup of Gondwana), and according to Vithanage (1970), has resulted from neo-tectonic movements that have modified the ancient Precambrian landscape.

Interaction between abundant rainfall and the youthful landscape of central Sri Lanka has lead to a self-perpetuating cycle of continuous rock exposure, mass wasting, intense weathering and erosion.

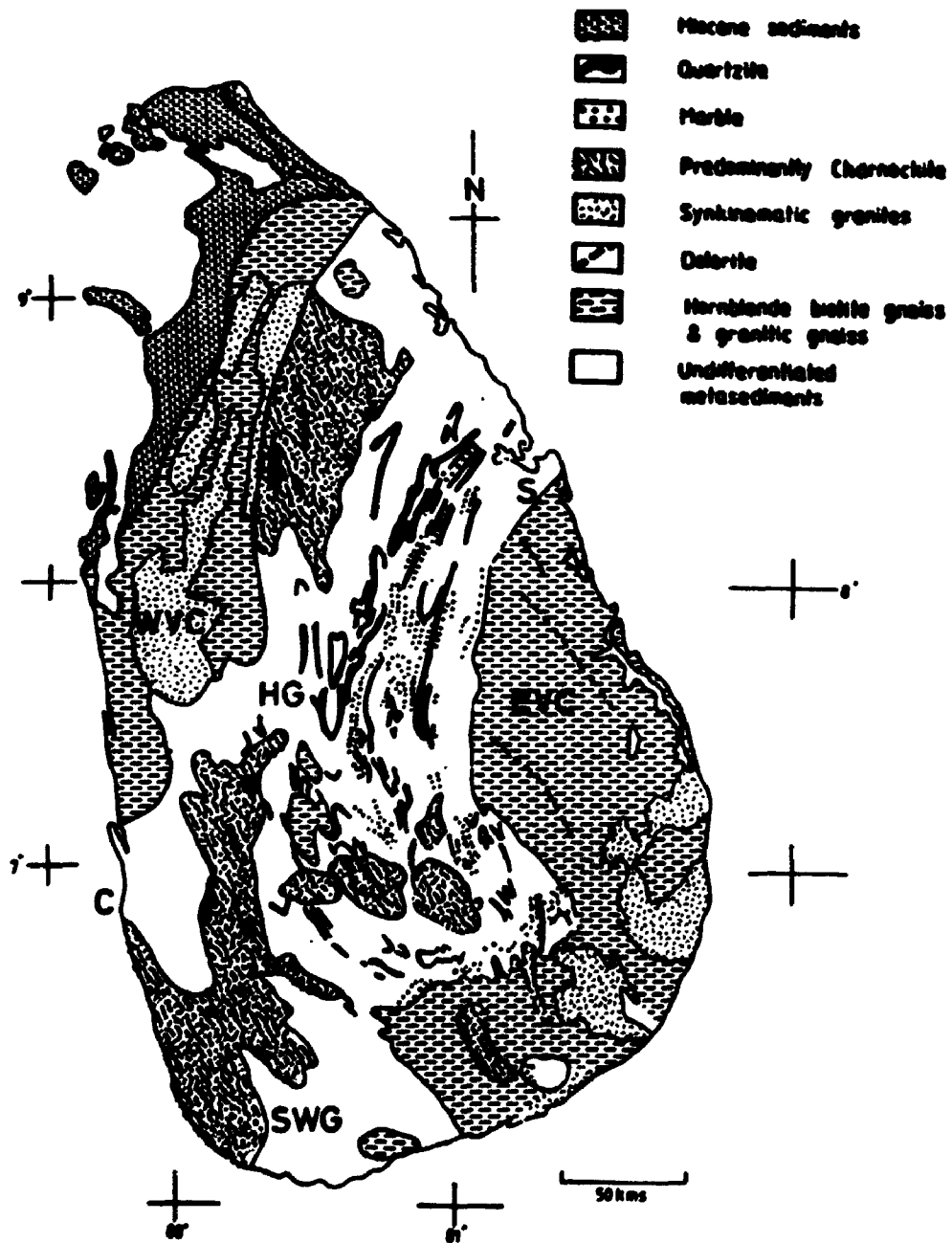


Map 1. The 3 main morphological regions (stippled boundaries) and climatic zones (dashed boundaries) of Sri Lanka. Morphological regions: I - Lowlands, II - Uplands III - Highlands. Contours of annual rainfall in mm.

The island can be divided into three physiographic units: lowlands, uplands and highlands (Map 1, Vithanage (1970)), on the basis of height and slope characteristics and the observable regional topographic discontinuities. Accordingly, the lowlands range in elevation from 0 to 270 m above msl; isolated ridges with gentle slopes ($0-10^{\circ}$) occur in a large peneplained area interrupted by sluggish streams and rivers. The uplands lie at elevations between 270 and 1060 m above msl and are characterised by mainly NNW and NNE trending parallel ridge and valley topography. Narrow arena like structures controlled mainly by lithology, structure and subsequently highlighted by weathering are also present. Slopes range from 10 to 35° . Waterfalls and rapids are prominent along their well developed steep scarps. The arena floors are flat and undulating with gentle slopes ranging from 0 to 10° . The highlands are typified by a series of plateaus well defined by high level topographic discontinuities (as much as 600 m) and by rimming mountain peaks and ridges ranging in elevation between 910 and 2420 m above msl both characterised by vigorous waterfalls.

2.3 Bedrock Geology and Surficial Deposits

Nine-tenths of the island is underlain by Precambrian rocks divided into three major units by Cooray (1978), the Vijayan Complex, Highland Group and Southwestern Group, while the remainder is covered by a narrow coastal strip of Jurassic and Miocene sedimentary rocks located in the NE (Map 2). The Vijayan Complex consists of hb-bt microcline granites, gneisses and migmatites that outcrop as isolated ridges and hills in the lowlands, which is otherwise mantled mainly by Reddish Brown Earths in the dry zone and Red Yellow Podsoils in the wet zone which are in part lateritic reaching depths of 40 m in places. The Highland Group comprises charnockites, hb-bt+garnet gneisses and granulites, khondalites, quartzites and marbles, that is continually exposed in the uplands and highlands by rapid mass wasting and erosion. Low ridges trending NE outcrop in the NE lowlands as well.



Map 2. Geological units (simplified) of the Precambrian of Sri Lanka (WVC = western Vijayan Complex; EVC = eastern Vijayan Complex; HG = Highland Group; SWG = Southwest Group; C = Colombo). Modified after Dissanayake and Munasinghe, 1985.

Cordierite gneisses, charnockites, quartzites and calc-silicate gneisses form the Southwestern Group.

2.4 Climate

The climate of Sri Lanka is tropical humid to sub-humid. The island is seasonally influenced by the southwest(SW) monsoon (May to September) and the northeast(NE) monsoon (December to February). Rainfall distribution (Map 1) is governed by the prominent physiography described in section 2.2. Most of the rain is derived from the SW monsoon in the western part of the island reaching its maximum at the boundary between the uplands and the highlands as a result of the blocking effect of the steep scarps and high ridges that constitute their boundary. Intermonsoon rainfall is derived from cyclones and thunderstorms. Marked rainfall fluctuations over a hundred year period, have been recognised by Suppiah and Yoshino (1984). Other than a 3-4 year periodicity noted over the whole island, other cycles differ from region to region. Biennial and ten year fluctuations have been observed in the wet zone; ten year cycle minima and maxima correspond to less than 2000mm to over 3500mm for the zone. Maximum mean precipitation reaches above 5000mm in the Watawala area (Map 1) averaging 2500mm for the rest of the region in the wet zone. Hence cyclic variation does not deviate excessively from the mean. The remaining segments of the lowlands are located in the rain shadow of the SW monsoon. These segments do not receive comparable precipitation from the NE monsoon, spent as it crossed the Asian continent and hence are marked by both a prominent dry season lasting at least 4 to 5 months of the year and an annual precipitation of less than 1875 mm. These segments comprise the dry zone, where an additional quasi-five year oscillation has been noted. The intermediate zone encompasses the region receiving between 1875 and 2500 mm of rainfall annually.

A detailed diagram from Suppiah and Yoshino (1984) showing seasonal spatial variation in rainfall is given in fig. 2A.

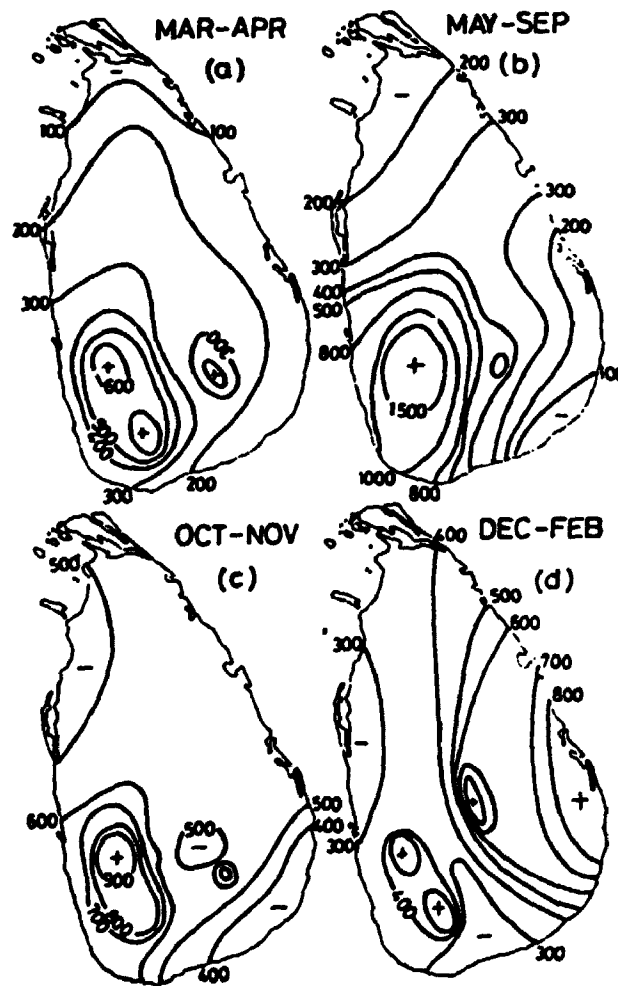


Fig. 2A. Seasonal rainfall (mm) of Sri Lanka. (a) First inter-monsoon season, (b) Southwest monsoon season, (c) second inter-monsoon season, and (d) Northeast monsoon season (Suppiah and Yoshino, 1984).

Cumulative rainfall over the entire island derived from the October to November intermonsoon and the NE monsoon varies between 700mm to 1400mm (fig. 2A, c and d). A similar amount of rain is derived from the SW monsoon for the wet zone alone, peaking in June, during the months of May to September, (fig. 2A, b). The diagram shows most explicitly that there is no appreciable dry period in the wet zone.

Mean monthly rainfall data during the period 1870-1956 from Moorman and Panabokke (1961), for a wet and dry zone station respectively are listed below. The lack of a 'dry month' in the wet zone is re-emphasised.

Dry Zone (Asparai station)

(1875-1956)

	J	F	M	A	M	J	J	A	S	O	N	D	Y
Mean Rainfall (mm)	354	123	95	88	88	43	43	70	90	178	272	361	1810

Wet Zone (Palmadulla station)

(1870-1956)

	J	F	M	A	M	J	J	A	S	O	N	D	Y
Mean Rainfall (mm)	160	120	228	260	390	378	263	238	278	353	338	240	3240

Daily rainfall fluctuations during critical months of the monsoons for a wet and dry zone station are presented in fig. 2B. Clearly the accumulated rainfall per day is greater in the wet zone and reach up to 150 mm per day.

2.5 Site Selection and Sampling Procedures

A reconnaissance sampling of soils within the three main climatic zones was undertaken to determine the differences in, and assess the quality of, soils in different agro-ecological zones of Sri Lanka. For comparative purposes samples were taken from constant depths at 10cm,

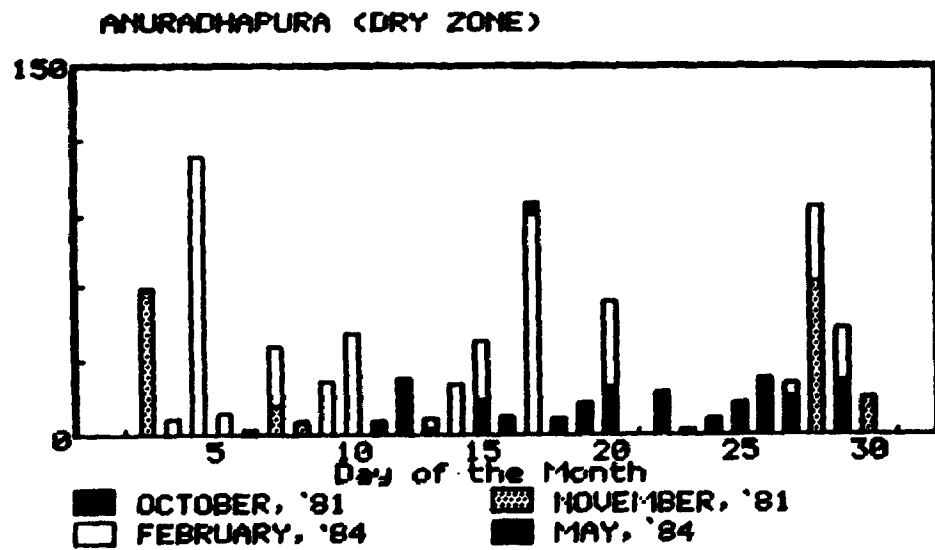
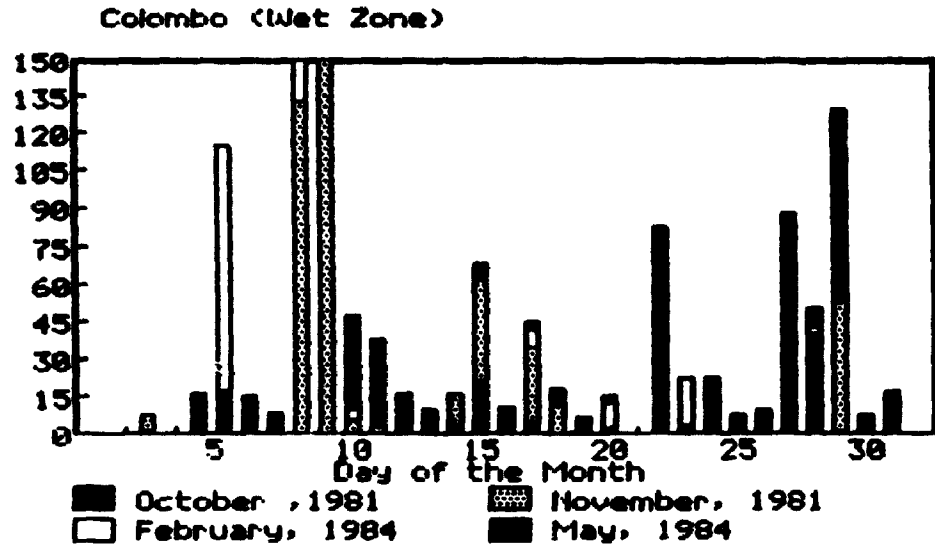


Fig. 2B. Daily rainfall fluctuations (mm) during critical months of the year.

30cm and 100cm within the root zone, using a hand auger or from undisturbed sequences along road cuts. Samples were collected below 100 cm where it was thought significant - the soft laterite at locations 148 and 145, the laterite/altered charnockite contact at location 145 and from 600cm within the decomposed rock zone at location 153 in the absence of fresh rock. River sediment samples and a sequence from the beach which constitutes prime coconut land were also sampled for comparison. The actual sample sites were constrained by the need to locate them near fresh rock outcrops. Two sequences (112 and 112a) were collected close to and away from a fresh rock outcrop at location 112, to assess the bearing of site location near a fresh rock outcrop. The two variables, parent rock and type of cultivation, were alternately kept constant at several locations for comparative purposes. Thus, sequences were sampled under identical types of cultivation, with different parent rock types and vice versa, within the same climatic zone. Conversely, sites were chosen near rock types under similar cultivation conditions where possible for comparison between climatic zones. At selected sites thunderstorm conditions were broadly simulated by agitating top soil samples with local water, and allowing to settle for 10-20 minutes prior to sampling both the suspension and residue separately. Fig.2.1 indicates the locations of each of the sequences examined. A synopsis of site characteristics is given in Table 2.1.

2.6 Preliminary Geochemical and Pedological Characterisation of Samples

The samples were air dried in the University of Peradeniya laboratories, but were subsequently oven dried at 150° C after learning of the strict entry requirements by Canadian customs.

Prior to detailed analysis a preliminary x-ray fluorescence study

Table 2.1 Site Location Characteristics of Sequences Used for Detailed Analysis

Sequence	Physiographic Unit	Rainfall (mm)	Climatic Zone	Rock Type	Cultivation Status
Samples used only for preliminary analysis					
145	Lowlands	1875-2500	Wet	Charnockite	Coconut
142	"	"	"	Hb-Bt Gn	Uncultivated
147	"	"	"	Beach Sand	Coconut
114	"	1875	Intermediate	River Sediment	-
63	Uplands	1875-2500	"	Charnockite	Uncultivated
115	"	2500-3125	Wet	Calc Gn	Coconut
116	"	"	"	River Sediment	-
49	Highlands	2500	"	Quartzite	Tea
123	"	2500-3125	"	Charnockite	Tea
125	"	"	"	"	Vegetables
125A	"	"	"	"	Uncultivated
126	"	"	"	"	Vegetables
71	Uplands	1875-2500	Intermediate	Alluvium	Coconut
84AG	Lowlands	"	"	River Sediment	-
90	"	1250-1875	Dry	Hb-Bt Migmatite	Vegetables
100	"	"	"	Unknown	Coconut
104	"	"	"	Augen Gn	"
139	"	"	"	Granitic Gn	Sugar Cane
131	"	"	"	Hb-Bt Migmatite	"
Samples used for detailed analysis					
88	Upland	1875-2500	Intermediate	Marble	Coconut
112	Lowlands	"	"	Granitic Gn	"
61	Uplands	2500	Wet	Hb-Bt Migmatite	"
132	Lowlands	1250-1875	Dry	Granitic Gn	Uncultivated
132scf	"	"	"	"	Sugar Cane
16	"	"	"	Hb-Bt Migmatite	"
99	"	"	"	Granitic Gn	Uncultivated
148	"	2500-3125	Wet	Laterite	Coconut
153	Highlands	>5000	"	Gt-Sil-Gr-Gn	Tea

Table 2.2A Major Oxide Analyses of Sequences¹

Sample:depth	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	H ₂ O	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Cr ₂ O ₃	Total
145 :-5 ²	40.60	2.41	19.50	23.20	0.05	0.12	0.08	0.02	0.14	0.10	13.90	0.05	100.17
" :10	41.70	2.62	19.30	21.00	0.05	0.18	0.13	0.04	0.13	0.10	14.40	0.05	99.7
" :30	38.00	1.45	19.10	27.20	0.02	0.14	0.01	0.01	0.07	0.07	13.50	0.06	99.53
" :100	27.30	1.59	21.70	33.90	0.02	0.14	0.01	0.01	0.07	0.06	15.00	0.06	99.86
" :>100	30.80	2.66	22.50	26.50	0.03	0.38	0.25	0.01	0.02	0.17	16.10	0.03	99.45
" :200	28.10	0.93	38.60	11.20	0.02	0.16	0.01	0.01	0.17	0.11	20.80	0.01	100.10
145FR ³	47.90	1.73	13.10	15.30	0.22	6.88	10.60	2.08	0.19	0.14	0.23	0.02	98.39
142 :-5	62.60	0.99	15.30	8.40	0.04	0.40	0.22	0.05	0.43	0.07	11.30	0.04	99.8
" :10	62.90	0.97	15.20	8.09	0.04	0.40	0.16	0.01	0.42	0.07	12.30	0.04	100.56
" :30	58.10	1.13	18.70	9.04	0.04	0.37	0.08	0.01	0.43	0.07	12.60	0.04	100.57
" :100	51.70	1.40	22.90	9.96	0.03	0.54	0.05	0.01	0.52	0.06	13.30	0.04	100.47
142MR ⁴	57.00	1.07	20.60	8.61	0.09	1.37	0.16	0.07	0.99	0.07	10.60	0.03	100.63
142FR	63.90	0.91	16.00	6.91	0.11	2.39	3.28	3.18	2.14	0.05	0.54	0.02	99.41
147 :-5	79.30	0.43	3.87	2.68	0.02	0.52	5.81	0.20	0.52	0.07	5.62	0.04	99.08
" :10	76.00	1.15	4.87	3.54	0.04	0.73	6.00	0.25	0.57	0.09	6.00	0.04	99.28
" :30	75.90	1.13	4.61	3.60	0.03	0.65	6.29	0.26	0.58	0.09	6.23	0.04	99.41
" :100	75.20	0.74	3.77	2.57	0.02	0.57	7.78	0.21	0.53	0.07	7.16	0.02	98.64
61 :-5	54.20	0.86	18.40	8.26	0.14	1.12	2.09	1.16	1.36	0.17	12.20	0.03	99.96
" :10	54.50	0.83	18.00	8.15	0.14	1.09	2.10	0.17	1.41	0.17	12.50	0.03	99.06
" :30	55.60	0.82	17.80	8.27	0.14	1.02	1.89	1.09	1.35	0.16	12.50	0.03	100.64
" :100	51.20	0.89	20.00	8.70	0.13	1.99	2.70	1.28	1.53	0.13	10.70	0.03	99.25
61fr	51.40	1.07	17.40	9.12	0.15	4.11	7.46	3.74	2.48	0.54	0.77	0.01	98.24
63 :-5	50.10	1.57	20.10	11.60	0.15	1.17	1.96	0.81	0.47	0.16	11.80	0.02	99.89
" :10	49.00	1.51	20.70	11.50	0.15	1.18	1.93	0.81	0.47	0.17	12.50	0.02	99.92
" :30	53.10	1.57	18.30	12.40	0.16	0.84	1.21	0.49	0.31	0.15	11.50	0.02	100.03
" :100	45.10	1.70	23.20	12.60	0.16	0.88	1.14	0.44	0.28	0.15	14.20	0.02	99.85
115 :10	78.50	0.67	7.81	3.20	0.09	0.28	0.79	0.54	2.13	0.05	4.70	0.03	98.79
" :30	74.70	0.64	9.56	3.82	0.11	0.54	1.44	0.84	2.28	0.07	5.16	0.02	99.18
" :100	73.50	0.65	9.61	3.73	0.09	0.67	1.78	0.84	2.25	0.07	4.85	0.01	98.05
84115FR	57.30	0.63	11.70	5.56	0.07	4.17	11.40	2.14	4.53	0.16	0.93	0.01	98.6
8449-5	73.70	0.66	10.80	7.12	0.01	0.10	0.03	0.01	0.10	0.07	7.16	0.03	99.76
" :10	55.90	1.32	17.50	11.50	0.04	0.19	0.02	0.01	0.20	0.13	13.20	0.03	100.04
" :30	70.60	0.76	11.00	7.76	0.02	0.12	0.02	0.01	0.11	0.08	7.77	0.02	98.27
" :100	60.60	0.96	15.00	13.10	0.02	0.05	0.02	0.01	0.13	0.11	9.54	0.03	99.57
49FR	97.00	0.05	0.38	0.31	0.01	0.01	0.01	0.01	0.01	0.02	0.62	0.03	98.46
123 :10	52.70	0.98	17.10	8.84	0.04	0.76	0.44	0.37	0.97	0.18	17.90	0.04	100.32
" :30	54.40	0.87	16.90	8.99	0.04	0.75	0.49	0.44	1.05	0.17	16.20	0.04	100.34
" :100	50.90	0.96	22.30	9.18	0.03	0.15	0.09	0.05	0.27	0.20	16.60	0.04	100.77
" :200	58.60	0.95	20.00	8.36	0.05	0.16	0.08	0.11	0.57	0.11	11.20	0.03	100.22
123FR	69.70	0.44	14.40	3.13	0.04	1.24	3.05	4.07	2.31	0.09	0.16	0.02	98.65
123B:-5	25.50	1.79	33.00	14.00	0.26	3.62	0.96	0.52	2.11	0.29	17.90	0.02	99.97
123MR	27.90	1.71	31.70	13.30	0.28	4.21	1.06	0.39	2.36	0.27	17.10	0.02	100.3
123FR	66.30	0.63	14.00	4.01	0.06	1.33	2.79	2.93	4.69	0.14	1.47	0.01	98.36

1 Analyzed at X-Ray Assay Laboratories, Canada
 2 Top soil agitated with local water

3 FR = Fresh Rock
 4 MR = Weathered Rock
 5 River Sediment

Table 2.2A (contd) Major Oxide Analyses of Sequences ¹

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Cr ₂ O ₃	Total
125 :-5(A)	40.10	1.28	21.50	11.80	0.08	0.65	0.88	0.06	0.66	0.55	23.00	0.07	100.56
" :10(A)	40.90	1.45	21.30	11.80	0.09	0.62	0.82	0.04	0.67	0.55	22.40	0.07	100.64
" :>100(A)	20.10	1.69	36.70	19.10	0.11	0.36	0.01	0.01	0.29	0.38	21.50	0.15	100.25
" :10	44.60	1.45	16.60	11.80	0.03	0.44	0.10	0.02	0.45	0.21	24.70	0.06	100.4
" :30	41.00	1.44	21.00	11.00	0.09	0.62	0.81	0.06	0.73	0.53	22.70	0.06	99.98
" :100	51.80	1.66	18.70	10.50	0.05	0.58	0.17	0.01	0.64	0.18	16.30	0.05	100.59
126 :10B	63.00	1.19	15.70	7.58	0.01	0.16	0.10	0.01	0.22	0.19	11.70	0.04	99.86
" :30B	61.30	1.22	16.90	7.60	0.02	0.17	0.09	0.01	0.24	0.17	12.50	0.04	100.22
71 :-5	51.70	1.41	20.30	13.10	0.38	0.36	0.08	0.01	0.06	0.38	12.80	0.03	100.7
" :10	52.50	1.46	20.20	12.30	0.54	0.31	0.10	0.03	0.13	0.37	12.20	0.03	100.17
" :30	49.90	1.51	21.40	13.10	0.40	0.32	0.05	0.01	0.08	0.28	12.50	0.03	99.58
" :100	51.40	1.82	22.70	11.90	0.28	0.39	0.05	0.01	0.08	0.21	11.70	0.03	100.57
84fr	5.93	0.12	1.55	0.76	0.01	10.70	41.00	0.04	0.71	0.02	39.40	0.01	100.25
90 :-5(2)	76.30	0.46	9.18	3.19	0.12	0.56	1.03	1.14	1.61	0.11	4.60	0.02	98.3
" :10(2)	73.70	0.53	10.10	3.75	0.15	0.72	1.17	1.12	1.73	0.14	6.16	0.02	99.27
" :30(2)	75.80	0.62	10.70	3.48	0.09	0.61	1.06	1.42	1.69	0.07	4.47	0.02	100.01
" :100(2)	77.80	0.46	9.52	3.14	0.08	0.64	0.83	1.13	1.72	0.08	4.23	0.02	99.63
90FR	75.30	0.59	10.20	4.08	0.08	1.43	1.46	2.58	2.32	0.11	0.31	0.02	98.60
100 :-5(A)	65.20	1.19	14.30	3.67	0.12	0.63	2.12	3.12	3.17	0.24	5.70	0.01	100.00
" :10(A)	65.50	1.45	13.90	3.69	0.11	0.81	2.37	3.35	3.01	0.29	4.77	0.01	99.80
104 :-5	71.80	0.40	11.80	2.05	0.06	0.57	1.71	2.39	2.95	0.18	5.08	0.01	99.30
" :10	72.60	0.68	13.60	2.55	0.01	0.30	0.34	0.57	0.93	0.04	7.93	0.01	99.70
" :30	70.80	0.48	13.00	2.47	0.06	0.62	1.68	2.44	3.02	0.15	5.23	0.01	100.30
" :100	70.90	0.31	13.80	1.87	0.02	0.54	2.06	2.93	3.25	0.07	4.08	0.01	100.10
104FR	65.40	0.62	13.80	2.76	0.05	1.36	2.12	3.62	6.75	0.37	0.54	0.01	98.80
139 :-5	75.90	2.48	9.51	2.78	0.17	0.09	0.71	2.02	3.72	0.03	1.39	0.01	99.10
139-0	67.00	1.46	13.20	3.19	0.14	0.06	0.88	2.46	4.55	0.08	5.39	0.02	98.60
" :10	74.30	3.01	9.51	3.21	0.21	0.04	0.77	1.97	3.66	0.03	1.54	0.02	98.50
" :30	76.50	1.35	10.60	1.91	0.11	0.03	0.73	2.13	3.98	0.03	1.62	0.02	99.01
" :100	76.00	1.31	11.00	1.94	0.10	0.03	0.74	2.19	4.11	0.03	1.47	0.01	98.93
139FR	61.30	0.96	15.30	6.36	0.13	1.08	1.89	3.08	6.82	0.23	0.85	0.01	98.01
112 :-5	77.90	0.79	8.49	4.05	0.15	0.11	0.76	1.12	0.85	0.04	4.85	0.01	99.11
" :10	82.68	0.97	6.72	2.41	0.10	0.31	0.51	1.85	1.14	0.03	3.74	n.d	100.47
" :30	84.40	0.77	4.46	1.28	0.03	0.18	0.53	0.53	1.20	0.04	2.54	0.01	95.96
" :100	82.30	1.82	6.61	2.34	0.03	0.09	0.70	1.06	1.79	0.03	2.31	0.01	99.08
112fr	74.50	0.07	13.20	0.72	0.03	0.10	1.00	3.05	5.14	0.02	0.39	-	98.22
114D-C ⁵	83.00	0.73	6.40	3.34	0.04	0.61	0.88	0.59	1.16	0.06	2.93	0.01	99.74
84AG ³	72.80	1.38	11.00	5.35	0.09	1.11	1.34	0.94	2.08	0.09	3.16	0.03	99.6
8486 ⁵	33.60	1.34	15.60	37.80	0.08	0.42	0.03	0.01	0.01	0.38	11.20	0.03	100.5

1 Analysed at X-Ray Assay Laboratories, Canada
 2 Top soil agitated with local water

3 FR = Fresh Rock
 4 WR = Weathered Rock
 5 River Sediment

Table 2.2B Major Oxide Analyses of Samples used for Detailed Study¹

Sample:depth	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	H ₂ O	MgO	CaO	K ₂ O	P ₂ O ₅	Na ₂ O	LOI	Total
88 :10	48.37	1.62	16.75	12.74	0.25	2.65	1.76	3.10	0.17	0.00	12.90	100.29
" :30-1	48.27	1.52	17.00	13.07	0.27	2.54	1.53	3.06	0.15	0.00	13.00	100.41
" :100-1	51.38	1.22	16.67	12.15	0.23	2.37	1.65	3.95	0.10	0.15	10.31	100.17
" :100	51.19	1.35	16.29	12.94	0.25	2.43	1.58	3.17	0.09	0.37	10.58	100.23
88fr	11.57	0.04	0.16	0.49	0.03	20.86	33.15	0.14	0.09	0.00	33.73	100.25
112 :10	77.42	0.85	9.64	3.47	0.10	0.24	0.87	1.41	0.03	0.15	5.69	99.87
" :30	73.67	1.00	12.14	3.44	0.18	0.22	1.19	1.67	0.03	1.08	5.09	99.70
" :100	86.48	0.25	5.80	2.82	0.33	0.17	0.07	0.17	0.00	0.00	3.80	99.89
" :100-1	86.61	0.21	5.79	2.84	0.33	0.19	0.08	0.19	0.00	0.00	4.20	100.43
100 :30A-1	67.57	1.29	13.68	3.65	0.10	0.86	2.19	3.07	0.25	1.55	4.51	98.71
" :30A	67.70	1.29	13.55	3.64	0.10	0.79	2.18	3.06	0.26	2.91	4.30	99.77
" :100A	66.75	1.34	13.79	3.67	0.11	0.86	2.26	3.14	0.27	2.27	4.68	99.14
132 :10	68.04	1.13	14.11	3.51	0.17	0.45	0.90	5.09	0.10	1.42	4.80	99.70
132 acf	77.50	0.85	10.06	2.20	0.04	0.25	0.37	5.28	0.04	0.92	2.10	99.61
" :100	70.24	0.66	13.66	2.85	0.09	0.26	0.79	5.87	0.05	2.49	2.89	99.85
132fr	71.57	0.52	13.05	3.40	0.05	0.66	1.42	5.78	0.09	2.67	0.74	99.97
16 :10	54.33	3.54	16.03	9.75	0.15	1.53	3.16	2.53	0.92	1.95	5.88	99.76
" :20	54.92	3.55	15.55	9.69	0.15	1.50	3.32	2.56	0.95	2.60	5.69	100.48
" :30	55.76	3.69	15.46	9.62	0.15	1.48	3.28	2.61	0.95	2.22	5.00	100.23
" :50	55.17	3.23	16.54	9.53	0.14	1.52	2.80	2.53	0.85	2.01	6.19	100.51
99 :10	66.33	1.30	14.52	5.24	0.09	0.64	1.14	4.19	0.09	1.92	4.91	100.38
" :30	74.39	0.78	11.29	3.64	0.05	0.34	0.65	3.32	0.05	0.63	3.79	98.92
" :100a	76.09	0.58	11.43	3.54	0.02	0.42	0.47	2.73	0.05	0.00	4.10	99.43
" :100	72.07	0.66	13.03	4.26	0.03	0.39	0.51	3.14	0.04	0.00	4.90	99.03
99fr	70.15	0.51	13.43	3.91	0.05	0.85	2.37	3.53	0.11	3.99	0.30	99.20
99fr-1	70.07	0.47	13.51	3.93	0.05	1.06	2.39	3.56	0.09	3.29	0.70	99.10
131 :10	65.31	0.70	14.97	5.37	0.20	1.08	2.00	3.41	0.05	1.39	5.59	100.08
" :30	66.97	0.63	14.10	5.69	0.13	0.94	1.61	3.14	0.05	1.04	5.90	100.20
" :30-1	66.49	0.62	14.17	5.61	0.12	0.81	1.63	3.18	0.05	1.92	5.79	100.39
" :100	64.89	0.68	15.32	6.55	0.05	1.14	1.98	2.83	0.03	0.53	5.31	99.32
131 WR	56.11	1.15	16.92	8.49	0.10	2.96	3.32	3.17	0.07	2.37	5.59	100.24
131fr	65.05	0.82	14.72	5.45	0.07	2.34	3.93	3.72	0.13	2.33	0.74	99.30
148 :10	50.58	1.34	18.77	16.09	0.03	0.25	0.00	0.10	0.06	0.00	13.09	100.31
" :30	40.19	1.21	18.81	26.25	0.03	0.59	0.08	0.10	0.35	0.00	12.63	100.23
" :100-1	40.51	0.95	19.09	20.40	0.02	0.49	0.00	0.08	0.06	0.00	13.40	95.00
" :100	44.79	0.98	19.95	21.97	0.02	0.49	0.00	0.08	0.07	0.00	12.19	100.54
" :>100-y	41.10	2.07	36.25	5.46	0.01	0.36	0.00	0.25	0.04	0.00	17.14	102.69
" :>100r	19.95	1.78	33.82	28.85	0.03	0.77	0.00	0.04	0.05	0.00	17.66	102.96
153 :10	50.12	1.41	22.65	13.55	0.07	1.16	0.14	0.09	0.11	0.00	11.09	100.38
" :30	54.42	1.41	21.31	11.38	0.05	0.89	0.14	0.12	0.11	0.00	10.58	100.42
" :30-1	54.65	1.44	21.42	11.37	0.06	0.89	0.12	0.11	0.12	0.00	10.28	100.46
" :100	55.79	0.77	24.97	6.86	0.02	0.33	0.01	0.07	0.05	0.00	11.49	100.36
" :<600	58.15	1.09	21.44	10.76	0.03	0.33	0.04	0.04	0.04	0.00	8.31	100.23
" :<600a	33.64	0.65	29.46	23.20	0.04	1.02	0.10	0.02	0.07	0.00	12.00	100.22
150fr	51.83	1.00	22.49	10.28	0.26	3.22	3.51	3.55	0.08	3.98	0.20	100.40

¹ Analysed at the U.W.O Laboratories, Canada
 4 WR = Weathered Rock

3 FR = Fresh Rock

of a representative batch of soils was carried out through X-ray Assay Laboratories Ltd, Canada and at The University of Western Ontario. Major oxide results including duplicates are detailed in Table 2.2 A and B, while trace element data inclusive of major oxides is given in Table 4.1.

2.6.1 Geochemical Differentiation of Sequences

An immediate differentiation of samples emerges, in figs. 2.2A and B, when oxide ratios are plotted in the Kronberg and Nesbitt (1981) weathering diagram. According to Kronberg and Nesbitt (1981), primary minerals plot high along the y-axis due their relatively high content of the nutrient elements Ca, K, Mg and Na. Removal of these elements during weathering by ground water results in partitioning of primary mineral elements between residual soil minerals and river water. This results from the uptake of mobile elements from fresh minerals by ground waters which accumulates as river water. This in turn drives the residual soil composition directly away from that of river water. This is expressed in the diagram by opposing evolutionary trends of (a) river water and (b) residual soil minerals. They branch out on either side of the plots of primary minerals. The residual soil weathering trend from unweathered rock to highly weathered residues such as gibbsite and kaolin evolves 'down' the diagram while the river solution evolves 'up' the diagram as it continually extracts Ca, K, Mg and Na from the soils.

Chemical weathering of the parent rock yields a convex downward trend directed to the left joining river water, primary minerals and gibbsite. Conversely, physical processes of winnowing and sorting are indicated by trends joining river water to quartz through primary minerals.

In figs. 2.2A and B samples are grouped into three fairly

In figs. 2.2A and B samples are grouped into three fairly distinct fields designated 1, 2 and 3. Fresh rock samples regardless of the climatic conditions of their sampling sites, plot in a relatively tight cluster in field 3. They cluster close to feldspar along the mixing curve between primary feldspars and quartz with the exception of the quartzite sample, FR49.

Soil samples on the other hand clearly fall into 3 distinct fields. Additionally it is noted that the soil trends have arrows pointing both up and down. In sequence 104 (fig.2.2 A) the upward directed arrows indicate that the surface layer has lower nutrient content and is more weathered than the subsurface layer that plots close to fresh rock. Hence upward directed arrows in the direction of greater depth (in an evolutionary sense the trend is 'downward', i.e. the least weathered soil layers are at the bottom of the sequence) indicate the presence of a high nutrient content at depth, signifying possibly the proximity of relatively fresh material at depth. The reverse (downward facing trends in the direction of depth) which is the dominant trend implies extensive leaching and accumulation of aluminum at depth and is seen in the most highly weathered lateritic sequences, 145, 148 and even more strikingly by sequence 49 developed on a quartzite precursor (FR49), that is exceptionally low in nutrient elements and aluminum, (figs. 2.2 A and B).

Superimposition of the interpretation of the up and down facing trends onto the original significance of the left and right facing trends of Kronberg and Nesbitt, (1981), gives four alternative routes of weathering. In the dominant downward left facing trends (fig. 2.2 A - eg. sequence 145), the surface samples are farthest along both y and x axes, implying that they have greater nutrient and silica contents than the subsurface samples which plot closer to gibbsite. They imply increase in chemical leaching of mobile constituents in the direction of greater depth which is superimposed by accumulation of silica at

the surface possibly through physical processes that remove aluminum bearing particles. Hence it is inconsistent with the expected aluminum enrichment in the surface layers which would be found in an idealised chemical only weathering system, where the weathering front moves downward enriching the surface material with more and more aluminum as it proceeds compared to the subsurface material. As noted previously in an idealised chemical only weathering system where the weathering front moves downward, an upward facing trend in the direction of depth would result indicating proximity to fresh material with greater depth.

Since samples collected from the Wet Zone, plot in field 1, the field of kaolinite and gibbsite; it indicates their probable mineralogy and the fact that they have lost most essential elements, Na, K, Ca and Mg during the process of weathering regardless of their parent rock type, rendering them to be indistinguishable from each other. The exception is sequence 115, which has developed on a calc-silicate gneiss. The intensity of leaching that proceeds in the wet zone can be gauged by the plot of weathered rock samples (WR), that are still structurally coherent but are far removed from the fresh rock plots (142WR, 123bWR, and 153WR in figs. 2.2 A and B). Wet and intermediate zone river sediment samples that are seen to carry visible primary minerals plot high along the y-axis outside field 1, testifying to the intensity of erosion. Beach sand samples containing Ca bearing shells plot above field 1.

Sequences sampled from the Wet Zone close to the Wet/Intermediate boundary (field 2), plot in the smectite-illite zone giving a possible indication of their mineralogy. Sequence 112, collected away from the fresh rock outcrop and presently under coconut cultivation (fig. 2.2a), is more enriched in nutrient elements than the sequence collected at the outcrop (fig. 2.2E). The direction of arrows with depth is also reversed reflecting possibly the complex interplay of

factors such as direction of ground water movement, abundance of unweathered primary minerals, and the replenishment of nutrient elements from leaf decay. More detailed work is required to explain the reversal of arrow direction.

Samples from the Dry Zone, field 3, plot just below the fresh rock samples, indicating either the presence of abundant unweathered primary minerals and/or the presence of clays with very high exchange capacities. A convex downward curvature directed to the right towards greater abundance of silica, is noted in some of the sequences of the Dry Zone (sequence 139, fig. 2.2A). This implies the dominance of physical weathering over chemical weathering, (Kronberg and Nesbitt, 1981). A vertical differentiation between levels and fresh rock is more often observed in dry zone sequences 104, 100 (fig.2.2A) and 99 (fig.2.2B).

Trends to the left or right are not however, mutually exclusive, (even though such a tendency exists), to either one of the climatic zones as noted in the cases of sequences 16 and 88 (fig.2.2B) from the dry zone, which have left directed trends and sequences 115 and 112 (fig. 2.2A) from the wet and the intermediate zones respectively that have right directed trends.

The overall dominance of climate in determining soil characteristics in tropical regions irrespective of parent rock type, is clearly brought out in this diagram.

The distinct character of soil samples belonging to the three main climatic zones of Sri Lanka is further demonstrated by plotting the oxide analyses according to Chesworth et al., (1981) in figs. 2.3 A and B. Since sequences in fig. 2.2B follow the same behavioural patterns established in fig. 2.2A further discussion at this stage will be restricted to sequences plotted in fig. 2.2A. In fig. 2.3A samples approaching pure quartzite or beach sand plot high along

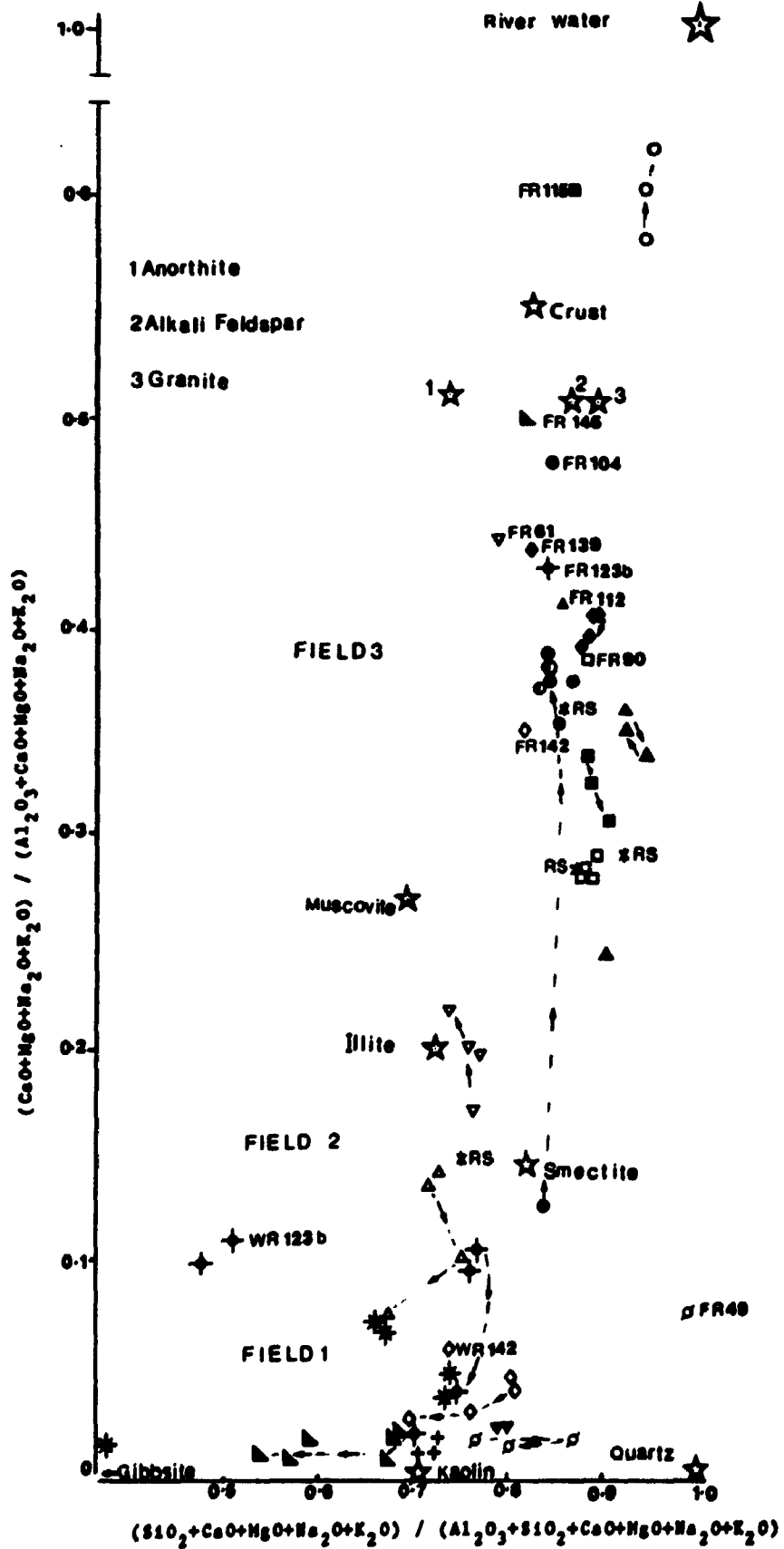
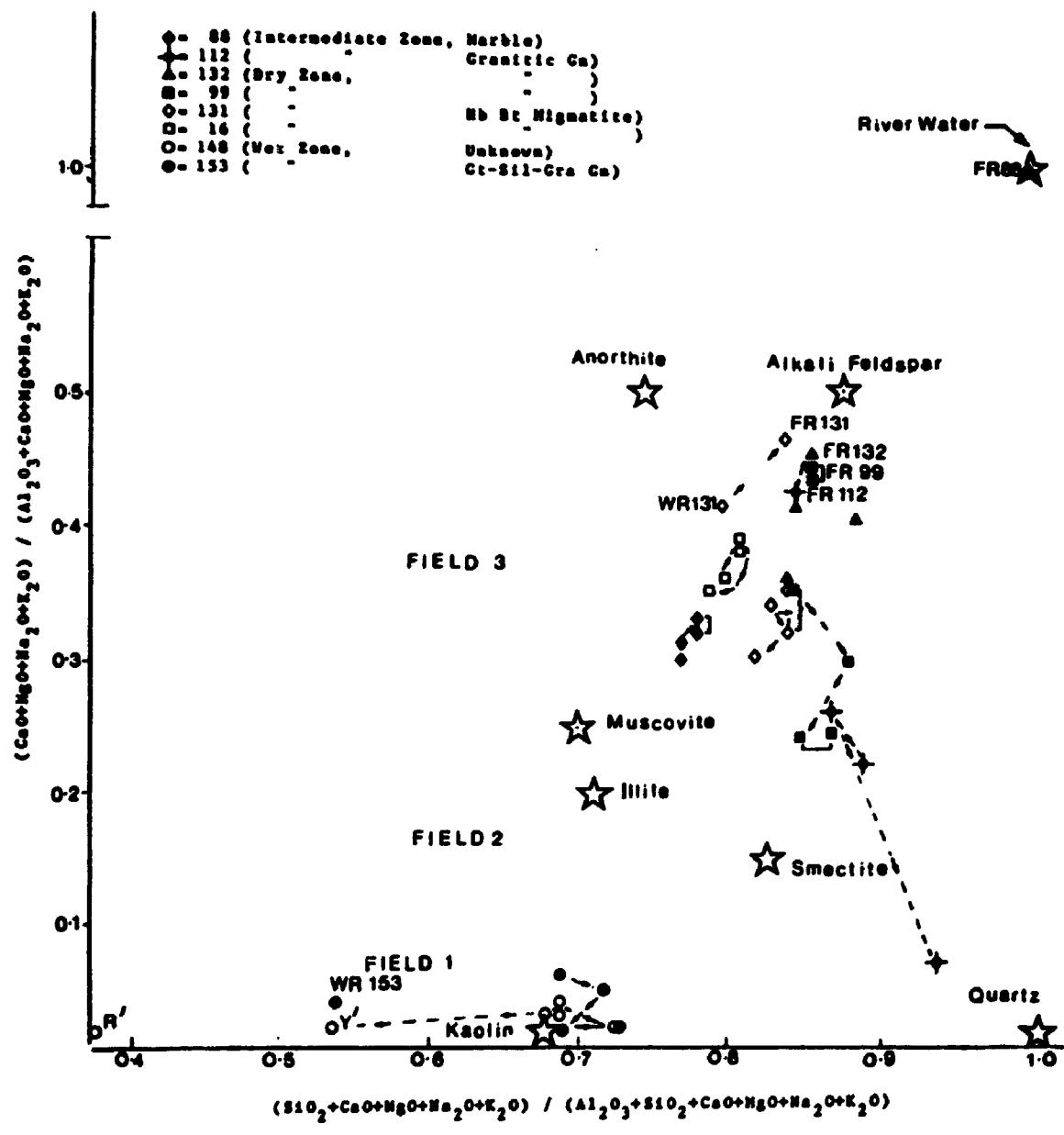


Fig. 2.2B Sample distribution plot on a Weathering Diagram modified after Kronberg and Nesbitt, (1981). Sequences are represented by symbols designated at the fresh rock (FR). Arrows indicate down depth direction. RS = River Sediment; WR = Weathered Rock; R' = Sample 148>100 red nodules; Y' = Sample 148>100 yellow matrix. (Duplicate analyses bracketted).



the y-axis and highly weathered samples with increasing amounts of residual oxides plot farthest along the x-axis. A pure bauxite will have an x-axis value of 100.

The amount of silica is strongly inversely correlated with the amount of sesquioxides present and group the soils into fields both along the horizontal and vertical axes. This diagram shows that the total sesquioxide amount can be used to uniquely define sequences from the two main climatic zones. The Dry Zone samples fall into a distinct group by having both a wide range in silica concentrations and the lowest sesquioxide totals that hardly differ from that of the parent rock. Highly weathered Wet Zone soils have very high sesquioxide totals, much higher than their parent rock and a low range in silica concentrations.

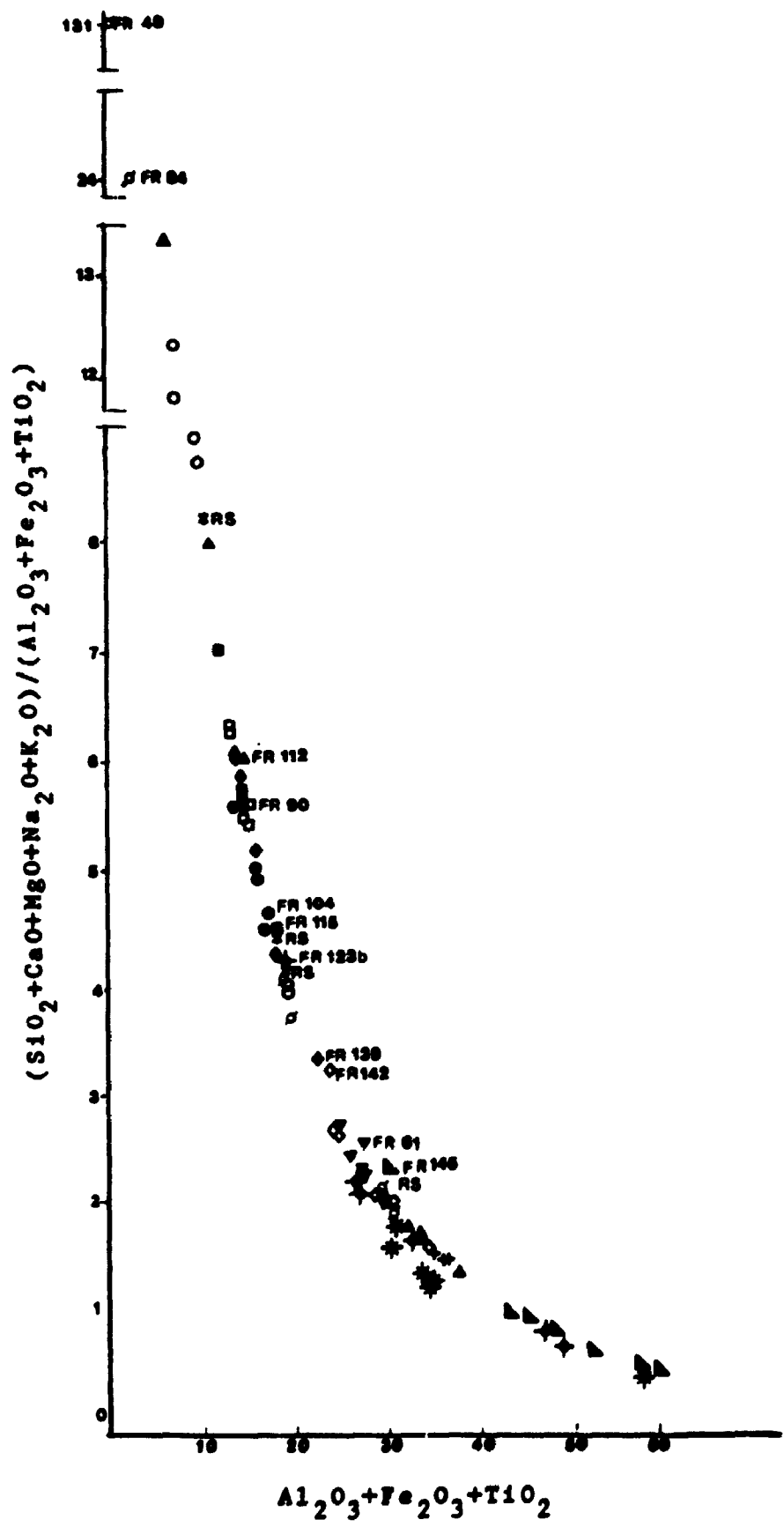
The Dry Zone samples show a different behaviour pattern from the others. Silica is gained with respect to the residual oxides in the weathered residue compared to the parent material, whereas in the Wet Zone samples, the reverse trend is observed.

The near identical reproduction of fig. 2.3A in fig. 2.3B underscores the fact that the other major oxides constitute only a very minor part of the soils' constituents, thus explaining the reciprocal relationship observed between silica and the sesquioxides in fig. 2.3A.

All soil samples have less of the oxides of the essential elements Na, K, Ca and Mg than their precursors, (figs. 2.2A and B), which contrasts with the behaviour of silica. The extent of leaching of these essential elements in the Wet Zone soils is to be gauged by comparing the differences along the y-axis between the precursor material and the soil samples.

Fig 2.3A Rates of silica loss or gain with respect to
 $Al_2O_3 + Fe_2O_3 + TiO_2$ used here as an index of weathering
after Chesworth, et al., (1981). FR = Fresh Rock.
RS = River Sediment.

Fig 2.3B Rates of major oxide loss or gain with respect to $Al_2O_3 + Fe_2O_3 + TiO_2$ used here as an index of weathering after Chesworth, et al., (1981). FR = Fresh Rock. RS = River Sediment.



2.6.2 Conclusions from Geochemical Investigation

The differences between the soil samples from the Wet and the Dry Zones point to the following facts:

- (a) Wet Zone samples are the most weathered in that they have lost most major nutrient elements regardless of parent rock type. They are unlikely to contain free silica and would most probably be characterised by the presence of kaolin and free oxides. These samples provide a dramatic illustration of the stripping power of humid tropical weathering, which show that weathering appears to be almost completed while the rock itself is still structurally coherent. This observation has not been noted previously in the case of Sri Lankan soils.
- (b) Dry Zone samples are the least weathered and in addition to silica must contain either residual primary minerals that contain nutrient elements and/or clay minerals with greater cation exchange capacity than kaolin, such as smectite or vermiculite.
- (c) Compared to the oxides SiO_2 , Al_2O_3 , and Fe_2O_3 , the total of the remaining nutrient oxides do not amount to a significant amount in all weathered samples.

In addition;

- (d) fresh rocks plot in a relatively tight cluster along the mixing line between quartz and other primary minerals. The overall dominance of climate in determining soil characteristics in tropical regions irrespective of parent rock type, is clearly brought out in these diagrams.

2.8 Routine Pedological Analyses

The following sections describe techniques and results of routine pedological analyses of representative samples that were carried out with the intention of:

- o relating soils of the present study, to available literature on Sri Lankan soils
- o and furthering the understanding of weathering processes operative in the different climatic zones that led to such distinction between the soils analysed so far.

To enable evaluation of the current set of results laboratory conditions used by Moorman and Panabokke (1961) were emulated as far as possible.

Description of sequence locations used for detailed analyses is given in Appendix 2. These samples constitute a segment of the samples taken during the reconnaissance survey mentioned in section 2.5. Sample location is given in fig. 2.1. Plate 1 provides an indication of colour and texture of the samples.

2.8.1 Laboratory Analysis and Evaluation of Results

Routine analysis at the University of Western Ontario involved determination of (1) pH , (2) particle size , (3) cation exchange capacity , (4) extractable acidity and (4) exchangeable bases , on the <2 mm fraction of the samples.

Determinations of pH were carried out in 1:2 H₂O and 1:2, 1N KCl solutions using a Corning pH meter 140. A direct 1:1 suspension as

Plate 1

General textural view of samples used for detailed analysis showing contrast in degrees of Fe oxidation as revealed by colour and preservation of primary minerals, between climatic zones.

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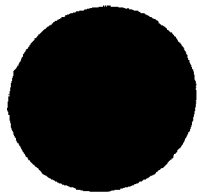
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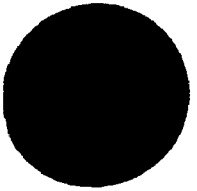
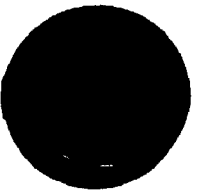
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Wet Zone

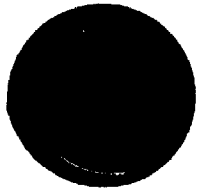


14810

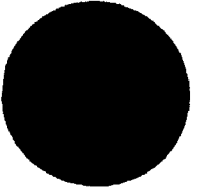
14830



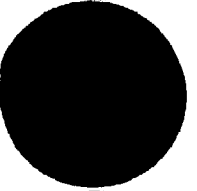
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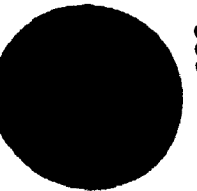
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15330

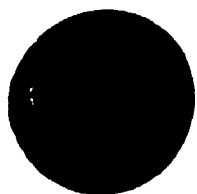


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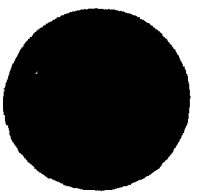


153< 600

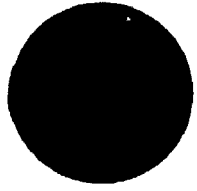
Int. Zone



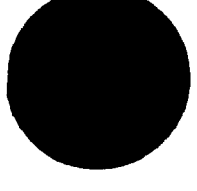
11210



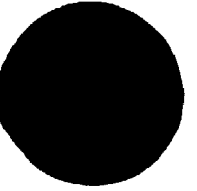
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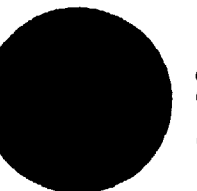
112100



6110

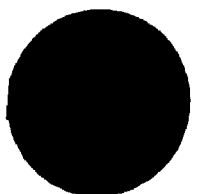


6130



61100

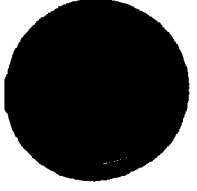
Dry Zone -



8810



8830



88100



9910



9930

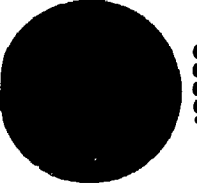


99100

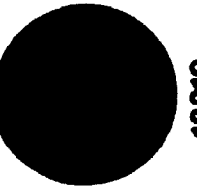
Dry Zone



132 scf



13230



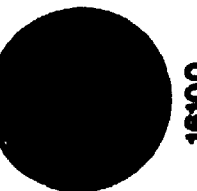
13210



1610



1630



16100

used by Moorman and Panabokke (1961) could not be emulated for fear of damaging the microelectrode.

Particle size analysis was carried out by a combination of dry sieving for the sand fractions and pipette analysis for the silt ($44\mu\text{m} - 2\mu\text{m}$) and total clay fractions ($<2\mu\text{m}$), (Singer and Janitzky, 1986). It was decided not to pretreat the samples to remove organic matter, since examination of the samples showed that very little organic matter was present. This was confirmed also by the colour of the soils, and by Moorman and Panabokkes' (1961) results. Cementing carbonate was not expected in any of the samples excepting in sequence 88 which had a marble precursor. Treatment to remove binding free oxides was not carried out to avoid altering clay minerals since the clay fraction was used subsequently for mineralogical analysis.

All samples were dispersed for 10 minutes in an ultrasonic bath, before and after soaking them overnight in diluted sodium metaphosphate, to obtain a clean sand fraction devoid of oxide coatings and partially dispersed aggregates, when examined under a microscope. Fractionation of the samples was performed according to the USDA grade scale after which data were aggregated into %sand, %silt and %clay. The arbitrary boundary between sand and silt at $50\mu\text{m}$, could not be kept due to the lack of the requisite sieve, hence a $44\mu\text{m}$ mesh sieve was substituted.

In the present analysis exchangeable bases were determined by displacing exchangeable bases/cations into solution using 0.5N BaCl_2 buffered at pH 8.1 (Janitzky, 1986). Individual cations were quantified by atomic absorption. Total exchangeable bases/cations was obtained by summing individual cations.

Total cation exchange capacity was subsequently determined according to Janitzky, (1986) by displacing Ba in the soil residue by saturating with a known amount of calcium and determining loss of

calcium subsequently.

Moorman and Panabokke (1961) used a separate method (Bray and Wilhite method) to obtain total exchangeable bases instead of summing exchangeable cations. These authors determined total cation exchange capacity by displacing exchangeable cations/bases into solution by sodium saturation at pH 8.2 followed by displacement by ammonium acetate and determination of displaced sodium.

In the present analysis, the pH was buffered to 8.1, to comply with Moorman and Panabokke, and current international practice, even though for the slightly acidic soil samples from Sri Lanka, this is a pH value highly unlikely to be encountered under natural conditions. A separate check for the validity of the current set of results was made by analysing the samples for exchangeable acidity by Ba displacement at pH 8.2 followed by HCl titration against a blank (Janitzky, 1986). Summation of exchangeable acidity and exchangeable bases approximate total cation exchange capacity within ± 1.0 meq/100g. A few anomalous total CEC results that were not within this range were found to be in error, when replicated subsequently. Results are tabulated in Tables 2.2 and 2.3.

2.9 Evaluation of Results

2.9.1 pH

Comparison of pH between the present study and that of Moorman and Panabokke (1961) was not possible since the same dilution could not be used as discussed in section 2.8.1. Upward drifting of the pH value with progressive settling when the reading was taken after 15 minutes of settling, as recommended by McLean (1982), makes dependability of these results suspect. Values for pH after settling overnight were generally higher but no systematic variation was detected. The depth at which the electrode rested made a significant

Table 2.3A. Physical and Textural Properties of Sequences.

Sample	Colour	Texture	Particle Size Distribution				
			stone %	sand %	silt %	clay %	
8810	5YR 3/4	dk rd br	sandy clay loam	0.88	47.57	22.52	29.91
8830	5YR 3/3	dk rd br	sandy clay loam	0.43	45.58	21.33	33.09
88100	5YR 3/3	dk rd br	sandy clay loam	6.08	53.64	19.97	26.39
11210	10YR 4/3	br-dk br	sandy loam (med)	10.38	74.52	13.89	11.59
11230	10YR 4/3	br-dk br	sandy loam (med)	11.22	72.18	11.59	16.03
112100	10YR 4/3	br-dk br	sandy clay	47.72	58.08	2.12	39.80
6110	7.5YR 4/4	dk br	sandy clay loam	1.32	57.12	18.92	23.96
6130	7.5YR 4/4	dk br	sandy clay loam	5.01	52.86	17.92	29.21
61100	7.5YR 4/6	st br	clay	3.30	42.56	8.13	49.31
13210	10YR 5/3	br	sandy loam (med)	6.26	70.41	15.72	13.87
13250	10YR 5/3	gr br	sandy loam (med)	15.30	72.64	12.43	14.93
132acf	10YR 5/2	br	loamy sand	10.27	83.75	9.75	6.50
1610	10YR 4/3	dk br	sandy clay loam	0.73	65.91	9.06	25.03
1630	10YR 4/4	dk yl br	sandy clay loam	0.21	70.26	9.14	20.60
1650	7.5YR 5/4	br	sandy clay loam	0.34	62.58	9.20	28.22
9910	7.5YR 4/4	br	sandy loam (med)	4.86	69.78	14.58	15.64
9930	5YR 4/4	rd br	sandy clay loam	34.78	66.31	11.86	21.83
99100	2.5YR 4/6	rd	sandy clay loam	23.13	60.97	10.56	28.46
14810	10YR 6/4	lt yl-br	sandy clay loam	43.57	59.18	11.09	29.73
14830	10YR 5/4	yl-br	sandy clay loam	53.93	65.52	8.18	26.30
148100	10YR 6/6	br-yl	sandy clay loam	56.06	63.74	7.20	29.05
15310	10YR 5/4	yl-br	sandy loam (med)	18.77	75.34	15.55	9.11
15330	10YR 5/4	yl-br	sandy loam (med)	28.25	77.69	15.44	6.86
153100	7.5YR 6/6	rd-yl	sandy loam (med)	17.39	68.93	17.20	13.87
153600	5YR 6/6	rd-yl	sandy loam (med)	18.00	73.73	15.00	11.26

Table 2.3B. Chemical Properties of Sequences.

sample	pH H ₂ O 1:2	pH KCL ¹ 1:2	Exchangeable cations m.e./100g					Extract. Acidity me/100g	CEC me/ 100g	CEC me/100g clay	Base Sat. %
	Mg	Ca	K	Na	Al						
8810	5.69	5.45	7.35	11.00	0.50	0.19	0.25	9.46	27.81	93.0	69.6
8830	5.62	5.46	6.77	10.31	0.23	0.16	0.28	8.07	25.11	75.9	68.4
88100	5.77	5.08	5.50	10.48	0.28	0.25	0.15	5.77	21.99	83.3	75.1
11210	5.20	4.88	1.00	2.18	0.10	0.04	0.41	5.47	9.10	78.5	35.9
11230	5.19	4.91	0.94	2.51	0.04	0.09	0.04	5.93	8.51	53.1	45.7
112100	4.62	4.81	2.82	3.61	0.05	0.21	0.20	5.93	11.61	29.2	57.6
6110	5.91	5.53	1.63	6.33	0.51	0.00	0.20	7.61	15.93	66.5	53.3
6130	5.52	5.32	1.57	5.80	0.45	0.09	0.04	8.07	17.42	59.6	45.4
61100	5.25	5.12	1.07	3.71	0.31	0.03	0.39	10.94	14.04	28.5	36.5
13210	5.95	5.57	1.02	5.37	0.35	0.03	0.27	4.38	11.12	80.0	60.9
13230	5.71	4.68	0.76	4.20	0.19	0.07	0.20	3.00	8.02	53.7	65.1
132scf	6.46	5.60	.29	0.96	0.06	0.14	0.35	7.15	5.32	81.9	27.2
1610	6.14	5.79	2.30	7.27	0.57	0.02	0.22	2.54	12.96	51.8	78.3
1630	6.29	6.26	1.72	8.02	0.82	0.04	0.24	1.61	11.88	57.7	89.3
1650	6.14	5.76	2.82	6.77	0.42	0.08	0.17	3.46	13.37	47.4	75.2
9910	6.26	5.40	1.49	4.28	0.51	0.01	0.28	3.19	9.18	58.7	68.5
9930	6.14	5.73	1.08	4.71	0.18	0.04	0.21	4.10	10.53	48.2	57.1
99100	6.23	5.40	1.29	4.91	0.16	0.02	0.15	4.10	10.26	36.1	62.2
14810	4.77	4.14	0.00	0.08	0.02	0.02	1.09	8.21	8.91	30.0	1.3
14830	4.42	4.19	0.00	0.16	0.01	0.02	0.86	5.93	6.80	25.9	2.8
148100	4.41	4.35	0.00	0.13	0.01	0.03	0.70	5.01	5.59	19.2	3.0
15310	4.82	4.41	0.06	0.49	0.15	0.04	0.82	1.61	7.75	85.1	9.4
15330	4.84	4.46	0.04	0.34	0.17	0.04	0.75	4.84	5.32	77.6	11.0
153100	4.78	4.24	0.00	0.27	0.03	0.05	0.57	4.38	3.78	27.3	9.2
153600	5.09	5.26	0.00	0.39	0.02	0.06	0.51	2.08	2.21	19.6	20.0

1. 0.01 N KCL solution

difference. The pH dropped significantly as the soil water interface was approached. These observations indicate the probable existence of H^+ concentration gradients associated with charged colloidal aggregates that causes interference. Although the solution should be constantly agitated during pH measurement, this would place the soil in suspension and hence this step is avoided in soil pH measurement. Perhaps the soil suspension should be filtered before measurements are made if dependable results are required.

When the results are viewed even within these limitations trends are observed (Table 2.2). The wet zone sequences 148 and 153 are the most acidic and change little in the KCl determination, indicating that the clays have low exchange capacity. The dry zone samples, sequences 16 and 99 have comparatively high pH values and are 1 to 2 pH units higher and show a significant change when pH is determined in salt solution.

2.9.2 Cation Exchange Capacity and Base Saturation

Results are summarised in figs. 2.4 to 2.7B. The correspondence in range and trend (exchangeable $Ca > Mg >> K > Na$) between the present analyses and that of Moorman and Panabokke (1961), for both the wet and dry zone soils, is remarkable considering that different techniques were used.

The average total CEC for the present set of analyses is approximately 10 meq/100g, excluding the sequence developed on a calcareous parent rock, (fig. 2.4). This range compares very favourably with the results in fig. 2.5 (details of which are given in Appendix 3), of Moorman and Panabokke (1961), and is typical of tropical soils (USDA ref). The percent base saturation of dry zone soils is above 50%, and falls gradually through the intermediate zone soils to less than 10% for the wet zone soils, excepting in the shallow 0-4" surface horizons where sampled, (fig. 2.5, sample numbers

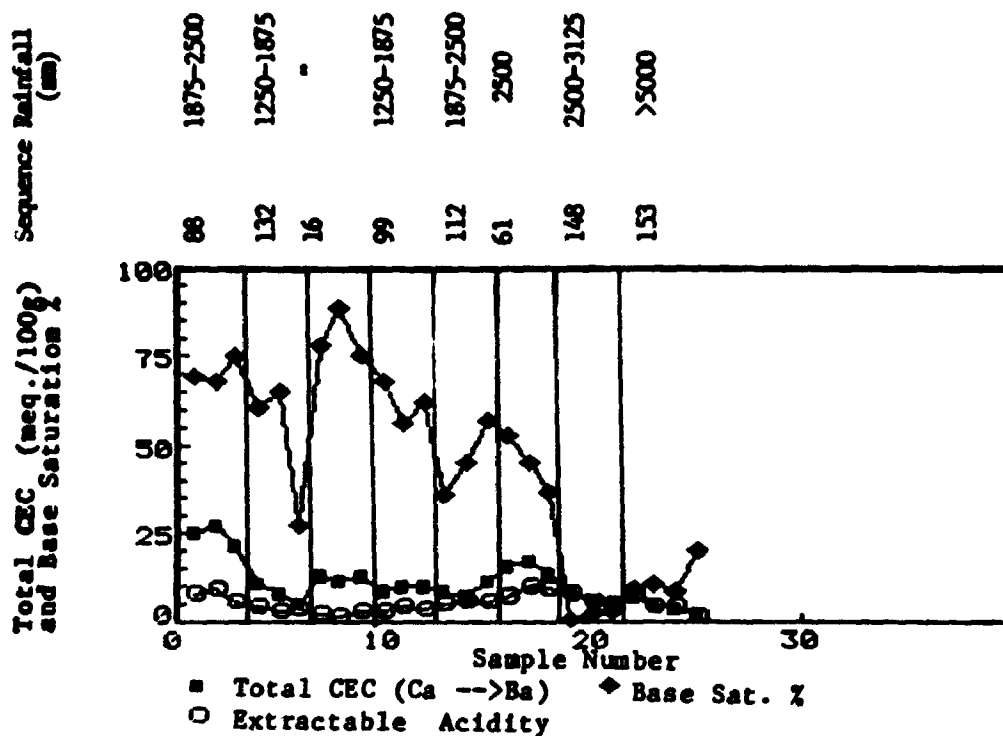


Fig. 2.4 Cation exchange capacity and base saturation % from the present study of some Sri Lankan soils.

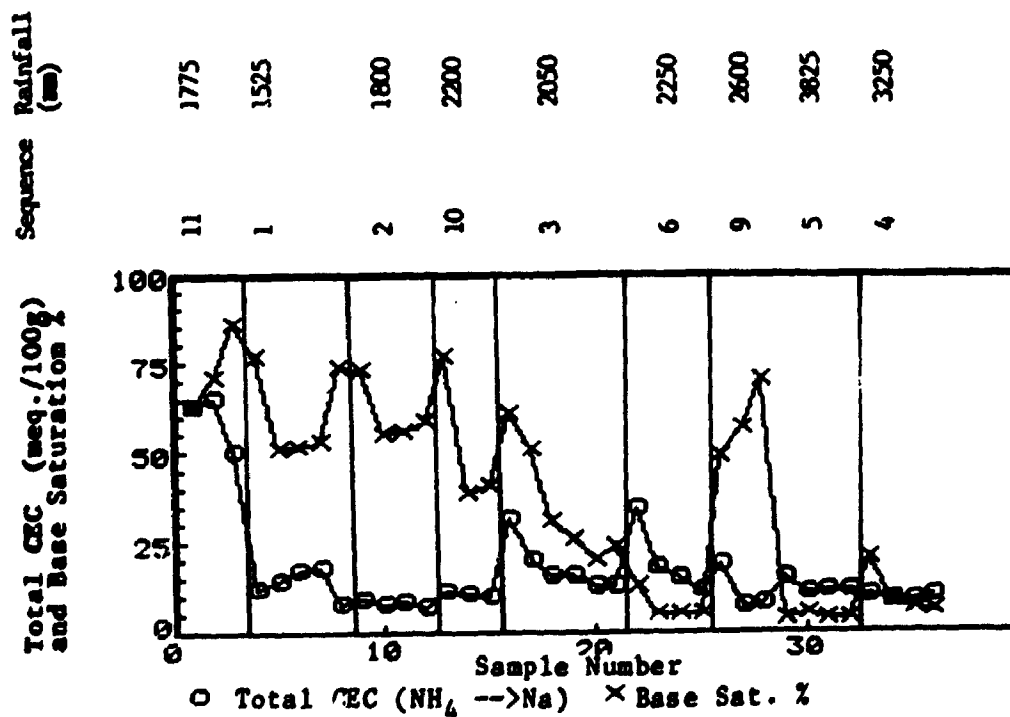
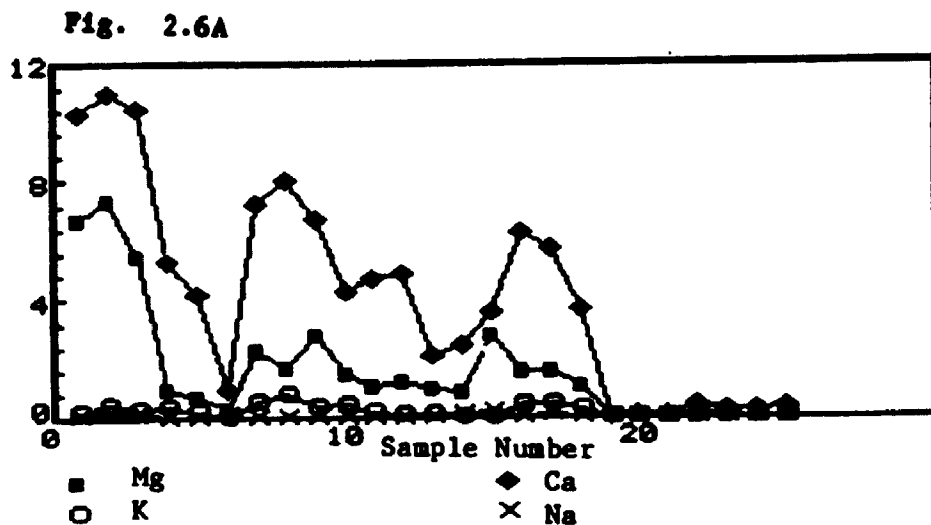


Fig. 2.5 Cation exchange capacity and base saturation % of some Sri Lankan soils (Moorman and Panabokke, 1961).

Exchangeable Cations (meq./100g)



Sequence Rainfall (mm)

1875-2500	1250-1875	"	1250-1875	1875-2500	2500	2500-3125	>5000
88	132	16	99	112	61	148	153

Exchangeable Cations (meq./100g)

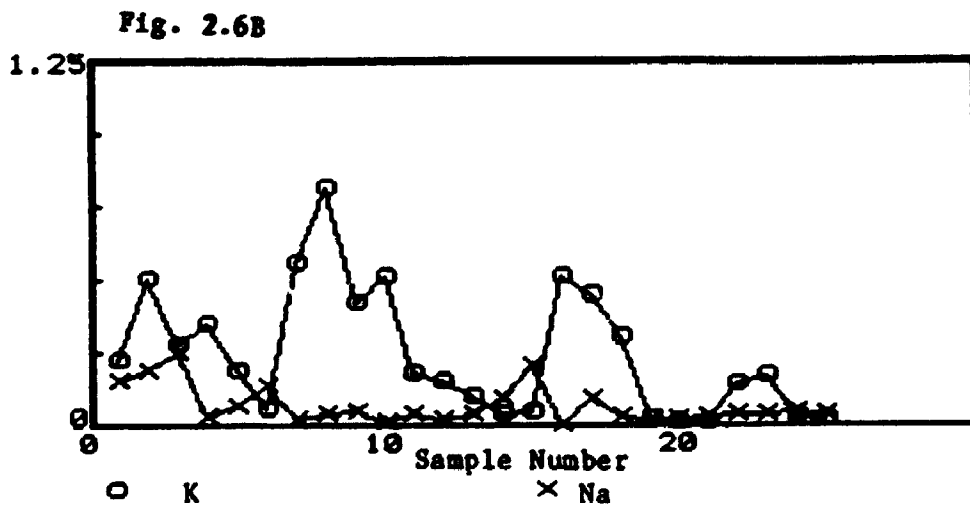
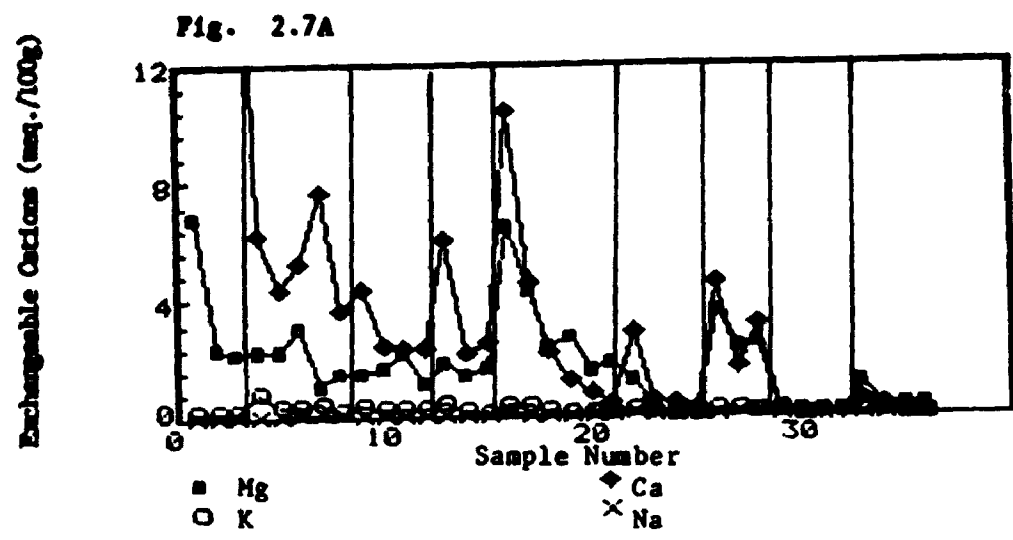


Fig. 2.6A Exchangeable cations, Mg, Ca, Na and K from the present study of some Sri Lankan soils.

Fig. 2.6B Exchangeable cations, Na and K on an expanded scale.



Sequence	Rainfall (mm)
11	1775
1	1525
2	1800
10	2200
3	2050
6	2250
9	2600
5	3025
4	3250

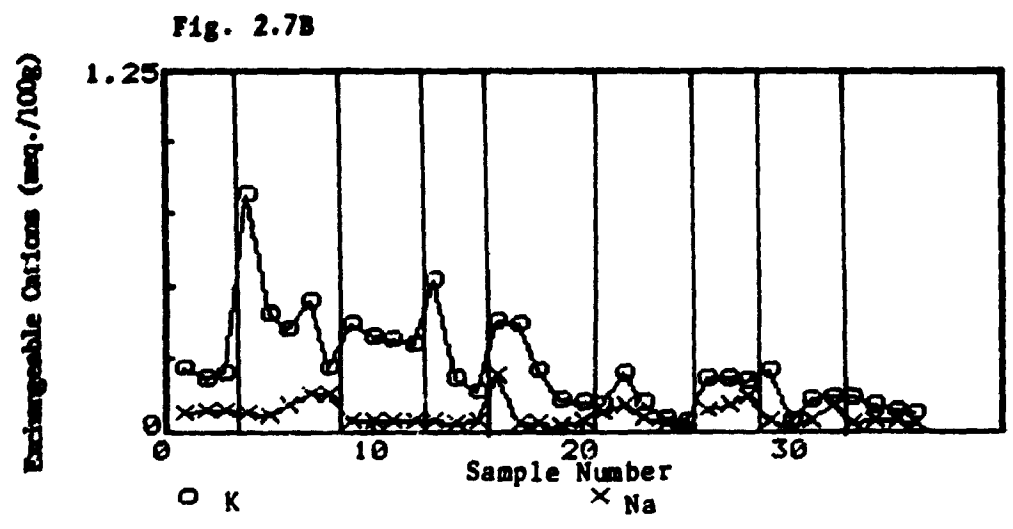


Fig. 2.7A Exchangeable cations, Mg, Ca, Na and K of some Sri Lankan soils (Moorman and Parabolke, 1961).

Fig. 2.7B Exchangeable cations, Na and K on an expanded scale (Moorman and Parabolke, 1961).

22 and 33). These results reinforce the findings from geochemical analyses (figs. 2.2 A and B); wet zone soils are heavily leached. In the lateritic sequence 148, (sample numbers 19-21, fig. 2.4) where coconut palms grow, base saturation is as low as 1-3%. Most of the total CEC in the wet zone soils comprise 'extractable acidity' since base saturation values are near zero. This, together with low pH values suggests, that exchangeable sites are occupied by H^+ and Al^{3+} -OH polymers that are considered to represent 'extractable acidity'. Sequence 153 (sample numbers 22-25), sampled in the wettest location in Sri Lanka where annual rainfall exceeds 5000mm, has a higher total CEC and base saturation, than the lowland lateritic sequence.

Sequences developed on calcareous precursors, have very high CEC and base saturation values, (figs. 2.4 to 2.6A and fig. 2.7A: sample numbers 1-3). On the other hand sequences 16 and 61 developed on highly micaceous migmatitic parent rocks have high exchangeable potassium (fig. 2.6B, samples 7-9 and 16-19).

The relation between % clay and total CEC shown in fig. 2.8 suggests that CEC is governed by the amount of clay present, and is to be expected.

2.9.2.1 Influence of Parent Rock on CEC

The unexpectedly high CEC in sequence 153 may be a result of rock residue retaining its structural coherence still observable within the sequence, in this highland site. The intensity of the rate of weathering at this site is reflected by comparing this site with that of another wet zone immature sequence, no.9 of Moorman and Panabokke (1961), fig. 2.5, samples 26-28, where the rainfall is less severe and the influence of the presence of residual parent rock is possibly reflected in the 'above average' total CEC and base saturation values of wet zone soils.

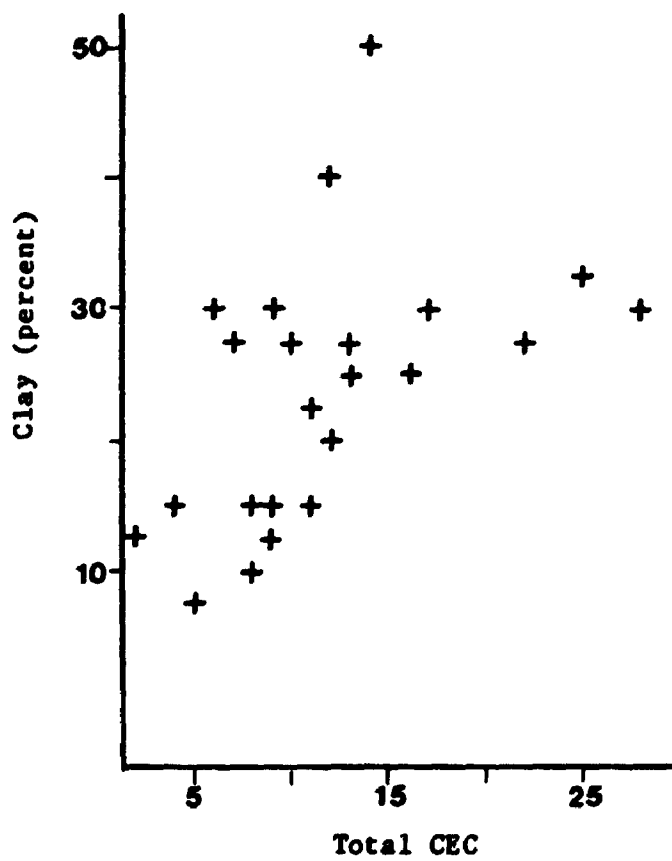


Fig. 2.8 Variation of Total CEC with Clay Percentage.

The influence of parent rock is further discernible in the calcareous sequences, figs. 2.4 to 2.6A and fig. 2.7A, (sample numbers 1-3), where the supply of Ca and Mg appears to supercede effects of leaching.

Highly micaceous migmatites appear to provide soils with relatively high CEC's, for example, samples 7-9, fig. 2.4, while soils on granitic parent material, samples 10-12, in the same climatic zone have lower values. Similarly the mica present in the parent migmatite is reflected in higher exchangeable potassium in sequences 16 and 61, (fig. 2.6B, samples 7-9 and 16-19).

Cultivation may have reduced CEC in sample 6 (fig. 2.4) taken from a sugar cane field, which is to be compared with samples 4 and 5 (sequence 132) taken from a forested grove from a profile 30 cm thick overlying its granitic gneiss parent, barely 3 meters away.

2.9.3 Particle Size Distribution and Its Correlation to Rock Type and Geochemistry

Samples group into sandy clay, sandy clay loam and sandy loam textural divisions when particle size analyses are plotted on a triangle diagram showing basic textural classes, (fig. 2.9). The dry zone samples reflect their higher silica content by consisting of a greater percentage of sand (sequences 132 and 99 and 16). There is no simple pattern to the distribution of the wet zone samples excepting their slightly higher silt and clay contents indicated by their plots that girdle those of the dry zone samples. Soils developed on micaceous migmatitic precursors are finer grained than the others as exemplified by sequence 61 from the wet zone and sequence 16 from the dry zone. The sample developed on dolomitic crystalline marble reflects the lack of abundant quartz by being the most silty (sequence 88). Similarly samples developed on granitic precursors have higher sand fractions as shown by sequences 112, 132 and 99. The dry zone

samples are sandy, and is in concert with the findings of Moorman and Panabokke (1961), fig. 2.10. Control by modifiers such as parent rock and the degree of maturity of the profile can be discerned as well. For example profile 9 is the sandiest, in spite of being a wet zone sample, the reason being its immaturity. Profile 11, is the siltiest derived as it is from a marble precursor lacking in resistant quartzo-feldspathic minerals.

Wet zone samples in fig. 2.10 from Moorman and Panabokke occupy clay, clay loam and loam divisions of the textural classification as well as those occupied in common with the present study. The extra divisions (fig.2.10) are occupied by the deep horizons, where increasing depth is denoted by ascending sequential numbers 3 to 6, and was not encountered in the present study since sampling was restricted to the upper 100cm. The sandiness of the upper horizons in the wet zone sequences of the present study hence may probably be the result of erosional and or eluviation processes.

The sandiness of the upper horizons in the wet zone sequences correlates with the surficial silica enrichment trends observed geochemically in fig. 2.2 B (section 2.6.1). This is noticeable in sequences 61, 99, and 112 (fig 2.9). They comprise several textural divisions and show vertical separation along the y-axis in fig. 2.2 B between levels. In these cases where the aluminum content increases with depth (downward facing arrows in fig. 2.2B) the clay content increases accordingly, ie. the upper horizons are sandier. A noteworthy correlation is found in the deepest level of sequence 112 which is geochemically richer in aluminum and silica compared to the surface levels (fig. 2.2 B). Texturally it corresponds to a sandy clay.

The corollary is also true. In sequences 16 and 88 sparse geochemical (fig. 2.2 B) and textural (fig. 2.9) separation occurs; the disordering in the weathering trends (fig.2.2B) is also reflected

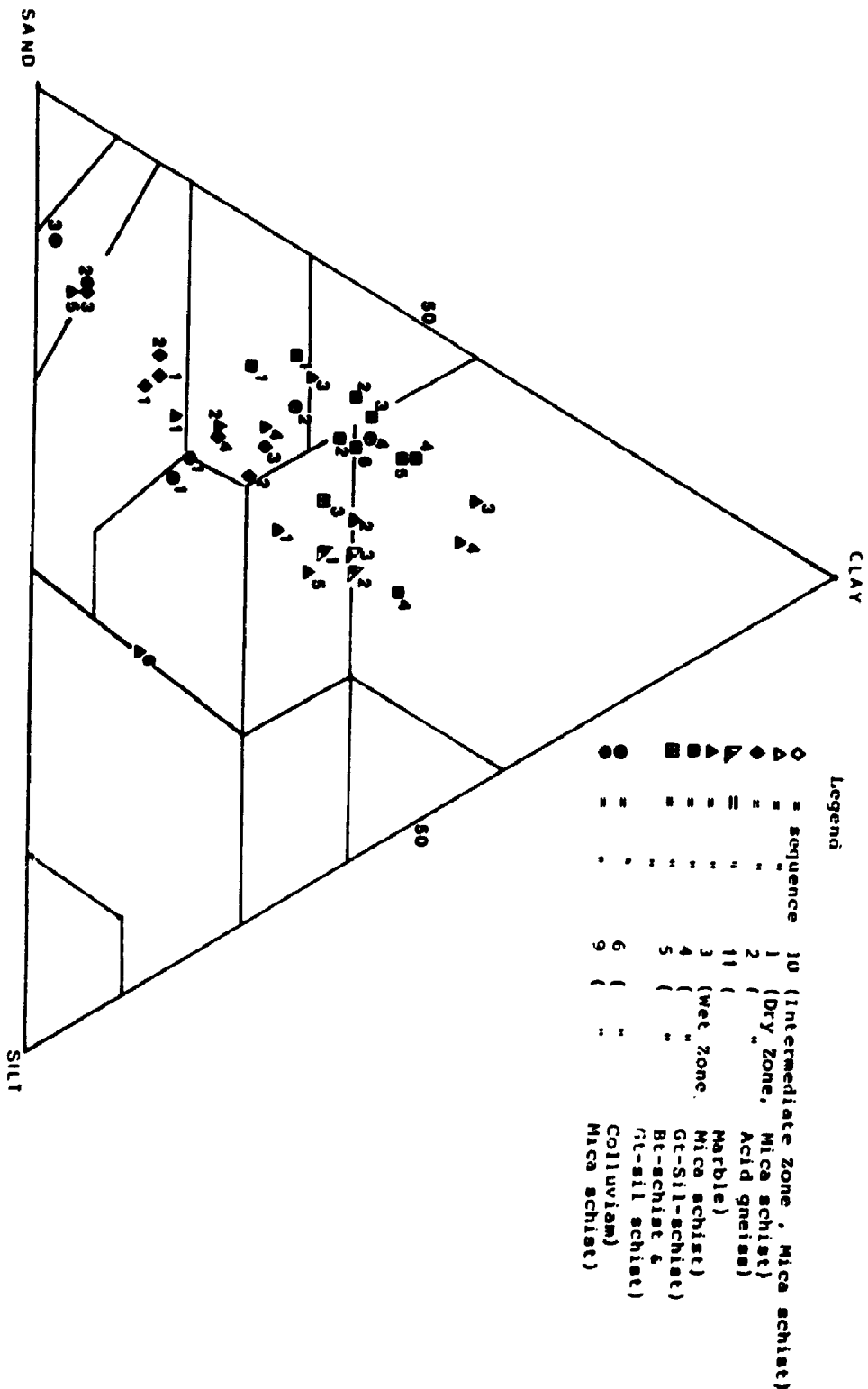


FIG. 2.10 Particle size distribution of some Sri Lankan soils from Moorman and Panabokke, (1961). Profiles are represented by symbols, followed by sequential digits indicative of increasing horizon depths. Triangle divisions same as in Fig. 2.9.

in these instances texturally. These examples show fairly convincingly that soil texture relates to soil mineralogy (which determines geochemistry) in a relatively straightforward manner.

2.10 Characterisation of Soil Sequences

In the following section, a tentative attempt to characterise the soils is made, according to the Sri Lankan system (Moorman and Panabokke, 1961). The principal features used in this system are: the nature and arrangement of the genetic soil horizons, colour, texture, structure, and consistence; hence this approach to classification is based on a soil morphological system. Other diagnostic characteristics utilised are content and nature of organic matter, presence of lime, soluble salts and the water regime. Chemical and physico-chemical properties mainly used are pH, in water and 1N KCl, cation exchange capacity (CEC), base saturation, conductivity, and free calcium carbonate content.

In the present study characterisation of the sequences is heavily dependent on soil properties determined such as colour, texture, pH, CEC, base saturation, parent material, and the spatial distribution of the Great Groups specified by Moorman and Panabokke (1961), determined through environmental factors that control their distribution: rainfall, temperature, parent material and relief.

Characterisation of the samples shows that the eight sequences studied in detail fall into five of the fourteen recognised great groups in Sri Lanka. According to Moorman and Panabokke (1961) they correspond to great groups within the Ultisol, Alfisol and Inceptisol Orders of the U.S.D.A. 7th Approximation (1960). The Sri Lankan Great Groups and corresponding 7th Approximation terminology are given in Appendix 7.

The five great groups in order of importance are:

1. Reddish Brown Earths
2. Red Yellow Podzolic soils
3. Reddish Brown Lateritic soils
4. Noncalcic Brown soils
5. Immature Brown Loams

The following description of the distribution of the five Great Groups of interest to this study, is paraphrased from Moorman and Panabokke (1961).

The Reddish Brown Earth Great Group (sequences 88 and 99) is in extent the most important soils of Sri Lanka. It occupies by far the largest part of the lowland dry zone in the Northern, North Central, Eastern and Southern provinces of Sri Lanka.

Two other sequences, sequences 148 and 153 belong to the Red-Yellow Podzolic Great Group, the dominant soils of the wet zone of Sri Lanka and also of the intermediate zones over elevations of 600 m. The subgroup with laterite (sequence 148) is concentrated mainly in the wet lowlands of the Sabaragamuwa and Western provinces of Sri Lanka, whereas the modal subgroup (sequence 153) is found throughout the wet zone though their largest extent is in the highlands and uplands of central Sri Lanka.

The Reddish Brown Lateritic Great Group is the dominant soil in the Kandy and Kegalle districts within the uplands and is best developed between the 1875-1000 mm isohyets within areas of rejuvenated relief expressed as mainly hilly

topography.

Noncalcic Brown Soils (sequences 112 and 132) and Immature Brown Loams (sequence 132) are Groups of lesser importance and occur in scattered localities mainly in the dry zone, the latter in close association with rocky outcrops. The former Great Group occurs in the Eastern Provinces, and in transitional areas to the lowland wet zone.

Table 2.4 Physico-chemical Properties of Sequence 148

sample	color	Texture	Particle size Distribution			
			stone%	sand	silt	clay
14810	10YR 6/4 lt yl-br	sandy clay loam	43.57	59.18	11.09	29.73
14830	10YR 5/4 yl-br	sandy clay loam	53.93	65.52	8.18	26.30
148100	10YR 6/6 br-yl	sandy clay loam	56.06	63.74	7.20	29.05

sample	pH H2O 1:2	pH INKCl 1:2	Exchangeable cations m.e./100g					Extract. Acidity m.e./100g	CEC m.e./100g	CEC m.e./100g clay	Base Sat.%
			Mg	Ca	K	Na	Al				
14810	4.77	4.14	0.00	0.08	0.02	0.02	1.09	8.21	8.91	30.0	1.3
14830	4.42	4.19	0.00	0.16	0.01	0.02	0.86	5.93	6.80	25.9	2.8
148100	4.41	4.35	0.00	0.13	0.01	0.03	0.70	5.01	5.59	19.2	3.0

2.10.1 (i). Sequence 148

Sequence 148 (Table 2.4) taken from the surface horizons of a productive laterite pit, is characterised as part of a Red-Yellow Podzolic profile on the basis of colour (yellowish brown in the A horizon), sandy clay loam texture, pH which ought to be less than 5.5 and very low CEC values. The occurrence of soft laterite at less than 250 cms would place the sample in the subgroup with soft laterite (cabook). The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Table 2.5 Physico-chemical Properties of Sequence 153

sample	color		Texture	Particle size Distribution				Extract. Acidity m.e/100g	CEC m.e/100g	CEC m.e/100g clay	Base Sat.%
				stone%	sand	silt	clay				
15310	10YR 5/4	yl-br	sandy loam (med)	18.77	75.34	15.55	9.11	1.61,	7.75	85.1	9.4
15330	10YR 5/4	yl-br	sandy loam (med)	28.25	77.69	15.44	6.86				
153100	7.5YR 6/6	rd-yl	sandy loam (med)	17.39	68.93	17.20	13.87				
153600	5YR 6/6	rd-yl	sandy loam (med)	18.00	73.73	15.00	11.26				
sample	pH H ₂ O 1:2	pH 1NKCl 1:2	Exchangeable cations m.e/100g				Extract. Acidity m.e/100g	CEC m.e/100g	CEC m.e/100g clay	Base Sat.%	
			Mg	Ca	K	Na					Al
15310	4.82	4.41	0.06	0.49	0.15	0.04	0.82	4.84,	5.32	77.6	11.0
15330	4.86	4.46	0.04	0.34	0.17	0.04	0.75				
153100	4.78	4.24	0.00	0.27	0.03	0.05	0.57				
153600	5.09	5.26	0.00	0.39	0.02	0.06	0.51				

2.10.2 (11). Sequence 153

Sequence 153 (Table 2.5), that has yellowish brown surface horizons that transform to reddish yellow horizons with depth, would constitute parts of the A and B horizons of a Red-Yellow Podzolic profile, on the basis of pH, sandy loam texture, very low CEC values and occurrence within the ultra wet zone of the country. Absence of prominent dark horizons and soft laterite at depth would place this sequence in the modal subgroup of the Red Yellow Podzols. The presence at greater depths (>100 cm) of highly weathered aggregates retaining structural coherence but stripped of bases as indicated by low base saturation, is uncharacteristic, unless this sequence is an example of the rapidity of weathering that takes place on rejuvenated relief subject to erosion, in the ultra Wet Zone, which can reduce a fresh rock to an exceedingly weathered soil that belonging to the Red-Yellow Podzolic Great Group implies. The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Table 2.6 Physico-chemical Properties of Sequence 112

sample	color	Texture	Particle size Distribution			
			stone%	sand%	silt%	clay%
11210	10YR 4/3 br-dk br	sandy loam (med)	10.38	74.52	13.89	11.59
11230	10YR 4/3 br-dk br	sandy loam (med)	11.22	72.18	11.59	16.03
112100	10YR 4/3 br-dk br	sandy clay	47.72	58.08	2.12	39.80

sample	pH H ₂ O 1:2	pH .01N HCL 1:2	Exchangeable cations m.e/100g					Extract. Acidity me/100g	CEC me/ 100g	CEC me/100g clay	Base Sat.%
			Mg	Ca	K	Na	Al				
11210	5.20	4.88	1.00	2.18	0.10	0.04	0.41	5.47	9.10	78.5	35.9
11230	5.19	4.91	0.94	2.51	0.04	0.09	0.04	5.93	8.51	53.1	45.7
112100	4.62	4.81	2.82	3.61	0.05	0.21	0.20	5.93	11.61	29.2	57.6

2.10.3 Sequence 112

Sequence 112, (Table 2.6), is tentatively characterised as a Noncalcareous Brown Soil, by its dark brown to brown colour, sandy loam texture and base saturation that is greater than 40% in the lower levels. The presence of clay coatings, between the coarse grains, distinguishes this Group from the Immature Brown Loams. The lowest level consisting of decomposed acid gneiss, in this instance granitic gneiss, is also distinctive. However as in the case of sequence 132, the CEC is greater than 40 me/100g clay, and is atypical in this respect. The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Table 2.7 Physico-chemical Properties of Sequence 61

sample	color		Texture	Particle size Distribution			
				stone%	sand%	silt%	clay%
6110	7.5YR	4/4 dk br	sandy clay loam	1.32	57.12	18.92	23.96
6130	7.5YR	4/4 dk br	sandy clay loam	5.01	52.86	17.92	29.21
61100	7.5YR	4/6 st br	clay	3.30	42.56	8.13	49.31

sample	pH H ₂ O	pH	Exchangeable cations				Extract. Acidity	CEC	CEC	Base	
	1:2	.01N KCL	Mg	Ca	K	Na					Al
6110	5.91	5.53	1.63	6.33	0.51	0.00	0.20	7.61	15.93	66.5	53.3
6130	5.52	5.32	1.57	5.80	0.45	0.09	0.04	8.07	17.42	59.6	45.4
61100	5.25	5.12	1.07	3.71	0.31	0.03	0.39	10.94	14.04	28.5	36.5

2.10.4 (vi). Sequence 61

Sequence 61, (Table 2.7), is tentatively characterised as a Reddish Brown Lateritic Soil, instead of characterising it as an Immature Brown Soil (wet zone subgroup), which is distinguished by its marked sandy loam texture in the B horizon. Sequence 61, has a sandy clay loam which transforms to a clay texture, in the 100cm level and is typical of the Bt horizon of Reddish Brown Lateritic Soils. Its dark brown colour and pH between 5 and 6 is however common to both Groups of soils. Both, CEC and base saturation, which ought to be, less than 40 me/100g clay and less than 45% respectively, in the Bt horizon, are typical of Reddish Brown Lateritic soils, if the 100cm level is considered as part of the B horizon. The presence of partially weathered mica flakes in the silt and sand fractions is also characteristic even though it is more typical of the Immature Brown Soils which are developed according to Moorman and Panabokke (1961), on mica schists a general term, equivalent to a migmatite, the precursor material of sequence 61 in this instance. The site location, close to Kandy, conforms to its locale, for both soil groups, in terms of typical occurrence.

Table 2.8 Physico-chemical Properties of Sequence 88

sample	color		Texture		Particle size Distribution			
					stone%	sand%	silt%	clay%
8810	5YR 3/4	dk rd br,	sandy	clay loam	0.88	47.57	22.52	29.91
8830	5YR 3/3	dk rd br,	sandy	clay loam	0.43	45.58	21.33	33.09
88100	5YR 3/3	dk rd br,	sandy	clay loam	6.08	53.64	19.97	26.39

sample	pH H ₂ O		n.e./100g					Acidity me/100g	me/ 100g	me/100g clay	Sat. %
	1:2	.01N KCL 1:2	g	Ca	K	Na	Al				
8810	5.69	5.45	7.35	11.00	0.50	0.19	0.25	9.46	27.81	93.0	69.6
8830	5.62	5.46	6.77	10.31	0.23	0.16	0.28	8.07	25.11	75.9	68.4
88100	5.77	5.08	5.50	10.48	0.28	0.25	0.15	5.77	21.99	83.3	75.1

2.10.5 (v). Sequence 88

Sequence 88, (Table 2.8) forms part of a Reddish Brown Earth sequence, characterised by colour, pH which is normally between 6 and 7, but which can be as low as 5.5, high base saturation (ought to be above 40%, but usually is higher than 70%), and high CEC, (which ought to be above 45 me/100g clay in the B horizon). The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Table 2.9 Physico-chemical Properties of Sequence 99

sample	color		Texture		Particle size Distribution							
					stone%	sand%	silt%	clay%				
9910	7.5YR	4/4	br		sandy loam (med)	4.86	69.78	14.58	15.64			
9930	5YR	4/4	rd br		sandy clay loam	34.78	66.31	11.86	21.83			
99100	2.5YR	4/6	rd		sandy clay loam	23.13	60.97	10.56	28.46			

	Extract- 1:2	CEC .01N KCL 1:2	Base m.e/100g				Acidity me/100g		me/ 100g	me/100g clay	Sat. %
			Mg	Ca	K	Na	Al				
9910	6.26	5.40	1.49	4.28	0.51	0.01	0.28	3.19	9.18	58.7	68.5
9930	6.14	5.73	1.08	4.71	0.18	0.04	0.21	4.10	10.53	48.2	57.1
99100	6.23	5.40	1.29	4.91	0.16	0.02	0.15	4.10	10.26	36.1	62.2

2.10.6 (vi). Sequence 99

Sequence 99, (Table 2.9), an immature sequence developed on a granitic precursor, (Table 2.1) is characterised as a Reddish Brown Earth, due to its reddish brown colour, pH between 6 and 7, CEC, above 45 me/100g clay in the upper two levels, and base saturation which is above 40%. The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Table 2.10 Physico-chemical Properties of Sequence 132

sample	color		Texture	Particle size Distribution			
				stone%	sand%	silt%	clay%
13210	10YR 5/3	br	sandy loam (med)	6.26	70.41	15.72	13.87
13230	10YR 5/3	gr br	sandy loam (med)	15.30	72.64	12.43	14.93
132scf	10YR 5/2	br	loamy sand	10.27	83.75	9.75	6.50

sample	pH H ₂ O	pH	Exchangeable cations				Extract- Acidity me/100g	CEC me/ 100g	CEC me/100g clay	Base Sat. %	
	1:2	.01N KCL 1:2	Mg	Ca	K	Na					Al
13210	5.95	5.57	1.02	5.37	0.35	0.03	0.27	4.38	11.12	80.0	60.9
13230	5.71	4.68	0.76	4.20	0.19	0.07	0.20	3.00	8.02	53.7	65.1
132scf	6.46	5.60	.29	0.96	0.06	0.14	0.35	7.15	5.32	81.9	27.2

2.10.7 (vii). Sequence 132

Sequence 132, (Table 2.10) is characterised as a weakly developed Noncalcic Brown Soil, because of its brown to greyish brown colour, sandy loam texture, base saturation which is above 40%, and its characteristic occurrence on a granitic gneiss precursor within the d₁ zone. It is weakly developed in that feldspathic grains are present in the upper level and the sequence itself is not more than 30cm thick and because of it, has a CEC above 40 me/100g clay and hence is atypical. The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Table 2.11 Physico-chemical Properties of Sequence 16

sample	color	Texture	Particle size Distribution			
			stone%	sand%	silt%	clay%
1610	10YR 4/3 dk br	sandy clay loam	0.73	65.91	9.06	25.03
1630	10YR 4/4 dk yl br	sandy clay loam	0.21	70.26	9.14	20.60
1650	7.5YR 5/4 br	sandy clay loam	0.34	62.58	9.20	28.22

sample	pH H ₂ O 1:2	pH .01N KCL 1:2	Exchangeable cations m.e./100g					Extract. Acidity me/100g	CEC me/ 100g	CEC me/100g clay	Base Sat.%
			Mg	Ca	K	Na	Al				
1610	6.14	5.79	2.30	7.27	0.57	0.02	0.22	2.54	12.96	51.8	78.3
1630	6.29	6.26	1.72	8.02	0.82	0.04	0.24	1.61	11.88	57.7	89.3
1650	6.14	5.76	2.82	6.77	0.42	0.08	0.17	3.46	13.37	47.4	75.2

2.10.8 (viii). Sequence 16

Sequence 16, (Table 2.11), is characterised as an Immature Brown Loam (dry zone subgroup) by its dark brown colour, sandy clay loam texture in the upper level, absence of clay coatings between grains and its soft consistency when dry, in the lower levels . It also has a base saturation above 40% and a CEC value higher than 40 me/100g clay, both typical of the Great Group. The absence of clay coatings, the soft consistency, and the typical CEC and base saturation values differentiate this Great Group from that of the Noncalcic Brown Soils. The site location falls within the areal extent of its occurrence as described by Moorman and Panabokke (1961).

Chapter III

Mineralogy of the Clay and Silt Fractions and their Significance Relative to the Currently Accepted Concepts of Weathering

2.1 Introduction

In this chapter techniques and results of mineralogical analyses will be presented, followed by a comparison of results with the currently accepted division of clay mineral provinces in the island. Correlation with results obtained in Chapter II will be made, prior to discussion of the significance of these results within the context of currently held concepts of weathering.

3.1.1 Literature Review

Analytical results from preliminary geochemical investigations and cation exchange studies suggest a major mineralogical distinction between dry and wet zone samples as has been previously demonstrated by Herath and Grimshaw (1971). In their classic paper the island was divided into three clay mineralogical provinces that closely follow the climatic divisions. Gibbsite was used as the indicator mineral. Only alluvial soils were sampled. The wet zone was found to correlate with the occurrence of the mineral pair kaolin - gibbsite. A mixed layer mineral identified as vermiculite-mica was also found to be present. The dry zone was characterised by the complete absence of gibbsite and the predominance of montmorillonite together with kaolin. The intermediate zone was characterised by kaolin, a lower abundance of gibbsite, + montmorillonite and mixed layer minerals. Previous work by Panabokke(1959) on a soil catena developed in the dry zone confirmed the absence of gibbsite and the presence of

the mineral pair kaolin and montmorillonite in the upper slope; montmorillonite superceded kaolin in abundance both at depth and lower down slope. The formation of smectite was considered to be the result of impeded drainage lower down in profiles next to the zone of rock decomposition and also at the base of slope. The findings of Kalpage et al., (1963) who analysed four of the more widespread fourteen soil groups of Sri Lanka, viz. a young and a mature Reddish Brown Earth profile from the dry zone, a Red Yellow Latosol from the dry zone and a Red Yellow Podzol from the wet zone, agree on the whole with Herath and Grimshaw's (1971) classification, excepting that they note a discrepancy that emerges between differential thermal analysis and x-ray diffraction results regarding identification of the smectite found in the dry zone samples. Mention is also not made of mixed layer minerals from the wet zone. In a more recent study of Red Latosol sequences from the dry zone, De Alwis and Pluth (1976), reported the co-existence of kaolin and a vermiculite-smectite intergrade (instead of pure smectite). The latter point will be further discussed in section 3.5.

The presence of gibbsite was taken to indicate advanced stages of weathering by Kalpage et al., (1963) and was assigned to the extreme end of the weathering scale - the final end product - by Panabokke, (1959).

Samples were prepared for x-ray analysis to establish whether predictions made regarding mineralogy based on geochemistry and cation exchange studies in Chapter II, which appear to be substantiated by previous research work could be further justified. It was also intended to add to the existing knowledge in Sri Lanka, if possible, regards both the concept of a weathering scale and weathering processes that were considered to be operative that led to such mineralogical distinction, as discussed above.

3.1.2 X-ray Analysis Techniques

Clay mineral identification was carried out on an aliquot of clay taken at the time of particle size analysis. Hence the clay suspension was Na-saturated at the start. Extra samples were selected from sequences used for preliminary geochemical analyses only.

X-ray traces of oriented clay mounts were produced per sample for the following conditions, for all depth levels, excepting condition 3 for levels 30 and 100cms, to identify minerals according to the criteria given in Brindley and Brown (1982). The rationale behind the procedure followed is given in detail in section 3.1.3.

1. Na-saturated and air-dried at room temperature (Na-ADPO)
2. Na-saturated and solvated in 1:1 ethylene glycol-ethanol solution (Na-GPO) for $14 \overset{\circ}{\text{A}}$ peak shift characteristics
3. K-saturated and air-dried (K-ADPO) for $14 \overset{\circ}{\text{A}}$ peak shift characteristics
4. Na-saturated and heated to $300 \overset{\circ}{\text{C}}$ (Na-300) to confirm oxide and hydroxide identification
5. Na-saturated and heated to $450 \overset{\circ}{\text{C}}$ (Na-450) to observe $14 \overset{\circ}{\text{A}}$ peak collapse.
6. Na-saturated and heated to $550 \overset{\circ}{\text{C}}$ (Na-550) to observe 7 and $14 \overset{\circ}{\text{A}}$ peak collapse.

In addition conditions 4 and 6 were repeated for the 10 cm level on K-saturated samples. It was noted that peak collapse was more prompt

with K-300 treatment compared to Na-300 treatment (fig. 3.3); however differences between Na-saturated and K-saturated samples disappeared on heating to 550 °C. Samples were further heated to 600 °C if either the 7 Å or 14 Å remained.

To ensure that the same thickness of oriented clay film remained common for all the samples during clay mineral analysis, a volume of clay suspension containing 42 mg of clay was passed through a 0.4 µm semi-permeable cellulose membrane of a Millipore filter system (Drever, 1973). The membrane was then removed from the suction apparatus and pressed against a glass slide to transfer the clay film.

K-saturated samples were produced by centrifuging the same volume of clay in a centrifuge tube to which sufficient 1N KCl was added to flocculate the clay. This step was repeated 4 more times and was followed by washing with deionised water and centrifuging, thrice to remove excess KCl (Janitzky, 1986).

Traces were produced using Ni filtered $\text{CuK}\alpha$ radiation and a Rigaku X-ray diffractometer, geigerflex CN2029 D/MAX-1A. Scanning was performed from 2° (2θ) to 42° (2θ), at a speed of 2° per minute and a count rate usually of 400cps, which had to be varied to maximize peaks in some instances.

3.1.3 Interpretation of X-ray Traces

Minerals were determined by criteria given in Brindley and Brown, (1982). Kaolinite was identified by its 7 Å peak that collapsed on heating to 550 °C. Mica/illite was identified by its 10 Å peak that resisted collapse when heated to 550 °C. Gibbsite and goethite were identified by their 4.82 Å and 4.15 Å peaks respectively, that collapsed on heating to 300 °C. 14 Å Peaks with expansion

characteristics towards 18 Å with ethylene glycol were assigned to smectite while 12-14 Å peaks that collapsed towards 10 Å with K-saturation at room temperature were identified as vermiculite. The absence of chlorite was determined by the behaviour of the 14 Å peak during heat treatment; collapse of the 14 Å peak towards 10 Å indicated smectite or vermiculite, and the absence of chlorite. Characteristic secondary peaks of chlorite, not in common with kaolin were also checked. Characteristic peaks remaining after heat treatment at 550-600 °C were assigned to chlorite. Serpentine group minerals were not expected under the pH conditions of the soils.

Initial analysis of x-ray diffractograms of many sequences soon indicated atypical behaviour of the 14 Å peak as described for either pure smectite or vermiculite, (Brindley and Brown, 1982). The presence of Al-hydroxy interlayered smectite/vermiculite, or possibly an interstratification of smectite and vermiculite was suggested by the existence of a broad ill-defined peak between 13 Å and 15 Å that showed continued resistance in collapsing to 10 Å when heated, by drifting of peaks between 14 Å and 10 Å. It resulted in some instances in a plateau between this range, on heating even up to 550 °C.

Presence of interlayered clays formed by partial filling of interlayer spaces with Al-hydroxy "islands" complicates the simple identification procedure given in Brindley and Brown (1982) as discussed by Averack(1983), by producing minerals that have intermediate properties between chlorite and vermiculite and chlorite and smectite. The existence of partially filled interlayers increases resistance to collapse, to 10 Å, upon heating which is readily observed in both pure smectites and vermiculite. The degree of interlayering can be determined both by the temperature at which "the mineral achieves its maximum collapse and the amount of collapse obtained at a given temperature", (Ibid). The more complete the filling the greater the resistance to collapse.

De Alwis and Pluth (1976) describe similar behaviour of the 14^oÅ peak in their dry zone profiles. A vermiculite-smectite intergrade is described, that gives a broad diffuse peak between 14.7 and 19.2 Å (with maximum at 17^oÅ) upon glycolation and collapse to 10^oÅ on K-saturation. A mixed-layer mineral is described occurring side by side, identified from a series of small peaks "between 10^oÅ and 18^oÅ" which on heating formed a plateau with some enhancement of the 10^oÅ peak. Presence of pure smectite was not noted.

It is difficult to distinguish between Al-hydroxy interlayered smectite/vermiculite that has similar x-ray characteristics to vermiculite-smectite interstratification without further complication by the use of undefined terms such as "intergrade and mixed layer minerals" that, as discussed by Averack (1983) mean different things to different authors. Absence of x-ray traces compounds the problem.

Under these circumstances, no presumptions regarding the interpretation of the terms intergrade and mixed layer, will be made, in spite of the resemblance of the description of the peak behaviour to those found in the present study.

In this thesis, in concert with Averack (1983), the term interlayering will apply to the presence of incomplete hydroxy islands found in vermiculite and smectite, and the term interstratification will be applied to stacking sequences in which different clay species are mixed within one particle.

In this study the smectite component of the interstratification was identified by expansion of the 14^oÅ with ethylene glycol treatment and resistance to collapse upon K saturation at room temperature. The vermiculite component of the interstratification was identified by its opposite behaviour, ie. by its resistance to expansion with

ethylene glycol and significant degree of collapse to 10 \AA upon K saturation. Presence of Al-hydroxy interlayering was identified by resistance to heat treatment which results in a plateau between 10 and 14 \AA . In the presence of interstratification it was not possible to determine which of the component was interlayered.

Kaolin-smectite and kaolin-vermiculite interstratifications found recently in humid tropical and temperate regions, have been considered to be intermediate products in the transition from smectite to kaolin (Dixon, 1977; Wada and Kakuto, 1983; Herbillion et al., 1981). This mineral has been identified in Australia, Scotland, Japan, Florida, and Mexico. Wilson and Nadeau (1985) state that although this stratification has not been widely reported, it may be more common than is presently appreciated; because of its close behavioural similarity in XRD studies to 'chloritised vermiculite' and smectite-vermiculite interstratifications it could be easily misidentified. The presence of a broad band between $7.2 - 14 \text{ \AA}$ and the special dehydration characteristic which does not show collapse to 7.2 \AA after heating at $350 \text{ }^\circ\text{C}$ (halloysite) and, the occurrence of a peak above 10 \AA after heating at $550 \text{ }^\circ\text{C}$ have been attributed to this interstratification (Araki and Kyuma, 1987). In published reports of this mineral, partial expansion with ethylene glycol is observed in some instances (Altschuler et al., 1963, Araki and Kyuma, 1987), but not in others (Schultz et al., 1971). Since these characteristics are identical with X-ray characteristics used to identify smectite-vermiculite interstratification, the term 14 \AA mineral will be used in the following sections for the time being.

In the wet zone samples, the 14 \AA peak neither expanded with ethylene glycol nor collapsed with K-homoionisation. Resistance to heating even at $500 \text{ }^\circ\text{C}$ was noted. For identification purposes minerals exhibiting identical behaviour were termed "Al-hydroxy interlayered vermiculite" after Douglas (1977) who together

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with other workers note that this mineral is found to be more abundant than kaolin, in surface horizons of some intensive weathering environments. Similar behaviour in a 14 Å mineral has been reported by other workers (Tamura 1958; Karathanasis et al., 1983 (extensive bibliography); Averack, 1983).

3.2 Clay Mineralogy

The following sections examine X-ray traces of the clay fraction of sequences which have been grouped according to similarities displayed. The 450 °C trace was omitted from the trace diagrams in the interest of space. Similarly composite trace diagrams highlighting essential details were made for extra sequences within groups, where type sequence had already been presented in detail.

Many traces have been presented here, contrary to established practice in Sri Lanka. Lack of trace diagrams has been a severe hindrance in identification and it is hoped that this will set a precedent for future work with Sri Lankan soils.

According to the clay mineralogy, the sequences can be divided into five main groups as follows:

Wet and Intermediate Zones

- Group 1 - kaolin + gibbsite, trace Al-hydroxy vermiculite + Fe oxides
- Group 2 - kaolin, minor gibbsite, trace Al-hydroxy vermiculite + illite
- Group 3 - kaolin + smectite-vermiculite, minor illite (no gibbsite)

Dry Zone

Group 4 - Illite + kaolin + smectite-vermiculite (no gibbsite)

Group 5 - smectite + kaolin, trace illite (no gibbsite)

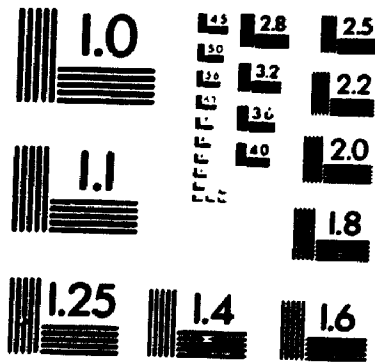
A summary of the abundances of clay and silt minerals is presented in Table 3.1. Abundances were calculated using peak heights only, and hence is semi-quantitative. Calculation of abundances using peak area was not attempted because of the suspected presence of amorphous oxide coatings likely to be present even in the dry zone samples judging by the colour of the samples.

Table 3.1 Relative Abundances of Clay and Silt Minerals

Sample	Clay Minerals			14Å ¹ Smectite	Silt Fraction				
	Goethite	Gibbsite	Keolin Illite		Quartz	Pelldapar Mica	HB	Others	Precursor
Wet Zone									
Group (i)									
14910	x	+++++	+	xx	+	-	Gib	unknown	
14830	x	++++	+	xx	-	-	Gib	"	
149100	x	++++	+	xx	-	-	Gib	"	
15310	x	+	+	x	-	-	Sil/Gib	Cr-611-Graphite Gs	
15330	x	+	+	x	-	-	Sil/Gib	"	
153100	x	+++	+	x	-	-	Sil/Gib	"	
153670	x	++	+	-	-	-	Sil/Gib	"	
Group (ii)									
6110	x	++	tr	x	x	-	Gib	HB-Bt Migmatitic Gs	
6130	x	++	tr	x	x	-	Gib	"	
61100	x	+++	tr	x	x	-	Gib/12.45Å	"	
Intermediate Zone									
11210	-	+++	-	xxx	+	-	-	Granitic Gs	
11230	-	++++	-	x	+	-	-	"	
112100	-	+++++	-	x	+	-	-	"	
Group (iii)									
8810	-	x	tr	x	+	-	12.25Å	Marble	
8830	-	x	tr	x	+	-	"	"	
88100	-	x	x	x	+	-	"	"	
Dry Zone									
9910	-	x	x	x	+	-	-	Granitic Gs	
9930	-	xx	x	x	+	-	-	"	
99100	-	xxx	x	x	+	-	-	"	
Group (iv)									
1610	-	xxx	xxx	xx	+	x	-	HB-Bt Migmatitic Gs	
1630	-	xx	xxx	x	+	x	-	"	
1650	-	x	xx	x	+	tr	-	"	
13210	-	xx	xx	x	+	tr	-	Granitic Gs	
13230	-	xx	xx	x	+	tr	-	"	
1326cf	-	xx	x	x	+	-	-	"	

1 14Å Interlayered smectite or vermiculite
+ = xxx

2



3.2.1. Group (1). Sequences 148 and 153

Information presented in Chapter II indicated that Red Yellow Podzolic sequences 148 and 153 collected from the wet zone which plot in field one in fig. 2.2B would consist mainly of kaolin and oxides consistent with its site location in the wet zone within the Red-Yellow Podzolic soil region. The clay mineralogy supports this view.

The clay fraction, based on figs. 3.1 and 3.3 is composed primarily of crystalline kaolin, and gibbsite. Minor amounts of goethite and or hematite(2.68Å), quartz and a 14Å mineral are present. The 14Å mineral resists both expansion with ethylene glycol (Na-ADPO, fig.3.1) and collapse to 10Å on K-saturation (K-ADPO). However its gradual and incomplete collapse to 10 Å on heating to 550°C (Na-550; fig. 3.1) suggests an interlayered clay, possibly with chlorite or Al-hydroxy "islands" as suggested by the right shoulder towards 14Å. As discussed in section 3.1.3 this mineral was identified as "Al-hydroxy interlayered vermiculite".

Variation with depth is not present within the top 100cms as indicated by the uniformity between traces in figs. 3.2. and 3.3.

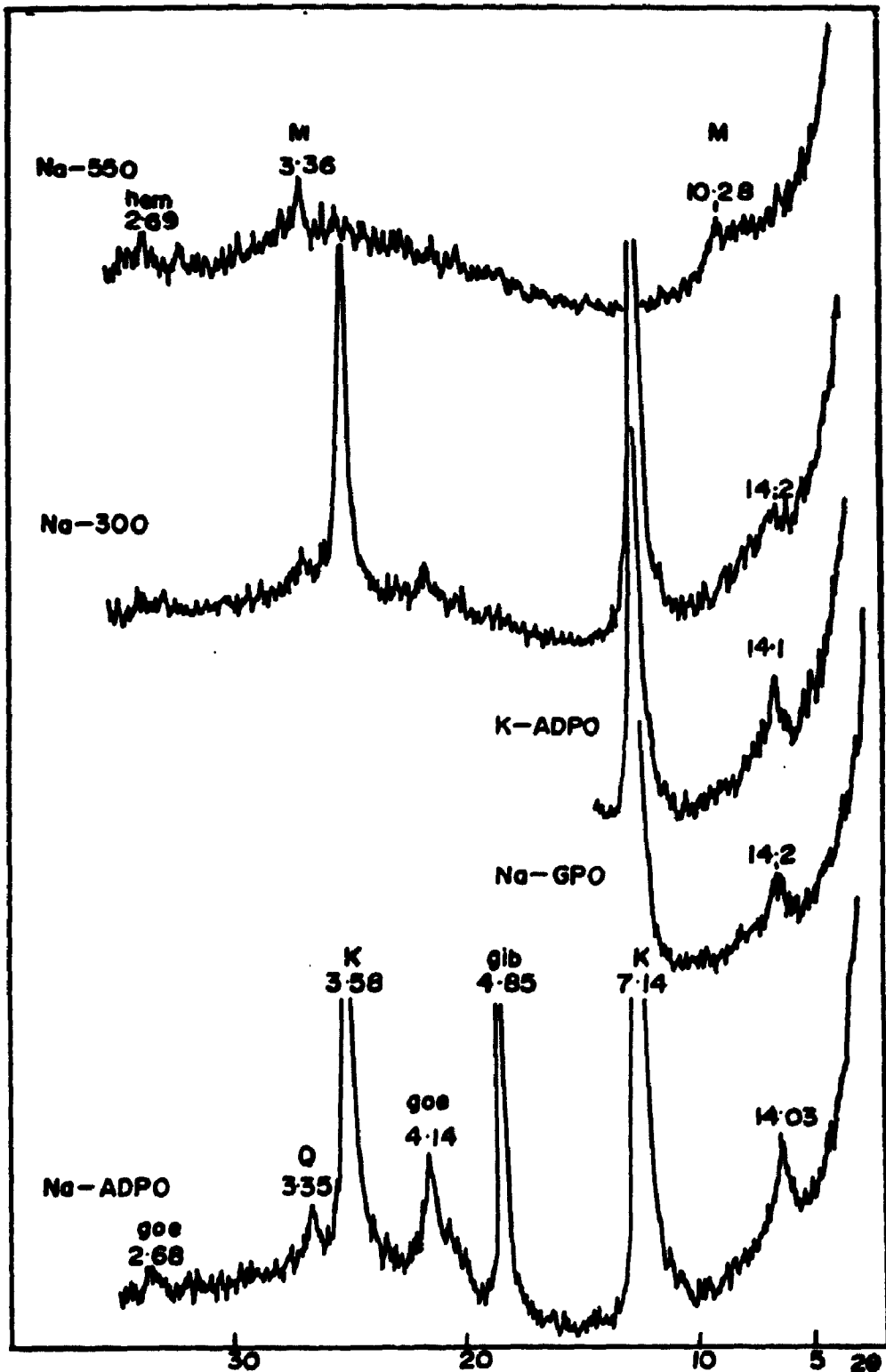


Fig. 3.1. X-ray Diffractograms of the 10 cm clay fraction in sequence 153. K=kaolin; gib=gibbsite; goe=goethite; hem=hematite; M=collapsed smectite or vermiculite.

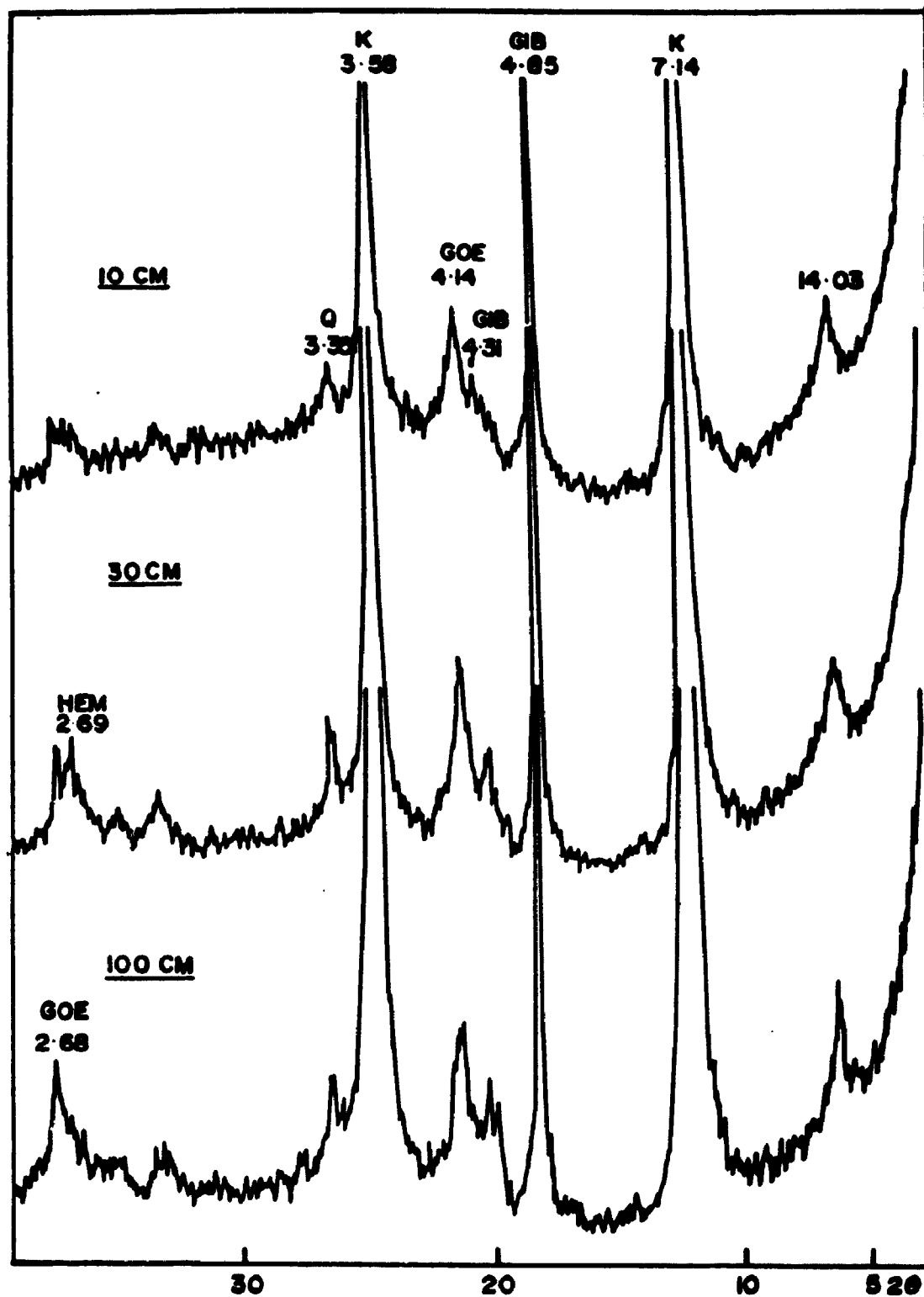


Fig. 3.2. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 153. K=Kaolin; GIB=Gibbsite; GOE=Goethite; HEM=Hematite

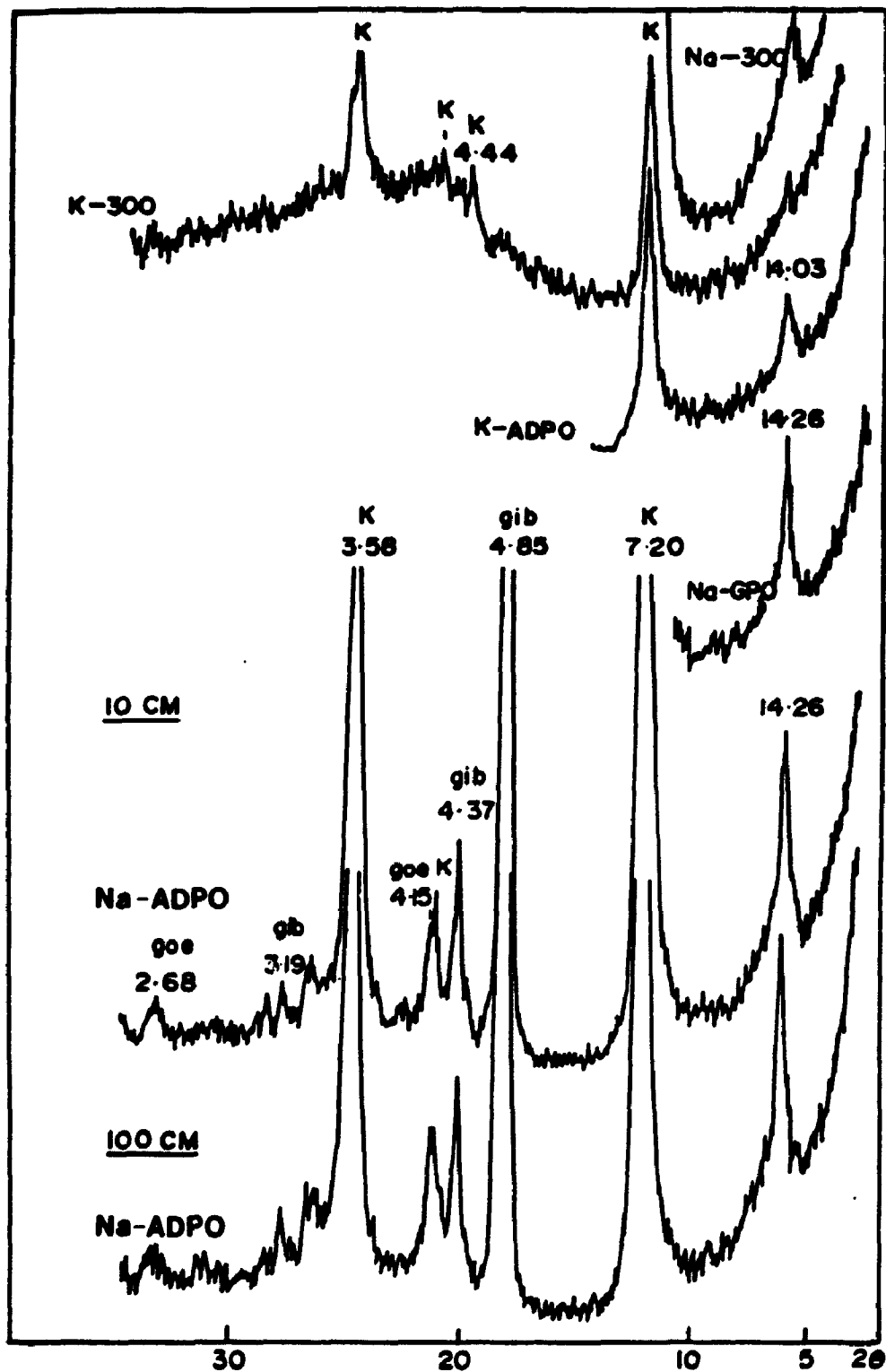


Fig. 3.3. X-ray Diffractograms of the 10 cm clay fraction and variation with depth of the clay fraction in sequence 148. Symbols as in Fig. 3.1.

3.2.2 Group (11). Sequences 61 and 112

Information presented in Chapter II indicated that sequences 61 (Reddish Brown Lateritic soil) and 112 (Noncalcic Brown soil) collected at the border between the wet and intermediate zones which plot in field 2 in figs. 2.2 A and B, would consist mainly of montmorillonite and illite clays consistent with its site location close to and within the intermediate zone. The clay mineralogy does not support this view.

The clay fractions in sequences 61 and 112 are dominated by kaolin (figs. 3.4 and 3.8). Trace amounts of gibbsite and "Al-hydroxy interlayered vermiculite" are present in both samples. In addition sequence 61 contains trace amounts of illite ($10.28 \overset{\circ}{\text{Å}}$) and goethite. These two samples are differentiated from group (1) by the absence of major amounts of gibbsite. It is of interest to note that no other sequence analysed, besides sequence 112 (fig. 3.8) contained such abundant amounts of kaolin to the exclusion of all other minerals in the clay fraction.

Variation with depth is not present within the top 100cms as indicated by the uniformity between traces in figs. 3.5 and 3.9 except in quantitative terms. The 100 cm sample in sequence 112 contains approximately twice as much kaolin as indicated in fig. 3.9 in terms of peak heights (note different count rates used).

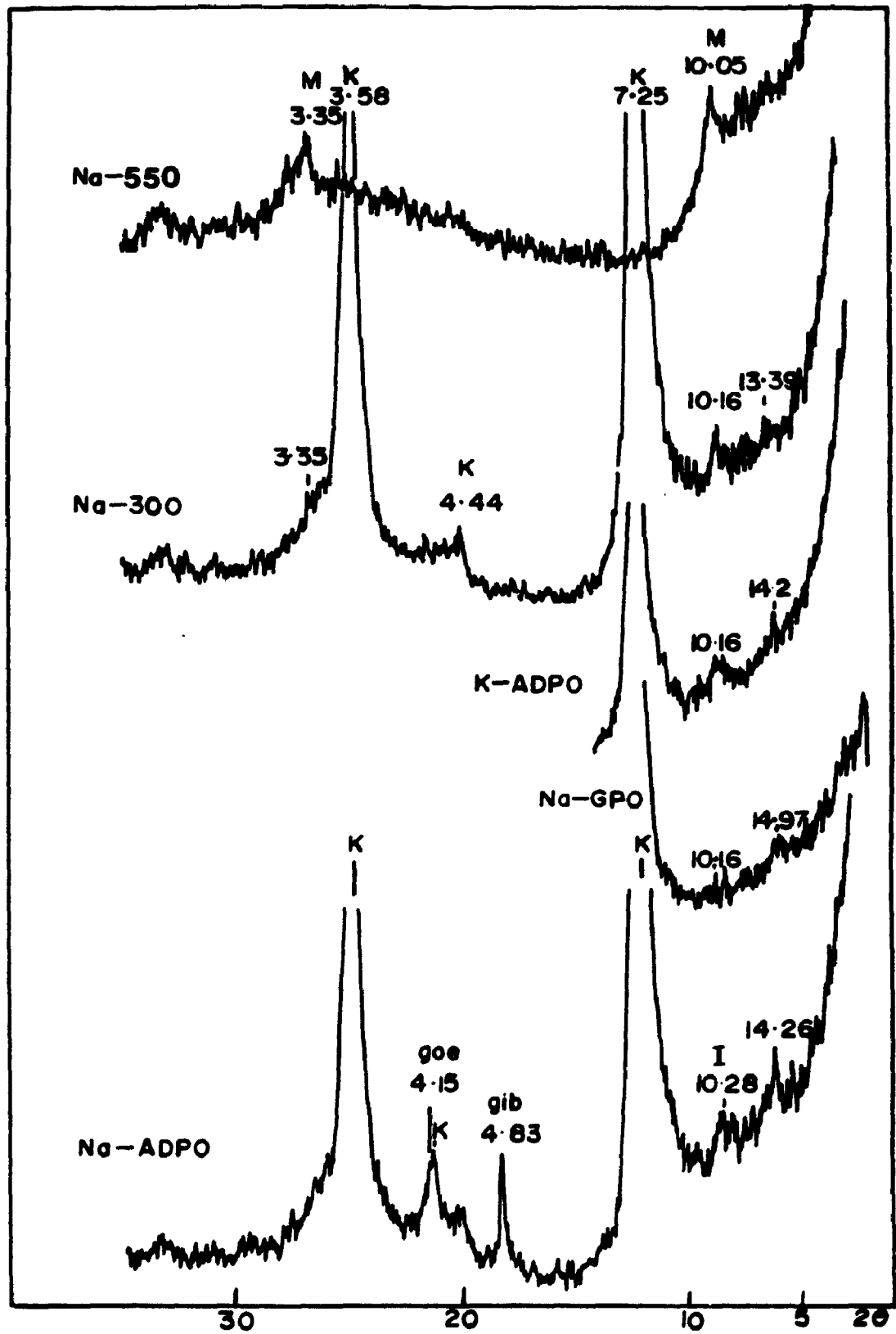


Fig. 3.4. X-ray Diffractograms of the 10 cm clay fraction in sequence 61. K=kaolin; gib=gibbsite; goe=goethite; I=illite/mica; M=collapsed smectite or vermiculite.

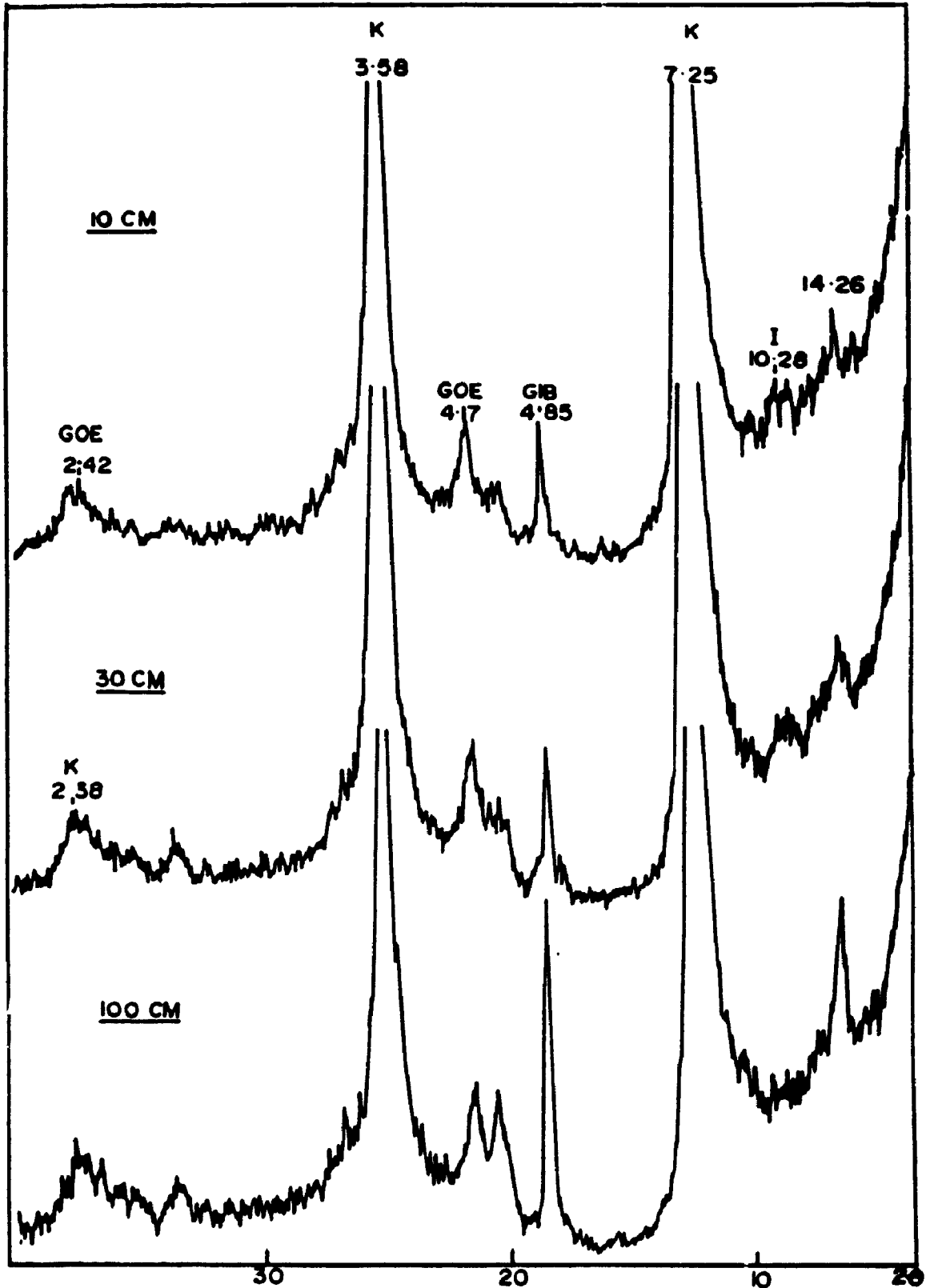


Fig. 3.5. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 61. K=Kaolin; GIB=Gibbsite; GOE=Goethite; I=Illite/mica.

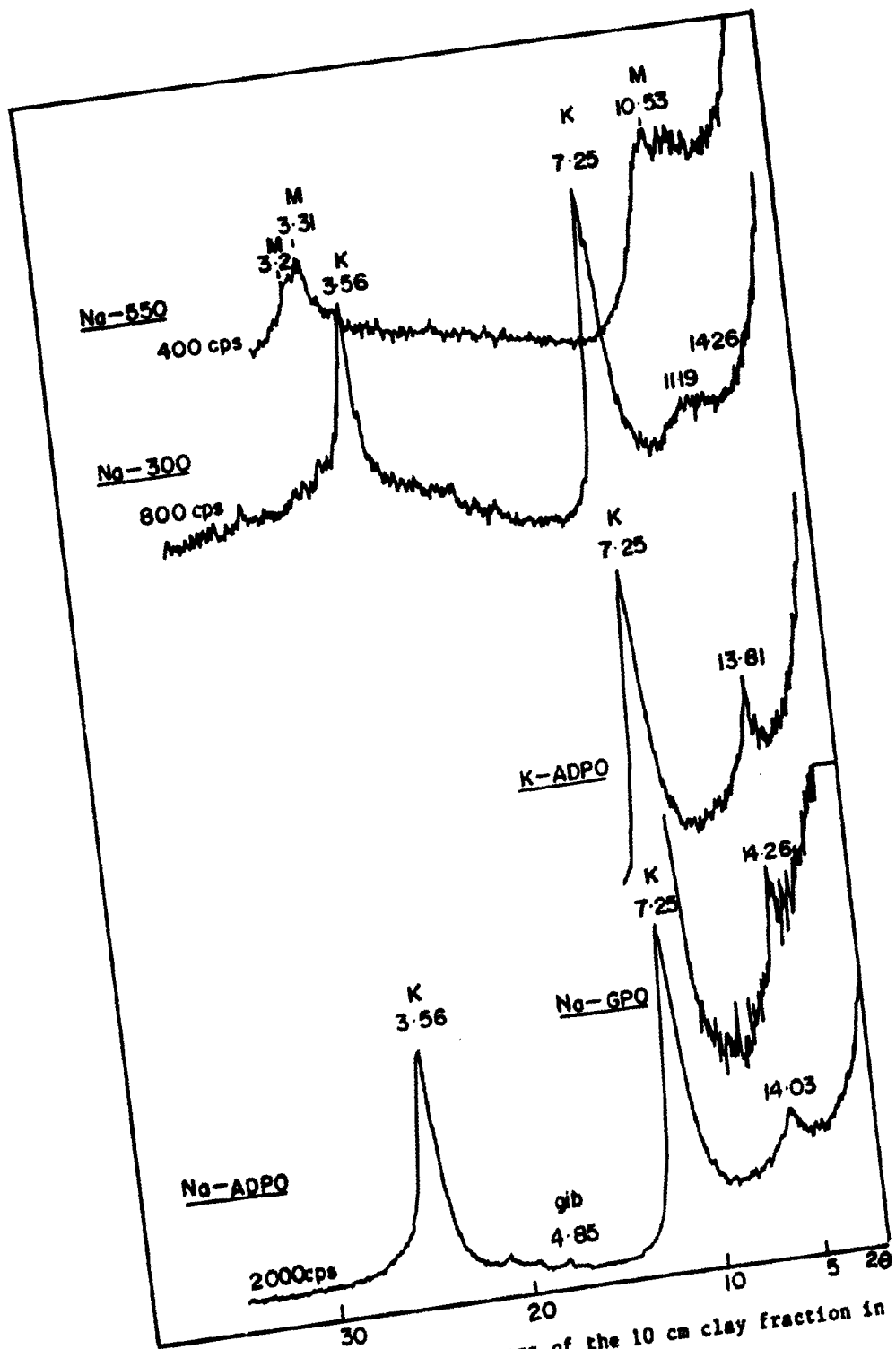


Fig. 3.8. X-ray Diffractograms of the 10 cm clay fraction in sequence 112. Symbols as in Fig. 3.4.

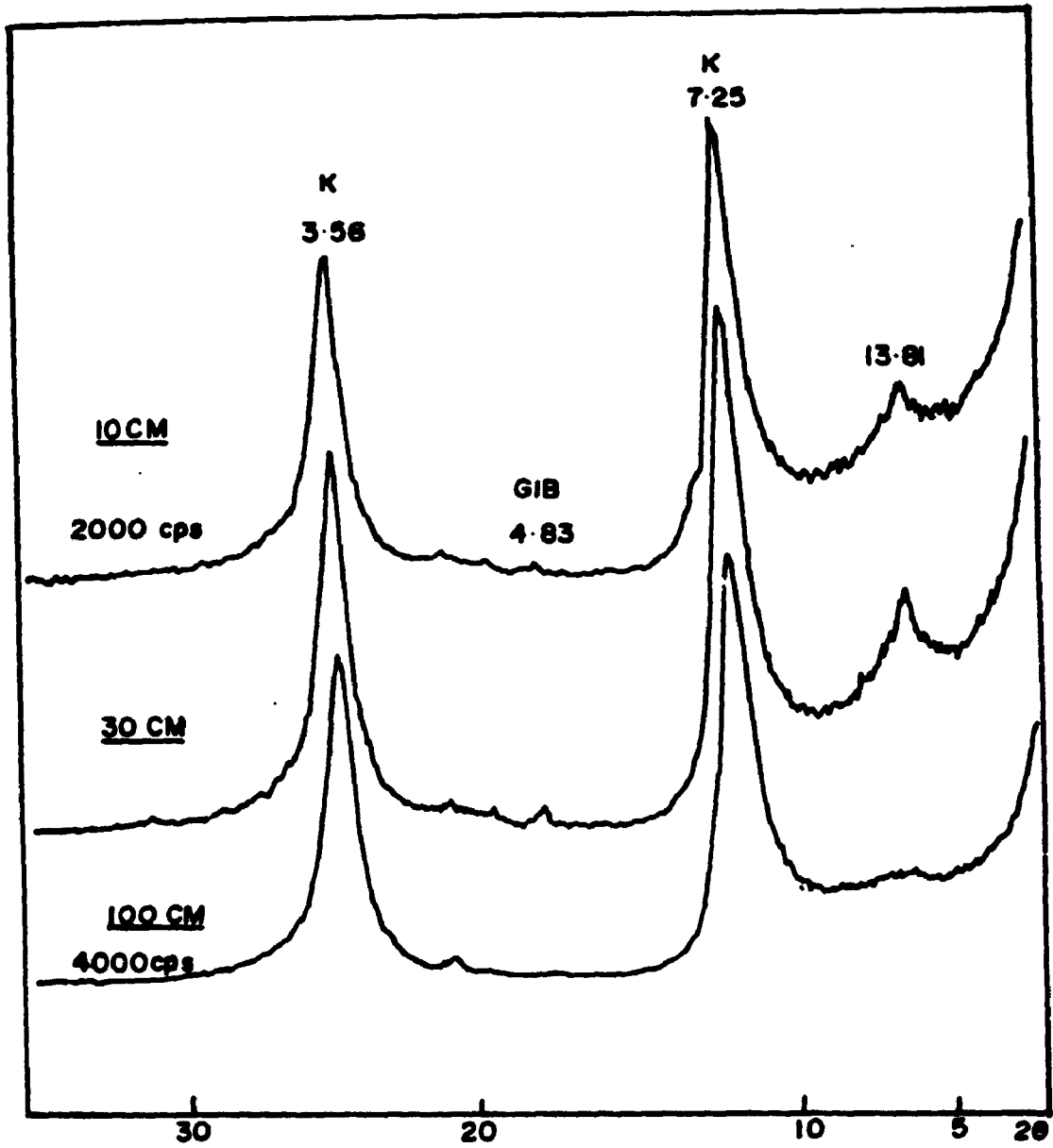


Fig. 3.9. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 112. Symbols as in Fig. 3.5.

3.2.3 Group (iii). Sequences 88 and 99

Information presented in Chapter II indicated that both these Reddish Brown Earths, collected at the border between the intermediate and dry zones and the dry zone respectively which plot in field 3 in fig. 2.2B would consist mainly of clays with high cation exchange capacity and/or primary minerals, consistent with its site location. The clay mineralogy partially supports this view.

Unlike Groups (i) and (ii), which were delineated by the presence of major or minor gibbsite together with "Al-hydroxy interlayered vermiculite", Group (iii) sequences (figs. 3.6 and 3.10) are characterised by the lack of gibbsite and a poorly defined $14\overset{\circ}{\text{A}}$ mineral as indicated by the very broad peak shape, that semi-quantitatively, is not dominated by kaolin as in the former two groups. In fact the $14\overset{\circ}{\text{A}}$ minerals dominate over kaolin in sequence 88 (fig. 3.6) but assume a less dominant position in sequence 99 (fig. 3.10). The $14\overset{\circ}{\text{A}}$ mineral is differentiated from the Al-hydroxy interlayered vermiculite of Groups (i) and (ii), by its ability to partially expand (Na-GPO) and collapse on K-saturation (K-ADPO). Expansion to a broad $18.8\overset{\circ}{\text{A}}$ peak still encompassing $14\overset{\circ}{\text{A}}$ (fig. 3.6, NA-GPO) with ethylene glycol, and clear separation to two peaks resulting from partial collapse to $10\overset{\circ}{\text{A}}$ upon K-saturation (K-ADPO), one at $10\overset{\circ}{\text{A}}$, the other remaining at $13.4\overset{\circ}{\text{A}}$ implies the presence of both a swelling component and vermiculite, i.e. inter-stratification. The swelling component is identified as smectite instead of chlorite by the absence of the $14\overset{\circ}{\text{A}}$ peak in the Na-550 trace. Interstratification of the smectite and vermiculite is suggested by the resistance to collapse expressed in the

Na-300 trace. Trace quantities of illite ($\sim 10 \overset{\circ}{\text{A}}$, Na-ADPO in figs. 3.6 and 3.10) and goethite are present. Interstratification of clay minerals is further suggested by the high order peaks. It is perplexing that hematite peaks are not present in the XRD traces since the characteristic reddish colour from which the pedogenic name of this soil group derives is inexplicable otherwise.

Variation with depth is minimal in the clay fraction as indicated by figs. 3.7 and 3.11 excepting the assumption of dominance of the vermiculite component ($12 \overset{\circ}{\text{A}}$ peak) in the clay fraction, either in abundance or degree of crystallinity at depth (fig. 3.7, 100cm) in sequence 88.

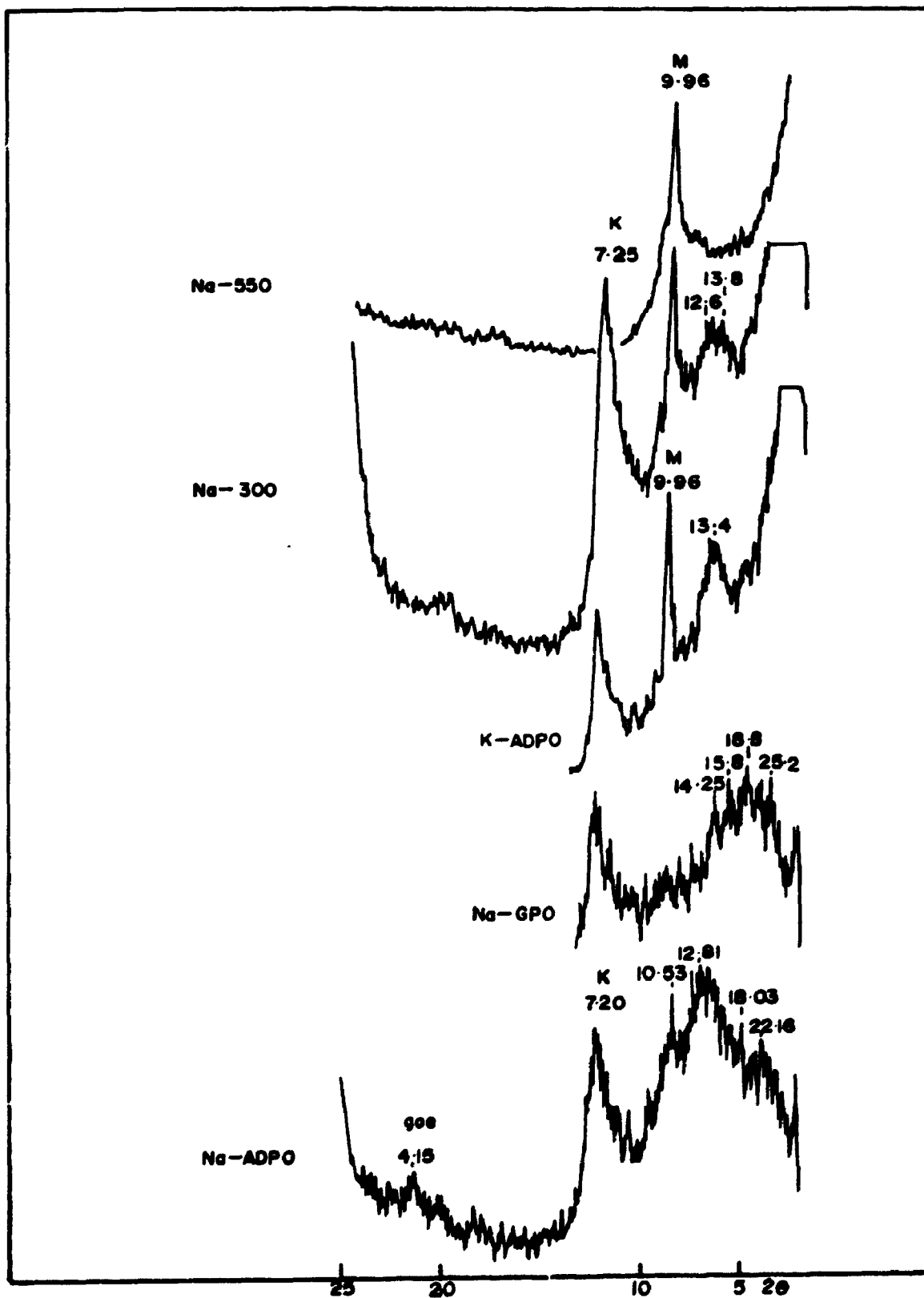


Fig. 3.6. X-ray Diffractograms of the 10 cm clay fraction in sequence 88. Symbols as in Fig. 3.4.

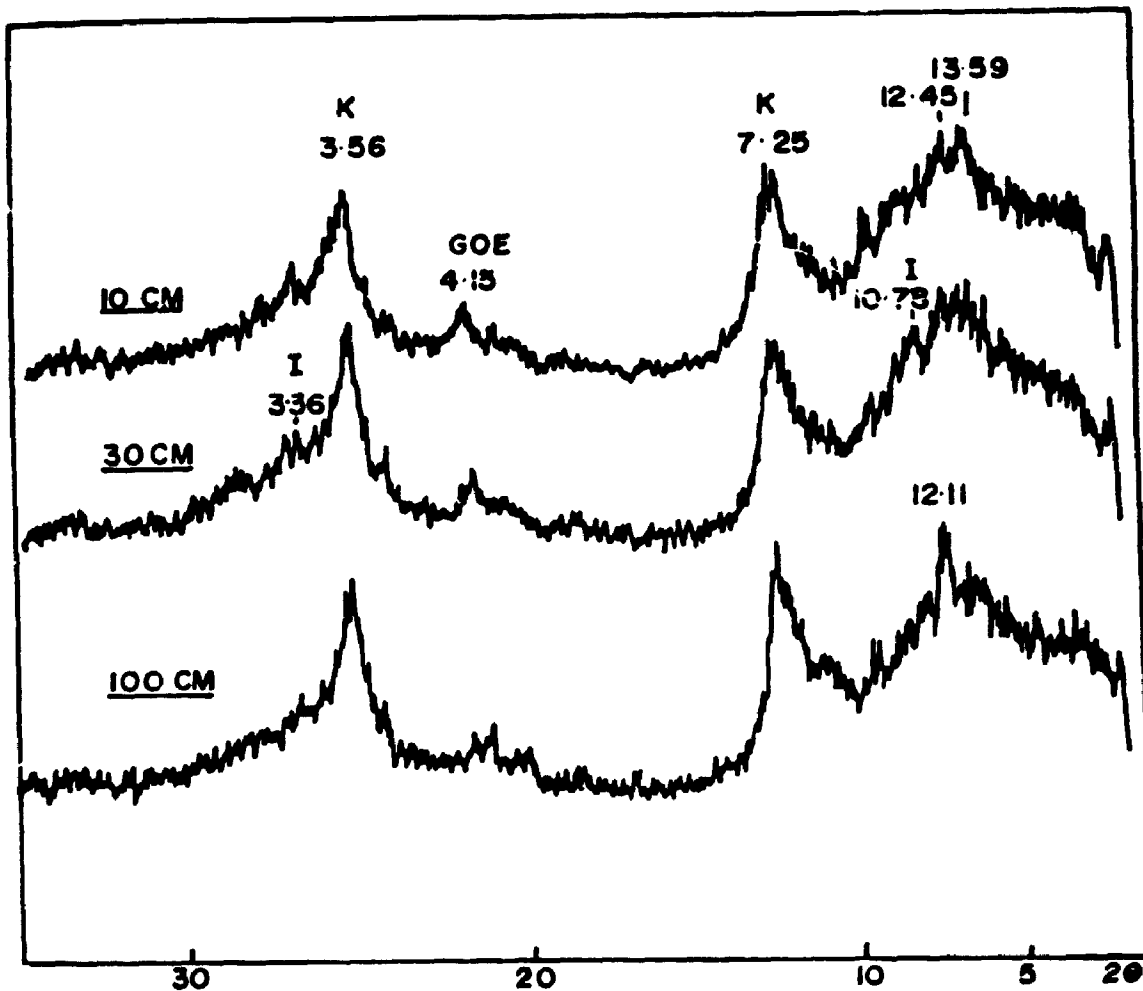


Fig. 3.7. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 88. Symbols as in Fig. 3.5.

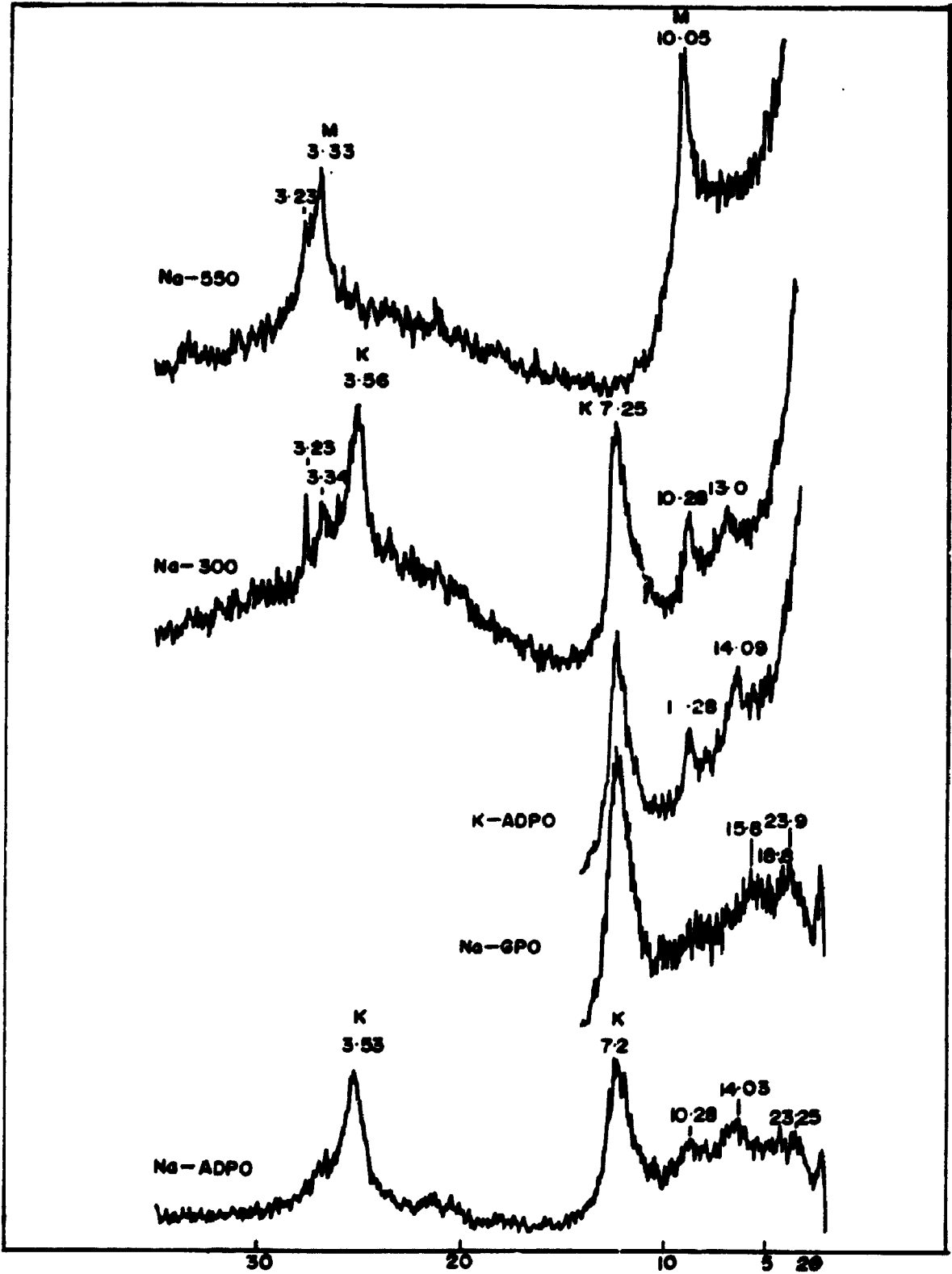


Fig. 3.10. X-ray Diffractograms of the 10 cm clay fraction in sequence 99. Symbols as in Fig. 3.4.

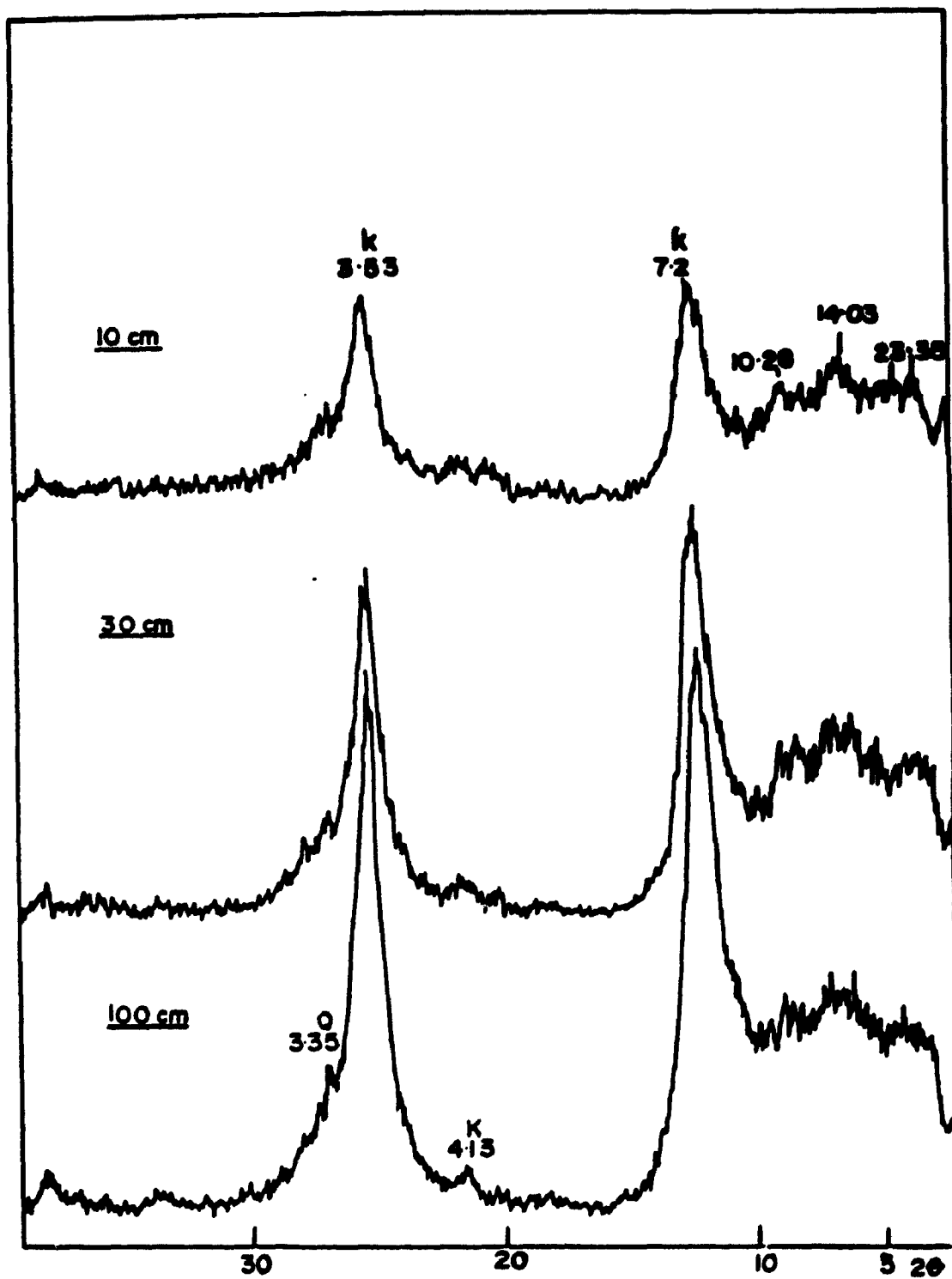


Fig. 3.11. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 99. Symbols as in Fig. 3.5.

3.2.4 Group (iv). Sequences 16, and 132 (and 135)

Information presented in Chapter II indicated that sequence 16 (Immature Brown Loam) and sequence 132 (Noncalic Brown soil) collected from the dry zone, which plot in field 3 in fig. 2.2B, would consist mainly of clays with high cation exchange capacity and/or primary minerals, consistent with its site location. The clay mineralogy partially supports this view.

Sequences in Group (iv), figs. 3.12, and 3.14, are differentiated from Group (iii) by the presence of illite together with kaolin as the dominant minerals. Gibbsite is conspicuously absent. The broad peak between $12\overset{\circ}{\text{A}}$ and $14\overset{\circ}{\text{A}}$ enhanced at $13\overset{\circ}{\text{A}}$ in sequence 16, (fig. 3.12), is identified as an interstratified smectite.

Several other differences are noted in sequence 16 (fig. 3.12) when compared to Group (iii) sequences, such as the non-definition of the $13\overset{\circ}{\text{A}}$ peak (expressed as the shoulder on the low angle side of the $10\overset{\circ}{\text{A}}$ peak) in the K-ADPO trace, which collapses less readily at $300\overset{\circ}{\text{C}}$; the peak position at $13\overset{\circ}{\text{A}}$ compared to the normal $14\overset{\circ}{\text{A}}$ peak as in the previous group and in fig. 3.14; These possibly imply interstratification of smectite with kaolin. The opposite is true of sequence 132 (fig. 3.14), where peak behaviour, especially good expansion on glycolation and resistance to collapse on K saturation and heat treatment (even in the K-300) trace suggests the presence of smectite instead of interstratification.

Sample 135 (fig. 3.18) comprising river sediment, and sequence 132 are placed in this group, because of the

abundance of illite in spite of the presence of smectite instead of the interstratified 14⁰Å mineral.

Within sequence mineralogical variation excepting in quantitative terms is slight (fig. 3.13). As shown in fig. 3.13, the 50 cm level has a smaller abundance of illite, which is surprising since it was sampled near the soil parent rock interface.

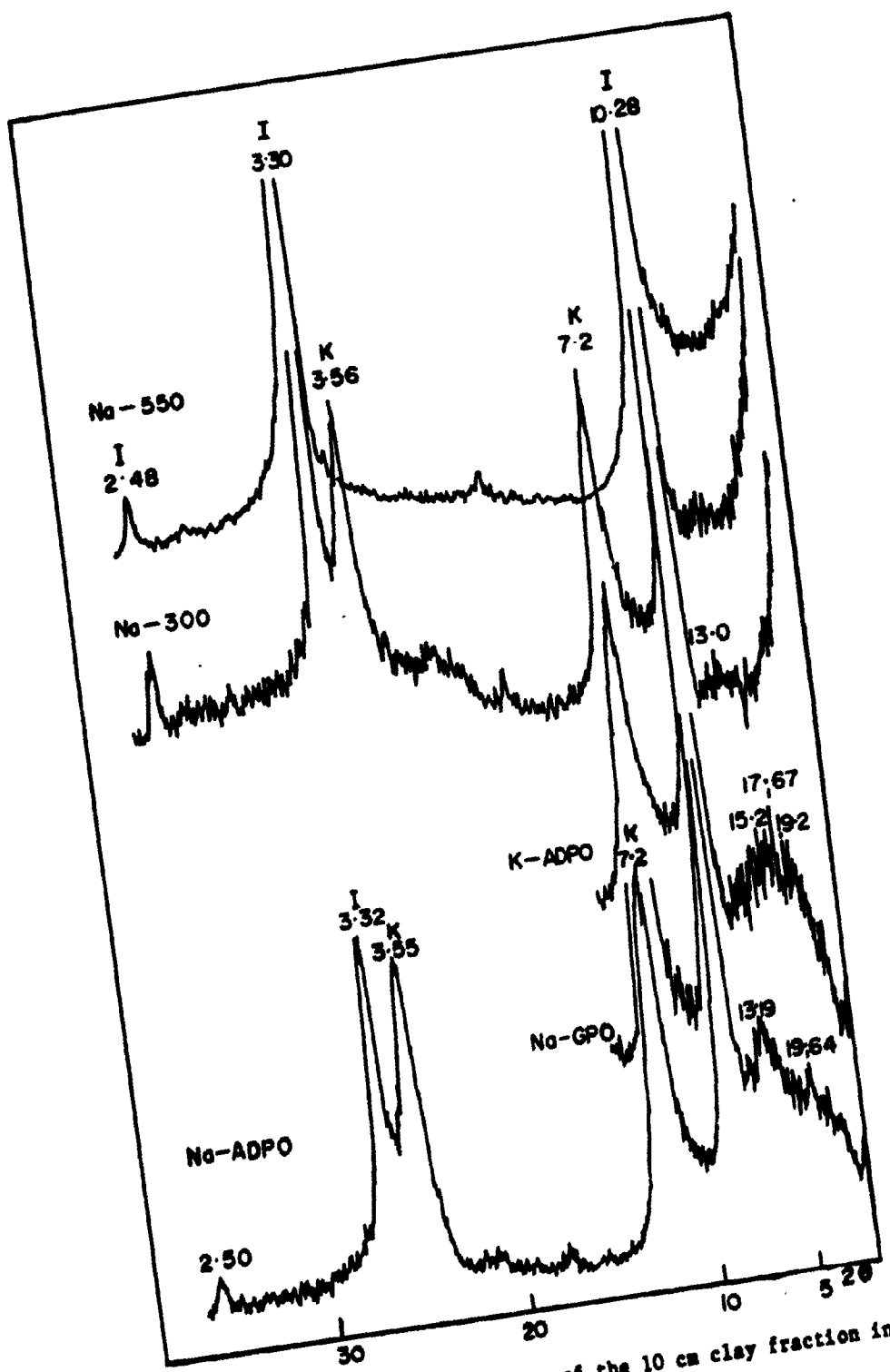


Fig. 3.12. X-ray Diffractograms of the 10 cm clay fraction in sequence 16. Symbols as in Fig. 3.4.

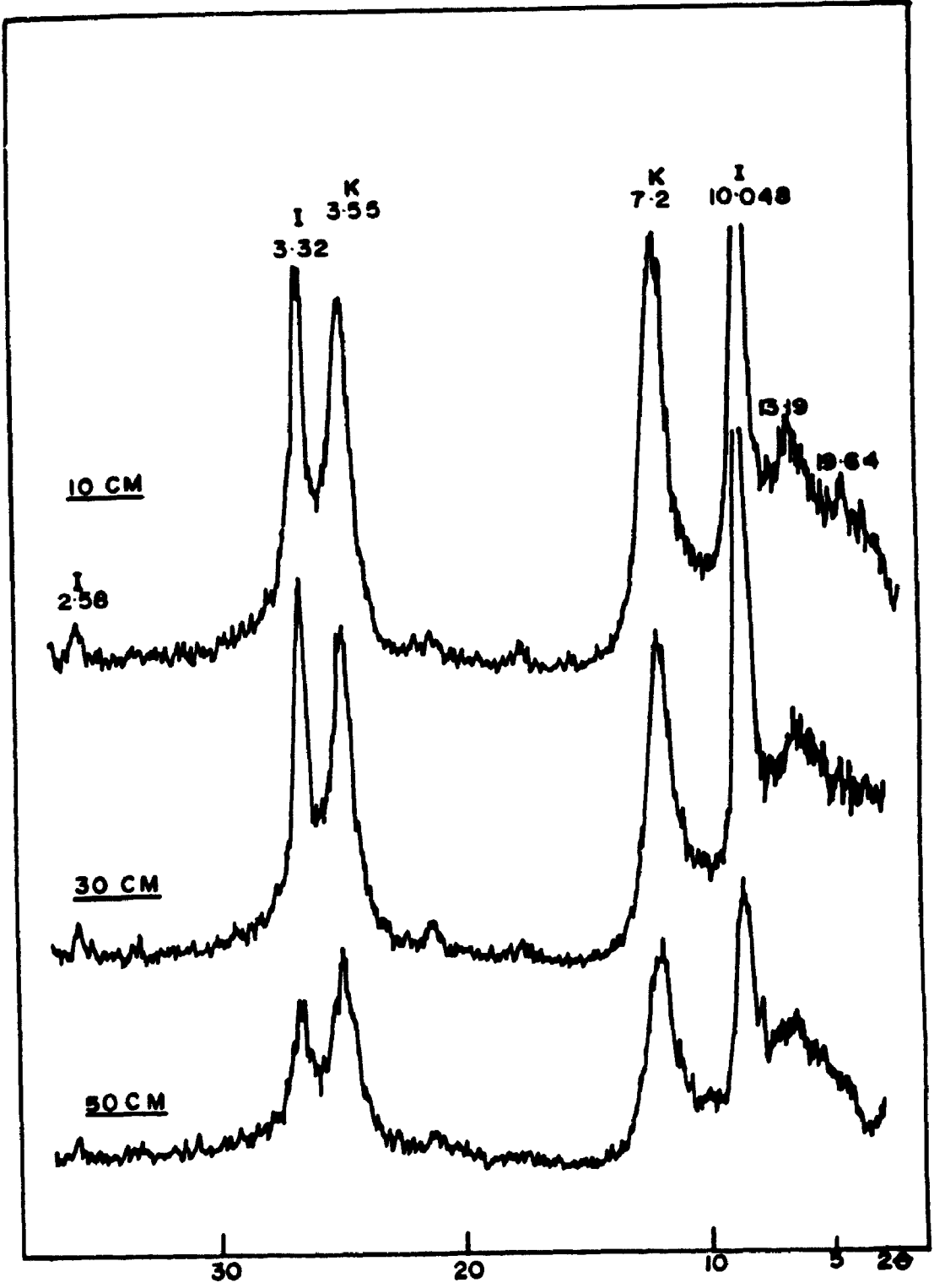


Fig. 3.13. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 16 Symbols as in Fig. 3.5.

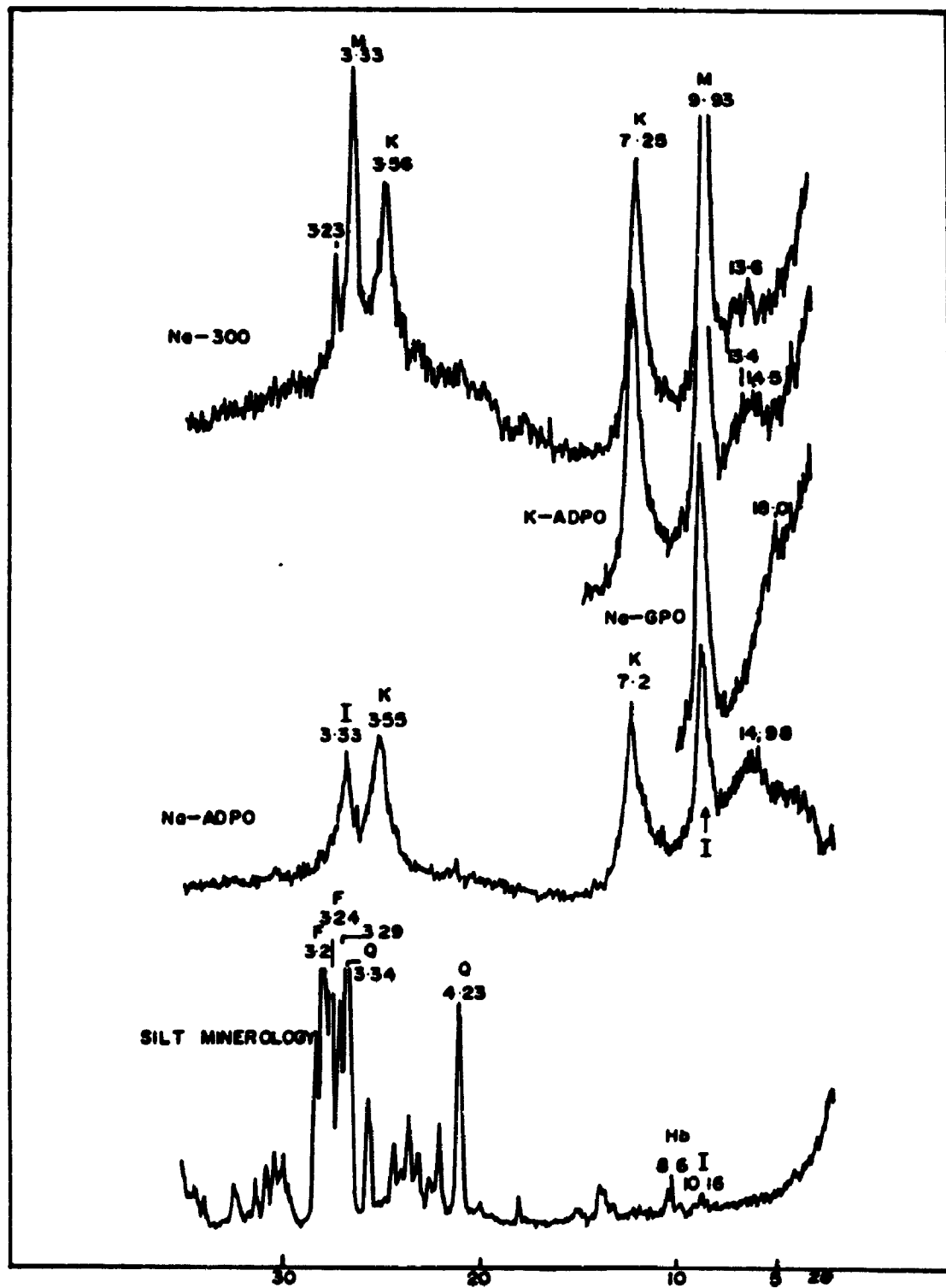


Fig. 3.14. X-ray Diffractograms of clay and silt fractions in sequence 132. K=kaolin; F=feldspar; Q=quartz; I=illite/mica; M=collapsed smectite or vermiculite; S=smectite; Hb=hornblende.

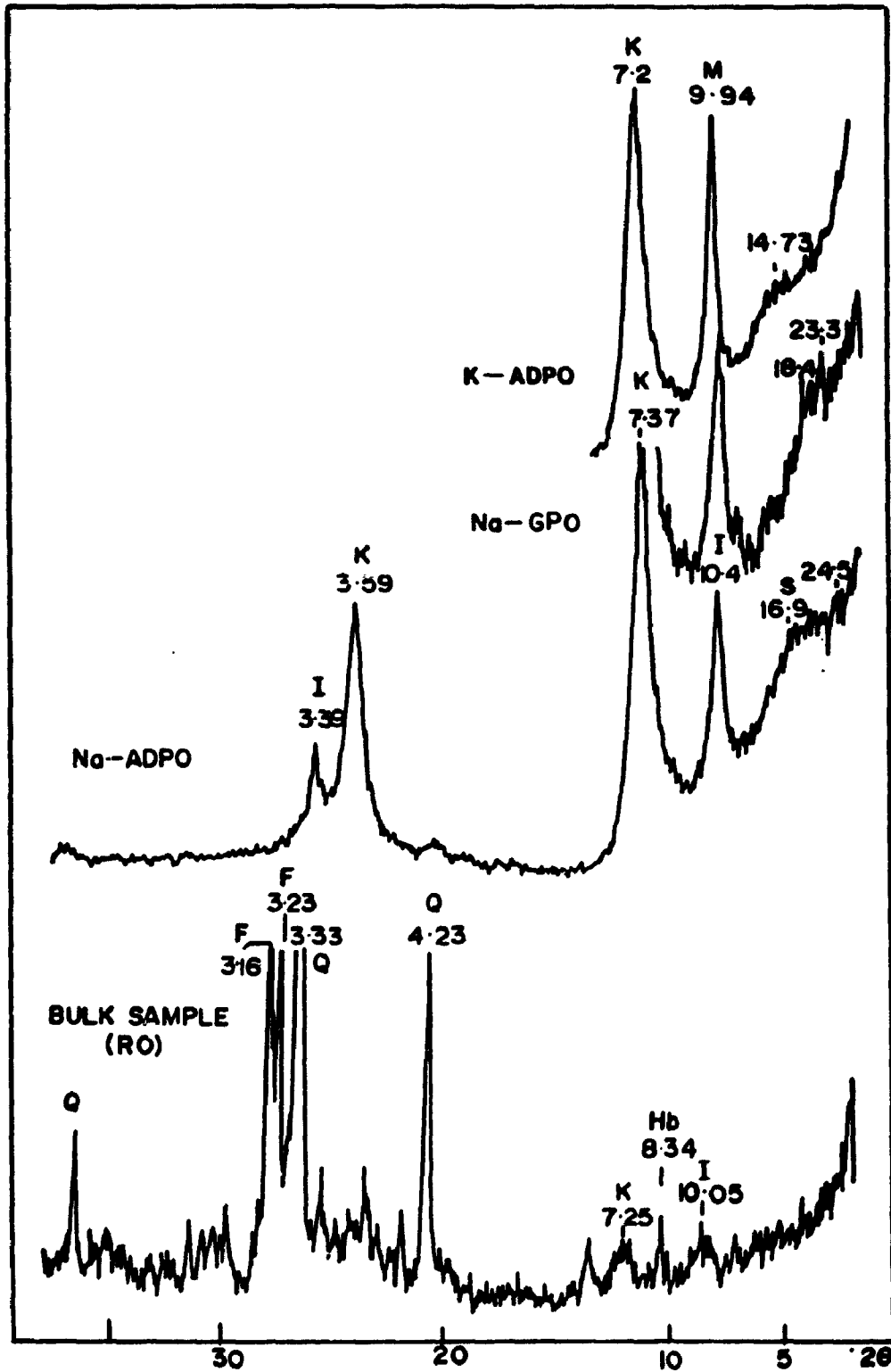


Fig. 3.18. X-ray Diffractograms of clay fraction and bulk sample (random orientation) in sequence 135. Symbols as in Fig. 3.14.

3.2.5 Group (v). Sequences 104, 100

Information presented in Chapter II indicated that sequence 104 and 100 collected from the northwestern dry zone which plot in field 3 in fig. 2.2A would consist mainly of clays with high cation exchange capacity and/or primary minerals, consistent with its site location. The clay mineralogy supports this view.

Group (v) sequences (figs. 3.15 and 3.17) are differentiated from the rest by the absence of gibbsite, the subordinate role of kaolin and illite and by the characteristic presence of dominant smectite in the absence of vermiculite. Absence of vermiculite is established by the complete expansion of the 14-16^oÅ peak on ethylene glycol solvation to a relatively well defined peak at 18.4^oÅ compared to the Na-GPO traces in other Groups, the definite resistance to peak collapse after K-saturation (K-ADPO), and the complete collapse to a mica structure (9.9^oÅ) on heating to 550^o C.

Variation with depth (fig. 3.16) in clay mineralogy other than in quantitative terms is not very marked.

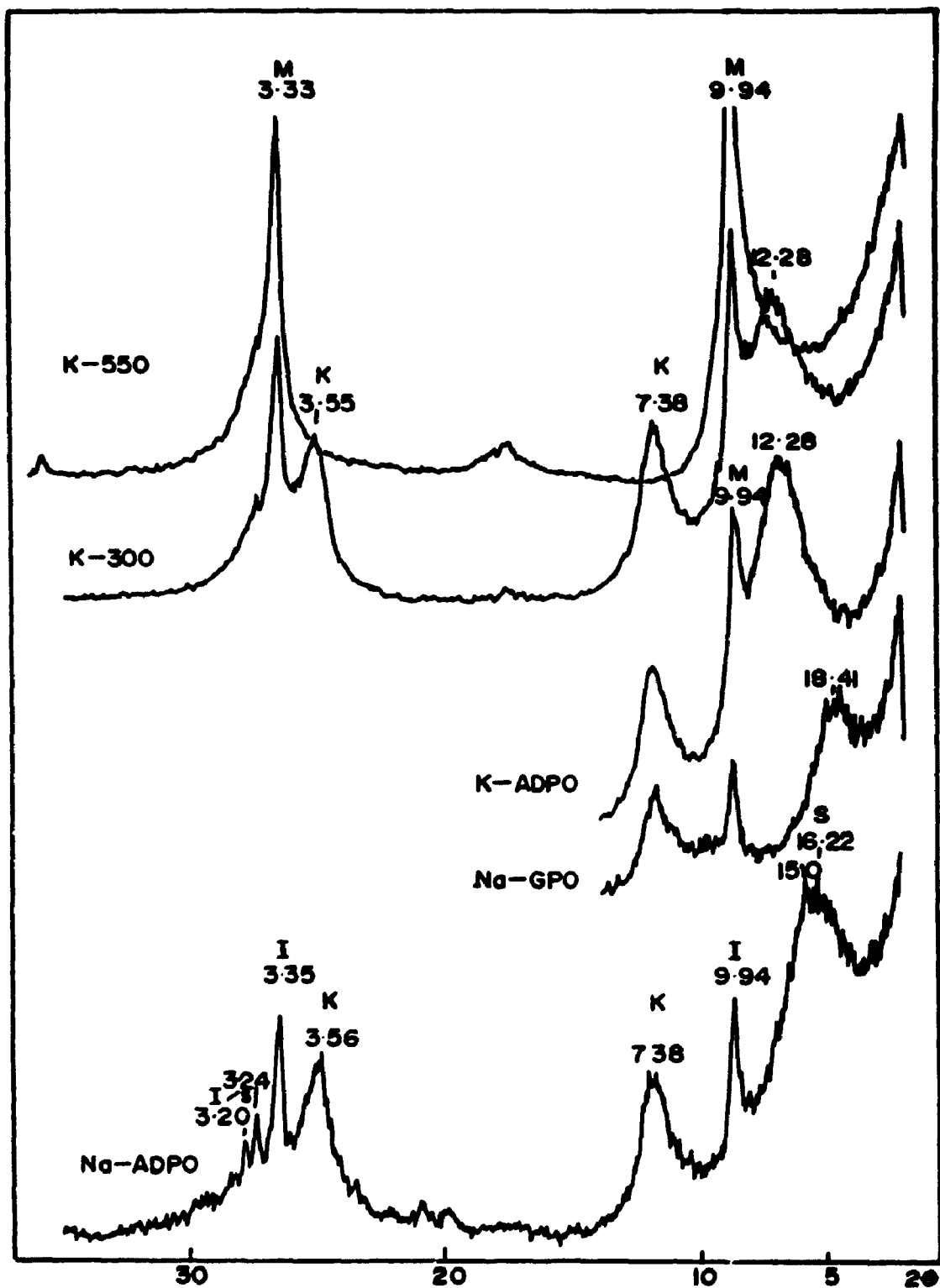


Fig. 3.15. X-ray Diffractograms of the 10 cm clay fraction in sequence 104. Symbols as in Fig. 3.14.

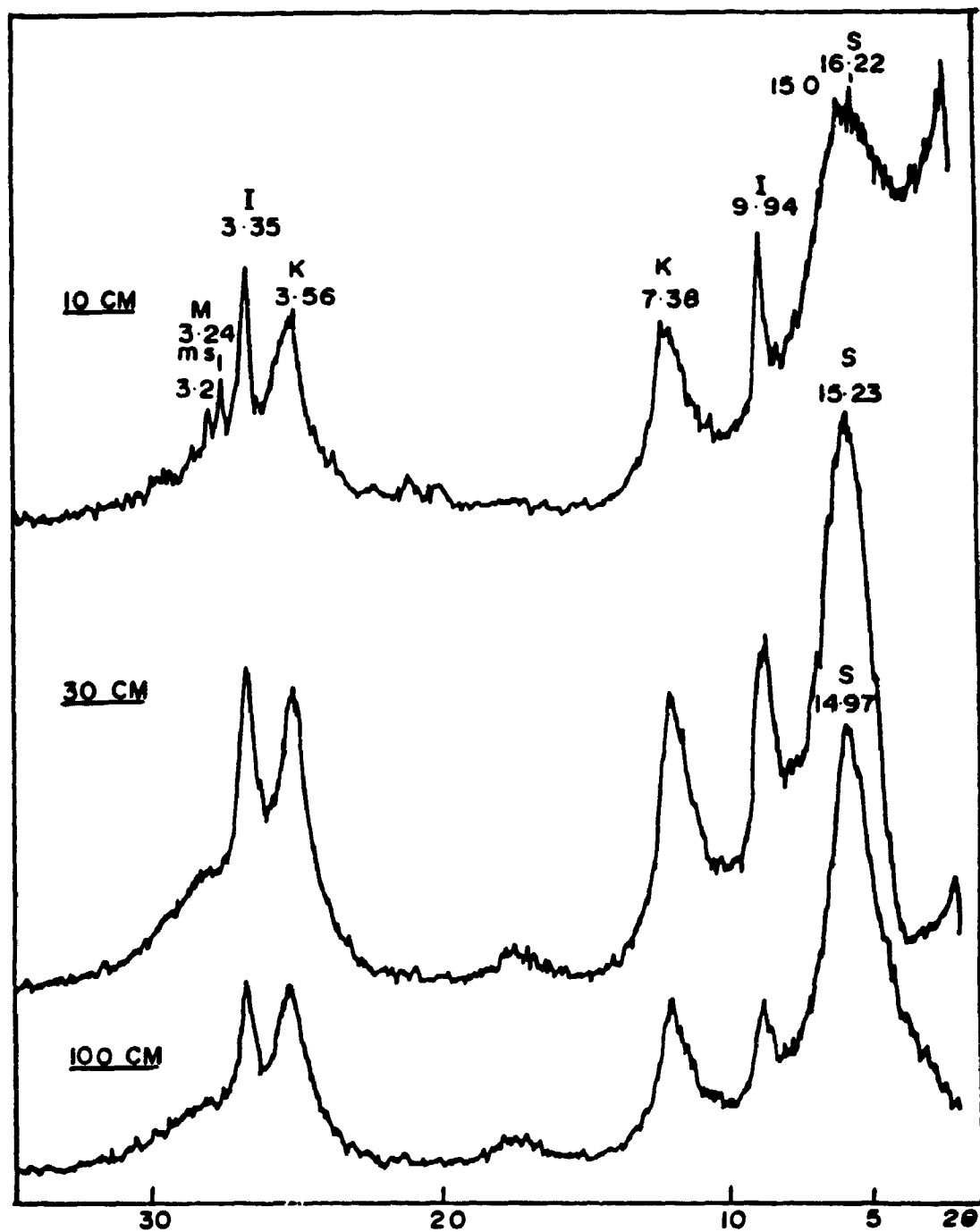


Fig. 3.16. X-ray Diffractograms of clay fractions (Na-ADPO) from varying depths in sequence 104. Symbols as in Fig. 3.14.

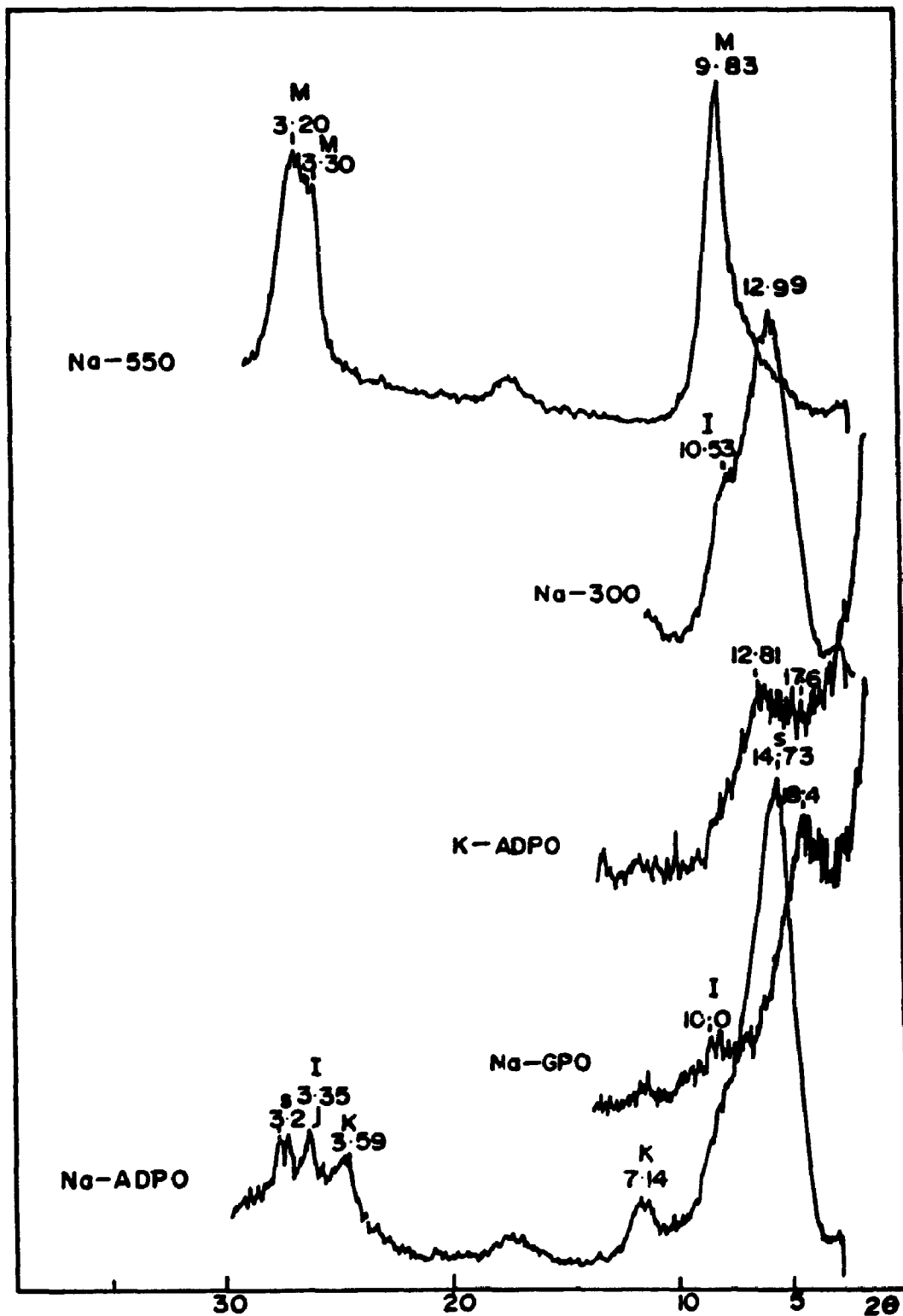


Fig. 3.17. X-ray Diffractograms of the 10 cm clay fraction in sequence 100. Symbols as in Fig. 3.14.

3.3 Silt Mineralogy

Mineralogy of the silt fraction was found by air drying the silt fraction obtained after repeatedly washing the residue remaining after particle size analysis, free of clay, and subsequently crushing the sample gently in an agate mortar prior to X-ray diffraction analysis of the sample, mounted as a randomly oriented powder. In sequence 104 the bulk sample was used for mounting. X-ray diffraction records presented in figs. 3.21 to 3.26, were obtained under the same conditions as the clay fractions excepting that most samples were run at 800 counts per second other than sequence 61 (fig. 3.21) and the 100 cm level in sequence 88 (fig. 3.22) which were run at 400 counts per second to maximize peaks.

The same grouping of sequences used in presenting the clay mineralogy is maintained even though dramatic differences between groups in silt mineralogy are not observed as in the clay mineral grouping, excepting between Group (i) and the rest. A summary of the silt mineralogy is given in Table 3.1 in addition to that given below.

- Group (i) - Quartz + gibbsite + sillimanite (no major primary minerals)
- Group (ii) - Quartz + feldspar + mica + hornblende
- Group (iii) - "
- Group (iv) - "
- Group (vi) - "

3.3.1 Group (i) Sequences 148 and 153

The silt consists primarily of quartz and gibbsite (fig. 3.20), in contrast to the clay fraction (fig. 3.3). Hence the simplest silt mineralogy lacking in primary minerals other than quartz is observed in this sequence, pedogenically placed within the soft laterite subgroup of Red Yellow Podsoles. Variation is not present in the silt fraction within the non-indurated upper segment of the lateritic sequence. However in the soft laterite at depths >100cms a distinct mineralogical differentiation is observed corresponding to the red nodules and yellow matrix of typical laterite, as shown in fig. 3.20. The red nodules consist of gibbsite, quartz and hematite (that gives the red pigment to the red nodules) and lacks kaolin; the yellow matrix comprises kaolin, more quartz and gibbsite but lacks hematite.

The silt fraction of sequence 153, a Red Yellow Podzol, also of the wet zone, collected from the rainiest location in Sri Lanka is comparable to that of sequence 148 ; however in addition to quartz and gibbsite it contains sillimanite (fig. 3.19). Feldspar is notably absent and appears to be less resistant than sillimanite, to weathering. This is true even at depths of 600cm (fig. 3.19) which contains highly weathered clasts retaining primary micro-structure and visible garnet grains originating from the parent garnet sillimanite graphite gneiss.

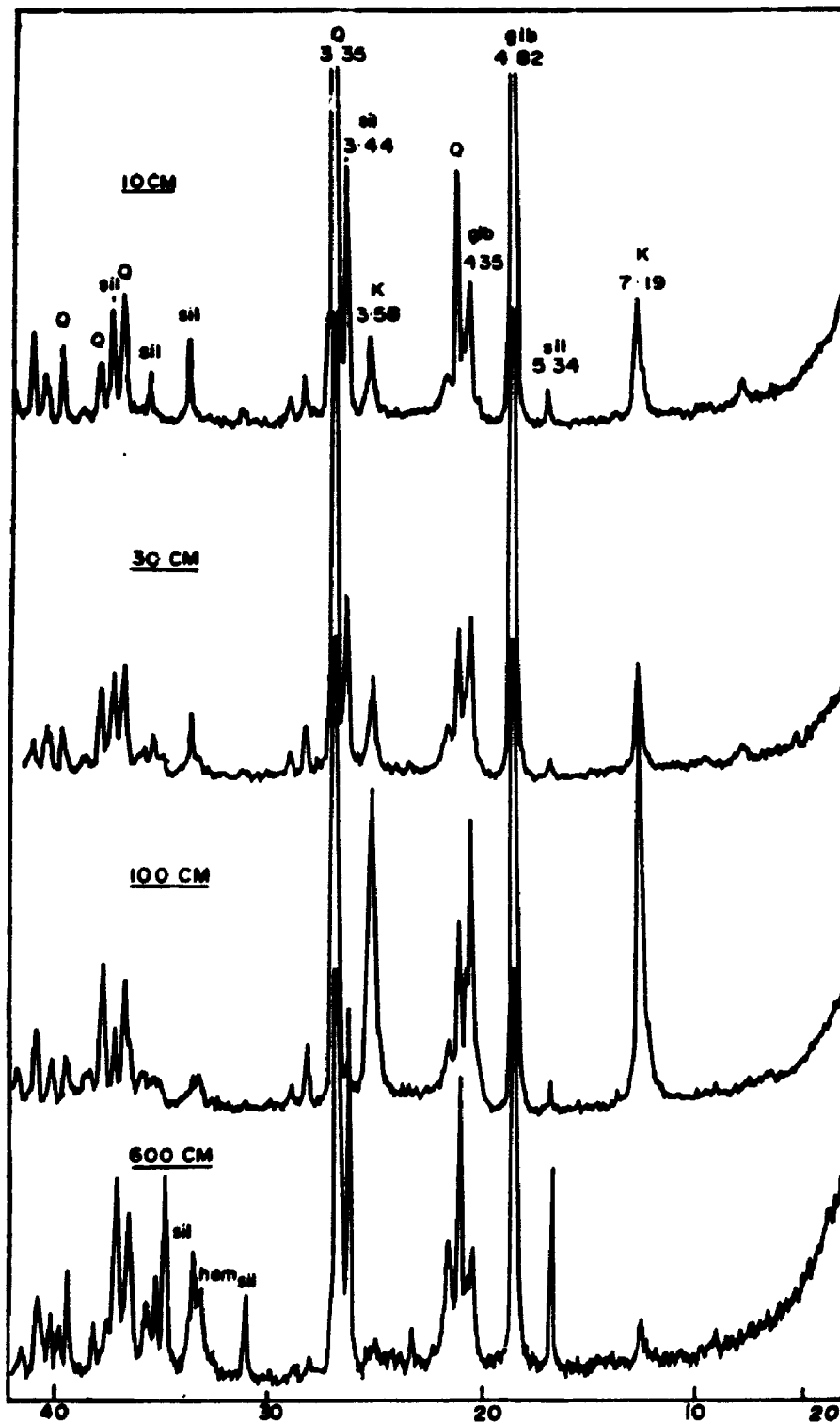


Fig. 3.19. X-ray Diffractograms from silt fractions from varying depths in sequence 153. Q=Quartz; sil=Sillimanite; gib=Gibbsite; K=Kaolinite; hem=Hematite.

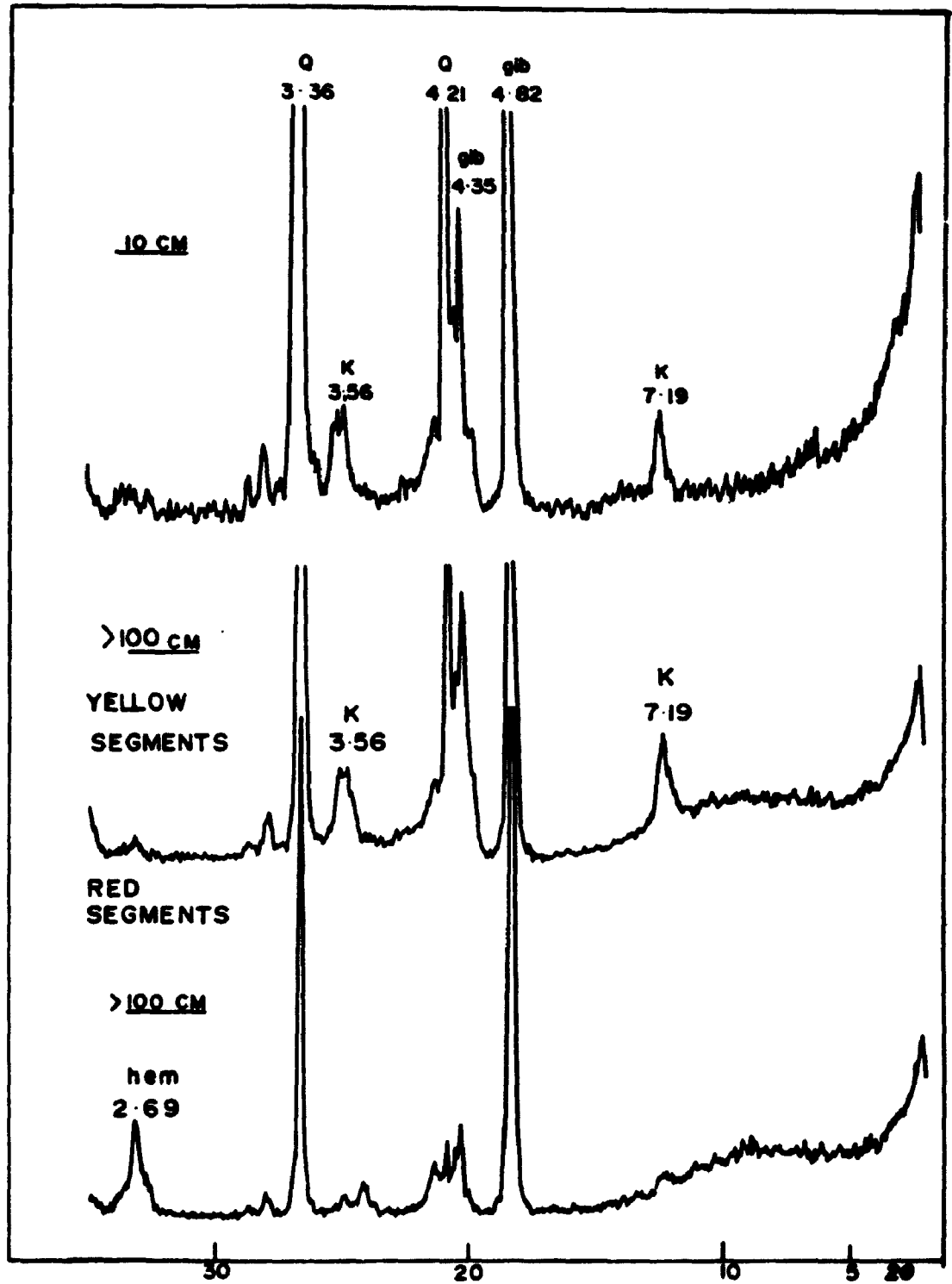


Fig. 3.20. X-ray Diffractograms from silt fractions from varying depths in sequence 148. Symbols as in Fig. 3.19.

3.3.2 Group (ii) Sequences 61 and 112

Sequences 61 and 112 were grouped together because of similarities in the clay fraction, in terms of mineralogy and proportion of kaolin to gibbsite (section 3.2.2). However primary minerals besides quartz are present such as feldspar, hornblende and degraded mica in sequence 61 (fig. 3.21) and only abundant feldspar in sequence 112 (fig. 3.23), which can be related directly to their parent rock types, a hornblende biotite migmatitic gneiss and a granitic gneiss respectively. The illite and interlayered vermiculite trace found in the clay fraction of sequence 61 (fig. 3.5) possibly originated from the degraded mica, 12.4\AA ⁰, still detectable in the less weathered 100cm level (fig. 3.21). Illite was not found in the clay fraction of sequence 112 (figs. 3.8 and 3.23) which derives from a granitic gneiss that lacks abundant mica. The abundance of feldspar (fig. 3.23) inherited from the granitic parent of sequence 112 possibly explains the abundance of kaolin in the clay fraction (fig. 3.8) which is not found in any other sequence studied.

Variation with depth is very noticeable in the 12\AA ⁰ degraded mica, in sequence 61.

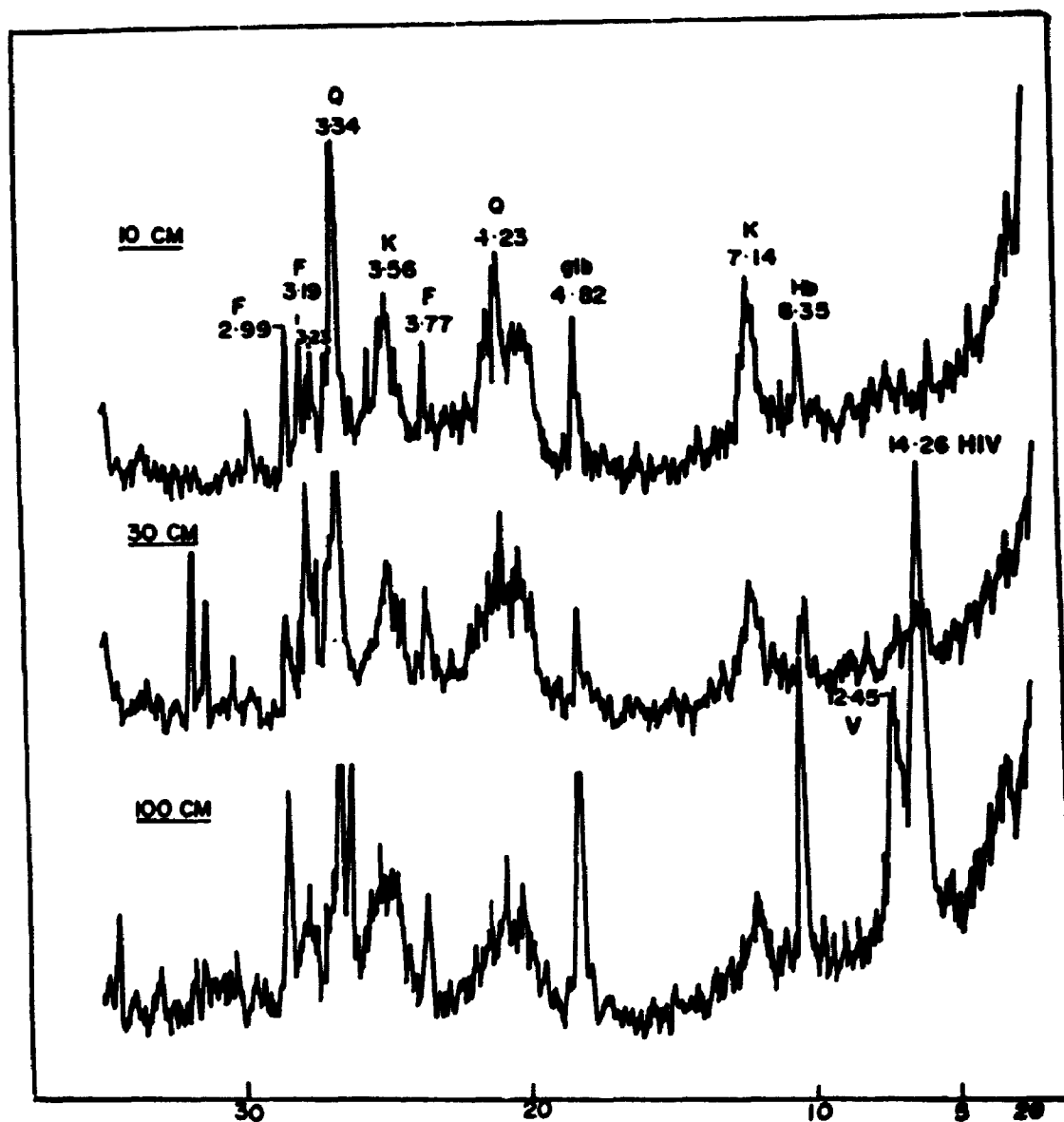


Fig. 3.21. X-ray Diffractograms of silt fractions from varying depths in sequence 61. Q=Quartz; K=Kaolin; gib=Gibbsite; F=feldspar; Hb=hornblende. V=Vermiculite; HIV=Hydroxy Interlayered Vermiculite.

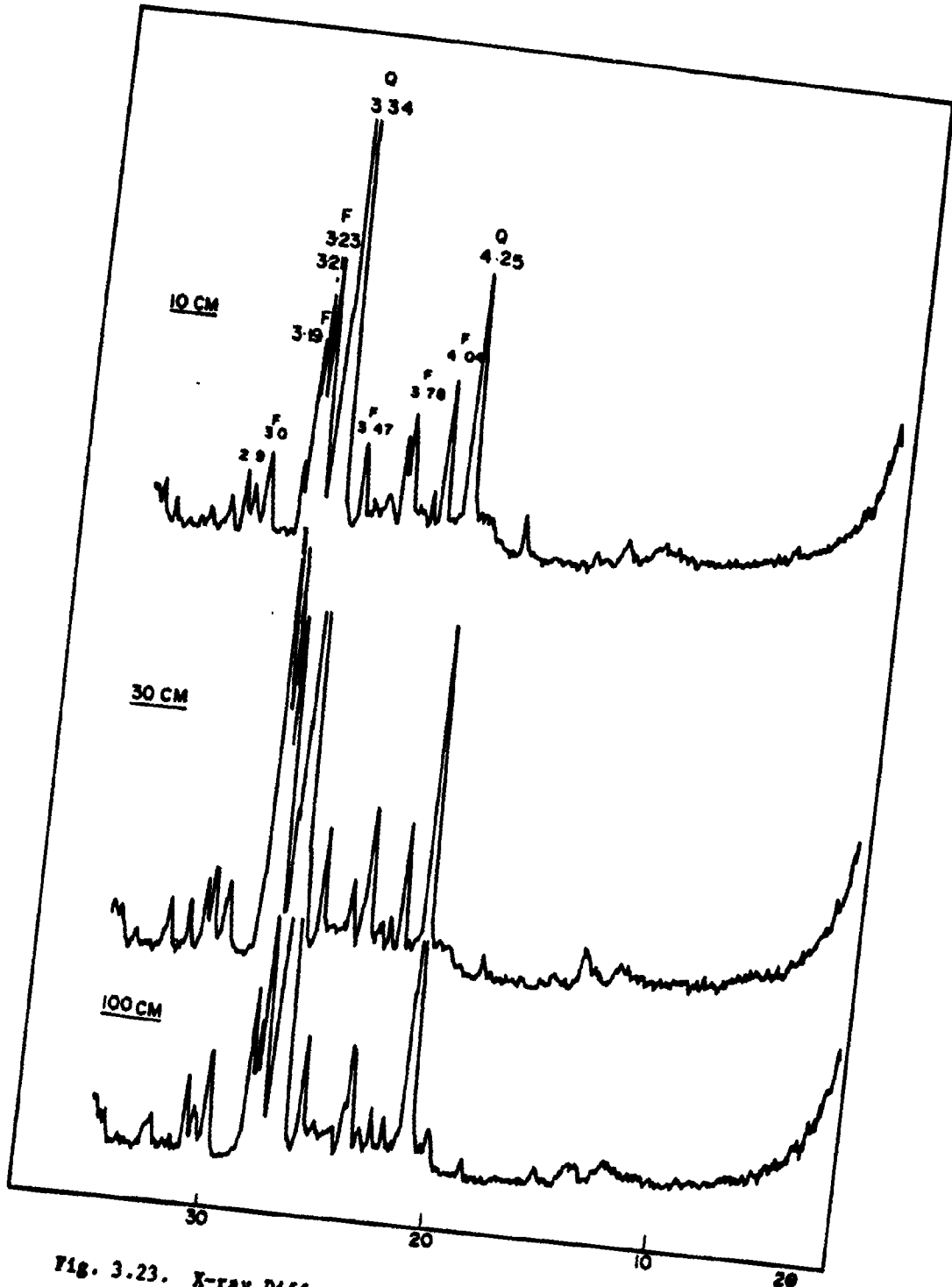


Fig. 3.23. X-ray Diffractograms from silt fractions from varying depths in sequence 112. Symbols as in Fig. 3.21.

3.3.3 Group (iii). Sequences 88 and 99

Group (iii) sequences, both characterised as Reddish Brown Earths, showed near identical clay mineralogy. Feldspar and quartz dominate the silt mineralogy of both sequences (figs. 3.22 and 3.24) but trace amounts of hornblende and degraded mica are only present in sequence 88. As with sequence 61 (fig. 3.21), the presence of minor illite in the clay fraction (fig. 3.6) in sequence 88 can be related to the presence of degraded mica (12.28A^o) in the silt fraction. This is however not possible for sequence 99, which also contains illite in its clay fraction. The latter sequence which derives from a granitic gneiss parent lacks mica in the silt fraction (fig.3.24) which however does not preclude its existence in the sand fraction.

Variation with depth is very noticeable in the 12A^o degraded mica, in sequence 88.

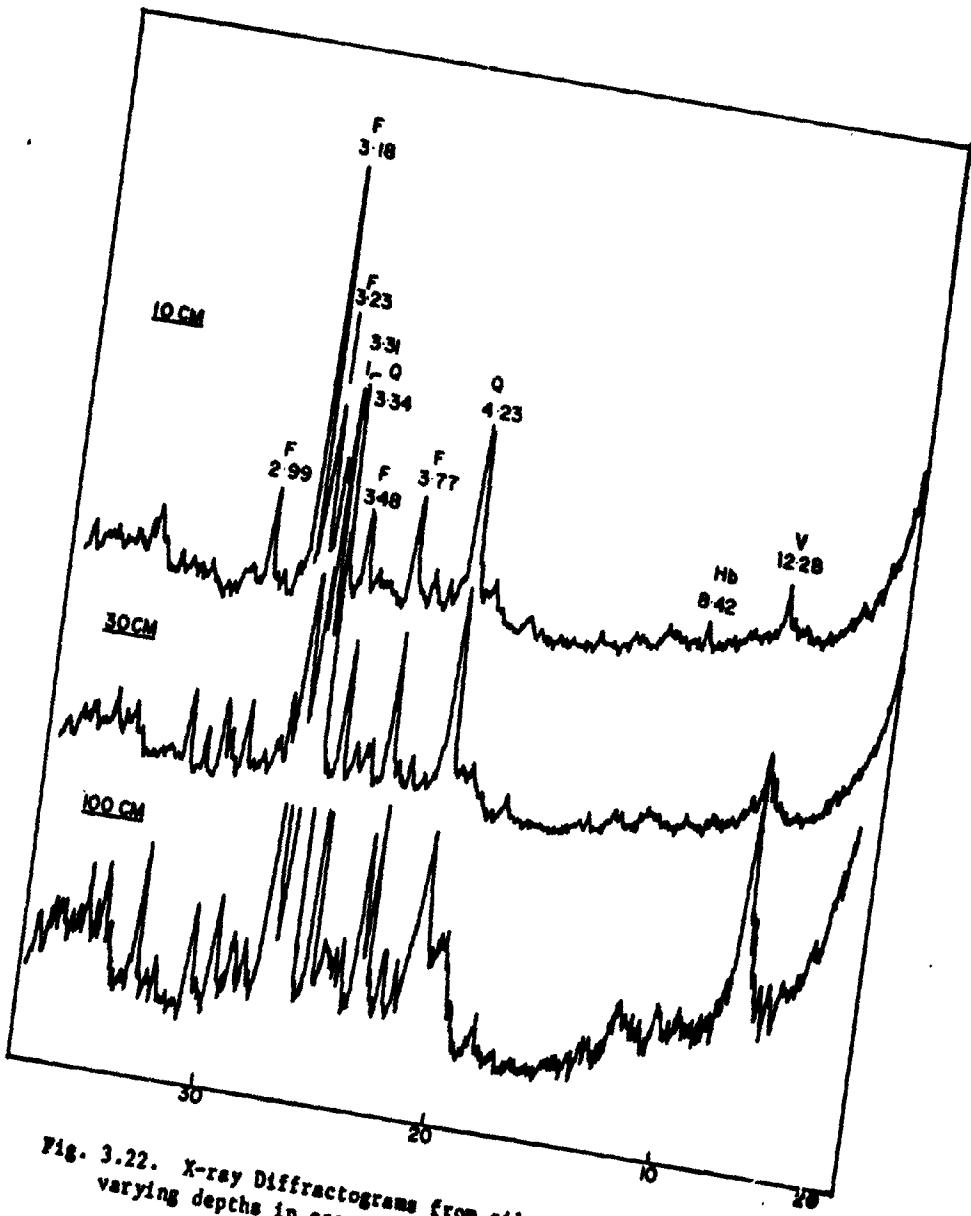


Fig. 3.22. X-ray Diffractograms from silt fractions from varying depths in sequence 88. Symbols as in Fig. 3.21.

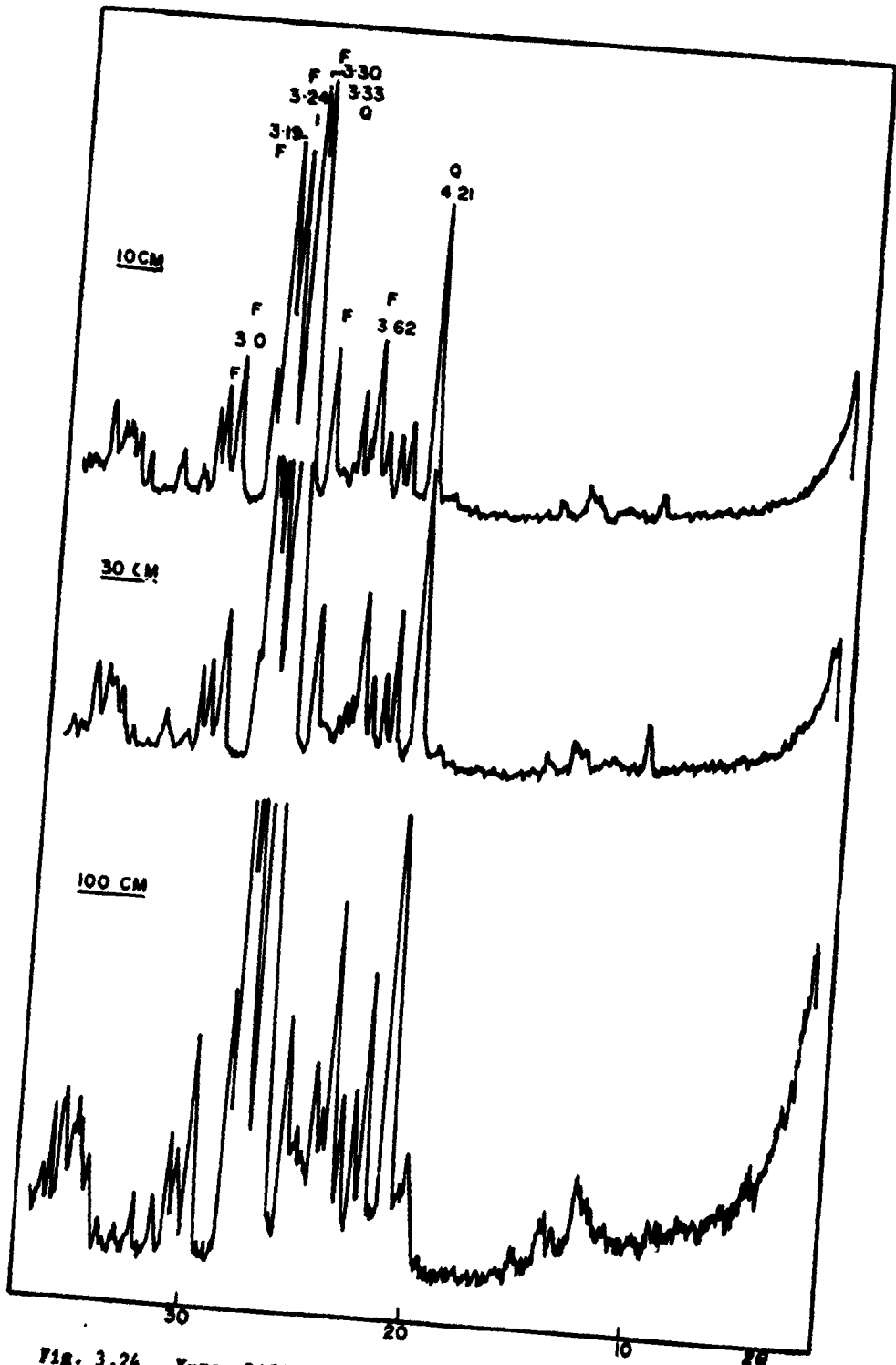


Fig. 3.24. X-ray Diffractograms from silt fractions from varying depths in sequence 99. Symbols as in Fig. 3.21.

3.3.4 Group (iv). Sequences 16 and 132

Dominance of mica/illite over kaolin was used to group both these sequences into this group in section 3.2.4. A complementary abundance of mica/illite, together with hornblende is present in the silt fraction of sequence 16 (fig. 3.25) derived from a migmatitic hornblende biotite gneiss. As in sequence 112, mica is undetectable excepting at depth in sequence 132 (fig. 3.14) derived from a granitic gneiss precursor. In both instances the primary mineral feldspar, clearly dominates over mica and hornblende in the silt fraction, even though illite is more abundant than kaolin in the clay fraction.

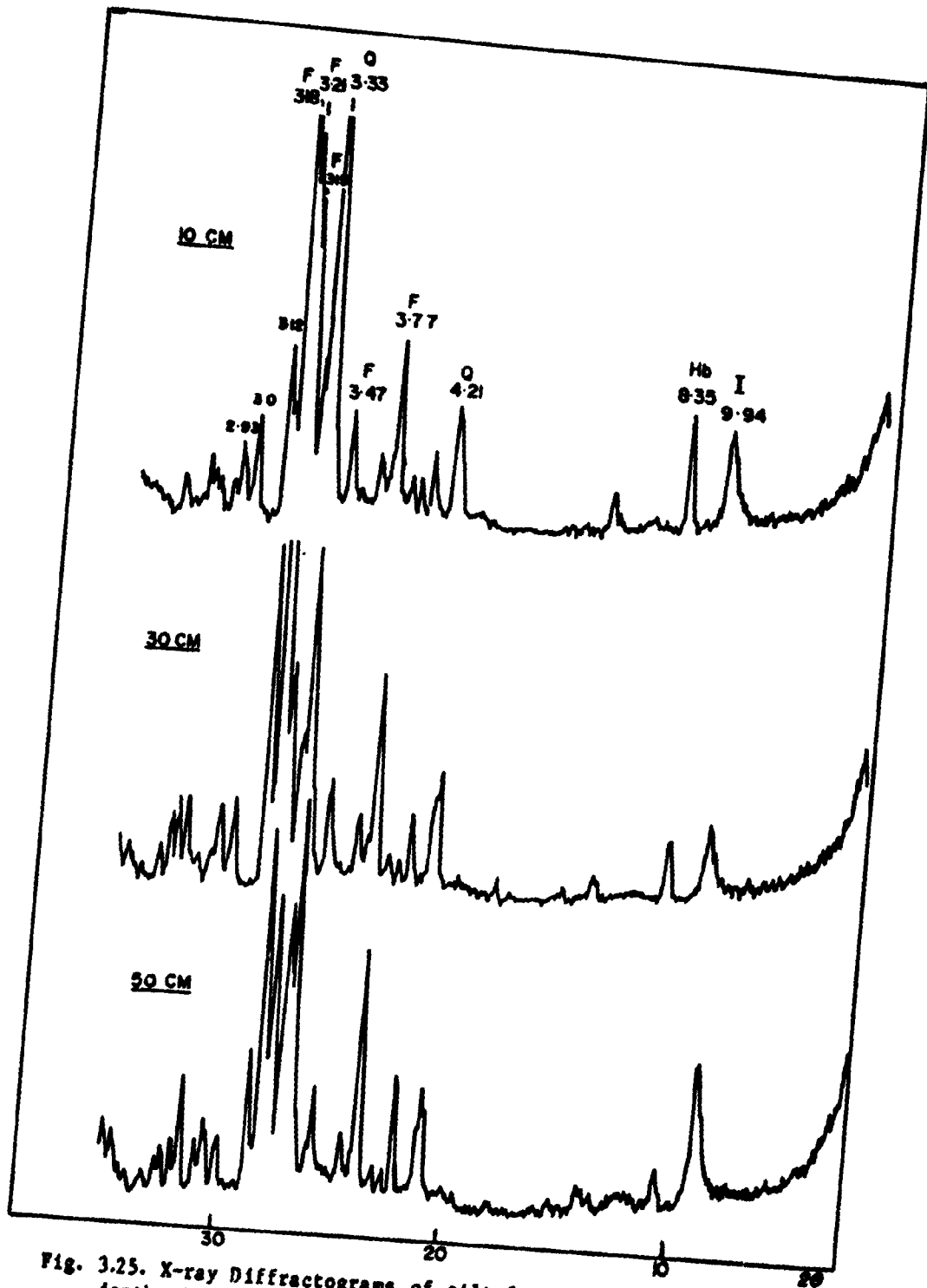


Fig. 3.25. X-ray Diffractograms of silt fractions from varying depths in sequence 16. I=Illite/mica; other symbols as in Fig.3.21.

3.3.5 Group (v) Sequence 104

In section 3.2.5 the predominance of smectite over kaolin was used to differentiate this group. However a trace of mica is detectable only at the 100 cm level (fig. 3.26) probably resulting from the use of the bulk sample instead of only the silt fraction. Feldspar dominates the silt fraction in the deeper levels whereas quartz is more abundant in the 10 cm level (fig. 3.26), where surprisingly a trace of gibbsite is also noted.

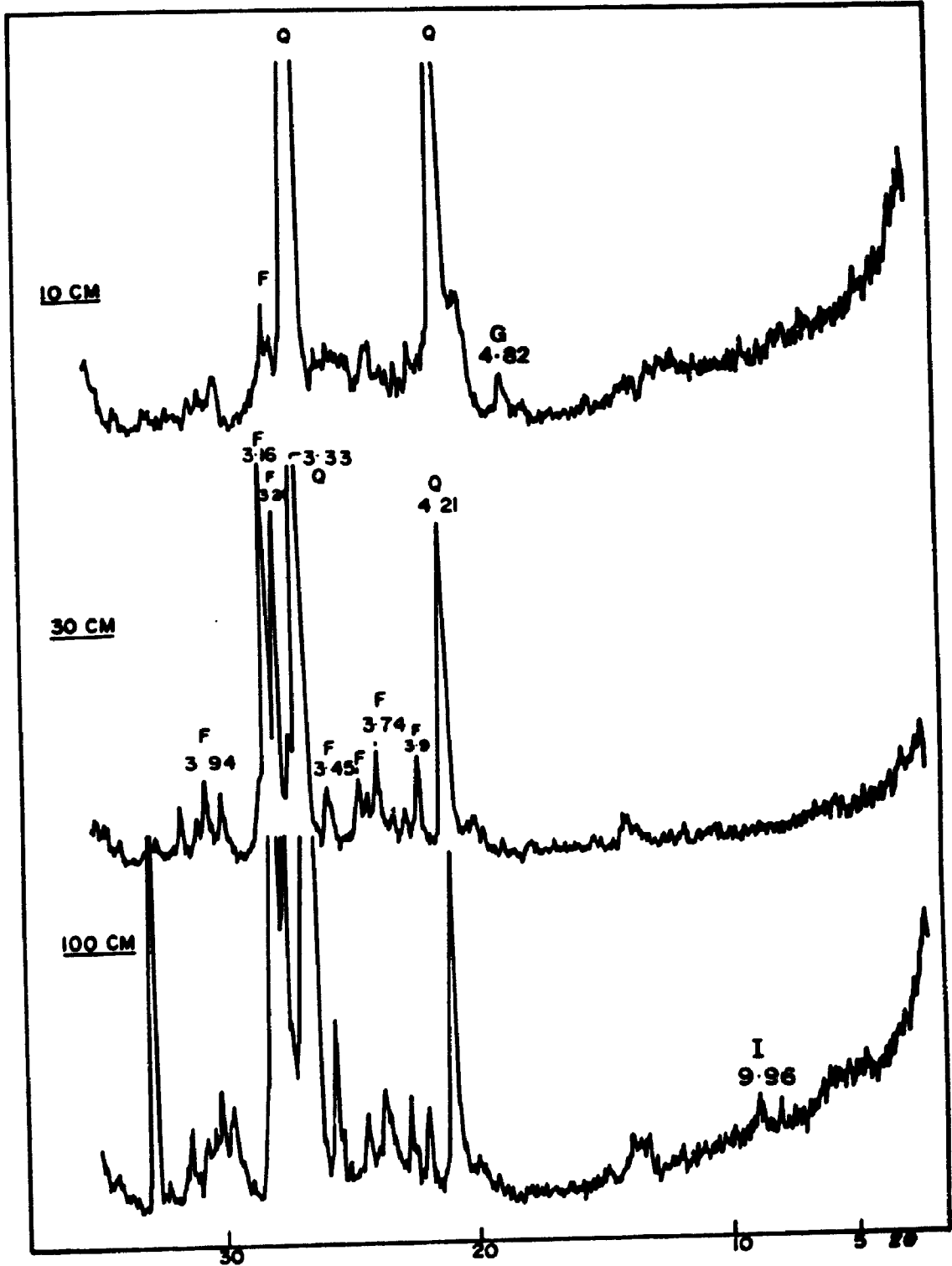


Fig. 3.26. X-ray Diffractograms of silt fractions from varying depths in sequence 104. I=illite/mica; G=Gibbsite; other symbols as in Fig.3.21.

Table 3.2 Relative Abundances of Clay and Bulk Sample Minerals

Sample	Goethite	Gibbsite	Clay Minerals			Smectite	Bulk Sample (-Clay Minerals)					Precursor	
			Kaolin	Illite 1A ¹	Smectite		Quartz	Feldspar	Mica	Hb	Others		
<u>Wet Zone</u>													
Group (I)													
14510	x	x	+	-	tr	-	+	-	-	-	-	-	Hyp-Flag Charno-Gn
145100	x	xx	++xx	-	x	-	++xx	-	-	-	-	-	"
145>100	x	+	++xx	-	tr	-	++xx	-	-	-	-	-	Hyp-Flag Gn
14210	x	x	++x	-	-	-	++x	-	-	-	-	-	"
142100	x	xx	++x	-	tr	-	++x	-	-	-	-	-	Calc Gn
142NR	x	xx	++x	-	tr	-	++x	-	-	-	-	-	Quartzite
11510	x	x	++x	-	tr	-	++x	-	-	-	-	-	
4910	x	x	++x	-	x	-	++x	-	-	-	-	-	
<u>Intermediate Zone</u>													
7110	x	tr	++	-	tr	-	++	-	-	-	-	-	Unknown River Sediment Paddy Field
848A	-	-	xxx	tr	-	-	xxx	n.d	n.d	n.d	n.d	n.d	
848A10b	-	-	xxx	tr	tr	-	xxx	n.d	n.d	n.d	n.d	n.d	
<u>Dry Zone</u>													
Group (v)													
10016	-	-	xx	+	-	+++xx	xx	+	-	-	-	-	Unknown Augen Gneiss (Hb-Bt-Qtz-Field)
10410	-	-	x	x	-	x	x	x	x	x	x	x	
10430	-	-	++x	++	-	+++xx	++x	++	++	++	++	++	
104100	-	-	xxx	+++	-	+++xx	xxx	+	+	+	+	+	
Group (iv)													
13130	-	-	++x	x	x	-	++x	x	n.d	n.d	n.d	n.d	Hb-Bt-Migmatite
131100	-	-	++	xx	xx	-	++	xx	n.d	n.d	n.d	n.d	"
131NR	-	-	++x	x	x	-	++x	x	n.d	n.d	n.d	n.d	Granite (Hb+Bt) River Sediment
13910	-	-	xxx	xx	xx	-	xxx	xx	x	x	x	x	
87	-	-	xx	x	x	-	xx	x	n.d	n.d	n.d	n.d	

+++xx
I 14X Interlayered Smectite/vermiculite

3.4 Verification of Clay Grouping and Identification

Summary of the mineralogical data in Table 3.1 shows that Group (i) clays correspond to wet zone sequences. Group (ii) sequences correspond to sequences collected near the intermediate and wet zone boundary and that Groups (iii) - (v) correspond to samples collected from the dry zone of Sri Lanka.

3.4.1 Verification of Clay Grouping

In order to verify the grouping of clay minerals further samples used for geochemical characterisation in Chapter 11 were analysed for clay minerals using techniques outlined in section 3.2. However since particle size analysis was not performed the amount of suspension used per slide could not be kept homogeneous. Relative abundances tabulated in Table 3.2 are comparative only for minerals within each level in a sequence, and not between levels. To obtain the minerals present other than clay sized minerals, bulk samples were gently crushed in an agate mortar and mounted as random powder mounts. Results are presented in Table 3.2. It can be seen that the random selection of samples can be divided into analogous groups, that fit into corresponding climatic divisions, although all of the groups designated in Table 3.1 are not represented.

3.4.2 Verification of mineral identification

As Tables 3.1 and 3.2 show smectite identified from X-ray analysis is not as prevalent in the dry zone samples as one would expect according to Herath and Grimshaw (1971). A 14^oÅ smectite interstratification is more common. De Alwis and Pluth (1976), who studied the surface horizons of some dry zone soils did not report pure smectite. They observed a smectite-vermiculite "intergrade" and mixed layer minerals between the 10^oÅ and 14^oÅ range.

Smectite was observed by Panabokke (1959) at depth in the rock decomposition zone and under impeded drainage conditions in the dry zone. Similarly Kalpage et al., (1963) noted the presence of smectite only in an immature Reddish Brown Earth. The mature profile studied contained a trace of vermiculite in all but the lowest horizon which contained a small amount of smectite. It would appear then that a discrepancy exists between the findings of Herath and Grimshaw (1971) and most other workers regarding the abundance of smectite in dry zone sequences. Smectite seems to be abundant mostly at depth, close to and in the zone of rock decomposition, and under conditions of impeded drainage.

In this respect it should be emphasized that Kalpage et al., (1963) report a discrepancy between conclusions reached XRD and DTA studies. X-ray diffraction showed a smectite (18⁰Å on glycerol saturation) but differential thermal curves did not show an endothermic peak at 680⁰ C which is the normal dehydroxylation temperature for montmorillonite. They conclude that the mineral present is either nontronite (an Fe-rich dioctahedral smectite) with an endothermic peak at 450-500⁰ C or an "abnormal" montmorillonite referenced to Mackenzie (1957).

Herath and Grimshaw (1971) who divided the island into the currently accepted clay mineralogical provinces present identical differential thermal curves without the dehydroxylation endothermic peak at 680⁰ C but fail to comment on it. Unfortunately since X-ray diffraction traces are not presented in either publication comparison with the present work is not possible. Clearly, there is much uncertainty on the issue of the abundance of montmorillonite in the dry zone soils.

The issue is compounded by the similarity mentioned before in section 3.1.3 between X-ray characteristics of kaolin-smectite mixed layer minerals and vermiculite-smectite interstratification. Electron

microscopy was used by Araki and Kyuma (1987), to obtain clarification of this issue. Three stages were observed in their study: cloud-shaped material in the least weather horizon; tubular halloysite and irregular platy materials in the intermediate stage and dominance of halloysite over the platy material in the third stage. De Alwis and Pluth (1976) who studied Sri Lankan Dry Zone samples using electron microscopy identified a similar platy material with vague hexagonal outlines, which as mentioned before was termed a smectite-vermiculite intergrade. In a study of biotite weathering to kaolin through and intermediate stage of vermiculite by electron microscopy (Banfield and Eggleton, 1988), show that kaolinite crystallizes onto mica sheets where substantial amount of space has been created by dissolution of biotite. Unlike vermiculite, kaolinite was not found to be interstratified with biotite but only filling larger cavities.

3.4.3 TEM and SEM observation of soil minerals

To verify the 14 \AA mineral identification, samples were analysed using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDX) and Transmission Electron Microscope (TEM) techniques. SEM micrographs were obtained with an ISI DS-130 instrument at 20-30 KV accelerating voltage, equipped with an EDX analyser. Grains were hand picked and mounted on stubs and coated with Au. TEM micrographs were obtained using a JEM 100C instrument with an accelerating voltage of 80 KV. Distilled water clay suspensions were mounted on Cu grids, and carbon coated for examination by TEM.

Sequences 100 and 104 (Group v) were chosen to verify the identification of smectite (that showed classic X-ray diffraction characteristics of smectite) and feldspar. It was observed that characteristic peaks both for K-feldspar (3.24 \AA) and Plagioclase ($3.18 \text{ \AA} - 3.19 \text{ \AA}$) were present in the silt fraction. However a complete suite of peaks was not present for either mineral. 131WR from sequence

131 from Group (iv) was chosen to further examine the interlayered 14\AA ^o mineral. Sample 135 was used to examine the nature of clay minerals in river sediment since Herath and Grimshaw (1971) identified smectite from alluvial soils. Minerals were identified by reference to the Atlas of Electron Microscopy of Clay Minerals (Beutelsfacher, 1968) using both morphological characteristics and electron diffraction grating patterns. Plates 2 to 5 record observations of the above studies.

Plate 2-A shows smectite characterised by its crinkled surface that should correspond to the 14\AA ^o peak in the XRD trace in fig. 3.17. taken from a Group (v) sequence that exhibited classic XRD characteristics. The d- spacings in Table 3.3 were measured in this study from electron diffraction patterns in Plate 2-B(c) and Plate 2-C(c) of selected areas of grains with similar morphology to the grain in Plate 3-A. However the sequence itself belonged to Group (iv) characterised by interstratified smectite from XRD traces. They are comparable to d- spacings for Fe-saponite and nontronite given by Sudo (1971), but are different from the smectite given by Brindley and Brown (1982), and vermiculite. Plate 2-C also shows a commonly observed form of a whole grain identifiable by its sharp outline, in this instance identified as smectite, overlain by kaolin. This form is similar to the electron micrographs of the 'irregular platy material' with vague hexagonal outlines described by Araki and Kyuma (1987), considered to be transitional between smectite and halloysite. Electron micrographs of grains published by Yerima et al., (1985), and Wada and Kakuto (1983) also have similar morphologies. Altschuler et al.,'s (1963) description of these grains as "development of hexagonal morphology on grains with curls and wisps characteristic of montmorillonite" is very apt. De Alwis and Pluth (1976) identified similar morphology in Sri Lankan soils without the help of electron diffraction data as a smectite-vermiculite intergrade. It appears that the broad 14\AA ^o peak in XRD traces characteristic of Group (iv) sequences considered as interstratified smectite using XRD techniques

is likely a kaolin-smectite interstratification.

Plate 3 shows relatively fresh mica (3-A), and weathered mica (3-B). It is not possible to determine if the right hand edge of the mica grain in Plate 3-A, and the rim of the weathered mica grain in Plate 3-B is transitional to kaolin or not. The commonly observed form, a thin flaky mineral, apparently transformed to kaolin is present in Group (v) sequences (Plate 3-C) as well. This Group was defined by characteristic smectite behaviour (without any hint of interstratification) from XRD studies, previously. It is noteworthy that this form is present both in Group (vi) and Group (v) sequences.

In Plate 3-D the smectite component of the interstratification shows well developed crinkled morphology. The river sediment sample (Plate 4) contains a mixture of mineral forms. (ie. crinkled films of smectite and grains overlain by kaolin, as well as halloysite and amorphous material, possibly hematite).

Plate 5 shows that K-feldspar from sequence 104 consists of varying stages of alteration to minerals such as gibbsite, kaolin, corroborating XRD results presented in figs. 3.15 and 3.26. The presence of gibbsite is an unusual occurrence in the dry zone.

Plate 2. Transmission Electron Micrographs of:

- A. Smectite with characteristic crinkled surface
(Sequence 100/10cm).**

- B. (a) Crinkled film of smectite ; arrow indicates vague hexagonal outlines; (c) Electron diffraction grating of (a).
(Sequence 131 WR)**

- C. Whole grain outlined by relatively sharp edges transformed to hexagonal plates of kaolin minerals. Arrow shows selected area of electron diffraction pattern (sequence 131 WR).**

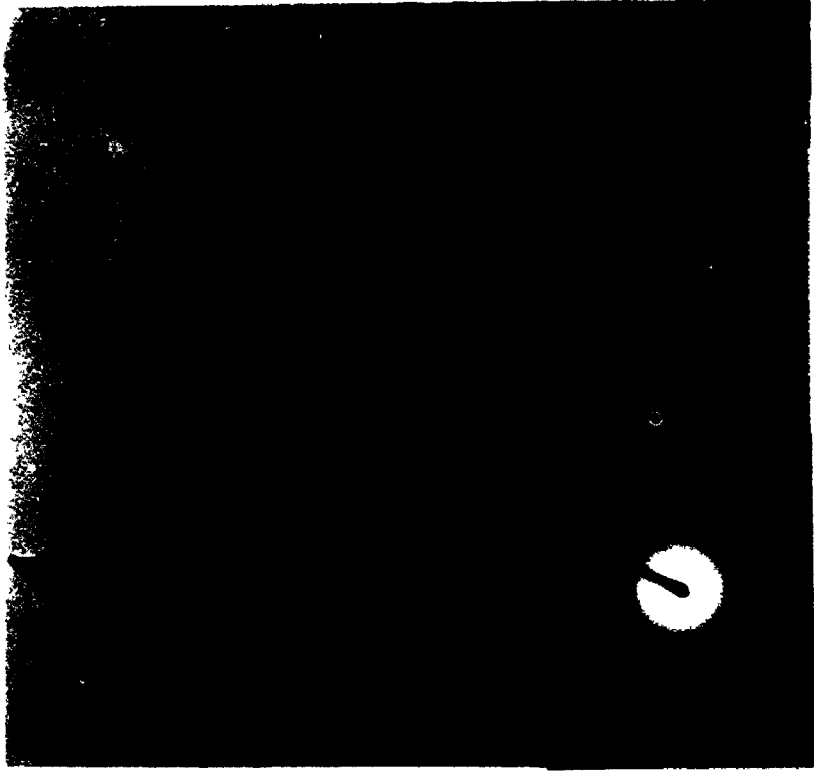


Plate 3. Transmission Electron Micrographs of:

- A. (a) Relatively fresh mica with thickness fringe; right hand edge suggestive of decomposition to small hexagonal plates of kaolin minerals (Sequence 104/30cm).
- B. Weathered mica showing dehydration indicated by miniscule holes on the surface . Note the development of small hexagonal plates near top and right hand edge rim. (Sequence 104/30cm).
- C. Whole grain transformed to hexagonal plates of kaolin minerals (Sequence 104/30cm).
- D. Smectite film overlying kaolin minerals; arrow indicates curled up rim;



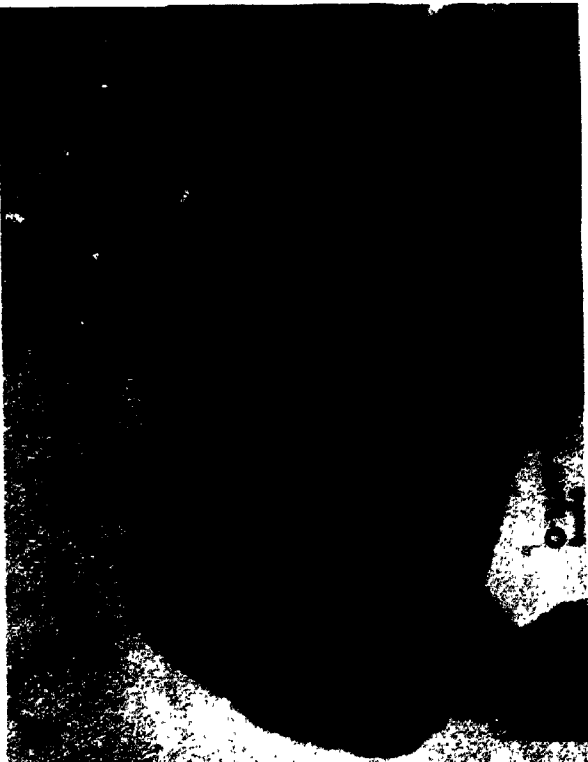
A



0.1µm



0.1µm

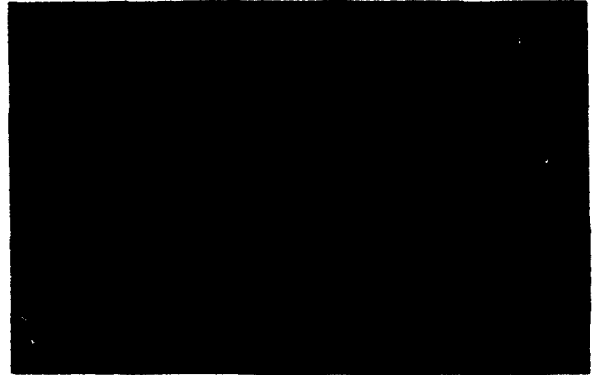
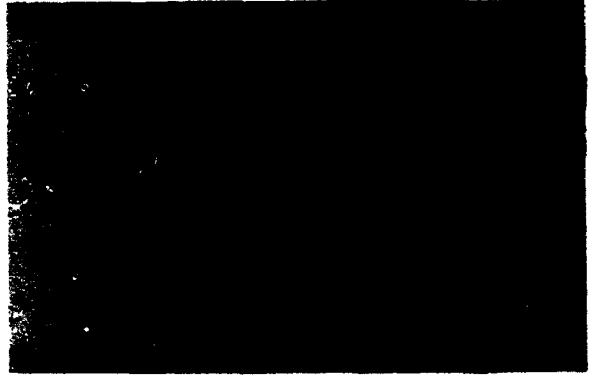


0.1µm

D

**Plate 4. Transmission Electron Micrographs of Clay Fraction
from a River sediment (sample 135).**

- A. General view of sample 135; (a) smectite;
(b) whole grain transformed to hexagonal plates of
kaolin minerals**
- B. (a) Thin platey grain without abundant hexagonal
outlines; arrow indicates relatively well formed
kaolin minerals.**
- C. Composite of (a) relatively fresh mica with moiré;
(b) curled up smectite; (c) Halloysite; .**
- D. Large weathered grain of mica with kaolin minerals on
surface.**
- E. Arrow indicates chain like aggregates of hematite.**
- F. (a) Tubular halloysite; (b) kaolin minerals; (c) smectite.**



**Plate 5. Scanning Electron Micrographs and their EDX data
from bulk sample 104/10cm.**

- A. Heavily altered K-Feldspar with etch pits on surface.**
- B. (a) Relatively fresh cleaved feldspar with arrow showing weathering product on surface.**
- C. Cubic minerals identified as gibbsite on altered surface; note inclusion of Fe in EDX.**
- E. Thin layer on K-Feldspar surface showing high silicon signal.**

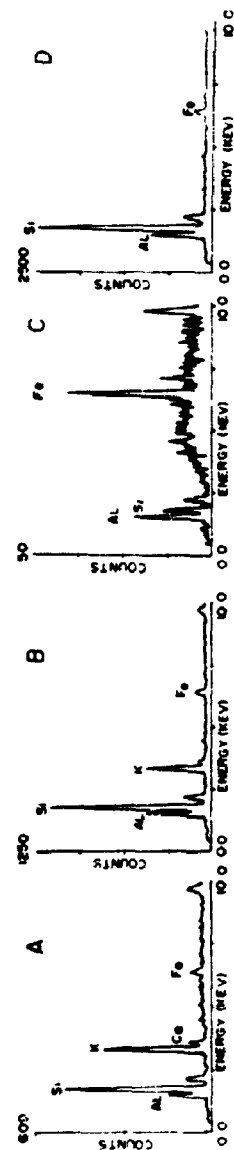


Table 3.3 Electron diffraction spacings for Vermiculite and Smectite.

Plate 3-C(c) ¹	Plate 3-B(c) ¹	Vermiculite ²	I	Montmorillonite		
				3	4	5
		4.77	15			
4.53(s) ⁶		4.60	40	4.51(s)	4.51	4.55
	4.48					4.33
		3.58	30			
		2.87	40			
2.64(s)	2.63(m)	2.65	18	2.61(s)		2.62
2.61	-					
		2.59	30	2.55(s)	2.58	
		2.55	30			
2.45	-					2.47
		2.39	50		2.40	
2.3(s)	-					
2.26		2.26	5	2.24	2.26	
					1.71	
					1.67	
1.54(s)	-	1.54	30			1.53
1.50}	1.50}	1.50	6	1.50(s)	1.51	
1.48}	1.47}					
1.31	1.31	1.32	10	1.29(m)	1.30	1.32

1 d-spacings from this study

2 Texas Vermiculite. Brindley and Brown (1982), p.101.

3 Unterruperoth Montmorillonite. Brindley and Brown (1982), p.182.

4 Japan, Fe-rich smectite. Sudo, T. (1971), p.145.

5 Miyagi, Japan Fe-saponite. Sudo, T. (1971), p.145.

6 (s) strong intensity; (m) medium intensity

3.5 Discussion

3.5.1 Identification of the 14⁰Å minerals

The electron diffraction patterns of smectite (identified from grain morphology) are similar to a Fe-rich saponite (trioctahedral smectite) and probably are not montmorillonite, vermiculite (Brindley and Brown 1982) or Fe-rich smectite (Sudo, 1971). This is in reasonable agreement with Kalpage et al., (1963), who from DTA curves suggest the presence of an Fe-rich dioctahedral smectite - nontronite. Further study using a Scanning Transmission Electron Microscope may be warranted to establish the chemistry.

Since Herath and Grimshaw (1971) based their work on alluvial soils, a river sediment sample was observed using TEM techniques to see if river smectite had a different morphology than soil smectite (Plate 4). It was noted in section 3.2.4 that the X-ray diffraction traces of the river sediment clays (fig. 3.18) show greater similarity to Group (iv) sequences particularly to sequence 99 where X-ray characteristics of smectite without interstratification was observed. On the other hand TEM micrographs (Plate 4) show that the river sediment consists of both forms - the typical smectite with a crinkled surface and the common platy whole grains which appear to be coated with kaolin; however they gave a smectite d-spacing at the margin free of kaolin, in a similar grain in sequence 131 (Plate 2); X-ray diffraction analysis of this sequence (131) however indicated the presence of only the 14⁰Å interstratified smectite; pure smectite characteristics were not observed.

The apparent contradictory evidence between XRD and TEM studies can be resolved if the XRD interpretation of the 14⁰Å interstratified mineral of Group (iv) sequences and river sediment sample 135 that surprisingly gives an electron diffraction pattern of smectite is considered to be a form of interstratified kaolin-smectite where the smectite component is not well developed. Accordingly Group (v)

sequences that have classic smectite from XRD studies and yet show both morphologies - ie. the crinkled filmy grains with associated kaolin and the platy grains with vague hexagonal outlines - could be considered as a further developmental stage of the kaolin - smectite interstratification, where the smectite dominates.

TEM and SEM studies indicate that both the mineralogy and the relationships between minerals comprise an interwoven mesh far more complex than that which is indicated by XRD studies alone. Further unraveling of these interrelationships requires both specific dissolution techniques in XRD work to observe the nature of interstratification and observation of samples using a coupled TEM - EDX system and or STEM.

3.5.2 Comparison of sequence grouping with existing classifications

The mineral groupings that emerge from X-ray diffraction studies summarised in Tables 3.1 and 3.2 re-establish most of the salient features of the currently accepted clay province classification of Herath and Grimshaw (1971) who based their work on the analysis of alluvial soils; the mineral pair kaolin and gibbsite is typically characteristic of the wet zone highly weathered Red Yellow Podzolic sequences; an Al-hydroxy interlayered vermiculite previously identified by Herath and Grimshaw (1971) as a mixed layer mica-vermiculite is a common accessory as well; gibbsite gradually disappears towards the intermediate zone in the clay fraction and disappears altogether in the dry zone; smectite too was observed in the clay fraction, only in the dry zone soils.

Variation with depth is not a prominent feature for most sequences, a fact that has been borne out by other researchers as well (Herath and Grimshaw, 1971). Panabokke (1959) noted that

mineral variation was not observed in the subsurface horizons until the horizon of rock decomposition was reached which is to be expected in regions of tropical weathering. However the latter observation was restricted to well drained locations of the catena studied. Exceptions were observed down slope where ground water levels fluctuated. This point will be further discussed in section 3.5.6.

Additions and exceptions were found in the course of the present study some of which are in concert with other researchers' observations.

Gibbsite was found in contact with primary feldspar in the dry zone soils which has not been noted before.

Smectite is not as common as indicated by Grimshaw and Herath (1971). Pure smectite has been observed in special circumstances, at depth or under impeded drainage or in immature soil sequences. A ⁰14A interstratification most likely of kaolin and smectite in lieu of pure smectite, was observed to be quite common in the dry zone in this study. Mixed layer minerals are noted by most authors but specific identification of a vermiculite-smectite intergrade (which as mentioned previously has similar X-ray behaviour to kaolin-smectite) was noted in the upper horizons only by De Alwis and Pluth (1976). Vermiculite takes the place of smectite in the upper horizons in most profiles (Panabokke, 1959; Kalpage et al., 196.). Since only DTA traces are presented in some of these publications subjective identification of clays termed intergrade, mixed layer and vermiculite cannot be further differentiated or compared with the present work.

The presence of primary minerals especially feldspar and ferromagnesium minerals in the silt fraction, can be used to differentiate the wet and dry zone soils of Sri Lanka. In the wet zone mature Podzolic soil profiles, feldspar and ferromagnesian minerals were

absent; consequently the silt fractions are similar and show no relationship to their parent rock types.

The influence of parent rock in varying the mineralogy of the silt and consecutively the clay fractions is apparent in sequences from the intermediate zone and more definitively from the dry zone of Sri Lanka. Examples are discussed in sections 3.3.2 - 3.3.5.

3.5.3 Correlation between Geochemistry, Cation Exchange and Mineralogy

It is apparent from the data presented so far that there is remarkable correlation among the geochemical, cation exchange and mineralogical characteristics. For example, the high potassium values detected in the exchangeable bases of sequences 16 and 132 in Table 2.3, can be linked to the abundant illite source in the clay fraction (Table 3.1 Group iv) and the mica source in the silt fraction (Table 3.1). The highest cation exchange values obtained from sequence 88 at a depth of 100cms - the Reddish Brown Earth consisting of expanding 14\AA clays (that are normally characterised by a high cation exchange capacity) and subordinate kaolin, that still retains abundant 12\AA degraded mica in its clay and silt fractions. Levels 10 and 30 cms of the same sequence have the second and third largest cation exchange values and are also characterised by the 12\AA degraded mica in the silt fraction. The 100cm level of sequence 61 contains abundant degraded mica as well in the silt fraction, but it shows the effect of being located in the wet zone by having a clay mineralogy dominated by kaolin and subsequently low cation exchange values.

A strong correlation exists between the mineralogy of the wet zone soils and their cation exchange capacity. Since the clay fraction consists of kaolin and gibbsite that have negligible exchange sites, and the silt fraction lacks primary minerals other than quartz (and

sillimanite) it is not surprising that the resulting soils have base saturation values of less than 3% in the case of the mature laterite sequence (148), and less than 11% in the case of the Podzolic sequence (153) that still retains garnet bearing fragments of decomposed parent rock, albeit without feldspar in it. Since extractable acidity is reciprocally high, (Table 2.2) this suggests that cation exchange sites of the wet zone soils are filled most likely with exchangeable Al-hydroxy polymers and hydronium ions. In contrast the dry zone soils have base saturation values above 50%, reflecting the presence of primary minerals and clays characterised by both expanding properties and concomitantly high ratio of exchangeable sites.

Mineralogical differences also explain the geochemical trends observed in figs. 2.2 A and B. The abundance of gibbsite and kaolin and the lack of primary minerals containing Ca, Mg and K in wet zone samples belonging to Group (i) result in their location within field 1 in figs. 2.2 A and B. The discrepancy noted in section 3.2.2 for Group (ii) sequences between the predicted clay mineralogy based on their bulk XRF plots within the illite-smectite field (field 2) in figs 2.2 A and B, and their observed mineralogy (Table 3.1) results from the mixing effect of the admixture of kaolin and gibbsite and a moderate presence of primary minerals containing Ca, Mg. and K, i.e. feldspars and mica. The partial success in predicting mineralogy based on figs. 2.2 A and B, in that the presence of kaolin was not predicted for sequences in Groups (iii) and (iv) result from the dominance of feldspars and mica minerals in the silt and probably sand fractions over the influence of kaolin. This tends to raise the y-axis values. The high x-axis value of all dry zone samples can be related to the presence of abundant quartz and framework silicates in the silt fraction and vice versa for wet zone samples. Hence the technique used to predict mineralogy based entirely on geochemical analyses of bulk samples, on fig. 2.2 type diagrams provides a good estimate as demonstrated for highly weathered sequences of field 1, and must be used with care for samples plotting in fields 2 and 3.

3.5.4 Control of Mineralogy by Weathering Dynamics

Discussion in the preceding sections emphasizes the need to examine the nature of weathering dynamics that causes such significant variations noted therein.

Explanations are required for:

- o the intensity of weathering in the wet zone; this is highlighted by sequence 153 sampled from the rainiest location in Sri Lanka, that at depths even of 600cm lacks feldspar in the abundant weathered garnet and sillimanite bearing, structurally coherent fragments, (derived from a feldspar bearing garnet-sillimanite graphite gneiss).

- o conversion of primary minerals other than quartz, directly to kaolin and gibbsite, without leaving a residue in the silt fraction which is in contrast to the presence of primary minerals in the silt fraction in the dry zone.

- o the dominance of feldspar over mica in the silt fraction in Groups (iv) and (v) where either illite or smectite dominates the clay fraction.

In this section pedogenic and geochemical concepts of weathering will be reviewed before attempting to explain the above observations.

From among many prevalent definitions of weathering it is sufficient to point out one that brings out the essence of the earlier and more broadly accepted concept of weathering. Birkeland (1974, p.52) defines weathering of primary minerals as "alteration to more stable

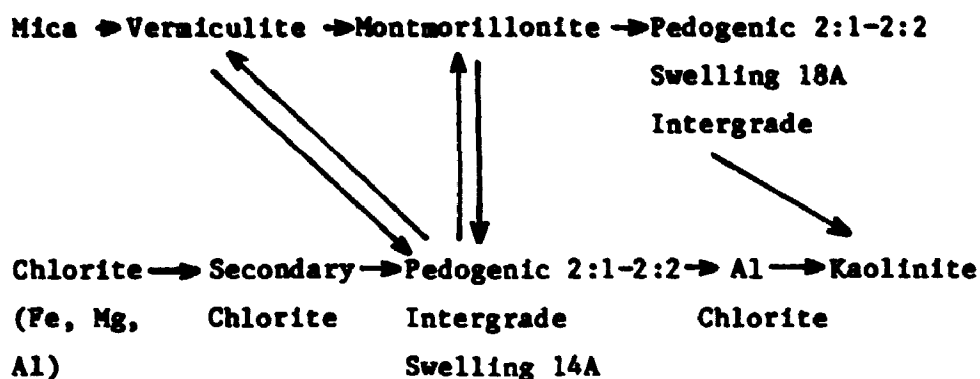
forms under the variable conditions of moisture, temperature and biological activity that prevail at the surface". This definition which is based on three variables epitomizes the absence of a single unifying concept, prevalent in the majority of the early literature of the 1960's and 1970's, both on discussions of pedogenic processes and more specifically on mineral alteration studies.

In pedogenic studies, soil formation, the end result of weathering, is considered as the product of the dynamic interaction of five state factors, climate, organic matter, slope morphology, parent material, and time. Jenny (1941) attempted a unifying concept by formulating a differential equation encompassing the above five factors that has eluded solution up until now because the contribution of each factor could not be estimated singly. Usually one or the other of the state factors is held more responsible, conveniently laying aside dealing with the concept of "soil formation as the result of complex interaction of all five state factors".

Hence in the example of the soil catena (Panabokke, 1959) from Sri Lanka, it was surmised that the dominant factor was slope morphology which in turn controls drainage. Thus impeded drainage, a condition in which montmorillonite is globally known to be more stable than kaolinite regardless of climatic type, was held responsible for the supercedence of montmorillonite over kaolinite in deeper horizons upslope and in all the horizons lower down sequence.

Thus one or the other state factor is recognised as being the major process controller to explain a given set of observations. Needless to say that this has led to an endless array of publications that emphasise differing sets of combinations of the state factors.

In the field of mineral alteration modeling of the interrelationships between minerals was spear-headed by Jackson (1962), who proposed the following model:



Kaolinite and its breakdown product gibbsite are considered as end products of extreme conditions of weathering, suggesting a sequence of alteration, the classic example often quoted being that of the Amazon soils rich in these minerals. The other clay minerals may be viewed as primary, intermediate or end products depending on soil conditions (Averack, 1983). In the early literature of the 1960's and even the 1970's clay mineral alteration studies tend to reason alteration of one mineral to another, or the stability of one type over the other mainly in terms of basic or acidic environments. This approach fails to explain satisfactorily the co-existence of minerals considered to be stable in one or the other of these two environments. For example, gibbsite, the end product of weathering in an acidic environment, was observed forming directly on primary K-feldspar (Plate 5) in a sequence characterised otherwise by the dominance of smectite (considered to be stable in a basic environment) over and above even kaolinite (another acid environment mineral). In addition this sequence was located in the dry zone of Sri Lanka defined in terms of clay provinces as completely lacking gibbsite in its clay fraction.

In the succeeding section it will be re-emphasized that a single unifying concept, slowly gaining acceptance in pedogenic literature exists (Kittrick, 1977). It is based on mineral-solution equilibria which derives from the work of Garrels and Christ (1965).

3.5.4.1 Control of Mineralogy by Weathering Processes as Determined by Mineral-Solution Equilibria

The concept mentioned above emerges from the knowledge that a soil solution is governed in its chemistry by the complex interaction of all five state factors, and being uniquely characteristic of them can in turn be substituted in their lieu. This leads to the next step, that since soil solutions are uniquely characteristic of the controlling state factors, reactions involving soil solutions can be used to study weathering phenomena, such as causes for the alteration or stability within or the very existence of, different mineral suites.

Such a possibility becomes apparent in one of the more recent definitions of chemical weathering, based on mineral saturation in soil solution given below. Nesbitt and Young (1984) define chemical weathering pertaining to horizons below the soil zone, "as the interaction between waters derived directly from precipitation (generally rain water containing inorganic and organic acids derived from decay of litter and organic materials in the soil zone) and rocks and their weathering residues". Interactions between groundwaters, rocks and materials of the weathering profile are considered as diagenetic reactions. Essentially this definition restricts chemical weathering to the zone of rock decomposition.

It is proposed to show in the course of this study, that the existence of different mineral suites in the 'soil zone' can also be explained in analogous terms.

The control on mineralogy by processes of weathering as determined by mineral-soil solution equilibria is demonstrated using the activity diagram constructed for the $MgO-Al_2O_3-SiO_2-H_2O$ system (fig. 3.27). Nesbitt (1984) discusses the application of this concept

to a much broader spectrum of 'weathering profiles' that exclude the soil zone, developed on diverse parent material. The construction of the diagram is given in Garrels and Christ (1965) and is based on thermodynamic principles. Rainwater low in cations and low in aqueous silica plots close to the lower left-hand corner of the diagram. These waters are undersaturated with respect to all major secondary soil minerals and particularly with primary minerals; consequently dissolution of the primary grains occur. As dissolution proceeds rainwater acquires dissolved solutes and evolves into a soil solution, along the hypothetical path indicated. The first mineral that may precipitate is gibbsite since it is the most likely mineral to be in equilibrium with the initial dilute soil solution as the latter evolves across the stability field of gibbsite. If profuse amounts of water continually pass through a given substratum throughout the year as in some of the Amazon regions, the likelihood of concentrating cations and dissolved silica in soil solution in quantities sufficient to cross from the gibbsite field into the kaolin field becomes remote. Most likely gibbsite will remain the first and only mineral to form instead of being the end product of a series of secondary minerals formed as weathering proceeds. If incipient stages of weathering (rainwater reacting with primary minerals) are investigated carefully, gibbsite may be found to form on primary mineral surfaces just as is observed in sequence 104 (Plate 5).

If a sufficiently long dry spell were to prevail seasonally, significant concentrations of cations and silica may be concentrated in soil solutions so that the gibbsite-kaolin boundary is encountered (fig. 3.27). At this point kaolin as well as gibbsite is equilibrated with the soil solution. In this circumstance the assemblage gibbsite-kaolin may form. If further concentration of the soil solution is not possible, due to the beginning of the next rainy season, gibbsite and kaolin will remain as the primary products of weathering.

Thermodynamic calculations of Al-hydroxy interlayered vermiculite

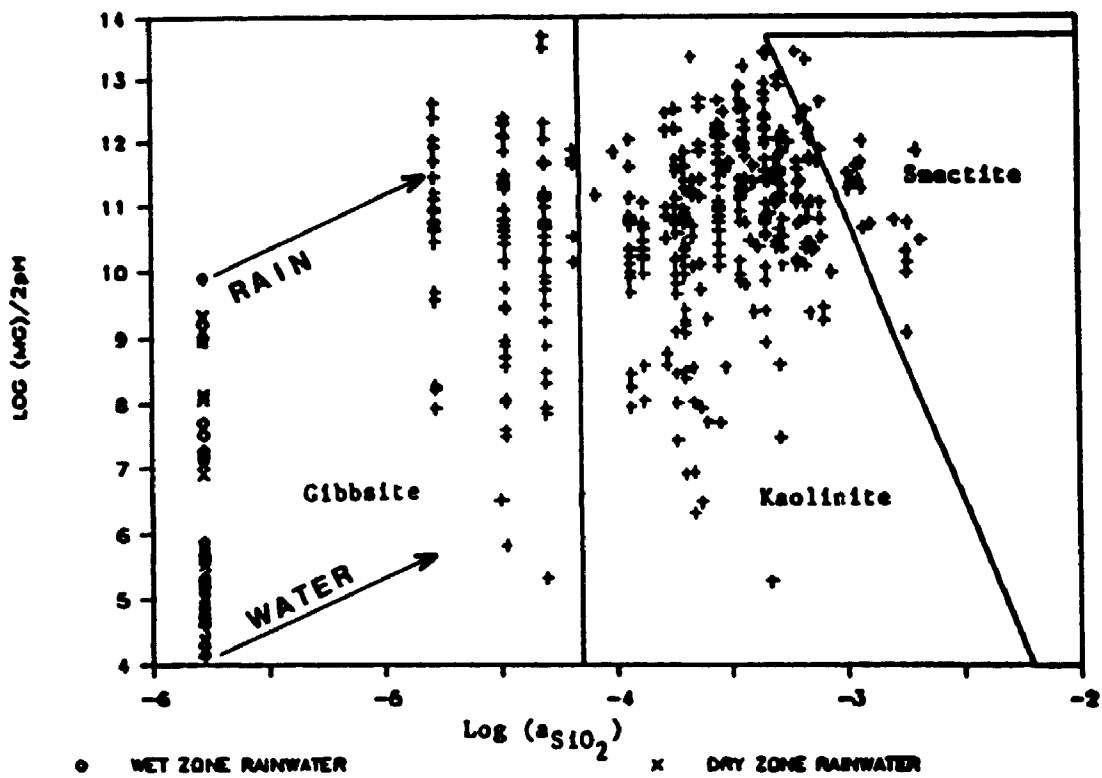


Fig. 3.27 Distribution of Sri Lankan Ground Water samples within a Mg - Activity Diagram compiled for equilibrium clay mineral assemblages at 25 °C and 1 atm. (After Nesbitt, 1984).

(Karathanasis, et al., 1983) show a complex inter-relationship between this mineral and gibbsite-kaolinite, depending upon the degree of interlayering. However according to the literature cited by these authors, Al-hydroxy interlayered vermiculite emerges as a common associate of kaolinite and gibbsite, a fact that has not received much recognition in studies of intense weathering environments.

For the soil water composition to cross into the kaolin field to permit kaolin to exist alone, any gibbsite previously formed would have to redissolve, (if equilibrium conditions prevail). Since gibbsite will react with additional aq. silica to form kaolinite silica activities cannot rise to values which would be in equilibrium with kaolin alone, in the presence of gibbsite.

In sub-humid tropical regions where rainfall is relatively low, and a pronounced dry season prevails as in the dry zone of Sri Lanka, rainwater can be concentrated and retained as soil moisture over a sufficiently long period to enable concentrations of cations to reach levels that, when plotted on activity diagrams, reach the smectite and kaolin stability fields (fig. 3.27). Under such conditions smectite and/or kaolin are likely to precipitate. Gibbsite reacts with these solutions to produce kaolin or smectite; hence it is expected to be relatively rare as observed in the dry zone mineralogy of Sri Lanka. Even if gibbsite precipitates initially, it may react out of the system when the solution concentrates cations and silica such that the solution evolves to stability fields of minerals other than that of gibbsite.

This concept could also explain the occurrence of smectite in regions of impeded drainage as in the lower slopes of soil catenas and its dominance over kaolin in the zone of decomposing rock as observed by Panabokke (1959) for a soil catena in Sri Lanka. Impeded drainage conditions allow for the concentration of cations to reach sufficiently high levels to allow smectite to precipitate directly as

will the presence of primary minerals in a zone of decomposing rock which constitutes a rich buffer of cations. The evolving nature of the soil solution can be substituted for such combinations as slope morphology, parent material and climate needed to explain the example discussed above. Vague terms such as extreme or intense weathering gain added meaning with the use of activity diagrams. For instance it was noted (section 3.3.1) that in the wet zone profiles even the silt fraction lacked primary feldspars. It would appear that the primary sand sized feldspars are converted to kaolin and gibbsite without decrease in size to silts. Prolonged continuation of rainfall throughout 8-10 months of the year without significant annual fluctuation has resulted in the formation of a thick lateritic cover in places reaching a maximum of 40 m (Dahanayake, 1982) in the lowlands. This has in turn blocked rainwater access to primary minerals. A partial result of this has been the formation of soft laterite at depths greater than 100 cm where a distinct mottling effect is observed. Mineralogical analysis of this zone described in section 3.3.1 shows that the red vermiform mottles comprise gibbsite, hematite and goethite, and are chemically distinct from the kaolin and gibbsite dominated yellow matrix. As Ambrosi and Nahon suggest (1986) it is likely that the red mottles represented pathways that carried soil water evolved hardly beyond the rainwater stage since it has only traversed a mantle composed of gibbsite and kaolin, which would be extremely unproductive in terms of cation buffers. The soil water greatly undersaturated in terms of dissolved silica, may cause the breakdown of kaolin and subsequent formation of gibbsite along its pathway resulting in the chemical differentiation observed.

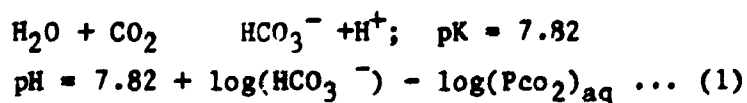
In the dry zone, by contrast, where the soil waters are less aggressive because there is a lesser volume of water competing for the same quantity of cations from primary minerals, the latter persist into the silt sized fraction as shown in Tables 3.1 and 3.2.

3.5.4.2 Ground Water Control on the Clay Mineralogy of Sri Lanka

The simultaneous occurrence of the clay minerals - kaolin-gibbsite and Al-hydroxy vermiculite in the wet zone and kaolin and smectite interstratification in the dry zone of Sri Lanka, implies the possible existence of equilibrium conditions among them. Activity diagrams can be used to test this hypothesis. Drever (1982) points out that for a mineral pair to exist in equilibrium, soil water compositions should plot at the common boundary of their stability fields.

To substantiate the theory of silica and cation activity control of secondary weathering products, ground water data compiled by Dissanayake and Weerasooriya, (1985) were plotted on activity diagrams. Ground water data were used since soil solution composition data were unavailable.

The ground water was sampled from dug wells open to the atmosphere. Unfortunately field pH measurements are not available, hence a pH value had to be calculated with available data. Calculation of pH was based on available HCO_3^- analyses by assuming a natural range for dissolved CO_2 . A partial pressure of 10^{-2} atm for dissolved CO_2 was adopted. Equilibrium between HCO_3^- and dissolved CO_2 was assumed (equation 1), from which a pH averaging 7.0 was obtained.



However because of the uncertainties associated with these assumptions, only broad generalisations can be made. The samples were

taken during the months of July to December, and it is most likely that it had a significant bearing on the results considering the temporal difference in peak rainfall regimes between the two climatic zones (see section 2.4). Activity coefficients of cations were calculated according to the Debye-Huckel equation. These were plotted in activity diagrams compiled by Nesbitt (1984a) for clay mineral assemblages at 25°C and 1 atm pressure (figs. 3.27 and 3.28 A-C), from which locations likely to be saturated with respect to gibbsite, smectite, muscovite and k-spar were identified (figs. 3.29 and 3.30 A-B).

Waters that plot in the gibbsite stability field (low dissolved silica contents) are confined mainly to the wet zone as was expected (fig. 3.29). Two unusually large areas of gibbsite saturation are also observed for the first time at the dry/intermediate zone boundary (fig. 3.29). Reasons for these anomalies cannot be postulated at present. The remaining areas have higher dissolved silica contents and are more likely to be saturated in kaolin, smectite and primary minerals rather than gibbsite. Ground waters are saturated with muscovite/illite (and to a lesser extent k-spar) over a larger areal spread in the dry zone (fig. 3.30 B) compared to Na, Ca and Mg bearing smectites (figs. 3.29, 3.30 A-B). This agrees with the well known fact of greater stability of muscovite and k-spar over other primary minerals. Illite was found to be a common mineral in many of the intermediate and dry zone profiles studied (Table 3.1 and 3.2). Ground waters saturated with smectite (figs. 3.29, and 3.30 A-B) are also confined to the dry zone as was expected but surprisingly the areal extent of predicted smectite stability appears to be very limited, even within the dry zone. A larger area of smectite saturated ground waters was expected from mineralogical studies. If the pH was assumed to be 6.5 hardly any localities would exist. It is interesting to note that smectite saturated ground waters are located close to the coastal regions classified by Dissanayake and Weerasooriya (1985) as the dominant N+K/Cl group that surrounds the coastal regions.

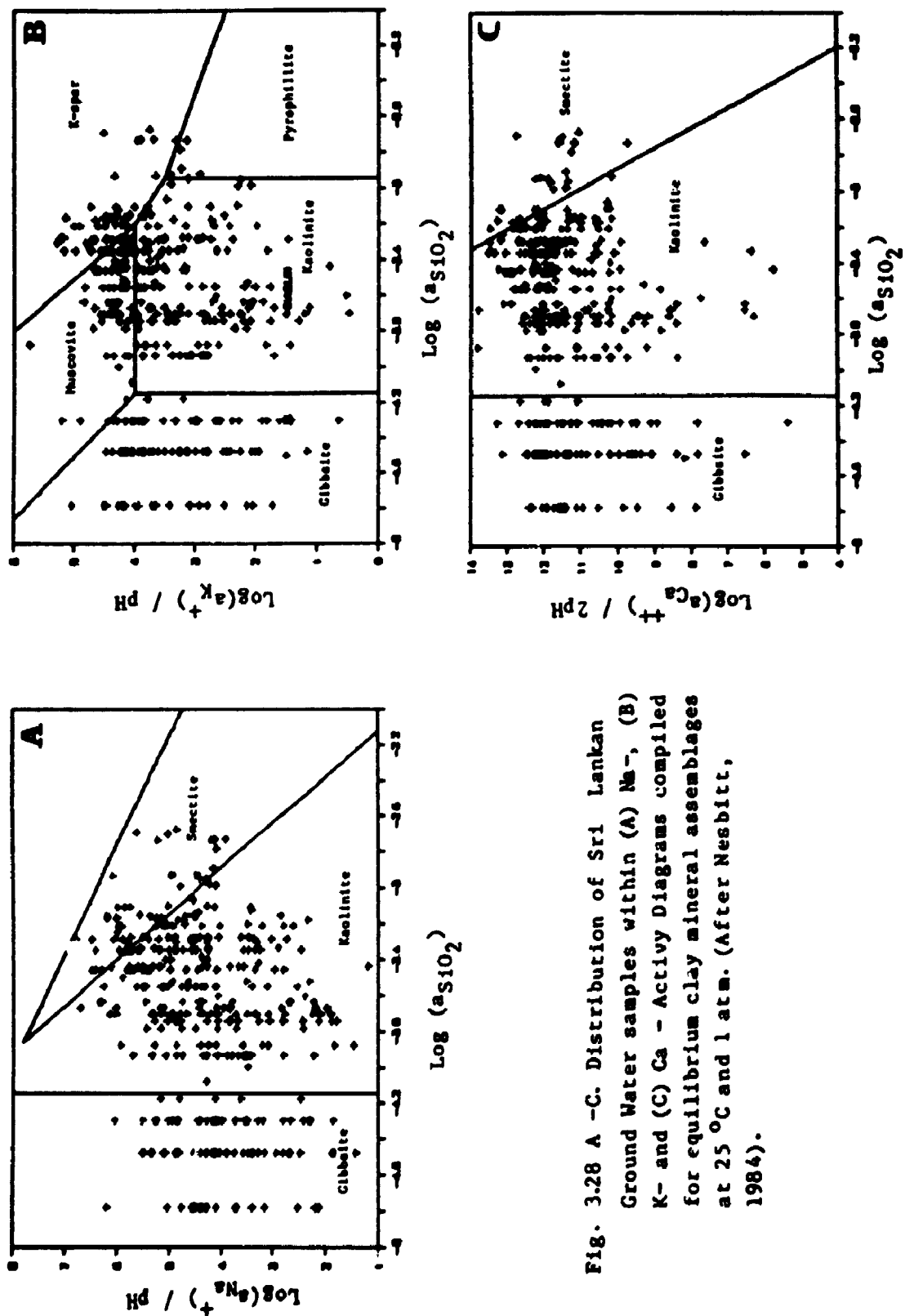


Fig. 3.28 A -C. Distribution of Sri Lankan Ground Water samples within (A) Na^+ , (B) K^+ and (C) Ca^{2+} - Activity Diagrams compiled for equilibrium clay mineral assemblages at 25 °C and 1 atm. (After Nesbitt, 1984).

The remaining blank area in figs 3.29 and 3.30 A-B contain waters predicted to be saturated with kaolin. Thus according to the data available ground waters of Sri Lanka are saturated with mostly kaolin which was also found to be the common mineral to both climatic zones in mineralogical studies.

These calculations suggest that wet zone waters are saturated with kaolin and gibbsite while dry zone waters are saturated with kaolin, illite, smectite and to a lesser degree k-spar. In spite of the non - availability of pH measurements these conclusions are in surprisingly good agreement with mineralogical data and common geological knowledge. They are compatible with the explanation of the mineral distribution proposed in section 3.5.4.1. which suggested that the clay mineralogical differences observed between the two climatic regions of Sri Lanka are controlled by soil solution composition as manifested through the chemistry of ground water.

Further work is required to explain why smectite saturated waters are limited in extent. Soil solution data as well as ground water composition during the months of January to June together with pH data are required. Also if thermodynamic data for natural smectites were used instead of data for pure smectite end members a larger area of smectite stability would be obtained.

The distribution of the majority of ground water analyses outside the boundary regions of the characteristic clay mineral pairs of the climatic zones contradict the implication of equilibrium between them that their simultaneous occurrence in the soils suggest. This is an important conclusion that arises from these plots. The strong seasonality of rainfall is likely to have a profound influence on the concentrations of elements in soil solutions as first pointed out by Tardy (1971), who suggested that one of the minerals comprising the mineral pair is likely to be metastable with the prevailing soil solution.

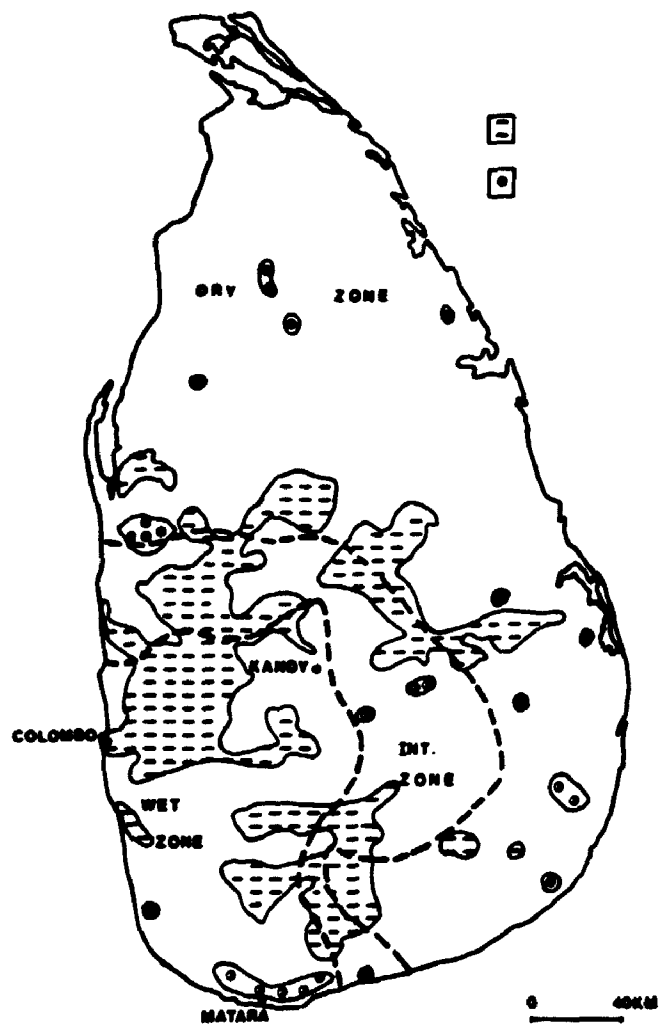


Fig. 3.29. Predicted localities of clay mineral saturation using ground water composition. Gibbsite (dashes); Mg-smectite (circles); Kaolin (blank).

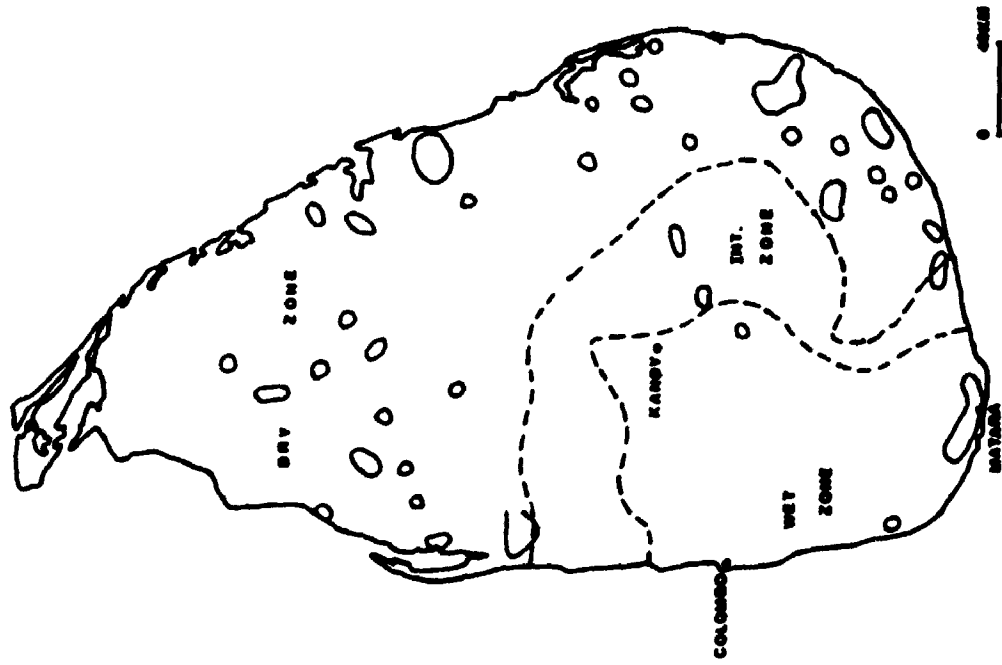


Fig. 3.30 A. Predicted localities of Na-smectite saturation using ground water composition.

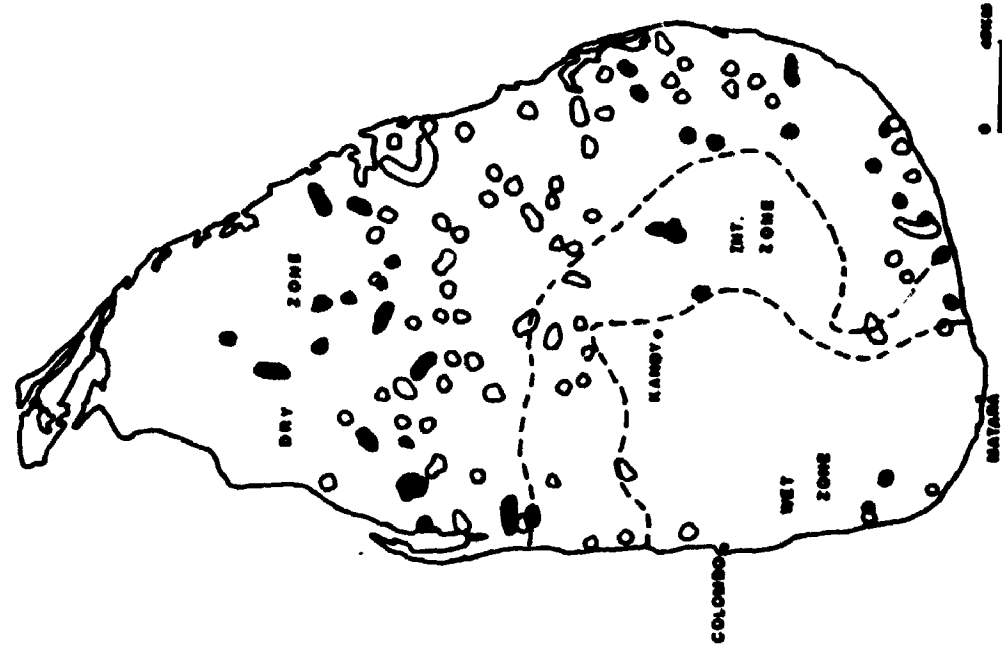


Fig. 3.30 B. Predicted localities of Muscovite and K-feldspar saturation using ground water composition.

3.5.4.3 Electron Microscope Observations of Mineral Relationships of Characteristic Assemblages

Disequilibrium between minerals may result from strong seasonal variations in soil/water composition; consequently a search for disequilibrium textures was undertaken to account for the co-existence of clay mineral pairs in soils, where ground water data predicted absence of equilibrium. There is no literature on micromorphological disequilibrium textures per se, but poorly defined grain shapes, overgrowths, and grain boundary dissolution features suggestive of instability of the host mineral were expected.

Sequence 104 was selected because of the wide range of minerals in it, as well as for its location in the dry zone which is marked by strong seasonality. Methods described in section 3.4.3 were used. Individual feldspar and mica grains as well as bulk samples were observed. In particular, since the 100 cm level comprised distinct brown and white granules, handpicked components were studied separately. Final observations were made on handpicked mica grains, cleaned 10 minutes in an ultrasonic bath.

In hand specimen the brown granules, often contain a core of weathered feldspar, whereas the white components comprise altered feldspar, golden brown mica and quartz bound by a creamy white cement.

X-ray traces (fig. 3.31) of the separated brown and white components indicate that feldspar, quartz, smectite and mica are common to both in varying proportions. The brown granules, contain more smectite and less mica in addition to minor hornblende than the white components. When the clay fraction alone of the bulk sample (brown and white components) was analysed kaolin was detected (fig. 3.15).

Several types of surfaces on feldspar grains were observed. They

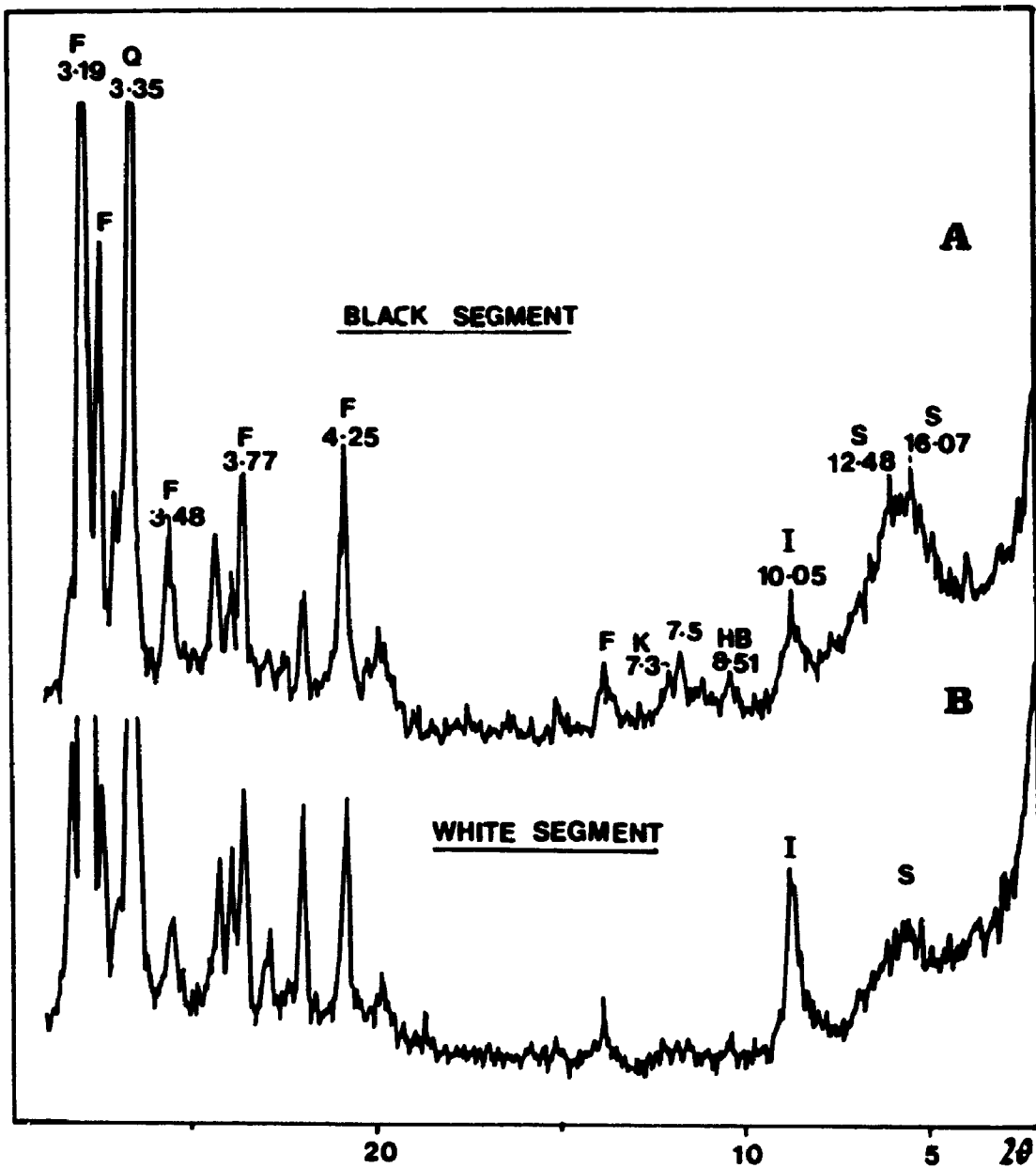


Fig. 3.31. X-Ray Diffractograms of crushed, oriented samples of (A) Black and (B) White handpicked segments (granules) from sequence 104 at 100cm depth. Q=Quartz; F=Feldspar; K=Kaolinite; HB=Hornblende; I=Illite; S=Smectite.

ranged from grains with relatively fresh surfaces partially covered with crusts (Plate 6) to etched surfaces (Plate 5). These crusts were present at all depths. The coatings were mostly silica rich (Plate 5 D, Plate 6B) with variable amounts of introduced Fe compared to the fresh surface that had little to no Fe and greater amounts of K and Ca. More than one kind of secondary weathering product could be observed on the same grain. For example the feldspar grain in Plate 6 contains a crust as well as a skin of honeycomb textured substance identified as smectite. The honeycomb textured substance contains introduced Fe compared to the fresh surface.

In the 10 cm depth level, gibbsite previously noted in X-ray traces (fig. 3.15) was observed on the surface of a K-rich feldspar (Plate 5 B-C: cubic morphology, compositionally rich in Fe, Al and Si) in addition to crusts. At lower depths gibbsite was not located but smectite recognised by the honeycomb morphology, was frequently observed forming directly both on feldspar (Plate 6 C-D) and mica (Plate 7), especially in the brown granules. Kaolin was not observed by SEM.

Microscopic kaolin was recognised by TEM and corroborates X-ray diffraction results. It was intimately associated with mica, (at all depths) and with smectite especially in the brown granules at lower depths (Plates 2, and 8 - 11).

Differing degrees mica alteration were noticeable in the white components. Fresh grains had less associated kaolin (Plate 8 A); in partially altered mica, the grain outlines are indistinct and kaolin is closely associated with them (Plate 8 B(c)). The partially altered grain composed of linked pseudo-hexagonal flakes previously identified as initial stages of kaolin-smectite interstratification (section 3.5.1) appears to separate out into kaolin (Plate 8 D). Note absence of crinkled edges.

In the black components different alteration degrees of mica exist . Plate 9 shows kaolin-smectite interstratification identified by the matted structure consisting of crinkled filmy surfaces associated with pseudo hexagonal kaolin-like flakes (Araki and Kyuma, 1987; Wada and Kakuto, 1983). The smectite component is well developed in the black components. This association is more prominent in sequence 100 (Plate 9 C-D). Curled up edges are noticeable around some linked pseudo-hexagonal flakes (Plate 9 D). Similar curled up edges around kaolin was observed by Inasuen (1987) in experiments designed to convert kaolin to smectite in the transitional stages.

Since it could not be determined whether the crinkled filmy surfaces supporting the hexagonal particles were an integral unit or resulted from precipitation of kaolin onto the films during mounting of sample onto Cu grids, handpicked mica grains cleaned ultrasonically were examined. A film-like form bridging and overlapping mica grains was observed (Plates 10 - 13). These films or nets were distinctly Ca rich (EDX data) as opposed to the associated biotite mica. Distinct hexagonal particles are supported by these amorphous nets (Plate 10 B-C, Plate 11 C, D) in addition to Fe rich particles (Plate 12 A -C'). Most of the film in photographs C and D in Plate 11 was damaged during STEM analysis (photograph A, Plate 11) but a relatively intact monolayer of film can be observed in Plates 12 A(B') and 13 A supporting varying amounts of kaolin particles. Stacks of these filmy substances appear to comprise the overlapping mats of linked pseudo-hexagonal particles as observed in Plate 12 B, Plate 13 B-D and Plates 2 - 4. These stacks are attached to or are separated from relatively fresh mica grains.

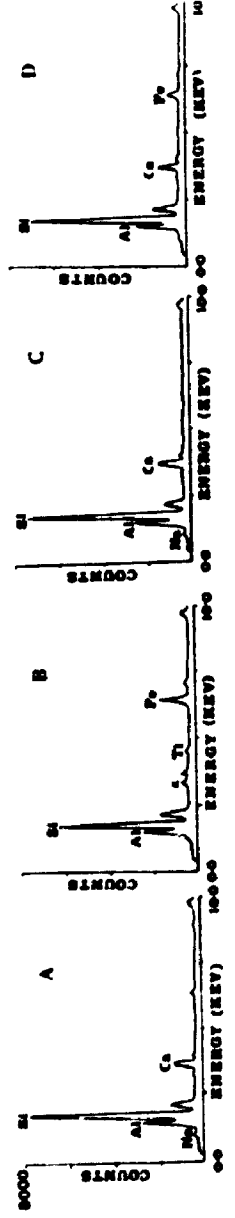
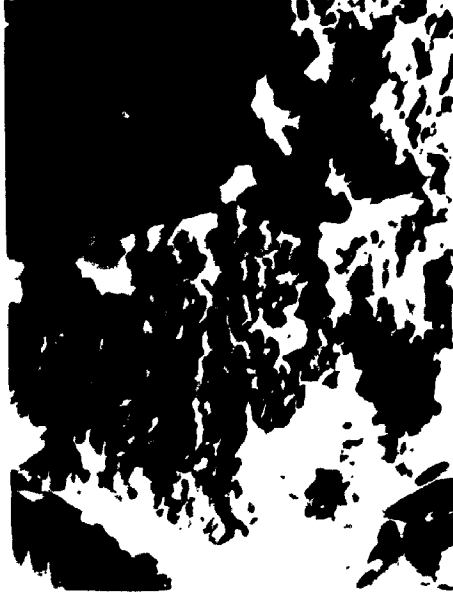
Before SEM and TEM results are tentatively pieced together two points need to be reiterated. Even though kaolin was found in XRD and TEM studies it was not detected using SEM. Crusts rich in Al, Si and Fe observed by SEM could not be linked to TEM studies unless microscopic kaolin and amorphous Fe commonly observed by TEM

Plate 6. Scanning Electron Micrographs and their EDX data
from black components of sample 104/30cm.

A. Feldspar grain with (a) Fe rich crust; (b) Honey comb texture.

B. Higher magnification of the crust. Note introduction of Fe, Ti, K in the crust (B') compared to the fresh surface that contains Ca and Na (A').

C and D. Higher magnifications of the honey comb texture showing introduction of Fe (D') suggestive of smectite. The fresher surface (C') has no Fe.



**Plate 7. Scanning Electron Micrographs and their EDX data
from the black components of sample 104/100cm.**

- A. Relatively fresh mica grain (A'- suggestive of biotite),
with a surface coating prominent to the right.**

- B. Higher magnification of surface coating showing honeycomb
texture, suggestive of smectite showing decrease of K and
Fe and introduction of Ca (B') compared to fresher surface
(A').**

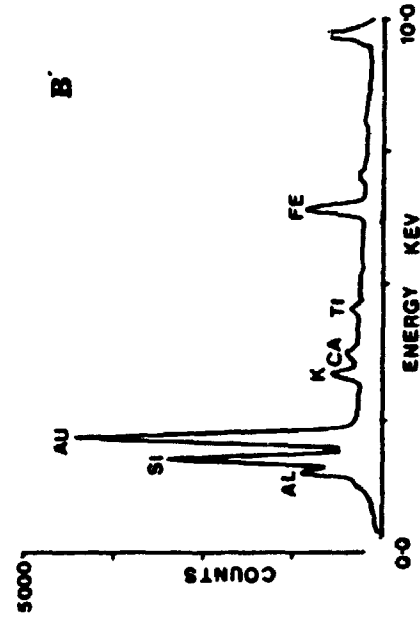
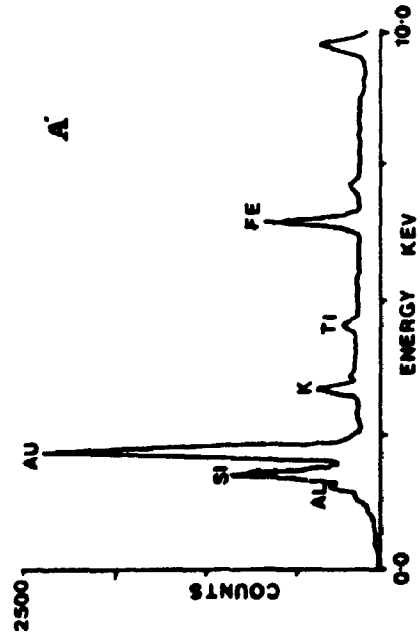


Plate 8. Transmission Electron Micrographs from the white components before ultrasonic cleaning of Sequence 104/30cm of:

- A. Fresh mica with moiré fringe. Note clean surface and sharp outlines.
- B. (a) Relatively fresh mica with moiré fringe; bottom edge shows sharp outlines; right hand edge suggestive of decomposition to small hexagonal plates suggestive of kaolin minerals that are (b)linked to form a mat; (c) separated.
- C. (a) Linked and or overlapping thick mat of hexagonal grains showing diffuse outlines; (b) separate sharply defined hexagonal grain suggestive of kaolin minerals. (c) thinner edge of linked or overlapping mat of hexagonal grains.
- D. Same features as in C viewed from a separate grain.

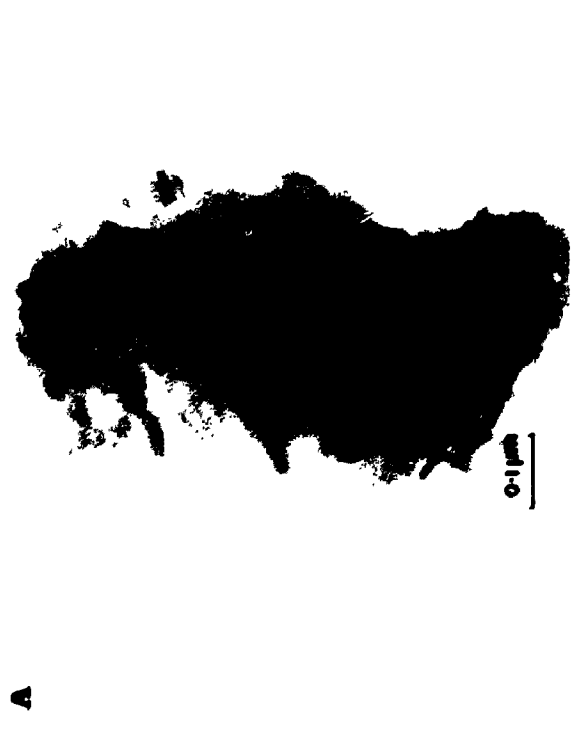


Plate 9. Transmission Electron Micrographs before ultrasonic cleaning of:

- A. (a) Mat with irregular outlines composed of layers containing pseudo hexagonal shaped particles attached to (b) relatively fresh mica grain showing sharper outlines. Note scatter of hexagonal grains on the surface. (from the black components of sequence 104/100cm).**

- B - C. Mat composed of (a), pseudo hexagonal particles with (b) some sections showing curled up edges and (c) crinkled edges (from the black components of sequence 104/100cm).**

- D. Pseudo hexagonal mat (a) associated with crinkled film suggestive of smectite (sequence 100/10cm).**

- E. Curled up edges of filmy substance supporting overlapping or linked mat of pseudo hexagonal particles (sequence 100/10cm).**



C



D



E



F



G

Plate 10. Transmission Electron Micrographs from the black components before ultrasonic cleaning of sequence 104/100cm:

- A. Layered amorphous net (b) supporting distinct hexagonal grains (a).**
- B. Higher magnification of area (b) from photograph (A). Note layered structure of net (a) and attached hexagonal particles (b).**
- C. (a) Crinkled edges of amorphous net; (b) overlying hexagonal particles; (c) pseudo hexagonal holes .**
- D. Isolated film, possibly carbon film for contrast.**



A



B



C



0.5 μm

0.5 μm

Plate 11. Transmission Electron Micrographs and EDX data of ultrasonically cleaned Mica grains from sequence 104/100cm:

- A. Ca-rich thin film bridging mica plates. Note Ca peak in bridge (EDX- A', C', D') compared to mica (EDX - B'). Also note linked pseudo hexagonal particles on bridge indicated by arrow. X' indicates area corresponding to area X in photographs (C) and (D) damaged by electron beam during X-ray scanning.
- B. Thin film distinguished by containing Ca (F') attached to edge of mica grain (biotite as suggested by E').
- C - D. Higher magnification of thin film on fresh mica surface prior to extensive beam damage. Note hexagonal particle supported by film (a).

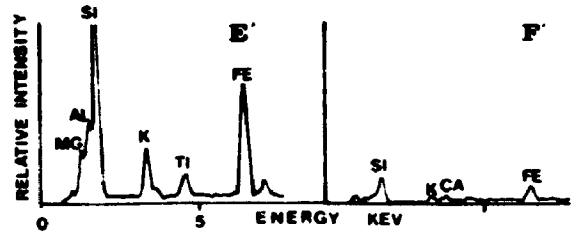
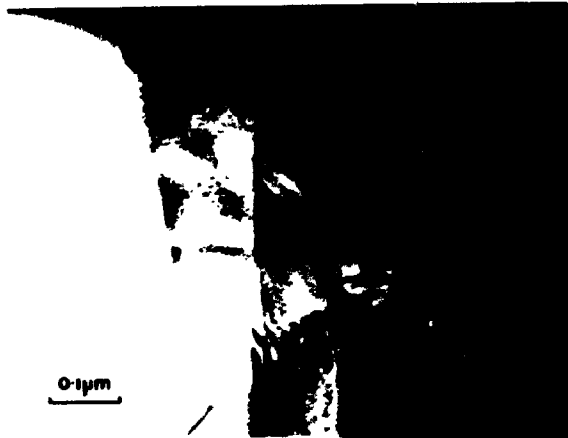
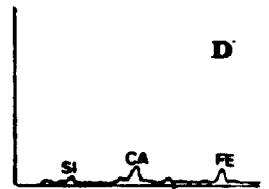
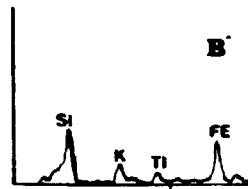
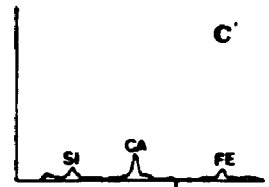
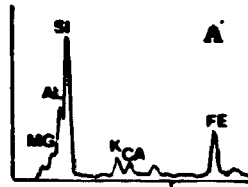
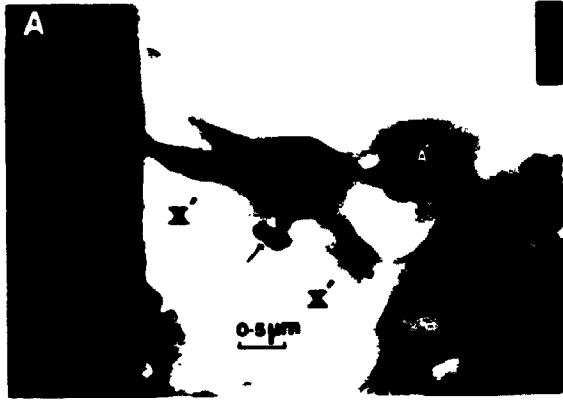


Plate 12. Transmission Electron Micrographs and EDX data of ultrasonically cleaned Mica grains from sequence 104/100cm:

- A. Ca-containing thin film (B') attached to edge of mica grain (A') supporting Fe rich minerals (C').**

- B. EDX data showing compositional difference between fresh mica grain (D') and mat (E'). Note that the thin film (B') and mat (E') both contain common cations Ca, K, and Fe.**

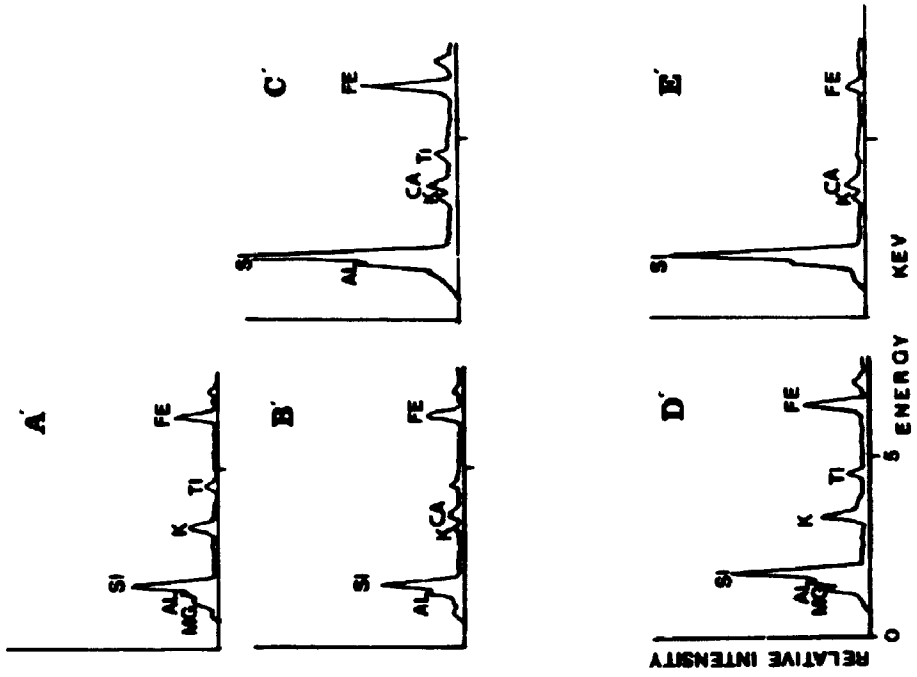
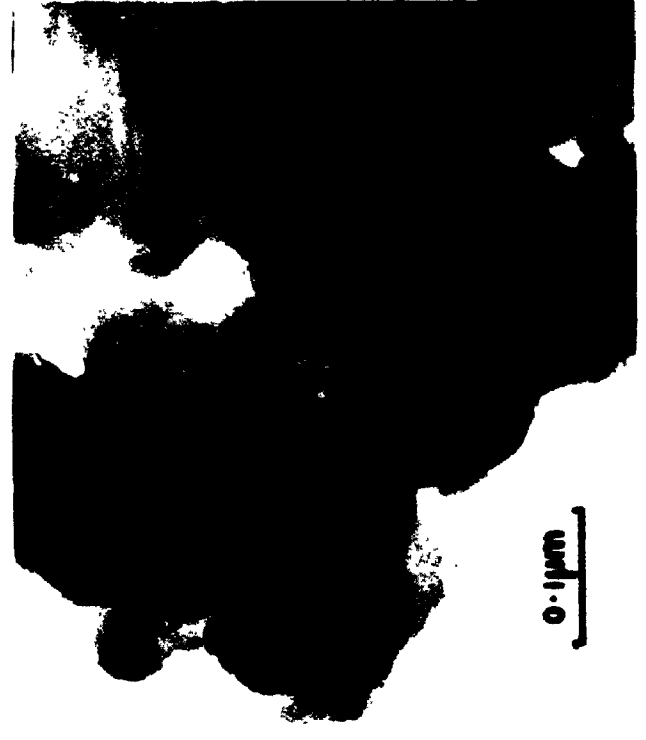
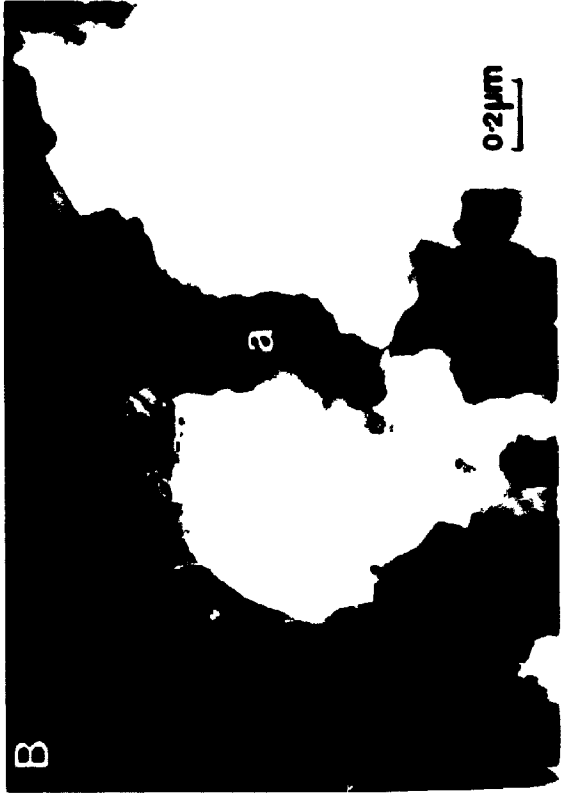


Plate 13. Transmission Electron Micrographs of ultrasonically cleaned mica grains from sequence 104/100cm showing different modifications of mica grain edges:

- A. Thin film attached to mica grain supporting isolated hexagonal particles indicated by arrows.
- B. Same as above but attachment composed of several overlapping layers.
- C. (a) Arrow indicates a point of attachment of the layered mat composed of pseudo hexagons to a relatively fresh mica grain as in Plate 12 B. Note sharper outlines to fresher mica grain. Outlines slightly modified by incipient outgrowths of film - like substance.
- D. Higher magnification of mat attachment to mica grain edge indicated by arrow and overlying layers of linked pseudo hexagonal particles.



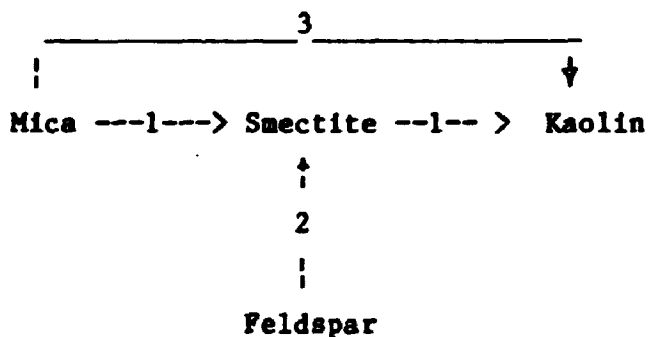
represented these crusts.

The following scheme represents the weathering pathways deduced from the results obtained.

Black Components

1. Mica -----> Smectite (Plate 7) + Kaolin (Plate 9,10)
2. Feldspar --> Smectite (Plate 6)
3. Mica -----> Kaolin (Plate 9)

ie.



White Components

5. Mica -----> Kaolin (Plate 2, 8)

Sharply defined crinkled surfaces identified as smectite were not commonly observed in the white components in SEM and TEM studies even though smectite was present in XRD traces.

The differences between the mineralogy of the black and white components appear to demonstrate the prevalence of micro-environments in weathering especially where primary minerals are abundant. They suggest that reactions are likely to follow different pathways controlled by the supply of elements in specific environments. For

example smectite was easily detected in the black granules where hornblende in addition to mica was present. In a similar study of feldspar weathering Anand et al., (1985) observed intimately associated gibbsite, halloysite and kaolinite within etch pits. They agree with other authors in concluding that differences in microenvironments even within a single grain affect the nature of secondary products. (Thus ground waters are likely the resultant of a composite suite of reactions where primary minerals are abundant).

The mechanism by which mica and or smectite weathers to form kaolin-smectite interstratification has not been addressed by Araki and Kuyuma (1987). Banfield and Eggleton (1988) propose that kaolin precipitates in cavities at dissolution sites and is not formed by direct modification of the tetrahedral sheets within biotite. If kaolin is a precipitate difficulty arises in explaining its coherence to the smectite surfaces and the vague definition of the pseudo hexagonal particles observed on the platy material not only in this study but in those of Araki and Kuyuma (1987), Wada and Kakuto (1983), Yerima et al., (1985) and De Alwis and Pluth (1976) where the samples underwent extensive pre-treatments. The composition of the thin amorphous Ca-rich film that supports kaolin particles is suggestive of an intermediary smectite. It is likely that stacking layers of this film-like substance leads to the familiar morphology of overlapping or linked pseudo-hexagonal structures (Plates 12 B and 13 B-D) identified as kaolin-smectite interstratification. The film may develop the crinkley morphology (Plate 10) of smectite when conditions are conducive. A similar morphological formational model of kaolin-smectite interstratification has not been presented before. However while Banfield and Eggleton, (1988) favour a dissolution-precipitation model, a transition model is favoured by most authors for interstratification (Wada and Kakuto, 1983; Wilson and Nadeau, 1985).

The vague pseudo-hexagonal particles formed on the smectite

to kaolin. This is the only disequilibrium feature found. It suggests that both mica and smectite are not in equilibrium with the prevalent soil solution. Hence the plots of groundwater in the center of the smectite field (fig.3.27) may be an artifact of the sampling time span (July-December) which are dry months in the area.

3.5.4.4 Summary

The control of weathering products by soil solution composition explains many weathering features instead of invoking a combination of state factors.

To summarise, four important points emerge from the above discussion.

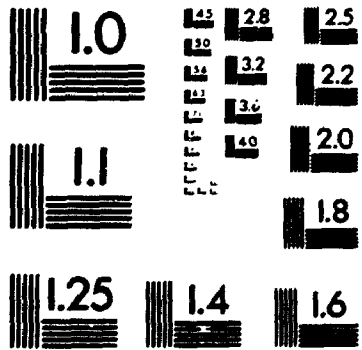
- (a). In the wet zone (where 57% of the population resides, since it forms the most important agricultural zone in the island dependent on an agricultural economy), rocks are stripped of virtually all essential nutrient elements, Na, K, Mg, and Ca regardless of rock type, and altered directly to kaolin and gibbsite bearing soils with essentially nil to very low base saturation while quartz remains in the silt fraction.
- (b). Gibbsite and kaolin traditionally considered to be the end product of extreme weathering, can in fact be the first and only minerals to form under intense weathering conditions, taken to mean conditions where a prominent dry period is not present and where rainfall averages 2500 mm annually.
- (c). The distribution of the majority of ground water analyses outside the common thermodynamic boundary regions of the characteristic clay mineral pairs of the climatic zones contradict the implication of equilibrium between them that their simultaneous occurrence in the soils suggest. The strong seasonality of

occurrence in the soils suggest. The strong seasonality of rainfall is likely to have a profound influence on the concentrations of elements in soil solutions. One of the minerals comprising the mineral pair is likely to be metastable with the prevailing soil solution if they coexist separately. In Nature seasonality in rainfall may be expressed by interstratification.

- (d). The successful application of the concept of weathering determined by mineral-soil solution equilibria to the sequences studied, endorses once again its capacity to unify many aspects of weathering and pedogenesis.

Finally it should be noted that though the definition of weathering in section 3.5.4.1 was restricted to horizons below the soil zone, i.e. to rocks and their weathering residues, the concept of weathering and its control on mineralogy as determined by activity diagrams can be successfully extended to the upper 100cm of profiles and even to profiles devoid of any trace of parent material as in the lateritic sequences found in humid to sub-humid tropical regimes.

3



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Chapter IV

Element Geochemistry, and Mass Changes during Weathering

4.1 Introduction

Preliminary geochemical and mineralogical studies have shown that differentiation of the soils in Sri Lanka is governed primarily by the activities of elements especially silica, in soil solutions, which in turn are heavily dependent on the rate of rainwater infiltration through a given soil sequence. In this Chapter, the geochemical status of the soils relative to crustal abundances and Amazon soils is established. Analysis of element abundance variation was carried out to obtain inter-relationships between elements and successive levels in sequences. Inter-relationships between elements were sought to delineate 'process related' element associations. Such associations were needed to identify suitable immobile index elements and sequences with horizons that are genetically related, so as to quantify the observed changes taking place during weathering. Index elements used in previous studies were not adopted on faith because of the diversity of the choice available as well as because of the range of the sample suite in the present study.

Several methods of analysing element variations, details of which are given in relevant sections, had to be used since neither approach gave sufficient insight by itself due to the complex origin of sample types. However the methods combined to provide a depth of information regarding processes at work during weathering, some of which was extracted from the methods used, for the first time in this study.

Finally, the challenge emerging from the results of this Chapter, to the concept of rock fertiliser is briefly discussed.

4.1.1 Brief summary of Methods of Investigation

Successive methods used to determine inter-element relationships were coefficients of variation analysis, element : Ti ratio analysis, cluster analysis and Spearman's rank coefficient analysis. Ti vs. Zr plots and enrichment factor analysis were used to seek out sequences with genetically related horizons (of common parent material).

Coefficients of variation indicated that Ti and Zr were the most suitable immobile index elements to use for mass balance calculations. Plots of element : Ti were used to check this observation, to search for other alternatives and to note the behaviour of other elements relative to Ti. However plots of Zr:Ti which should be uniformly flat had both Zr and Ti been immobile during weathering were quite non-uniform. Hence an unbiased statistical analysis - Spearman's rank coefficient analysis - was carried out to check if other element associations that could be used as index elements were present. Results obtained validated the previous choice of Zr and Ti. Enrichment factor analysis further indicated that Zr and Ti were the least immobile by generally giving the highest enrichment factors among the elements. XY-plots of these two elements and enrichment factors were used for subsequent delineation of sequences developed on the same parent material prior to mass balance calculations.

Oxide analyses recalculated to dry weight (Table 4.1) were used in all calculations. (It should be noted that the detection limits for trace elements as reported in Appendix 1 vary between the two laboratories where the samples were analysed).

Table 4.1 Geochemical Analyses Recalculated To Dry Weight Percent Per Major Oxides.

Sequence	Nb ¹	Sr	Y	Zr	Hf	Mo	Co	La	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CeO	H ₂ O	P ₂ O ₅	Cr ₂ O ₃	
Crust ²	78	364	31	162	20	390	19	35	58.50	1.05	15.80	6.50	0.14	4.57	6.51	3.06	2.22	0.23	0.02
14510	30	<	<	310	30	-	-	-	48.86	3.07	22.62	24.61	0.06	0.21	0.15	0.05	0.15	0.12	0.04
14530	20	<	<	170	40	-	-	-	44.11	1.86	22.17	31.57	0.02	0.16	0.01	0.01	0.08	0.07	0.07
145100	20	<	<	180	30	-	-	-	37.16	3.94	25.56	39.94	0.02	0.16	0.01	0.01	0.08	0.07	0.04
145103	20	<	<	130	40	-	-	-	36.94	3.19	26.99	31.79	0.04	0.20	0.01	0.01	0.02	0.14	0.01
145202	<	110	20	70	30	-	-	-	55.42	1.17	48.65	14.12	0.03	0.20	0.01	0.01	0.21	0.14	0.01
1457R	<	110	20	70	30	-	-	-	48.79	1.76	13.34	15.58	0.22	7.01	10.80	2.12	0.19	0.14	0.02
14810	8	1	11	627	27	35	28	35	57.94	1.53	21.50	18.43	0.03	0.29	0.09	<	0.11	0.07	-
14830	8	<	06	519	28	35	42	42	45.84	1.38	21.45	29.94	0.03	0.67	0.09	<	0.11	0.09	-
148101	8	<	07	635	23	<	46	46	49.61	1.16	23.38	24.98	0.02	0.60	0.09	<	0.10	0.07	-
148100	7	<	07	631	24	<	39	39	50.66	1.11	22.57	24.85	0.02	0.55	0.09	<	0.09	0.08	-
148107	13	20	15	504	34	<	61	61	48.01	2.42	42.34	6.38	0.01	0.42	0.00	<	0.79	0.05	-
148107	7	10	05	321	33	<	63	63	48.01	2.09	39.63	33.81	0.04	0.90	0.00	<	0.05	0.06	-
14210	40	<	20	360	<	360	<	360	71.23	1.10	17.21	9.16	0.05	0.45	0.18	0.01	0.48	0.08	0.02
14230	30	<	30	210	30	340	-	-	68.01	1.28	21.35	10.27	0.05	0.42	0.09	0.01	0.49	0.08	0.02
142100	40	<	20	280	30	400	-	-	55.28	1.41	26.16	14.42	0.03	0.42	0.06	0.01	0.60	0.07	0.02
1424R	30	30	50	210	20	680	-	-	63.29	1.19	22.87	9.58	0.11	1.52	0.18	0.08	1.10	0.08	0.02
1427R	30	390	20	210	20	620	-	-	64.58	0.92	16.17	6.98	0.11	2.42	3.32	3.21	1.16	0.05	0.01
4910	30	<	30	390	40	-	-	-	64.23	1.52	20.14	13.24	0.05	0.23	0.02	0.01	0.23	0.15	0.03
492040	20	<	20	210	20	-	-	-	71.99	0.86	12.15	14.54	0.02	0.13	0.02	0.01	0.12	0.09	0.02
49100	30	<	20	290	40	-	-	-	63.28	1.07	18.65	10.27	0.02	0.04	0.01	0.01	0.14	0.12	0.03
497R	<	<	<	80	20	-	-	-	99.13	0.05	0.39	0.52	0.01	0.01	0.01	0.01	0.01	0.02	0.03
7110	20	30	20	310	20	-	-	-	59.65	1.66	22.95	13.98	0.41	0.35	0.11	0.03	0.15	0.42	0.03
7130	20	30	<	340	40	-	-	-	57.78	1.77	24.55	13.98	0.46	0.33	0.04	0.01	0.09	0.32	0.03
71100	20	30	30	390	50	-	-	-	57.80	2.05	25.55	13.38	0.31	0.44	0.04	0.01	0.09	0.24	0.03
6310	20	230	<	200	30	630	-	-	56.02	1.73	23.66	13.15	0.17	1.35	2.31	0.35	0.35	0.19	0.01
6330	20	140	20	150	30	370	-	-	52.65	1.98	27.08	14.70	0.19	1.05	1.35	0.51	0.35	0.16	0.01
12310	40	60	<	240	50	-	-	-	63.91	1.19	20.74	10.72	0.05	0.92	0.53	0.45	1.18	0.22	0.05
12330	40	70	<	270	20	-	-	-	60.63	1.03	20.08	10.46	0.05	0.86	0.56	0.42	1.25	0.25	0.05
123100	30	<	<	370	20	-	-	-	60.48	1.07	22.98	10.90	0.04	0.18	0.11	0.02	0.32	0.24	0.05
123200	40	30	<	390	30	-	-	-	60.79	1.07	22.98	10.90	0.04	0.18	0.11	0.02	0.32	0.24	0.05
1237R	50	310	<	210	20	-	-	-	70.73	0.45	14.91	3.18	0.06	1.28	3.09	4.13	2.34	0.68	0.02
1238R	180	30	60	350	50	-	-	-	33.51	2.05	38.07	15.97	0.34	5.04	1.77	0.47	2.83	0.37	0.02
1238R	150	420	30	200	30	-	-	-	60.37	0.65	14.44	4.14	0.06	1.37	2.88	3.02	4.84	0.16	0.01
12510(A)	30	80	<	350	40	340	-	-	52.24	1.85	27.21	15.07	0.11	0.78	1.05	0.05	0.95	0.70	0.04
125100(A)	20	<	<	350	40	190	-	-	53.51	2.14	46.58	24.24	0.11	0.49	0.01	0.01	0.37	0.48	0.08
12510	40	<	<	300	20	230	-	-	58.89	1.91	21.92	15.58	0.04	0.58	0.13	0.03	0.58	0.28	0.02
12530	50	70	<	320	30	340	-	-	53.02	1.86	27.16	14.22	0.12	0.80	1.05	0.08	0.76	0.21	0.03
125100	60	<	<	560	40	290	-	-	61.40	1.97	22.17	12.45	0.06	0.69	0.20	0.01	0.76	0.21	0.03
126108	20	<	<	490	30	180	-	-	71.43	1.35	17.80	8.59	0.01	0.19	0.16	0.01	0.27	0.22	0.02
126308	40	<	<	600	20	180	-	-	69.85	1.35	19.35	8.64	0.02	0.19	0.16	0.01	0.27	0.22	0.02
145105 ^a	30	<	<	300	40	360	-	-	47.04	2.79	23.29	26.88	0.06	0.14	0.09	0.02	0.19	0.08	0.02
142455 ^a	20	<	<	190	30	360	-	-	70.70	1.12	17.28	9.49	0.05	0.45	0.23	0.01	0.08	0.03	0.02
71105 ^a	20	40	<	310	40	470	-	-	79.57	0.71	11.66	14.97	0.43	0.11	0.09	0.01	0.10	0.08	0.03
67105 ^a	40	530	<	270	30	640	-	-	54.87	1.08	23.87	14.97	0.07	0.41	0.23	0.01	0.08	0.03	0.02
67105 ^a	40	530	<	270	30	640	-	-	54.84	1.08	23.87	14.97	0.07	0.41	0.23	0.01	0.08	0.03	0.02
123105 ^a	150	40	50	330	50	350	-	-	31.05	2.18	20.18	17.05	0.32	4.41	1.13	0.43	0.18	0.01	0.01
1255(A) ^a	30	70	<	290	30	350	-	-	51.67	1.65	27.70	15.21	0.10	0.84	1.13	0.08	0.25	0.21	0.04

¹ Trace elements Bb-La in ppm values;

² Not determined
^a Topsoil mitigated with local water
< At or below detection limit

Table 4.1 continued

Sequence	Nb ¹	Sr	Y	Zr	Nb	Ba	Ga	La	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CeO	H ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃
Crust ²	78	364	31	162	20	390	19	35	58.50	1.05	15.80	6.50	0.16	4.57	6.51	3.06	2.22	0.25	0.02
12510(A)	50	80	20	330	40	340	-	-	52.24	1.85	27.21	15.07	0.11	0.79	1.05	0.05	0.86	0.70	0.04
125100(A)	20	<10	10	350	40	190	-	-	25.51	2.14	46.58	24.24	0.14	0.46	0.01	<0.01	0.37	0.48	0.08
12510	40	10	<10	300	20	230	-	-	58.89	1.91	21.92	15.58	0.04	0.58	0.13	0.03	0.59	0.28	0.03
12530	50	70	20	330	30	340	-	-	53.02	1.86	27.16	14.22	0.12	0.80	1.05	0.08	0.94	0.69	0.04
125100	60	10	<10	560	40	290	-	-	61.40	1.97	22.17	12.45	0.06	0.69	0.20	<0.01	0.76	0.21	0.03
12610B	20	<10	10	490	30	180	-	-	71.42	1.35	17.80	8.59	0.02	0.18	0.10	<0.01	0.25	0.22	0.02
12630B	40	10	<10	600	20	180	-	-	69.83	1.39	19.25	8.66	0.02	0.19	0.10	<0.01	0.27	0.19	0.02
6110	70	520	20	220	20	1160	-	-	62.90	0.96	20.77	9.61	0.16	1.26	2.42	0.20	1.63	0.20	0.01
6130	60	480	20	220	10	1100	-	-	57.02	0.93	20.16	9.37	0.16	1.16	2.14	0.24	1.33	0.18	0.02
61100	60	530	20	180	20	1190	-	-	57.77	1.00	22.57	9.82	0.13	2.25	3.05	1.44	1.73	0.15	0.02
611F	90	830	20	170	30	990	-	-	52.67	1.10	17.83	9.35	0.15	4.21	7.64	3.83	2.54	0.55	0.01
15310	7	<1	24	437	37	34	41	44	56.09	1.58	25.35	15.16	0.08	1.30	0.16	<0.01	0.10	0.12	-
15330	7	<1	26	404	37	<3	43	54	60.54	1.57	23.71	12.66	0.06	0.99	0.13	<0.01	0.13	0.13	-
153301	7	<1	26	404	37	<3	43	54	60.56	1.60	23.74	12.60	0.07	0.99	0.13	<0.01	0.12	0.13	-
153100	7	<1	11	201	19	<3	42	43	62.75	0.87	28.09	17.72	0.02	0.37	0.01	<0.01	0.08	0.04	-
153600	4	<1	15	392	27	<3	52	50	63.22	1.19	23.31	11.70	0.03	0.36	0.04	<0.01	0.04	0.04	-
153600a	6	<1	27	645	20	<3	57	136	38.10	0.74	33.37	26.28	0.03	1.15	0.11	<0.01	0.02	0.08	-
16710	50	710	10	510	30	-	-	-	81.36	1.23	5.21	3.79	0.04	0.78	6.42	0.27	0.61	0.10	0.04
16730	40	720	10	540	30	-	-	-	81.34	1.21	4.94	3.86	0.03	0.70	6.74	0.28	0.62	0.10	0.04
167100	30	830	10	590	20	-	-	-	82.09	0.81	4.12	2.81	0.02	0.62	8.49	0.23	0.58	0.08	0.02
11510	90	140	20	390	20	-	-	-	83.37	0.71	8.29	3.40	0.10	0.30	0.84	0.57	2.26	0.05	0.03
11530	100	150	50	400	10	-	-	-	79.39	0.68	10.16	4.06	0.12	0.57	1.53	0.89	2.42	0.07	0.02
115100	100	150	20	410	30	-	-	-	78.80	0.70	10.30	4	0.10	0.72	1.91	0.90	2.41	0.08	0.01
115PR	130	290	40	120	20	-	-	-	58.63	0.64	11.97	5.69	0.07	4.27	11.66	2.19	4.64	0.16	0.01
8484	30	510	<10	<10	<10	-	-	-	9.74	0.3	2.54	1.25	0.02	17.57	67.32	0.07	1.17	0.03	0.02
8486	<10	<10	<10	420	60	-	-	-	37.60	1.5	17.46	42.31	0.09	0.67	0.03	0.01	0.01	0.63	0.03
8810	140	133	50	233	16	731	29	55	55.26	1.84	19.13	14.55	0.29	3.03	2.01	<0.01	3.34	0.19	-
88301	127	118	46	205	14	613	25	37	55.15	1.74	19.42	14.93	0.31	2.90	1.75	<0.01	3.50	0.17	-
881001	118	125	41	132	12	644	26	44	57.10	1.36	18.53	13.50	0.26	2.63	1.83	0.17	4.39	0.11	-
89100	105	109	42	156	13	561	24	37	57.03	1.50	18.15	14.41	0.28	2.70	1.76	0.41	3.53	0.10	-
88F	6	52	4	<1	3	<10	0	17	17.39	0.24	0.06	0.74	0.05	31.35	49.92	<0.01	0.21	0.14	-
11210	37	135	11	401	13	728	14	25	82.09	0.90	10.22	3.68	0.11	0.25	0.92	0.16	1.50	0.03	-
11230	42	169	13	521	15	994	15	39	77.71	1.05	12.81	3.63	0.19	0.23	1.73	1.14	1.76	0.03	-
112100	5	4	4	064	4	619	9	16	89.93	0.25	6.03	2.93	0.34	0.18	1.07	<0.01	0.18	0.00	-
112101	5	4	5	066	4	626	9	23	89.92	0.22	6.01	2.95	0.34	0.20	0.08	<0.01	0.20	0.00	-
11230	50	60	10	350	30	370	-	-	90.30	0.82	4.77	1.37	0.03	0.19	0.37	0.57	1.28	0.04	0.01
112100	50	190	20	890	40	740	-	-	84.94	1.86	6.82	2.42	0.03	0.09	1.02	1.09	1.85	0.03	0.01
112F	120	90	30	70	20	380	-	-	76.13	0.87	13.49	0.74	0.03	0.10	1.02	3.12	5.25	0.02	0.00
60PDY*	90	260	40	270	10	800	-	-	61.83	1.11	19.46	8.60	0.08	2.26	2.88	1.45	2.10	0.16	0.02
61PDY*	60	380	20	130	20	910	-	-	51.97	1.30	28.01	11.88	0.12	1.82	2.15	1.04	1.36	0.27	0.02
61105*	70	500	30	250	20	1110	-	-	61.70	0.98	20.95	9.40	0.16	1.27	2.78	1.32	1.55	0.19	0.01
1475	40	700	10	210	10	-	-	-	84.76	1.44	4.14	2.86	0.02	0.56	6.21	0.71	0.16	0.07	0.04
1155*	160	120	30	270	40	-	-	-	54.11	1.47	26.46	11.92	0.02	0.92	0.95	0.61	2.19	0.19	0.01
112105*	20	120	10	360	30	870	-	-	82.59	0.84	9.00	4.29	0.16	0.12	0.81	0.90	1.19	0.04	0.01

1 Trace elements Nb-La in ppm values;
2 Fairbridge (1972).

- Not determined
* Topsoil agitated with local water
< below detection limit

Table 4.1 continued

Sequence	Rb ¹	Sr	Y	Zr	Nb	Mo	Ca	La	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Mn ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃
Crust 2	78	364	31	162	20	390	19	35	58.50	1.05	15.80	6.50	0.14	4.57	6.51	3.06	2.22	0.25	0.02
1410	73	1404	28	803	45	2069	24	123	57.59	3.75	16.99	10.33	0.16	1.62	3.35	2.07	2.68	0.98	-
1410Z	67	1325	28	794	41	2041	23	115	57.67	3.73	16.33	10.17	0.16	1.53	3.43	2.32	2.73	0.99	-
1430	66	1416	29	806	45	2190	24	126	58.27	3.86	16.16	10.05	0.16	1.55	3.43	2.32	2.73	0.99	-
1650	71	1284	30	714	39	2053	29	126	58.22	3.40	17.46	10.06	0.15	1.60	2.96	2.12	2.67	0.90	-
13110	163	229	28	860	9	482	24	49	68.98	0.74	15.81	5.67	0.21	1.14	2.11	1.47	3.60	0.05	-
13130	176	214	24	804	9	481	25	32	70.88	0.67	14.92	5.02	0.14	0.99	1.70	1.10	3.72	0.05	-
131301	150	206	24	887	9	487	20	42	70.15	0.65	14.82	5.02	0.13	0.95	1.72	2.04	3.74	0.05	-
131100	117	228	22	909	8	470	25	16	68.93	0.72	19.27	8.35	0.05	1.21	3.50	2.50	3.74	0.05	-
13110e	183	291	27	284	14	600	27	73	59.18	1.21	17.84	8.35	0.05	1.21	3.50	2.50	3.74	0.05	-
1311e	218	251	27	203	10	413	20	51	63.92	0.83	14.92	5.52	0.07	2.33	3.98	2.38	3.77	0.13	-
13210	218	82	68	1436	23	491	30	98	71.50	1.19	14.83	3.69	0.18	0.47	0.95	1.49	3.35	0.11	-
13210f	200	79	17	1007	19	465	18	25	75.33	0.87	10.30	2.25	0.04	0.26	0.38	0.94	3.40	0.04	-
132100	227	81	54	873	17	470	28	77	72.31	0.58	14.06	2.93	0.09	0.27	0.81	2.56	6.04	0.05	-
1321e	217	68	77	344	15	345	31	33	72.06	0.52	13.14	3.42	0.05	0.66	1.43	2.69	5.82	0.05	-
9010(2)	90	150	30	220	10	660	-	-	79.11	0.57	10.84	4.03	0.16	0.77	1.26	1.20	1.46	0.15	0.01
9010(2)	70	140	30	560	20	690	-	-	79.27	0.65	11.19	3.64	0.09	0.64	1.11	1.48	1.77	0.07	0.01
9010(2)	70	140	30	240	10	640	-	-	81.51	0.48	9.97	3.29	0.08	0.67	0.87	1.18	1.40	0.08	0.01
901e	90	190	20	170	30	590	-	-	76.68	0.60	10.39	4.15	0.08	1.46	1.49	2.63	2.36	0.11	0.01
9910	118	470	24	721	24	1407	23	66	69.28	1.36	15.17	5.47	0.09	0.67	1.19	2.01	4.38	0.09	-
9910a	91	294	22	430	16	1207	40	64	78.01	0.82	11.84	3.82	0.05	0.36	0.68	0.66	3.48	0.05	-
9910b	82	231	21	373	14	1294	23	65	78.67	0.71	11.97	4.52	0.02	0.44	0.49	0.01	3.86	0.05	-
9910c	82	231	21	373	14	1035	22	48	78.51	0.70	11.82	4.52	0.03	0.41	0.54	0.01	3.86	0.05	-
991e	61	393	33	263	13	806	19	41	80.81	0.51	13.76	3.65	0.05	0.88	2.39	4.03	3.56	0.11	-
991e1	63	411	31	264	13	833	25	53	71.07	0.48	13.70	3.99	0.05	1.08	2.42	3.36	3.61	0.09	-
13910	110	140	40	2310	80	-	-	-	76.66	3.11	9.73	3.31	0.22	0.04	0.79	2.03	3.78	0.03	0.02
13930	120	160	30	1300	40	-	-	-	78.42	1.34	10.87	1.96	0.11	0.03	0.73	2.18	4.08	0.03	0.02
139100	140	190	30	1320	30	-	-	-	77.84	1.34	11.27	1.99	0.10	0.03	0.76	2.24	4.21	0.03	0.01
1391e	2100	200	130	540	40	-	-	-	63.02	0.99	15.73	6.54	0.13	1.11	1.94	3.17	7.01	0.24	0.01
10410	60	40	30	370	20	450	-	-	79.20	0.74	14.84	2.78	0.01	0.33	0.37	0.62	1.01	0.04	0.01
10430	120	540	10	320	20	1520	-	-	74.67	0.51	13.71	2.60	0.06	0.56	1.77	2.57	3.18	0.07	0.01
104100	110	550	20	160	20	1180	-	-	73.98	0.32	14.40	1.95	0.02	0.56	2.35	3.06	3.39	0.07	0.01
104PDY	90	640	10	450	20	1800	-	-	82.31	0.35	9.57	1.17	0.03	0.28	1.13	1.98	2.96	0.09	0.00
104FR	180	2090	20	450	40	9330	-	-	67.33	0.64	14.21	2.84	0.05	1.40	2.18	3.73	6.95	0.38	0.00
10010	70	1550	30	560	30	2480	-	-	69.16	1.53	14.68	3.90	0.12	0.86	2.50	3.54	3.18	0.31	0.00
100301	67	1209	13	414	17	2104	20	34	71.43	1.34	14.46	3.69	0.11	0.90	2.32	1.64	3.25	0.26	-
100708	68	1359	14	468	18	2204	20	55	70.60	1.35	14.13	3.80	0.10	0.82	2.27	3.03	3.19	0.27	-
100100	70	1303	13	426	18	2218	19	57	70.36	1.41	14.54	3.87	0.12	0.91	2.38	2.39	3.31	0.28	-
116-H	50	370	10	360	20	-	-	-	71.17	1.03	12.62	6.21	0.09	1.53	3.10	2.28	1.77	0.09	0.02
116NO-C	30	120	20	390	30	480	-	-	81.69	0.73	6.93	3.25	0.04	0.21	0.91	0.21	1.70	0.06	0.01
84AC	90	140	<10	390	30	860	-	-	73.62	1.43	11.53	3.59	0.09	1.15	1.39	0.98	2.16	0.09	0.02
1-W	110	150	30	630	30	810	-	-	60.27	1.6	21.20	10.33	0.10	1.34	1.44	1.01	2.39	0.21	0.02
905(2)S ^a	70	130	30	250	30	710	-	-	81.39	0.49	9.79	3.40	0.13	0.60	1.10	1.22	1.72	0.12	0.01
909DY	180	390	60	670	50	1640	-	-	58.62	1.93	21.79	10.43	0.24	1.46	1.30	0.87	3.03	0.35	0.02
1395 ^a	130	130	20	1640	30	-	-	-	77.73	2.54	9.74	3.42	0.15	0.09	0.73	2.07	3.81	0.03	0.02
1395 ^b	130	190	20	1640	30	-	-	-	71.88	1.57	14.16	3.42	0.15	0.04	0.94	2.64	4.88	0.03	0.02
1045-S ^a	120	510	<10	240	20	1590	-	-	74.38	0.43	12.55	3.18	0.04	0.63	1.82	3.54	3.14	0.19	0.01
10010-S	80	160	20	430	20	2400	-	-	63.40	1.27	17.22	3.91	0.17	0.63	2.26	3.37	3.37	0.19	0.00
1009DY	40	280	20	480	20	780	-	-	63.82	2.46	17.68	11.88	0.17	0.50	1.26	1.16	0.37	0.12	0.02

1 Trace elements Rb-La in ppm values;
 2 Pb/Bi ratio (1972).
 - Not determined
 a Topsoil agitated with local water
 < below detection limit

4.2 Element and Oxide Status Relative to the Crust and Amazon Soils

To evaluate the element status of Sri Lankan soils they were compared to Amazon soils (Kronberg et al., 1987) and crustal abundances (Fairbridge, 1972) as in Kronberg (1979). The same seven categories were maintained denoting enrichment (e, 3-10 fold crustal abundance (CA); xe, 10-100 fold CA; xxe, 100-1000 fold CA;), depletion (d, 3-1 tenths CA; xd, 1-tenth to 1-hundreth CA; xxd, less than 1-hundreth CA) and relative uniformity (within 3-fold). Detailed results are tabulated in Table 4.2A and B and summarised in Tables 4.3 A-C and 4.4 as well as in figs. 4.1 A and B. Sixty one and thirty two samples in total were used for the wet zone and dry zone histograms respectively.

Analysis of relative abundances in soils provides information on the relative mobility of elements. A high degree of depletion of an element in soils developed 'across a range of parent rock types' implies its solubility and hence mobility whereas enrichment indicates the opposite. Stability implies an intermediate status between the two extremes. This analysis also provides a yardstick to judge the quality of the soils in terms of its suitability for agriculture.

Fig. 4.1A and Tables 4.3A and B show that, for both climatic zones, Si, Al, Y, La and Nb, with minor exception, remain unchanged with respect to the crust. Zr shows a marked enrichment (61%) in the

Table 4.2A Element and Oxide Abundances Relative to Crustal Abundances¹

Sample	Rb	Sr	Y	Zr	Nb	Ba	Ca	La	Si	Ti	Al	Fe	Mn	Hg	Ca	Na	K	P
Wet and Intermediate Zones																		
8414510	e	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
8414530	d	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
84145100	d	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
84145202	d	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
84145103	d	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
14810	d	xxd	e	e	e	xxd	e	e	e	e	e	e	d	xd	xd	xd	xd	e
14830	d	xxd	d	e	e	xd	e	e	e	e	e	e	d	d	xd	xd	xd	e
1481001	d	xxd	d	e	e	xxd	e	e	e	e	e	e	d	d	xd	xd	xd	e
148100	xd	xxd	d	e	e	xxd	e	e	e	e	e	e	d	xd	xd	xd	xd	e
148100y	d	xd	e	e	e	xxd	e	e	e	e	e	e	xd	xd	xd	xd	xd	e
148100r	xd	xxd	d	e	e	xxd	e	e	e	e	e	e	d	d	xd	xd	xd	e
8414210	e	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
8414230	e	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
84142100	e	xd	e	e	e	-	-	-	e	e	e	e	d	d	xd	xd	xd	e
844910	e	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
84492040	d	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
8449100	e	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
847110	d	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
847130	d	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
8471100	d	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
8486	d	xd	e	e	e	-	-	-	e	e	e	e	e	d	xd	xd	xd	e
846310	d	e	e	e	e	-	-	-	e	e	e	e	e	d	e	e	e	e
846330	d	e	e	e	e	-	-	-	e	e	e	e	e	d	d	d	d	e
8463100	d	e	e	e	e	-	-	-	e	e	e	e	e	d	d	d	d	e
8412310	e	d	e	e	e	-	-	-	e	e	e	e	e	d	xd	d	e	e
8412330	e	d	e	e	e	-	-	-	e	e	e	e	e	d	xd	d	e	e
84123100	e	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	d	e
84123200	e	xd	e	e	e	-	-	-	e	e	e	e	e	xd	xd	xd	xd	e
12510(a)	e	d	e	e	e	-	-	-	e	e	e	e	e	d	d	xd	e	e
125>100A	d	xd	e	e	e	-	-	-	e	e	e	e	e	d	xd	xd	xd	e
8412510	e	d	e	e	e	-	-	-	e	e	e	e	e	d	d	xd	e	e
84125100	e	xd	e	e	e	-	-	-	e	e	e	e	e	d	xd	xd	xd	e
8412610B	d	xd	e	e	e	-	-	-	e	e	e	e	xd	xd	xd	xd	xd	e
8412630B	e	xd	e	e	e	-	-	-	e	e	e	e	d	xd	xd	xd	xd	e
846110	e	e	e	e	e	-	-	-	e	e	e	e	e	d	e	e	e	e
846130	e	e	e	e	e	-	-	-	e	e	e	e	e	d	e	e	e	e
8461100	e	e	e	e	e	-	-	-	e	e	e	e	e	e	e	e	e	e
15310	xd	xxd	e	e	e	xd	e	e	e	e	e	e	e	d	xd	xd	xd	e
15330	xd	xxd	e	e	e	xxd	e	e	e	e	e	e	e	d	xd	xd	xd	e
153301	xd	xxd	e	e	e	xxd	e	e	e	e	e	e	e	d	xd	xd	xd	e
153100	xd	xxd	e	e	e	xxd	e	e	e	e	e	e	d	xd	xd	xd	xd	e
153600	xd	xxd	e	e	e	xxd	e	e	e	e	e	e	d	xd	xd	xd	xd	e
8414710	e	e	e	e	e	-	-	-	e	e	e	e	e	d	e	xd	d	e
8414730	e	e	e	e	e	-	-	-	e	e	e	e	e	d	e	xd	d	e
84147100	e	e	e	e	e	-	-	-	e	e	d	e	e	d	e	xd	d	e
8411510	e	e	e	e	e	-	-	-	e	e	e	e	e	xd	d	d	e	d
8411530	e	e	e	e	e	-	-	-	e	e	e	e	e	d	d	d	e	d
84115100	e	e	e	e	e	-	-	-	e	e	e	e	e	d	d	d	e	d
8810	e	e	e	e	e	e	e	e	e	e	e	e	e	e	e	xxd	e	e
88301	e	e	e	e	e	e	e	e	e	e	e	e	e	e	d	xxd	e	e
881001	e	e	e	e	e	e	e	e	e	e	e	e	e	e	d	xd	e	e
88100	e	d	e	e	e	e	e	e	e	e	e	e	e	e	d	d	e	e
11210	e	e	e	e	e	e	e	e	e	e	e	e	e	xd	d	xd	e	d
11230	e	e	e	e	e	e	e	e	e	e	e	e	e	xd	d	e	e	d
112100	xd	xd	d	e	d	e	e	e	e	d	e	e	e	xd	xd	xxd	xd	xxd
1121001	xd	xd	d	e	d	e	e	e	e	d	e	e	e	xd	xd	xxd	xd	xxd
8411210	e	e	e	e	e	-	-	-	e	e	e	e	e	xd	xd	e	e	d
8411230	e	d	e	e	e	-	-	-	e	e	e	d	d	xd	xd	d	e	d
112100	e	e	e	e	e	-	-	-	e	e	e	e	e	xd	d	e	e	d

Table 4.2A cont'd.

Sample	Rb	Sr	Y	Zr	Nb	Ba	Ca	La	Si	Ti	Al	Fe	Mn	Mg	Co	Na	K	P
<u>Dry Zone</u>																		
1610	s	e	s	e	s	e	s	e	s	e	s	s	s	s	s	s	s	s
161020	s	e	s	e	s	e	s	e	s	e	s	s	s	s	s	s	s	s
1630	s	e	s	e	s	e	s	e	s	e	s	s	s	s	s	s	s	s
1650	s	e	s	e	s	e	s	e	s	e	s	s	s	s	s	s	s	s
13110	s	s	s	e	s	s	s	s	s	s	s	s	e	d	s	s	s	d
13130	s	s	s	e	s	s	s	s	s	s	s	s	e	d	s	s	s	d
131301	s	s	s	e	s	s	s	s	s	s	s	s	e	d	s	s	s	d
131100	s	s	s	e	s	s	s	s	s	s	s	s	e	d	s	s	s	d
13210	s	d	s	e	s	s	s	s	s	s	s	s	e	d	s	s	s	d
132ecf	s	d	s	e	s	s	s	s	s	s	s	s	d	nd	nd	s	s	d
132100	s	d	s	e	s	s	s	s	s	s	s	s	e	nd	d	s	s	d
9010(2)	s	s	s	e	s	-	-	-	s	s	s	s	e	d	d	s	s	d
9030(2)	s	s	s	e	s	-	-	-	s	s	s	s	e	d	d	s	s	d
90100(2)	s	s	s	e	s	-	-	-	s	s	s	s	e	d	d	s	s	d
9910	s	s	s	e	s	s	s	s	s	s	s	s	e	d	d	s	s	d
9930	s	s	s	e	s	s	s	s	s	s	s	s	e	nd	d	nd	s	d
99100a	s	s	s	e	s	s	s	s	s	s	s	s	d	nd	nd	nd	s	d
99100	s	s	s	e	s	s	s	s	s	s	s	s	d	nd	nd	nd	s	d
841390	s	s	s	e	s	-	-	-	s	s	s	s	e	nd	d	s	s	d
13910	s	s	s	xe	e	-	-	-	s	s	s	s	e	xxd	d	s	s	d
8413930	s	s	s	e	s	-	-	-	s	s	s	s	e	xxd	d	s	s	d
84139100	s	s	s	e	s	-	-	-	s	s	s	s	e	xxd	d	s	s	d
8410410	s	d	s	e	s	-	-	-	s	s	s	s	nd	nd	nd	d	s	d
8410430	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	d
104100	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	d
10010(A)	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	d
100301	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	d
10030a	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	d
100100a	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	d
<u>River Sediment</u>																		
84114MOC	s	s	s	s	s	-	-	-	s	s	s	s	d	d	d	d	s	d
8484AC	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	s
1-MP	s	s	s	e	s	-	-	-	s	s	s	s	s	d	d	s	s	s
84116-M	s	s	s	s	s	-	-	-	s	s	s	s	s	s	s	s	s	s

1 Fairbridge (1972)

Table 4.2B Oxide Abundances relative Amazon Soils¹

Wet and Intermediate Zones						
Sample	Si	Al	Mg	Ca	Na	K
8414510	s	s	e	xe	s	s
8414530	s	s	e	s	d	s
84145100	s	s	e	s	d	s
84145202	s	s	e	s	s	s
84145103	s	s	xe	xe	s	d
14810	s	s	e	xxd	xxd	s
14830	s	s	xe	e	xxd	s
1481001	s	s	xe	xxd	xxd	s
148100	s	s	xe	xxd	xxd	s
148100y	s	s	xe	xxd	xxd	e
148100r	s	s	xe	xxd	xxd	s
8414210	s	s	xe	xe	d	e
8414230	s	s	xe	e	d	e
84142100	s	s	xe	e	d	e
84142WR	s	s	xe	xe	s	xe
844910	s	s	e	s	d	s
84492040	s	s	e	s	d	s
8449100	s	s	s	s	d	s
847110	s	s	xe	xe	s	s
847100	s	s	xe	e	d	s
847100	s	s	xe	e	d	s
8436	s	s	xe	e	d	d
846310	s	s	xe	xxe	xe	e
846330	s	s	xe	xxe	xe	e
8463100	s	s	xe	xxe	xe	e
8412310	s	s	xe	xe	xe	xe
8412330	s	s	xe	xe	xe	xe
84123100	s	s	e	xe	s	e
84123200	s	s	e	e	e	e
84123PWR	s	s	xe	xxe	xxe	xe
84123BWR	s	s	xxe	xxe	xe	xe
12510(A)	s	s	xe	xxe	s	e
125>100A	s	s	xe	s	s	e
8412510	s	s	xe	xe	s	e
8412530	s	s	xe	xxe	s	e
84125100	s	s	xe	xe	d	e
8412610B	s	s	e	xe	d	s
8412630B	s	s	e	xe	d	s
846110	s	s	xe	xxe	e	xe
846130	s	s	xe	xxe	xe	xe
8461100	s	s	xe	xxe	xe	xe
15310	s	s	xe	xe	xxd	s
15330	s	s	xe	xe	xxd	s
153301	s	s	xe	xe	xxd	s
153100	s	s	xe	s	xxd	s
153600	s	s	xe	e	xxd	s
153600a	s	s	xe	xe	xxd	d
8414710	s	d	xe	xxe	e	e
8414730	s	d	xe	xxe	e	e
84147100	s	d	xe	xxe	e	e
8411510	s	s	e	xe	xe	xe
8411530	s	s	xe	xxe	xe	xe
84115100	s	s	xe	xxe	xe	xe
8810	s	s	xe	xxe	xxd	xe
88301	s	s	xe	xxe	xxd	xe
881001	s	s	xe	xxe	e	xe
88100	s	s	xe	xxe	xe	xe
8411230a	s	d	e	xe	xe	xe
112100a	s	s	s	xe	xe	xe
11210	s	s	e	xe	e	xe
11230	s	s	e	xxe	xe	xe
112100	s	d	e	e	xxd	s
1121001	s	d	e	e	xxd	s

¹ Kronberg (1987)

Table 4.2B cont'd

<u>Dry Zone</u>	Si	Al	Mg	Ca	Na	K
1610	s	s	xe	xxe	xe	xe
161020	s	s	xe	xxe	xe	xe
1630	s	s	xe	xxe	xe	xe
1650	s	s	xe	xxe	xe	xe
13110	s	s	xe	xxe	xe	xe
13130	s	s	xe	xxe	xe	xe
131301	s	s	xe	xxe	xe	xe
131100	s	s	xe	xxe	xe	xe
131we	s	s	xe	xxe	xe	xe
13210	s	s	xe	xe	xe	xe
132scf	s	s	e	xe	xe	xe
132100	s	s	e	xe	xe	xe
9010(2)	s	s	xe	xxe	xe	xe
9030(2)	s	s	xe	xxe	xe	xe
90100(2)	s	s	xe	xe	xe	xe
9910	s	s	xe	xxe	xe	xe
9930	s	s	xe	xe	xe	xe
99100a	s	s	xe	xe	xxd	xe
99100	s	s	xe	xe	xxd	xe
841390	s	s	s	xe	xe	xe
8413930	s	s	s	xe	xe	xe
84139100	s	s	s	xe	xe	xe
8410410	s	s	e	xe	xe	xe
8410430	s	s	xe	xxe	xe	xe
104100	s	s	xe	xxe	xe	xe
10010(A)	s	s	xe	xxe	xe	xe
100301	s	s	xe	xxe	xe	xe
10030a	s	s	xe	xxe	xe	xe
100100a	s	s	xe	xxe	xe	xe
<u>River Sediment</u>						
84114MOG	s	s	xe	xe	xe	xe
8484AG	s	s	xe	xxe	xe	xe
1-MP	s	s	xe	xxe	xe	xe
84116-M	s	s	xe	xxe	xe	xe

1 Kronberg (1987)

dry zone samples, derived as they are from granitic precursors compared to a much lesser degree of enrichment in the wet zone, associated in this instance with highly weathered samples and beach sand (Table 4.2A). Hence the cause for the observed enrichment differs between the two zones. Ti is fractionally enriched (14%) in the dry zone, whereas Fe (20%) and Ca(11%) are only enriched in the wet zone.

Alkalis and alkaline earth elements show significant depletion in the wet zone soils. K and Rb are less depleted compared to Na as well as Mg and Ca (Table 4.3A). In striking contrast K and Rb and Na to a lesser extent, remain stable in the dry zone soils (Table 4.3B). Na shows the highest depletion among the wet zone soils (55% xxd category: Table 4.3A and fig. 4.1A) and is followed by Ca (32% xxd category) whereas the bulk of Mg (90%) remains within the xd and d range (none in the xxd category). On the other hand Mg is relatively more depleted than Ca in the dry zone soils (Table 4.3B and Fig. 4.1A). However the highest frequency of depletion only reaches the d category for both these elements in half of the dry zone soils and are hence less depleted than wet zone soils.

It is noted from Table 4.3C, that 30-45% of the depletion category of over 1-tenth crustal levels (xd+xxd) for Na, K, Rb, Ca, Mg, Sr and Ba(55%), is contributed by the highly weathered wet zone SW-lowland samples that comprise 24%, of the wet zone samples, (sequences 145, 148, and 142). Especially noteworthy, is their greater contribution of samples to both the depleted and highly depleted categories for K compared to Mg, indicative of the fact that Mg is less depleted than K in these samples contrary to the general trend observed. These samples were taken from the south west and western coastal lowlands, where extensive laterites occur. Classification of sequences 145 and 148 as typical laterites, the most weathered among the sample suite is substantiated by their chemistry. A high degree of depletion is also observed in sequence 153 (Table 4.2A) sampled

from the ultra wet zone (over 5000mm rainfall), and from sequences 49 and 71, developed on a quartzite and river terrace alluvium respectively.

Thus the order of depletion is:

- o wet zone soils $K < Mg < Ca < Na$
- o dry zone soils $K < Na < Ca < Mg$
- o sw-lowland soils $Mg < K < Na < Ca$

Kronberg (1979) determined the order of depletion for the Amazon region relative to the same values used in this study for crustal abundances as:

- o $K < Mg, Na, Ca$

For the same soils the order was found to resolve and bear much closer similarity to Sri Lankan soils when the upper crustal abundances were used as reference (Kronberg, 1987).

- o Bahia (Intermediate Weathering) $K < Mg < Na < Ca$
- o Amazon (Advanced Weathering) $K < Na < Mg < Ca$
- o Gois (Extreme Weathering) $K < Mg < Na < Ca$
- o Amazon Bauxite (") $Mg < K < Na < Ca$

In both the Amazon region and in Sri Lanka, K remains as the least depleted of the mobile major elements. The Amazon (advanced weathering) depletion order resembles that of the dry zone soils of Sri Lanka whereas the Brazilian Gois soils and wet zone samples have equivalent depletion orders. It is interesting to note that Mg is less depleted than K in the Amazon Bauxite. Identical changes are observed in Sri Lankan soils when the highly weathered wet zone sw-lowland sequences are considered.

Sr and Ba are also significantly depleted in the wet zone (Table

Fig. 4.1A. Distribution of elements in Sri Lankan soils relative to crustal abundances (CA)

Fig. 4.1B. Distribution of elements in Sri Lankan soils relative to Amazon Soils

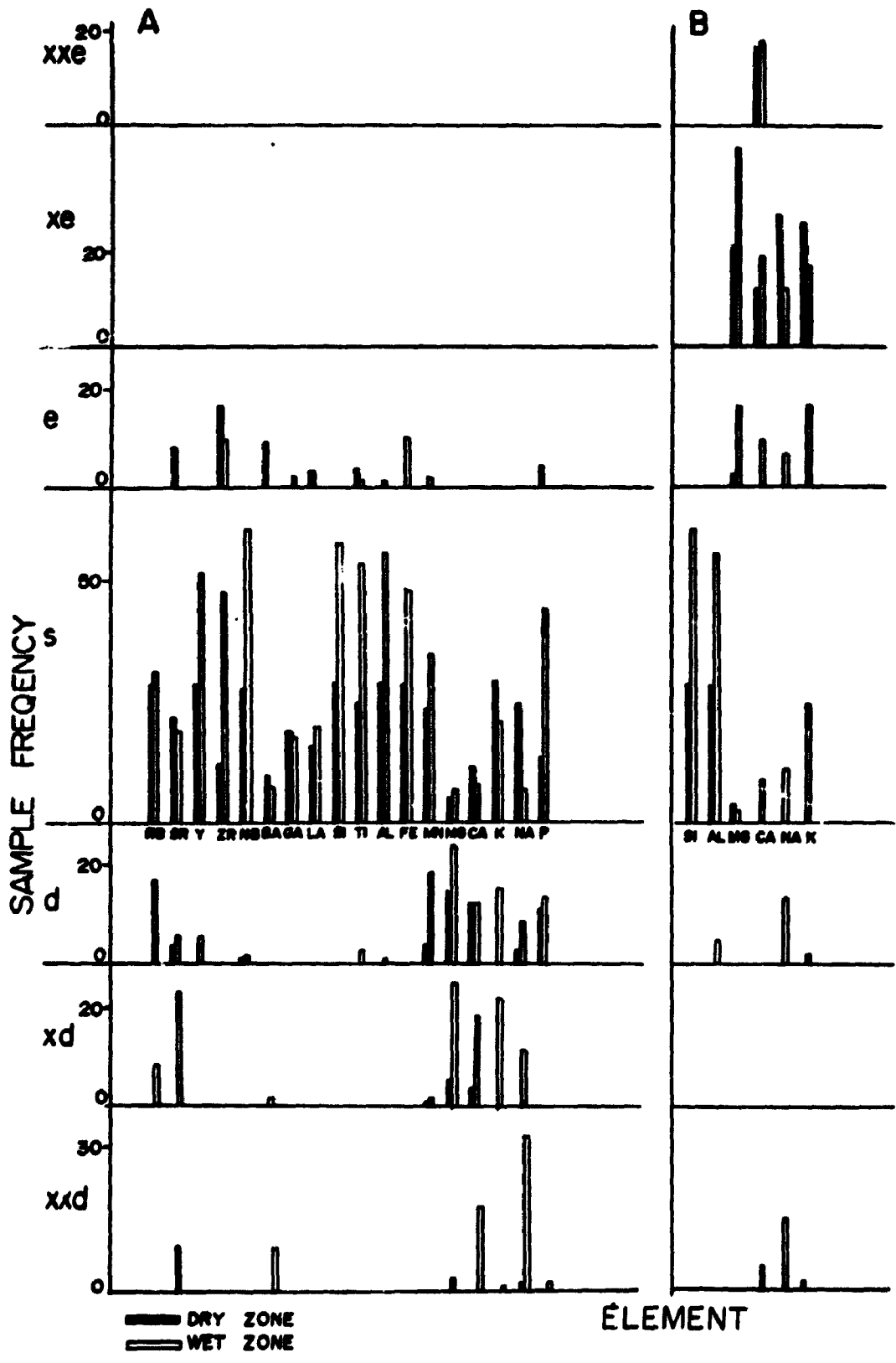


Table 4.3A. Geochemical Status of Sri Lankan Soils relative to Crustal Abundances (CA)¹

Element	xxd	xd	d	s	e	xe	xxe
<u>Wet and Intermediate Zones</u>							
Rb		16 ² (9) ³	31(18)	53(31)			
Sr	17(10)	41(24)	10(6)	31(18)			
Y			10(6)	90(52)			
Zr				83(48)	17(10)		
Nb			3(2)	97(56)			
Ba	47(9)	11(2)		42(8)			
Ga				89(17)	11(2)		
La				100(19)			
SiO ₂				100(58)			
TiO ₂			5(3)	93(54)	2(1)		
Al ₂ O ₃			2(1)	97(56)	2(1)		
Fe ₂ O ₃				83(48)	17(10)		
MnO		3.5(2)	33(19)	60(34)	3.5(2)		
MgO		46(26)	44(25)	11(6)			
CaO	32(18)	33(19)	23(13)	12(7)			
Na ₂ O	55(33)	20(12)	15(9)	10(6)			
K ₂ O	2(1)	38(23)	27(16)	33(20)			
P ₂ O ₅	3(2)		23(14)	73(44)			

¹ Fairbridge (1972)

xxd = <.01 CA xd = .01 - .1 CA d = .1 - .3 CA

s = .3 - 3 CA e = 3 - 10 CA xe = 10 - 100 CA

xxe = 100 - 1000 CA

² percentage frequency to nearest integer of each category

³ frequency, for N=58 (total sample number) except for Ba - La, where N=19

Table 4.3B. Geochemical Status of Sri Lankan Soils relative to Crustal Abundances (CA)¹

Element	xxd	xd	d	s	e	xe	xxe
<u>Dry Zone</u>							
Rb				100 ² (28) ³			
Sr			14(4)	57(16)		29(8)	
Y				100(28)			
Zr				39(11)		61(17)	
Nb				96(27)		4(1)	
Ba				50(9)		50(9)	
Ga				100(18)			
La				83(15)		17(3)	
SiO ₂				100(28)			
TiO ₂				86(24)		14(14)	
Al ₂ O ₃				100(28)			
Fe ₂ O ₃				100(28)			
MnO		4(1)	14(4)	82(23)			
MgO	11(3)	22(6)	54(15)	14(4)			
CaO		14(4)	46(13)	39(11)			
Na ₂ O	7(2)		10(3)	83(24)			
K ₂ O				100(29)			
P ₂ O ₅			45(13)	14(4)			

¹ Fairbridge (1972)

xxd = <.01 CA xd = .01 - .1 CA d = .1 - .3 CA

s = .3 - 3 CA e = 3 - 10 CA xe = 10 - 100 CA

xxe = 100 - 1000 CA

² percentage frequency to nearest integer in each category

³ frequency, out of N=28(total sample number) except for Ba - La, where N=18

Table 4.3C. Geochemical Status of Selected Elements in the Wet Zone SW - Lowland Soils Relative to Crustal Abundances

Element	xxd + xd	d	s	e	xe	xxe
Rb	22 ¹ (9) ²	44(18)	13(31)			
Sr	41(14)	17(6)	0(18)			
Ba	55(11)		0(8)			
MgO	35(26)	20(25)	0(6)			
CaO	38(37)	0(13)	0(7)			
Na ₂ O	33(45)	0(9)	0(6)			
K ₂ O	46(24)	25(16)	0(20)			
P ₂ O ₅		29(14)	23(44)			

1 sw-lowland sample frequency percentage

2 total wet zone frequency under each category out of N=58

Table 4.4 Geochemical Status of Sri Lankan Soils relative to Amazon Soils (AS)¹

Element	xxd	xd	d	s	e	xe	xxe
<u>Wet and Intermediate Zones</u>							
SiO ₂				100 ²			
Al ₂ O ₃			8	92			
MgO				3	28	69	
CaO	8			13	17	32	30
Na ₂ O	26		24	17	12	21	
K ₂ O			3	40	28	17	
<u>Dry Zone</u>							
SiO ₂				100			
Al ₂ O ₃				100			
MgO				11	11	78	
CaO						41	59
Na ₂ O						100	
K ₂ O	7					93	

¹ Kronberg, B.I. (1987)

xxd = <.01 AS; xd = .01 - .1 AS; d = .1 - .3 AS

s = .3 - 3 AS; e = 3 - 10 AS; xe = 10 - 100 AS

xxe = 100 - 1000 AS

² percentage frequency

4.3A) in contrast to Rb, while a fraction of dry zone soils have Sr and Ba enrichment. Within the wet zone, Ba appears much more depleted than Sr, however since the total number of samples analysed for Ba is low meaningful deductions cannot be made.

When Sri Lankan soils are compared to the Amazon soils (Kronberg et al., 1987), the majority of the soils are enriched 10-100 fold in the alkali and alkaline earths (Table 4.4 and fig.4.1A). In fact 50% of dry zone soils and 20% of wet zone soils are enriched by over 100-fold in Ca, the element found to be depleted next to Na in terms of crustal abundances. 60% of wet zone soils are enriched up to 100-fold in Mg, while for K which was the least depleted of the mobile elements compared to crustal levels, enrichment relative to Amazon soils is not as prominent compared to Mg and Ca. This is to be expected since K values are relatively high in the Amazon soils. Surprisingly ~50% of the wet zone soils are depleted in Na in comparison to Amazon soils. In contrast the dry zone soils are uniformly enriched in Mg, Ca, Na and K, by 10-100 times Amazon soils. Si and Al remain virtually the same for all soils.

4.2.1 Variability of Oxide and Element Abundances Within Sequences

Since a detailed geochemical investigation of the soils of Sri Lanka was not available for comparative purposes, it was necessary to understand the reasons for the degree of variation found in the geochemical results. The degree of variation of the individual elements concentrations within a sequence as well as among all the sequences was assessed by studying the coefficient of variation $\{(standard\ deviation * 100) / average\}$ and its mean respectively. Sequence 112 was not included in calculating means, because of anomalous concentrations (Table 4.1) as were individual elements with abundances below detection level.

Table 4.5A Standard Deviation of Element¹ And Major Oxide Analyses

Wet. and Intermediate Zones	Nb	Sr	Y	Zr	Nb	Ba	Ca	La	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	Cr
145-3ss	6.0	-	-	78.0	10.0	n-d	n-d	n-d	8.6	.75	1.84	7.67	.0203	.0273	-	-	.0407	.0244	.0067
145-3ss	7.0	-	-	72.0	15.0	n-d	n-d	n-d	6.8	.89	11.06	9.66	.0151	.1230	-	-	.0736	.0532	.0249
148-4ss	0.5	-	2.2	92.1	2.4	17.5	4.7	19.2	5.1	.20	.93	4.72	.0058	.1668	-	-	.0096	.1634	n-d
148-6ss	3.1	-	3.8	103.1	4.5	14.3	11.7	21.6	11.8	.53	9.75	9.68	.0105	2.103	-	-	.0636	.1367	n-d
142-3ss	6.0	-	6.0	40.0	12.0	n-d	n-d	n-d	6.0	.26	4.53	1.13	.0063	.1066	.0641	-	.0663	.0061	0
49-3ss	6.0	-	10.0	90.0	15.0	n-d	n-d	n-d	7.2	.34	4.01	3.14	.0138	.0816	.0005	-	.0573	.0307	.0068
71-3ss	0	6.0	6.0	40.0	15.0	n-d	n-d	n-d	1.2	.21	1.30	.84	.1494	.0461	.0328	-	.0328	.0922	.0004
63-3ss	0	55.0	6.0	78.0	15.0	n-d	n-d	n-d	3.7	.14	3.21	.78	.0072	.2123	.4958	-	.1154	.0131	0
123-3ss	6.0	32.0	-	84.0	13.0	n-d	n-d	n-d	2.2	.08	3.52	.12	.0085	.4202	2.661	2.489	.5158	.0178	.0006
123-4ss	5.0	28.0	-	142.0	10.0	n-d	n-d	n-d	2.3	.07	2.88	.70	.0079	.1104	.5097	.0345	.4430	.0500	.0071
125-3ss	10.0	35.0	-	45.0	10.0	n-d	n-d	n-d	4.3	.04	2.96	1.57	.0399	.6016	.6685	.1750	2.561	.0500	0
61-3ss	6.0	26.0	0	141.4	8.7	13.9	6.6	35.8	3.0	.39	1.24	.25	.0079	.6016	.4626	.098	.0254	.0371	0
153-6ss	1.2	-	6.8	94.6	8.2	15.2	4.4	5.3	2.8	.32	3.91	6.32	.0232	.4004	.0631	.044	.0371	.041	n-d
153-5ss	1.3	-	7.0	79.0	06.0	n-d	n-d	n-d	0.4	.24	0.57	.59	.0105	.0797	1.1145	.0259	.0223	.0115	.0122
147-3ss	10.0	67.0	17.0	10.0	10.0	n-d	n-d	n-d	0.4	.02	1.12	.37	.0120	2.139	.5423	.1866	.0090	.0125	.0106
115-3ss	6.0	6.0	4.5	52.1	2.0	61.2	2.1	7.0	2.5	.25	.45	.74	.0252	.204	.1332	.0981	.5027	.0416	n-d
88-4ss	11.1	93.9	4.4	233.8	5.8	175.4	3.2	9.6	1.1	.43	3.34	.41	.1145	.0311	.6022	.5465	.8382	.0173	n-d
112-4ss	19.5	-	-	-	-	-	-	-	6.1	-	-	-	-	-	-	-	-	-	-
Dry Zone																			
16-4ss	2.8	63.4	1.0	44.2	3.0	68.8	2.7	13.0	4	.20	.60	.13	.005	.0299	2.387	.3001	.0263	.0457	n-d
131-4ss	20.1	11.2	2.5	188.2	0.5	51.8	2.4	14.3	.9	.04	.66	.56	.0655	.1605	2.282	.6309	2.466	.01	n-d
90-3ss	12.0	6.0	17.0	191.0	06.0	n-d	n-d	n-d	1.3	.08	.63	.37	.0419	.0704	.1949	.1688	.0452	.0418	n-d
99-4ss	17.0	109.5	1.5	168.6	4.6	187.7	1.4	8.5	4.6	.34	1.59	.81	.0310	.1374	.3003	.9475	.6358	.0222	n-d
139-3ss	15.0	25.0	6.0	577.0	26.0	n-d	n-d	n-d	0.9	1.01	.80	.77	.0632	.0061	.0244	.1085	.2224	.0002	.006
104-3ss	32.0	292.0	10.0	110.0	0.0	n-d	n-d	n-d	2.8	.21	.57	.44	.0278	.1686	.9371	1.2893	1.3167	.0595	0

¹ ppm values

The second objective in calculating the mean coefficients of variation was (Table 4.5A and B) to quantify the observed partitioning of elements into categories in fig. 4.1. The extent of concentration or depletion of an element during chemical weathering will be reflected in a high degree of variation between levels, within a sequence from which inter-relationships between elements can be deduced. It appears that elements confined to one category in fig. 4.1, Si, for example, have low mean coefficients of variation (Table 4.5B), whereas elements distributed among the many categories, for example Ca, and Na have high mean coefficients of variation. Detailed analysis of the coefficients is given in Appendix 5.

4.2.1.1. Variation of Si, Ti, Al and Fe

The least variation among all sequences for wet and intermediate zone soils is observed in Si abundances, from among the relatively immobile major elements Si, Al, Fe and Ti, reflected in the mean value of the coefficient of variation of 8.69 (Table 4.5 B) . In comparison, Ti, Al and Fe have a higher degree of variability, shown by the mean values of 17.83, 14.4 and 16.86 respectively for wet zone and intermediate zone soils. Dry zone soils have surprisingly similar variation patterns in terms of the ordering in the degree of variation ($Si < Al < Fe < Ti$). The degree of variability (expressed by the mean coefficient of variation), is however, much lower for Si and Al in contrast to Ti, in the dry zone soils. This is also expressed in fig. 4.1A where Al, Si and Fe are confined to one category (category s), whereas Ti is not.

4.2.1.2 Variability of Some Trace Element Concentrations Within Sequences

It is surprising that the two elements Y and Nb, and Ga (where determined), differ by less than three orders of magnitude in

Table A-58 Coefficient of Variation of Element And Major Oxide Analyses

	Rb	Sr	Y	Zr	Nb	Ba	Ga	La	Si	Ti	Al	Fe	Mn	Mg	Ca	Nb	K	P	Cr
<u>Wet and Intermediate Zones</u>																			
145-3es	26.7	-	-	35.5	25.0	n-d	n-d	n-d	20.6	34.0	7.8	26.0	57.8	15.2	138.64	86.7*	38.6	27.2	10.1
145-5es	35.4	-	-	38.9	44.6	n-d	n-d	n-d	17.2	40.5	37.9	34.0	45.2	51.4	131.5*	82.3*	66.4	43.5	50.3
149-4es	6.6	-	28.6	18.3	9.3	n-d	11.5	43.0	25.6	15.1	4.2	19.2	23.1	31.4	-	-	9.3	105.4	n-d
149-6es	34.6	-	44.5	21.8	16.1	n-d	24.5	62.4	9.1	32.7	34.2	42.0	42.0	36.8	-	-	67.1	112.4	n-d
142-3es	15.7	-	24.7	12.8	49.5	n-d	n-d	n-d	10.3	19.3	21.0	11.0	15.2	21.4	58.4	-	12.7	8.1	n-d
49-3es	21.7	-	50.0	30.4	34.6	n-d	n-d	n-d	2.1	30.3	24.6	25.9	45.7	60.2	2.2	-	34.7	25.5	22.8
71-3es	0	21.7	34.6	11.7	41.7	n-d	n-d	n-d	6.5	11.4	5.3	5.6	32.3	12.0	43.3	69.4*	29.0	7.3	1.0
63-3es	0	33.1	64.8	14.7	49.5	n-d	n-d	n-d	3.6	7.5	13.5	1.1	4.3	19.2	30.3	74.3	28.5	7.3	n-d
123-3es	15.7	-	-	27.9	41.7	n-d	n-d	n-d	3.6	7.1	15.7	6.7	16.4	63.4	64.2	72.4	56.4	8.1	1.2
123-4es	13.3	-	-	27.4	36.9	n-d	n-d	n-d	3.6	6.8	12.8	1.1	18.1	77.4	81.1	80.1	52.4	25.6	16.0
125-3es	20.0	-	-	35.9	33.3	n-d	n-d	n-d	7.4	2.8	12.4	11.2	55.6	16.0	110.7	89.3*	22.9	65.3	n-d
61-3es	9.1	5.2	0	20.2	34.6	n-d	n-d	n-d	4.9	3.9	5.9	2.6	3.1	38.7	18.2	69.7	6.0	14.5	n-d
153-6es	19.1	-	31.5	34.2	29.4	n-d	14.2	56.4	16.8	30.6	14.9	44.1	44.8	46.6	62.0	-	53.9	40.5	n-d
153-5es	21.0	-	34.1	25.7	26.0	n-d	10.0	10.8	4.7	23.8	8.0	22.6	49.8	52.2	70.4	-	38.1	63.6	n-d
147-3es	25.0	8.8	57.7	16.5	21.7	n-d	n-d	n-d	3.5	22.0	12.0	16.9	32.6	11.4	15.4	10.0	3.7	12.8	33.9
115-3es	6.0	3.9	9.2	2.5	50.0	n-d	n-d	n-d	3.1	2.3	11.7	9.6	32.6	40.4	38.0	23.7	3.8	18.5	49.8
88-4es	12.0	8.4	53.6	25.3	12.4	11.2	8.3	19.5	1.9	13.6	3.1	4.2	17.3	6.5	6.6	133.8*	11.6	31.1	n-d
112-4es	85.6	113.1	53.6	88.9	64.8	23.6	27.2	37.4	7.1	70.6	38.1	12.5	46.7	14.5	103.4	168.8	92.1	115.5	n-d
mean	16.5	26.9	35.0	23.5	32.7	8.7	17.8	17.9	8.7	17.8	14.4	16.9	35.3	35.3	46.2	48.4	31.5	47.2	11.5
N	17	8	9	17	17	17	17	17	17	17	17	17	17	17	13	6	17	17	17
<u>Dry Zone</u>																			
16-4es	3.9	4.7	3.3	5.7	7.1	3.3	10.8	11.3	.6	5.4	3.6	1.3	3.2	1.8	7.2	13.0	1.0	4.7	n-d
131-4es	13.8	5.1	10.3	23.8	5.7	10.3	10.1	41.2	1.4	6.0	4.3	9.2	49.4	15.3	12.0	48.6	7.4	22.2	n-d
90-3es	15.1	4.0	43.3	36.1	43.3	n-d	n-d	n-d	1.7	14.7	5.9	10.1	37.1	10.2	18.1	13.1	2.5	40.8	n-d
99-4es	18.3	35.2	6.6	35.7	28.5	16.2	6.4	14.1	6.1	38.5	12.1	18.5	65.2	29.2	44.2	41.2	18.1	38.6	n-d
139-3es	12.4	15.4	17.3	35.1	52.9	n-d	n-d	n-d	1.2	51.8	7.5	32.0	43.9	17.8	3.2	5.0	5.5	34.9	n-d
104-3es	33.3	77.4	50.0	38.7	0	n-d	n-d	n-d	3.7	40.0	4.0	17.9	87.8	32.8	65.5	61.9	52.0	65.0	n-d
mean (N=6)	16.1	23.6	21.8	32.5	22.6	2.5	26.1	6.2	2.5	26.1	6.2	14.8	17.9	17.9	25.0	28.3	14.4	24.4	

* elements with abundances near detection limit not used for calculating mean
n-d element content not determined
- elements with abundances below detection limit

abundance relative to their parent rocks unlike Sr or Zr (Table 4.1). In this respect the results agree with those of Pendis et al., (1984) who note that especially for the trace element Nb which has a low crustal abundance (20 ppm) variation in global soil abundances is minimal. However in terms of the coefficient of variation for individual sequences, significant differences are noticed. Y coefficients are high and result from depletion whereas Nb coefficients appear to result from enrichment since abundances are well above detection limit. In fact Nb coefficients are larger than Zr and Ti in the wet zone, and equal in magnitude to Ti coefficients in the dry zone which in turn are both smaller than Zr.

Zr abundances are more variable than Ti (which had the highest variation among the resistate oxides) as expected of an immobile element, though it is lower than some of the mobile element coefficients, in both climatic zones (and Nb in the wet zone) when the mean coefficients of variation are considered .

The contrasts and comparisons in the coefficients between dry and wet zone soils is in itself significant since they reflect directly on the geochemical status of the soils relative to crustal abundances. However the preceding detailed examination of the differences in element concentration between levels suggests that the numerical value of variation in abundances observed, results (especially for the mobile elements) from many possible causes in addition to being simply the result of concentration or depletion during chemical weathering;

They could result from :

- o uneven interval differences between levels of the sampling design
- o unusual abundance or depletion levels in a single level (especially in the top most level as a result of plant interaction)
- o instrumental errors when abundances are close to detection limits

However the analysis of coefficients provides valuable insight on element geochemistry, by magnifying and thereby forcing attention on the nature of the differences that exist between levels in element abundances. Their significance is discussed in section 4.3.

4.3 Significance of the Geochemical Variation and Relevance to Further Geochemical Studies

To quantify the changes involved in soil formation in Sri Lankan soils an index element or suite of index elements has to be identified. Detailed reviews of published early literature on quantitative pedogenesis are found in Barshad (1965), Brewer (1964) and Hutton (1977). Most studies have used only one stable constituent often Zr (Chittleborough et al., 1984). SiO_2 and ZrO_2 have been preferred over TiO_2 because of demonstrated mobilisation of Ti during pedogenesis (Sudom and St.Arnaud, 1971; Bourne and Whiteside, 1962; Muir and Logan, 1982; Smeck and Wilding, 1980). Ti has been chosen over zircon on many occasions, because of its greater abundance and more even distribution in soils compared to zircon (Nesbitt, 1979). SiO_2 was chosen for the same reason. Inertness of SiO_2 was assessed by its unvarying distribution with depth. That this argument is incorrect is demonstrated below. Complete reliance on literature was avoided since an element range from Si and Al to Zr, Y and Ti and acid residue have been used, in many instances without sufficient justification. The trends indicated in abundance and element variation studies are assessed accordingly. In addition the Sri Lankan soils constitute a complex case-study because of the sampling design that encompassed a variety of soils.

If an element remains relatively immobile during weathering, it is self-evident that enrichment will be inevitable and variation within the sequence for the element will be relatively high (Krauskopf, 1967). Hence elements that show very low variability as in

Si, in the sequences studied are unlikely to have remained immobile. On the other hand elements that show extreme variability such as the alkalis and alkaline elements both major and trace are unlikely to have remained immobile, as demonstrated by their highly depleted geochemical status observed relative to crustal abundances. This limits consideration to 5 elements, Al, Fe, Ti, among the major elements, Nb and Zr among the trace elements. Nb has low elemental abundances (Table 4.1) and errors are likely in their determination. It is well established that Al and Fe have much higher solubilities than Ti and Zr, which an examination of river waters indicate. According to Drever, (1982) the corresponding solubilities are: Al 50 ppb, Fe 40 ppb, Ti 10 ppb; Relative mobility and fractionation of Al and Fe in addition to other elements can be demonstrated (Appendix 6) for the two most highly weathered laterite sequences in this study, sequences 145 and 148. Hence they are considered unlikely candidates as indices for mass balance studies.

The two remaining elements, Ti and Zr, are considered to remain within the soil sequence, even if dissolution takes place especially in the case of Ti bearing primary minerals, by reprecipitation as stable oxides and or hydroxides, that transform to stable mineral forms in soils where the pH remains above 5 (Kabata-Pendias and Pendias, 1984; Hutton, 1977; Tole, 1984; Craig and Loughnan, 1964). However according to Craig and Loughnan, (1964), if Ti is released from ferromagnesium minerals in the form of $Ti(OH)_4$, (solubility product 1.61×10^{-38} as opposed to 10^{-40} for $Ti(OH)_3$), in soils where the pH is between 4 - 5, movement of Ti relative to Al is a distinct possibility. It is noted that in the laterite sequences soil pH range in water is between 4-5 hence even Ti may not be stable. Another question that arises regarding the use of either of these elements as index minerals is that of the degree of dependence that can be placed in assuming even distribution of primary minerals in the parent rock, especially in a terrain that consisted of rocks that had a well developed gneissic texture. The need to develop a

technique to differentiate whether, for example, concentration trends of these two elements is a result of true enrichment or whether it is the result of original inhomogeneity within the rock becomes imperative. Ti has been chosen over zircon on many occasions, because of its greater abundance and more even distribution in soils compared to zircon (Nesbitt, 1979; Schorin and Puchelt, 1987).

4.4 Mass Balance Calculations: Initial Studies

Zr/Ti ratios will be constant through a profile if both elements have remained immobile, assuming that the horizons resulted from the same precursor. However Norton and Hall (1988) quote instances where Zr/Ti ratios have remained uniform across stratigraphic discontinuities. A similar check was carried out in this study for Ti and Zr immobility, assuming parent material homogeneity. Nb/Ti plots were used for comparison.

Since element:Ti plots encompass information on mineral transformation (Nesbitt et al., 1980) an analysis of all elements:Ti ratios was also carried out and detailed in Appendix 4.

Several significant results emerged. Progressive decrease of the y-axis values in figs. 4.2 A-E from dry to wet zone sequences (from 12.0 - 6.0) indicate depletion of cations Mg to K relative to Ti. Retention of Mg is highlighted more strongly than in section 4.2, compared to K, Na and Ca in the most weathered samples of the wet zone (fig. 4.2 A). This is compatible with results from Kronberg (1987, fig. 4) and Rimkus (1987) when Amazon bauxites were compared with less weathered sequences. K dominates in the dry zone soils (fig. 4.2 D). The complex pattern of variation between the climatic zones appear to reflect soil mineralogy and changes in composition. For example the dominance of K in the dry zone reflects the persistence of resistant K-feldspars in this granitoid terrain, compared to

Fig. 4.2 A-B. Changes in alkalis and alkaline earths relative to TiO_2 in Wet Zone sequences.

Fig. 4.2 C. Changes in alkalis and alkaline earths relative to TiO_2 in less weathered Wet and Intermediate Zone sequences.

Fig. 4.2 D-E. Changes in alkalis and alkaline earths relative to TiO_2 in Dry Zone sequences.

Sample depth increases to the right for each sequence.

FR = Fresh rock

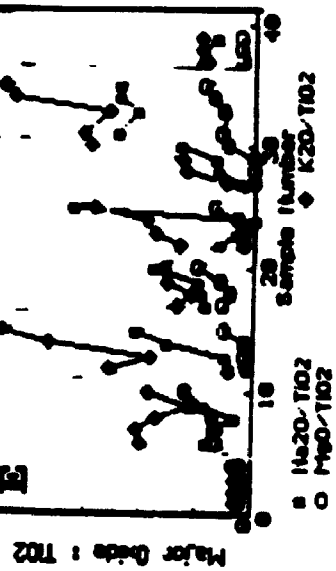
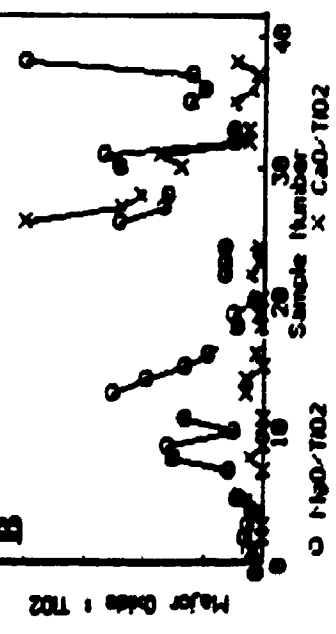
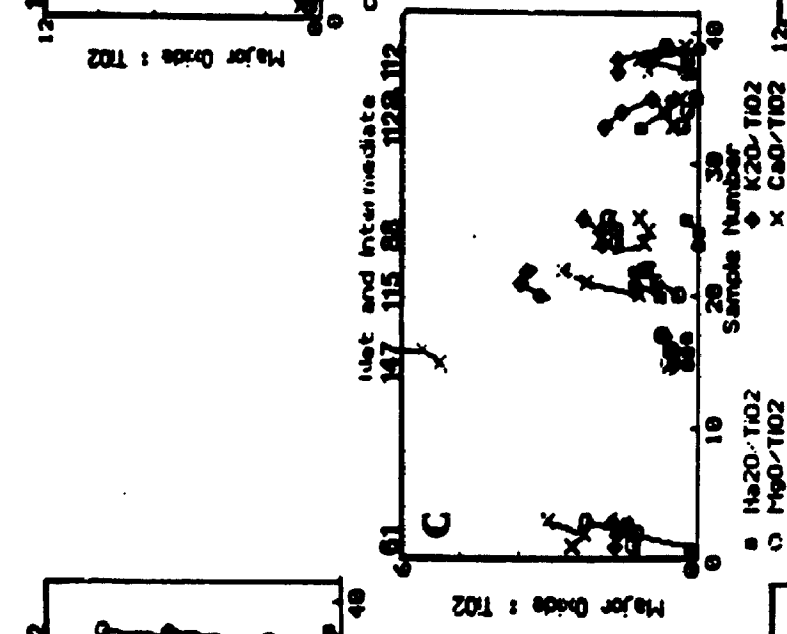
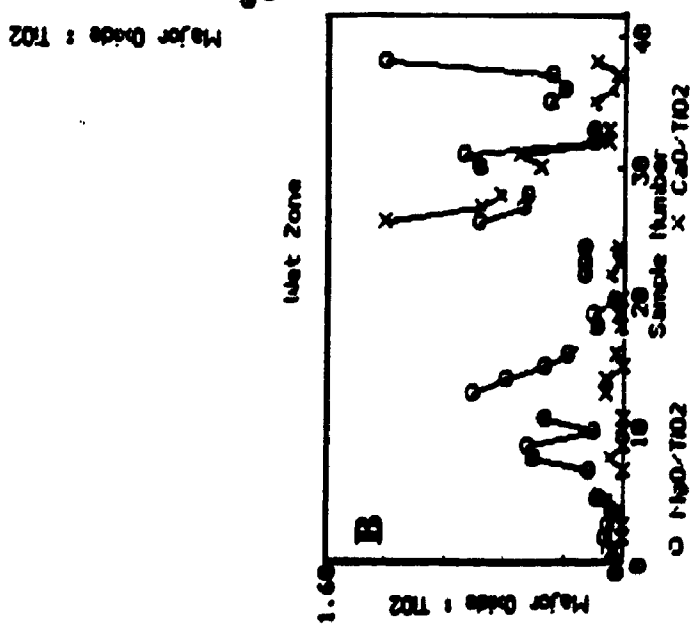
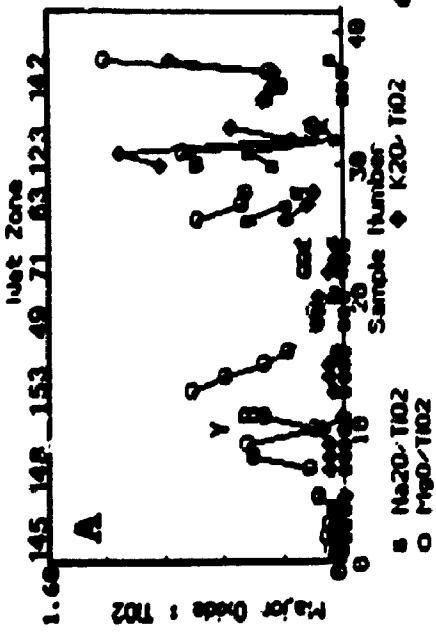


Fig. 4.3 A. Changes in aluminium(Al) and Iron(Fe) relative to TiO₂ in Wet Zone sequences.

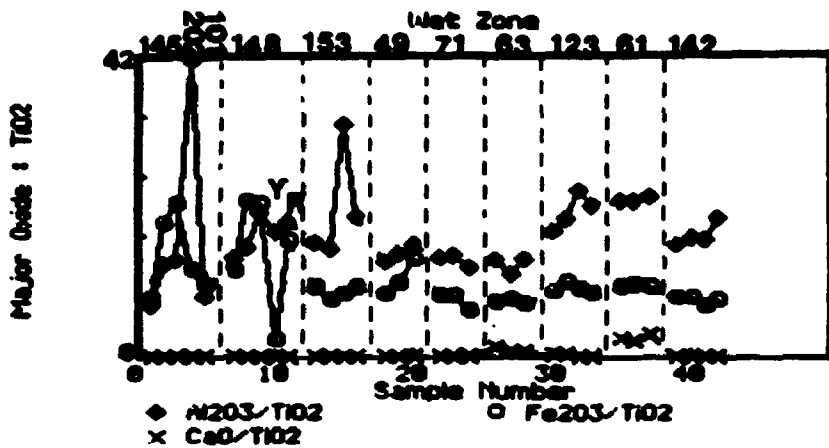
Fig. 4.3 B. Changes in aluminium(Al) and Iron(Fe) relative to TiO₂ in less weathered Wet and Intermediate Zone sequences.

Fig. 4.3 C. Changes in aluminium(Al) and Iron(Fe) relative to TiO₂ in Dry Zone sequences.

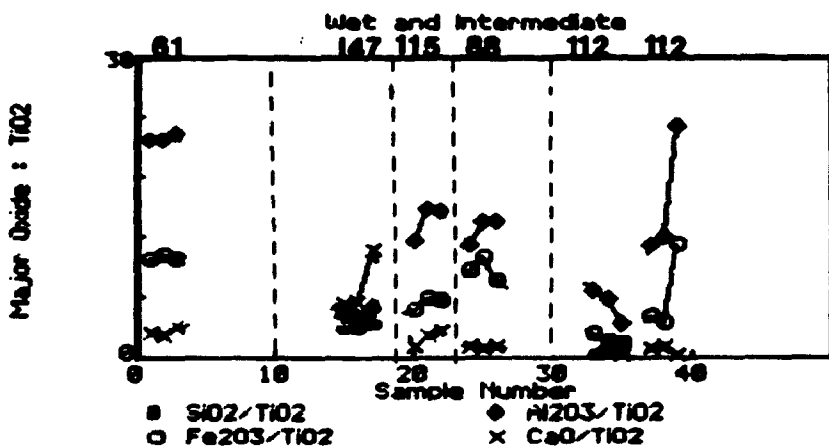
Sample depth increases to the right for each sequence.

FR = Fresh rock

(A)



(B)



(C)

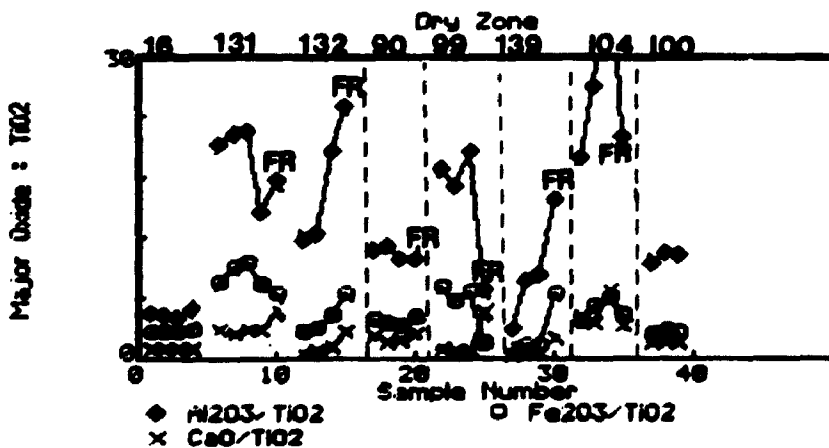


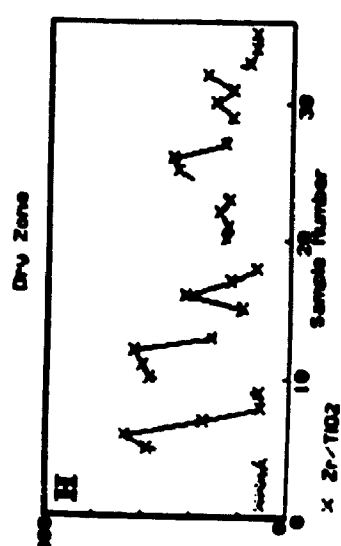
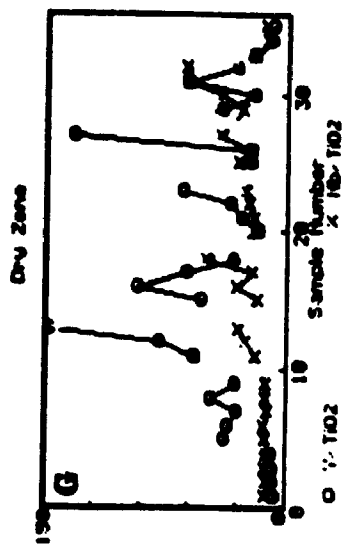
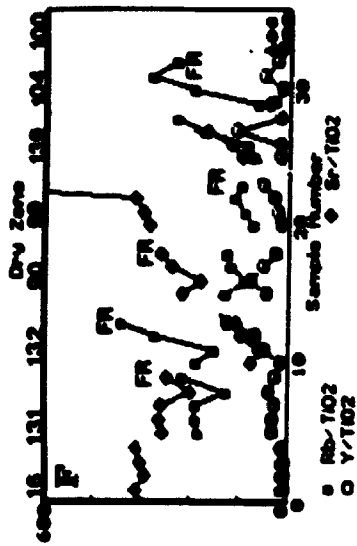
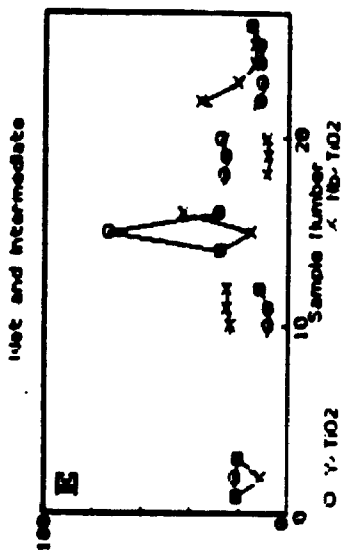
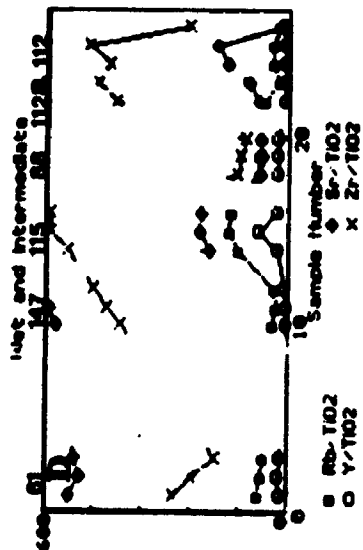
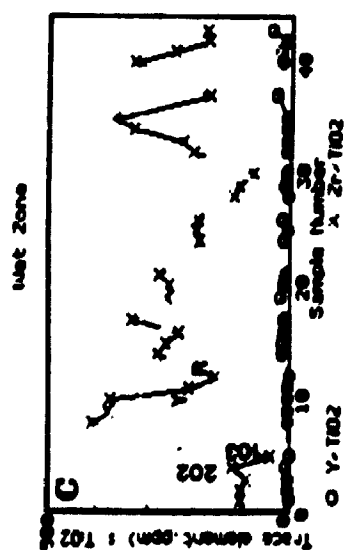
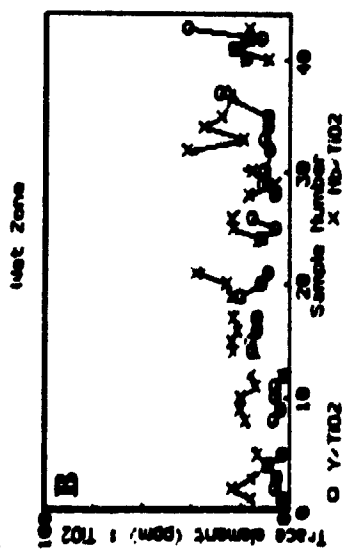
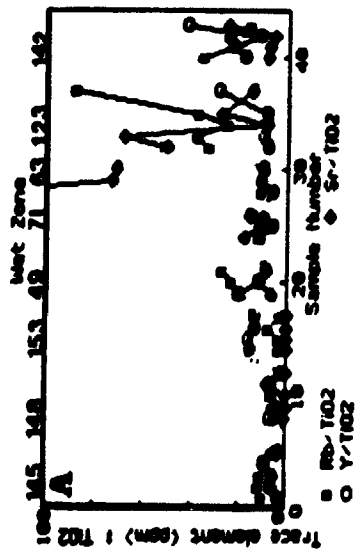
Fig. 4.4 A-C. Changes in trace elements relative to TiO_2 in Wet Zone sequences.

Fig. 4.4 D-E. Changes in trace elements relative to TiO_2 in less weathered Wet and Intermediate Zone sequences.

Fig. 4.4 F-H. Changes in trace elements relative to TiO_2 in Dry Zone sequences.

Sample depth increases to the right for each sequence.

FR = Fresh rock



Plagioclase. Similarly higher Mg content in the laterites suggest a change in mineralogy when primary minerals become unavailable. It is possible that Mg enrichment is concomitant with Fe enrichment during lateritisation.

Significant variation obtains in the deeper horizons in Al and Fe (sequence 145 levels 202 and 101, fig. 4.3 A) and is indicative of a compositional discontinuity as discussed in section 4.3.

Nb/Ti plots are more uniform compared to Zr/Ti plots (e.g. see figs. 4.4 B and C). The non-uniformity of Zr plots implies lack of simultaneous enrichment with Ti during weathering and is reason for much concern. Either the parent material is not homogeneous or Ti and Zr are not behaving similarly geochemically. An independent check using statistics was made to discern if Ti and Nb constitute a more suitable choice. While details of the statistical treatment are to be found in Appendix 4, section 4-2, results are summarised in Table 4.6.

4.4.1 Check on Choice of Suitable Index Element with Statistical Methods

High positive correlation between elements can be (i) process related, ie. can result from similar behaviour either depletion or enrichment from both physical and chemical processes, or, (ii) they can result from persistent association of an element pair within resistant minerals - Ti and Nb in rutile, for instance. An example of (i) would be enrichment of Zr and Ti through the sequence even though the elements originate and reside in minerals drastically different from one another. Ti derived from ferromagnesian minerals and resistant minerals is transformed and retained in oxyhydroxides and persistent resistant minerals whereas Zr usually occurs in Zircon and remains in Zircon within the heavy mineral suite. According to Wadehol (1978), the close association of Nb and Ti has long been recognised and a good correlation between Nb+Ta and Ti in rock forming

minerals as well as in bauxitic minerals, both residual and clay types, exists. Its geochemical behaviour is similar to Ti in that it occurs in ferromagnesium host minerals that release it during weathering to be absorbed onto clays, in addition to occurring in resistates such as Ti-minerals. A depletion order of $Si > Nb > Al = Fe$ is reported.

Some of the salient correlations relevant to the primary objective of the statistical analysis are summarised in Table 4.6. A high degree of index variability for a given pair is apparent among the groups. Ti, Al and Fe are positively correlated among one another in the wet zone where a more advanced stage of weathering prevails than in the dry zone. While Al - Fe are correlated in both zones, a negative correlation obtains between the pair in the ultra Group of the wet zone (the laterites) as observed in the Venezuelan bauxite profile (Schorin and Puchelt, 1987). In this group, surprisingly, Zr is correlated with Si.

The three elements Zr - Ti - Nb are well correlated only in Dry Zone Group 1 sequences where, as noted in Appendix 4, section 4-2, other strong correlations prevail. Ti and Zr have high correlation values only in this group. Ti correlation is more positive with Nb than Zr in most groups. Imasuen (1987) obtained the same high correlation between Ti - Nb ($r = .8$), -the highest for an element pair with Ti-, for Nigerian tropical soils, even though in that study no attempt had been made to calculate separate indices for soils sampled from three different climatic zones. Strong correlation between Zr-Ti, was absent ($r = .57$) as was any correlation of equal magnitude between Ti and any of the elements common to this study, other than Nb. In the present study also, near zero correlations occur between Zr - Ti in all groups except in dry zone Group 1 sequences and in the most weathered laterite group (ultra) in the wet zone where it turns negative (Table 4.6).

Table 4.6. Correlation Indices of Selected Element Pairs

	Ti-Zr	Ti-Nb	Ti-Al	Ti-Fe	Ti-P	Zr-Nb	Zr-Si	Zr-Al	Al-Fe	Al-Nb	Nb-P
Dry Zone - Group 1	.8571 ¹	.8880	-.1209	-.2527	-.5703	.7995	-.5604	-.0385	.2967	-.1217	-.4874
Dry Zone - Group 2	.0396	.3882	.1034	.1386	.6671	-.2378	-.0399	.5648	.5385	-.3711	.6093
Dry Zone	.4671 (.4116) ²	.7460 (.7681)	.3747 (.3533)	.4459 (.6910)	.4428 (.8676)	.3298 (.6279)	-.2958 (-.0980)	.2040 (-.0727)	.7039 (.6894)	.0712 (-.0137)	.3486 (.4205)
Wet Zone	.0177	.5401	.6033	.6296	.4235	.3083	.2198	-.1658	.6000	.3700	.3506
	(.1452)	(.5469)	(.5907)	(.5217)	(.4364)	(.3410)	(.1723)	(-.1665)	(.5585)	(.3533)	(.3605)
Wet Zone - Group 1	.0503	.4975	.5316	.5235	.2336	.1944	.1616	-.1158	.3492	.2853	.2315
Wet Zone - Group 2	.1342	.3732	.6488	.7596	.8687	.7410	-.1762	-.2341	.7750	-.1150	.5190
Wet Zone - Ultra	(-.2944)	(.8123)	(.0282)	(.0907)	(-.0092)	(-.1235)	(.6673)	(-.2495)	(-.4898)	(-.3915)	(-.0275)

1. Spearman's rank correlation indices

2. EMP Distance correlation indices (within brackets)

Dry Zone-Group 1: 99, 90, 139 (mmInJy)

-Group 2: 104, 100, 131, 132

Wet Zone-Group 2: 112, 115, 147

-Ultra: 145, 148

The features that are of interest are: the difference in type of element pairs with high correlation between the two climatic zones, especially that of the Al- Ti- Fe association in the wet zone compared to the strong correlation between Fe-Mg, Ca-Mg, Ti-Nb pairs in the dry zone; the greater number of strong correlations present in dry zone Group 1 and wet zone Group 2 samples; the unique correlation in the laterite (ultra) group between Si-Zr, AL-Fe and Ti-Nb; and the overall lack of strong correlation between Zr-Ti.

The negative correlation between Fe and Al found only in the laterite group (Table 4.6) is likely both a reflection of the Fe and Al enrichment observed in successive zones as discussed in Appendix 6 and also of their existence as two separate oxides at this stage of weathering, in contrast to their association in primary minerals as in biotite that appears to be reflected in the high positive correlation Fe and Al in the dry zone. A similar process related relationship between Zr and Ti may be operative in the laterite sequences. The negative correlation between Zr-Ti in this group combined with the positive correlation between Zr-Si suggest that at this stage of weathering, these correlations result from the difference in physical processes acting on Zr and Ti (Nesbitt, H.W., 1987, pers. comm.). Zircon and quartz possibly accumulate in the upper 100cms, to give a quartz rich zone as observed in xrf results, because Ti, and even possibly Al and Fe bearing oxyhydroxides are likely eluviated or leached out, in these sequences where the pH in soils agitated in water is between 4-5.

In most of the other groups the indices may reflect changes in mineralogy, ie. changes in terms of element associations in minerals more than process related associations caused by element enrichment or depletion as was expected from this study. This was deduced from the good correlations observed in dry zone Group 1 sequences where primary minerals are abundant, and from the contrast in type of correlated pairs between the wet and dry zone soils. For example the Ca - Mg

association in the dry zone is not observed in the wet zone (Group 1 and ultra group). This is likely a reflection of their association in primary minerals that occur in the dry zone, which are absent in the two highly weathered wet zone groups. If behavioural associations were reflected, then, since both these elements are lost during weathering they should still give high positive correlations in the wet zone. Similarly the positive correlation between Ti - Nb is likely a reflection of their association in a mineral that is resistant to weathering as it is prominent again in the laterite sequences (Table 4.6) even though a process related correlation cannot be ruled out. Hence the near zero correlation between Ti - Zr obtained in this study in most of the Groups, is possibly indicating that they are not process related ie. simultaneously enriched, in most of this sample suite.

4.4.2 Discrimination of Sequences With and Without Genetic Horizons

Because of the wide variation of element abundances observed within sequences, it is also necessary to screen horizons within a given sequence to check if they are genetically related, prior to quantifying changes taking place during weathering. Numerous recent soil genesis studies have been concerned with establishing parent material uniformity. Ti/Zr ratios have often been used but these ratios have been known to remain constant across stratigraphic boundaries (Norton and Hall, 1988). The premise used in this study for sequence discrimination is as follows:

If a sequence of horizons is derived from the same parent material, and if two elements X and Y are considered to be conserved, then, as a result of progressive enrichment of X and Y during weathering, the ratio Y_n/X_n will remain a constant, equal to that of the parent Y/X ratio

$$\text{ie. } \frac{Y_n}{X_n} = m \text{ (where } m \text{ is a constant) } \dots\dots\dots(1)$$

and a plot of X_n vs. Y_n (where $n=1,2,3\dots n$) will result in a linear array that passes through the plot of the fresh rock. The expression for the linear array will belong to the general class

$$Y = mX + C \dots\dots\dots(2)$$

In addition to being a linear array, the plot of X vs. Y has to pass through the origin, if the sequence of horizons are genetically related. The argument follows:

Rearranging eq. (1) gives

$$Y_n = mX_n$$

Comparison with eq. (2) shows that for Y_n/X_n to remain a constant, the term C in eq. (2) has to equal 0.

if 'C' of equation 2 is not equal to 0,

$$Y_n = mX_n + C.$$

$$\frac{Y_n}{X_n} = m + \frac{C}{X_n}$$

Then C/X_n will depend on X_n and Y_n/X_n will not remain constant through all the horizons of a given sequence. Hence the graph must pass through the origin.

Consequently a fan of lines as represented in fig. 4.5A that pass through the fresh rock and the origin can be generated to represent all possible types of parent rock and their weathering profiles consisting of genetically related horizons, if provided that X and Y remain immobile. Sequences originating from basic rocks will result in a linear array with a small positive slope, since Ti is abundant relative to Zr, are prevalent, whereas sequences from acidic rocks will have large positive slopes since Zr is abundant relative to Ti.

Thus two important conditions have to be met to prove a genetic relationship between horizons and parent rock.

- a. A plot of two immobile elements of a sequence of horizons must form a linear array, that includes the fresh rock.
- b. The extension of the line through the fresh rock must pass through the origin of the graph.

The importance of appreciating that both conditions as set out need to be met to establish genetic relations will be seen when the consequences of (i) contamination, (ii) inadequate sampling especially of inhomogeneous parent material, and (iii) preferential enrichment by translocation of amorphous material containing either X or Y from horizons, are discussed.

The consequences of contamination of selected horizons by extraneous elements other than X and Y, results in dilution, that

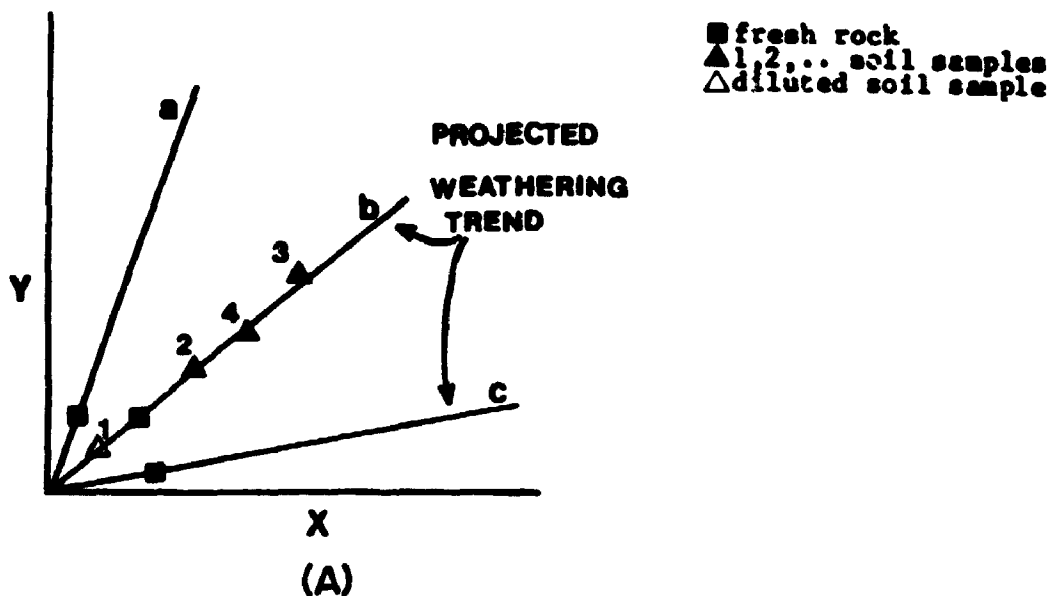


Fig. 4.5 A. Projected weathering trends derived from (a) acidic to (c) mafic rocks; (b) Weathering trend resulting from contamination.

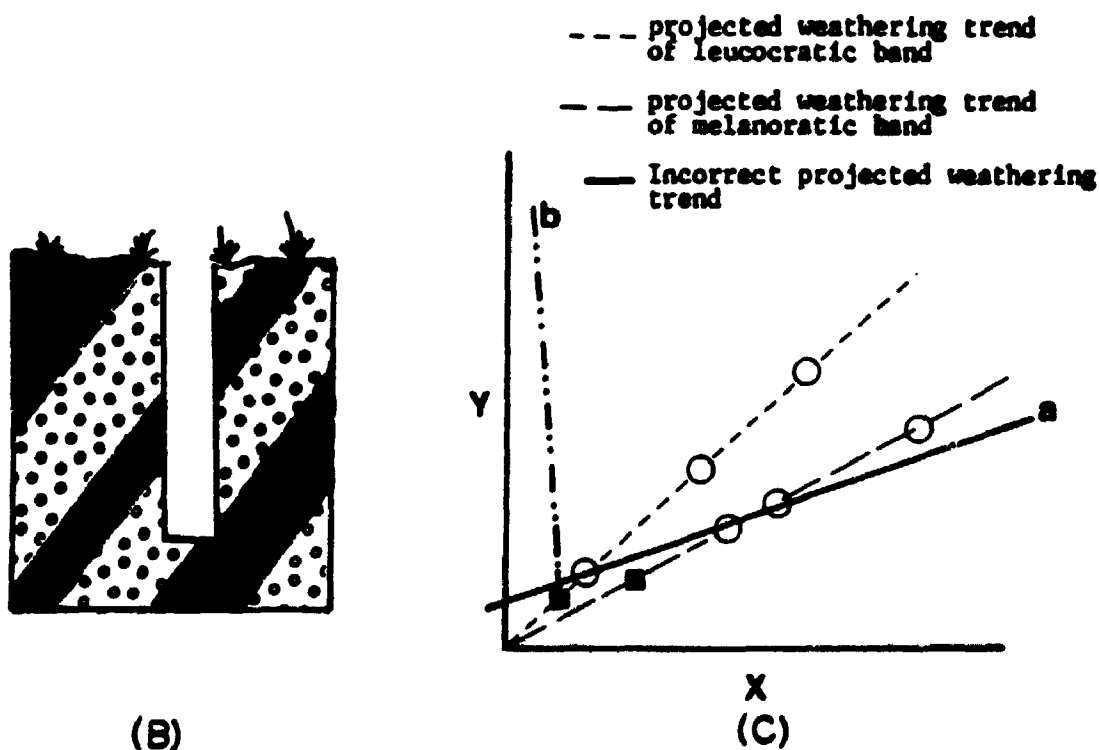


Fig. 4.5 B. Soil sequence forming in a complex geological terrain.

Fig. 4.5 C. Incorrect projected weathering trend (a); (b) Incorrect assumption of immobility in X with respect to Y.

would displace X and Y towards the origin (since the ratio still remains constant), leading to a disarray of horizon numbering relative to depth as indicated in fig. 4.5A.

If the sequence of horizons developed on a banded rock such as a gneiss, as sketched in fig. 4.5B, with different X:Y ratios between bands, at least two consequences can be envisaged. If samples were confined within the boundaries of each band in the profile, then a plot of X vs. Y of the parent rock bands and their weathered products will result in two separate linear arrays (fig. 4.5C). In the case of sampling across band boundaries, scattered points will be obtained. The scatter will be bounded by the projected weathering trends of the most melanocratic and leucocratic bands. If the number of samples are limited, the likelihood of obtaining an erroneous linear line by joining plots of the separate suites is high as depicted in fig. 4.5C. However, the likelihood of the line not passing through the origin of the graph is also high in this case, and demonstrates the importance of check (b) discussed previously.

Preferential enrichment of one of the elements considered as immobile can take place, by processes such as translocation of amorphous matter containing either X or Y, in regions of intense rainfall. Progressive removal of X would result in a negative to near vertical slope (fig. 4.5C) while removal of Y results in near horizontal to negative slope. The fact that these plots can indicate mobility of the chosen index element is an advantage. Hence the Zr - Ti pair was chosen over in spite of contrary indications in sections 4.4 and 4.4.1

Several types of trend are observed in figs. 4.6 A-C and 4.7.

1 Sequences with positive slopes indicating mostly enrichment of both Ti and Zr towards the surface:

Wet Zone - Sequences 49 112 (fig. 4.6C)

Dry Zone - Sequences 132 139 99 88 16 (fig. 4.7)

2 Sequences with a high negative to near vertical slope indicating rapid enrichment of Zr relative to Ti towards the surface:

Wet Zone - Sequences 115 61 63 (fig. 4.6B)

Dry Zone - Sequence 131 90 (fig. 4.7)

3 Sequences with a high negative to near vertical slope indicating rapid dilution of Zr and Ti towards the surface:

Wet Zone - Sequences 125 125A (fig. 4.6B)

Dry Zone - Sequence -

4 Sequences that have complex patterns:

Wet Zone - 145 148 123 (fig. 4.6 A),

142 (?) 153 (fig. 4.6 B,C)

Dry Zone - 100 104 131 (fig. 4.7)

Surprisingly, sequences that showed wide variation in element abundances in terms of high coefficients of variation (Table 4.5B) such as sequences 145 (fig. 4.6A), 88 (fig. 4.7) and 112 (fig. 4.6C), plot as positive slope graphs indicating that the levels are genetically related even if some levels are contaminated. Sequence 112 from a granitic gneiss has a high positive slope, whereas sequence 145 from a basic charnockite has a low slope as expected. However as with sequences 104 and 90 (fig. 4.7), sequences 112 and 49 (fig. 4.6C) show disordering of levels along the trend, and are likely contaminated or result from rocks that have undergone selective dilution of Ti and Zr during formation of the soil. It is noted

that rock sample 90 is a migmatite, while sample 104 is an augen gneiss, thus three of the four sequences result from highly altered and metasomatised rocks. High element abundance variation of Zr and Ti (Table 4.5B) in sequences with a positive slope, indicates the occurrence of large differences of these elements between levels from which it can be deduced, that large amounts of rock have undergone weathering to yield successive soil levels.

Type 2 sequences, with enrichment of Zr towards the surface relative to Ti are possibly examples of translocation of Ti in amorphous or adsorbed form.

Type 3 sequences are possibly examples of progressive dilution of surface levels from contamination with the introduction of material excluding Ti and Zr elements.

Type 4 sequences indicate complex soil forming processes in action. In the case of the laterite sequences 145 and 148 (fig. 4.6A), there is a marked discontinuity between the upper quartz rich layers (positive slope in fig. 4.6A plots 2-5, 33-36) and the vermiform, deeper, kaolin - Al/Fe oxide bearing layers [plot 6 (sequence 145) and plots 37-38 (sequence 148).] In sequence 145 which could most unusually be traced down to bedrock, level 06 (vermiform red and yellow level) is directly related to bedrock. The split level graph hence could indicate parent rock inhomogeneity. In a granulite grade terrain consisting of gneisses this hypothesis cannot be discounted. However, the difference in texture and composition between the deeper soft laterite level (37/38) and the quartz rich upper levels suggest that the difference could also be 'process related'. Acceptance of such a theory involves the explanation that the deeper levels result from enrichment of Ti by processes of amorphous phase and clay illuviation.

Discontinuity in sequence 123 is more likely genetic (fig. 4.6 A).

Plots 14 and 15 were from adjacent sloping bands of fresh rock where 14 was a leucocratic leptinite (123PWR) and 15, an Intermediate Charnockite. It appears that the deeper levels 11 and 12 are related to the fresh rock sampled whereas 09, 10 and 13 which align separately (line 'bb') are not.

It should be noted that levels 09, 10, 14, and 15 can be aligned to give a straight line 'aa' with a positive intercept. If condition (b) outlined above was neglected, it could have been surmised that these levels are genetically related. This could have been an example of consequence (ii) discussed earlier with respect to fig. 4.5C, of inadequate sampling in a complex geological terrain and subsequent surmise of genetic relationships between horizons that have clearly resulted from inhomogeneous parent material. Similarly if condition (b) had been ignored, the fresh rock in sequence 49 (quartzite) (fig. 4.6C - line aa) could have been used for erroneous mass balance calculations. The positive intercept on the y axis indicates that the sample used for xrf analysis of the fresh rock is not completely representative.

Sequences with likely contamination sequences are omitted in mass balance calculations. In the remaining sequences, the deepest genetically related soil horizon will be used to assess mass balances of the succeeding horizons.

It should be pointed out that, sequences 99, and 88 were two of the sequences that consisted of flat lying plots of Zr normalised to Ti (figs. 4.4 A -H). The reason that Zr to Ti plots were so non-uniform in figs. 4.4 C,D, and H, can now be explained as resulting from the inclusion of levels belonging to different parent material in one sequence and translocation of Ti out of the upper levels. In addition selective contamination of levels have contributed to the overall non-uniformity of plots.

7 4 2

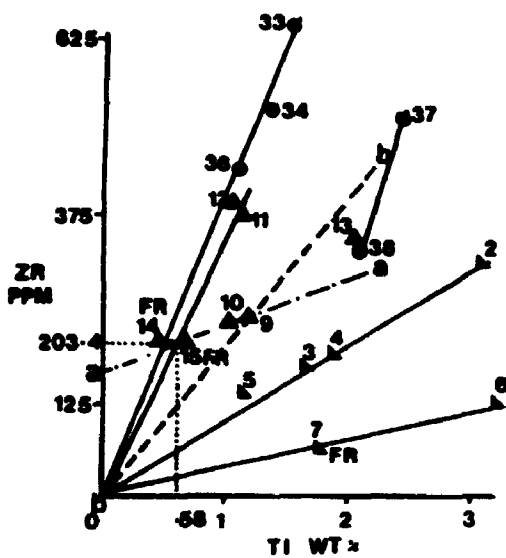
Fig. 4.6 A. TiO_2 (wt %) vs. Zr (ppm) plots of Wet Zone complex soils.

Line-aa Erroneous projection line of weathering (positive intercept).

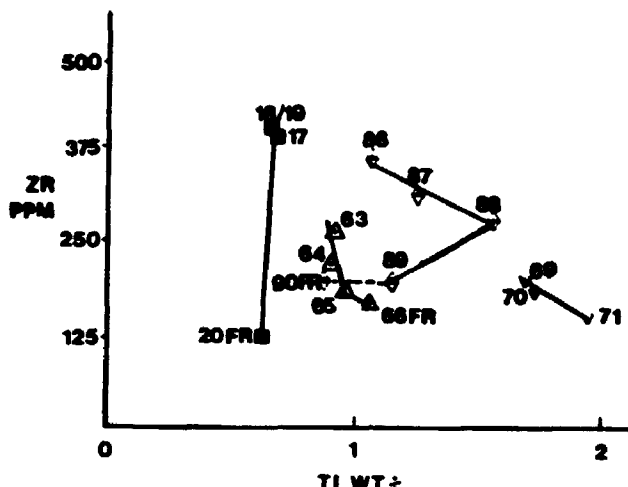
Fig. 4.6 B. TiO_2 (wt %) vs. Zr (ppm) plots of Wet Zone sequences with high slopes.

Fig. 4.6 C. TiO_2 (wt %) vs. Zr (ppm) plots of Wet Zone sequences with pronounced contamination.

Sequential numbering correlates with increasing depth levels in sequences, ending in fresh rock as in Enrichment Factor Tables 4.7 - 4.10.



(A)

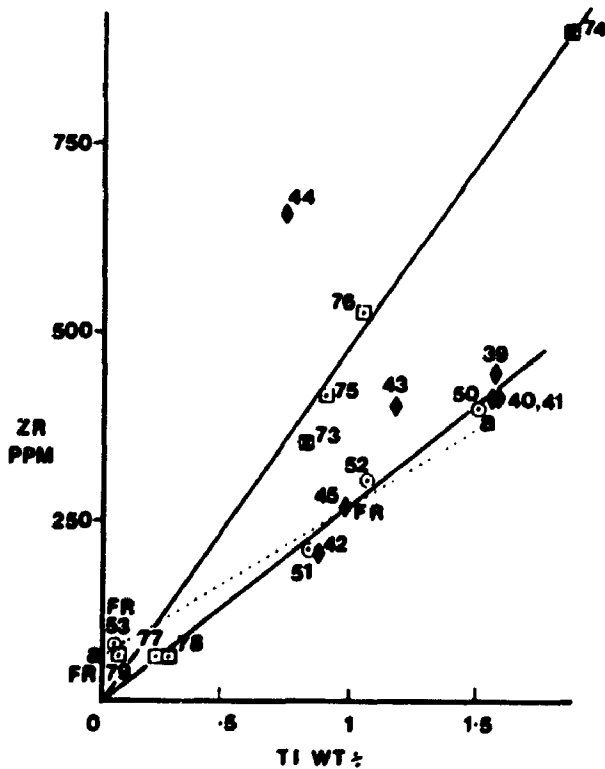


(B)

LEGEND
SEQUENCE

- 148
- ▲ 145
- ▲ 123
- 115
- ◇ 142
- △ 61
- ▽ 63
- 112, 112
- ◆ 153
- 49

FR FRESH ROCK



(C)

Table 4.7. Enrichment Factors of Samples Corresponding to fig.4.6 A

Fresh Rock as Parent Material										100 cm Soil Horizon as Parent Material											
	Zr	Ti	Nb	Si	Al	Fe		Zr	Ti	Nb	Si	Al	Fe		Zr	Ti	Nb	Si	Al	Fe	
02.14510	4.43	1.74	1.67	1.00	1.70	1.58		02.14510	1.72	1.64	1.52	0.88	0.62		03.14530	0.94	0.90	1.37	0.87	0.79	*
03.14530	2.43	.95	1.33	.90	1.66	2.03		03.14530	0.94	1.33	1.37	1	1		04.145100	1	1	1	1	1	1
04.145100	2.57	1.06	1.00	.66	1.92	2.56		04.145100	2.62	2.21	1.38	.46	1.74		02.14510	2.62	2.21	5.0	.46	1.74	
05.145202	2.00	.66	.33	.73	3.65	.91		05.145202	1.44	1.21	1.25	.46	2.24		04.14530	1.60	1.29	3.0	.53	2.83	
06.145103	1.86	1.81	1.33	0.76	2.02	2.04		06.145202	1	1	1	1	1		05.145202	1	1	1	1	1	
07.145RR	1	1	1	1	1	1		06.145103	2.73	.93	1.04	.55	2.25				4.0	1.04	.55	2.25	
11.123100	1.85	1.75	1.33	.88	1.83	2.63		33.14810	1.44	1.32	1.17	0.92	0.74		33.14810	1.44	1.32	1.17	0.92	0.74	
12.123200	1.95	1.65	1.0	0.96	1.55	2.27		34.14830	1.19	1.19	.92	0.92	1.2		34.14830	1.19	1.22	.92	0.92	1.2	
15.123RRR	1	1	1	1	1	1		35.148101	1	1	1	1	1		35.148101	1	1	1	1	1	
11.123100	1.82	1.96	1.48	.88	1.83	2.86		37.148100r	.64	.86	.97	.94	5.30		37.148100r	.64	.86	.97	.94	5.30	
12.123200	1.92	1.84	1.11	.95	1.55	2.46		38.148100r	1	1	1	1	1		38.148100r	1	1	1	1	1	
15.123new	1	1	1	1	1	1															

1 Fresh rock composition calculated from fig. 4.6 A

* Diluted

Table 4.8. Enrichment Factors of Samples Corresponding to Fig. 4.6 B

Fresh Rock as Parent Material		100 cm Soil Horizon as Parent Material											
	Zr	Ti	Nb	Si	Al	Fe		Zr	Ti	Nb	Si	Al	Fe
17.11510	3.25	1.11	1.0	1.42	.69	.60	17.11510	.95	1.01	.67	1.06	.80	.85 *
18.11530	3.33	1.06	.5	1.35	1.06	.85	18.11530	.98	.97	.33	1.01	.99	1.02 *
19.115100	3.42	1.09	1.5	1.34	.86	.70	19.115100	1	1	1	1	1	1
20.115fr	1	1	1	1	1	1							
63.6110	1.59	.87	.67	1.19	1.16	1.01							
64.6130	1.29	.85	.33	1.2	1.13	1.0							
65.61100	1.06	.95	.67	1.1	1.27	1.05							
66.61fr	1	1	1	1	1	1							
86.14210	1.71	1.2	.50	1.1	1.06	1.31	86.14210	1.71	.92	.50	1.13	.75	.96
87.14230	1.48	1.39	1.50	1.02	1.31	1.47	87.14230	1.48	1.08	1.50	1.04	.93	1.07
88.142100	1.33	1.75	1.5	.92	1.75	1.62	88.142100	1.33	1.35	1.5	.95	1.15	1.19
89.142NE	2.5	1.29	1	1	1.41	1.37	89.142NE	1	1	1	1	1	1
90.142fr	1	1	1	1	1	1							

* Diluted Sequences 125, 63 not considered

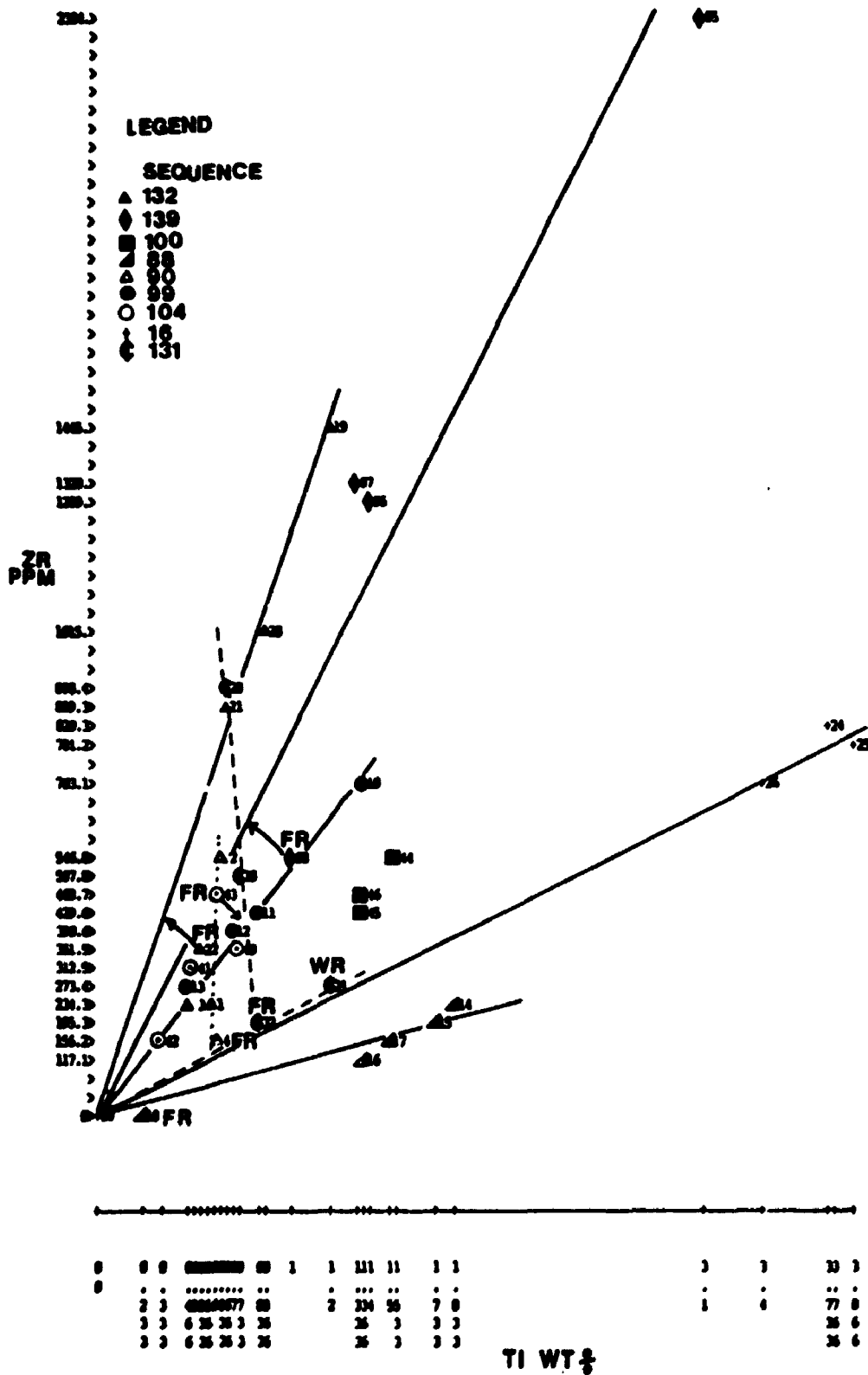


Fig. 4.7. TiO₂ (wt %) vs. Zr (ppm) plots of Dry Zone soils.

Table 4.10. Enrichment Factors of Samples Corresponding to Fig. 4.7

Fresh Rock as Parent Material		100 cm Soil Horizon as Parent Material										
	Zr	Ti	Nb	Si	Al	Fe	Zr	Ti	Nb	Si	Al	Fe
10.9910	2.74	2.67	1.85	.98	1.12	1.38						
11.9930	1.63	1.61	1.23	1.1	.87	.97						
12.991001	1.38	1.20	1.08	1.13	.88	.94						
12.99100	1.42	1.37	1.15	1.08	1.02	1.14						
13.99fr	1	1	1	1	1	1						
05.13910	4.28	3.14	2.0	1.22	.62	.51						
06.13930	2.41	1.39	1.0	1.24	.69	.30						
07.139100	2.44	1.35	.75	1.24	.72	.30						
08.139fr	1	1	1	1	1	1						
14.8810	1.49	1.23	1.23	.97	1.05	1.01						
15.88301	1.31	1.16	1.08	.97	1.07	1.04						
16.881001	.85	.91	.92	1	1.02	.94						
17.88100	1	1	1	1	1	1						
19.13210	4.17	2.29	1.53	.99	1.13	1.08	19.13210	1.64	1.75	1.35	.99	1.05
21.132100	2.93	1.67	1.27	1.1	.78	.66	21.132100	1	1	1	1	1
22.132fr	1	1	1	1	1	1						
40.10410	.82	1.16	.50	1.18	1.16	1.04 *	40.10410	2.31	2.31	1	1.07	1.03
41.10430	.71	.80	.50	1.11	.96	.92 *	41.10430	2.00	1.59	1	1.01	.95
42.104100	.36	.50	.50	1.10	1.01	.69 *	42.104100	1	1	1	1	1
43.104fr	1	1	1	1	1	1						
23.1610							23.1610	1.13	1.10	1.15	.99	.97
24.161020							24.161020	1.13	1.10	1.05	.99	.94
25.1630							25.1630	1.11	1.14	1.15	1.00	.9
26.1650							26.1650					
44.10010							44.10010	1.31	1.09	1.67	.98	1.01
45.100301							45.100301	.97	.96	.94	1.02	.99
46.10030							46.10030	1.10	.96	1.00	1.00	.97
47.100100							47.100100	1	1	1	1	1

Sequences 131, 90 not considered
 † Duplicates
 * Diluted

These examples demonstrate the need to use both concepts (a) and (b) to screen the sequences intensively before quantitative analysis so as to achieve meaningful estimates of weathering. Unfortunately sampling sequences without contamination is almost unavoidable since soil forming processes are synonymous with transport and translocation of material within sequences, especially in advanced weathering regimes. However the success achieved in differentiating genetic discontinuities in sequences by combining concepts (a) and (b) indicates that relatively 'immobile, elements can be used for this analysis, since their immobility is itself tested in this approach.

4.5 Estimation of Changes Taking Place During Weathering of Selected Sequences

The widely used Gresens (1967) technique of calculating mass balances can be rearranged to eliminate the superfluous specific gravity terms in it, if volume changes accompanying weathering is not required. Such a derivation is that used by Nesbitt (1979), with the added modification of calculating percent change relative to the original amount of starting parent material instead of giving absolute change and is adopted in this study. The same symbols as in Nesbitt (1979) a.e used.

In essence, if an element (I) remains immobile as weathering proceeds, then the percent change of an element X in a sample (s), compared to its concentration in the parent material (p) can be calculated by:

$$\% \text{ Change} = \left[\frac{X^s}{I^s} / \frac{X^p}{I^p} - 1 \right] 100$$

when x grams of parent material yield 100 grams of weathered material.

A simple calculation shows that in the instance that at least two elements have remained immobile, such that the ratio $Y:X = a$ constant for parent rock and derivative horizons, then, for all the horizons (Y^S, X^S) and their corresponding parent material (Y^P, X^P), the concentration factors of X and Y must remain equal.

Since

$$\frac{Y^S}{X^S} = \frac{Y^P}{X^P} \text{ equal a constant when X and Y are immobile,}$$

then

$$\frac{X^S}{X^P} = \frac{Y^S}{Y^P} \text{ must also equal a constant.}$$

ie. the concentration factors of the elements assumed immobile must also be equal. If the enrichment factors are both greater than 1 it implies enrichment of both elements relative to the fresh rock in spite of subsequent changes relative to one another.

Tables 4.7 to 4.10 give the concentration factors of elements considered likely to be immobile. When the concentration factors between Zr and Ti are considered as shown in Table 4.7 to 4.10, very few of the screened and selected sequences considered to be genetically derived, have concentration factors that are identical when the sampled parent rock is considered as the precursor material. This is especially true of sequences where the plot of the fresh rock lies outside of the line joining the origin to the soil levels (fig. 4.6C: sequence 49; fig. 4.7 : sequence 132, and 139). Dissimilarity is noted as well for sequences with a near vertical slope (fig. 4.6B :sequence 115) and for sequences with a negative slope (fig. 4.6B :sequence 61). In the latter case Ti concentration factors are all significantly less than 1. The same observation holds in sequences with a split level trend (fig. 4.6A). In most instances the Zr concentration factor is greater than that of Ti; generally both are

greater than 1.

The equality test mentioned above is an even more rigorous test to apply than the conditions discussed in section 4.4.2 since inequality can appear as a result of magnifying a slight analytical error or sampling error. Only close (not identical) correspondence in the mass factors of the immobile elements is likely to be achieved. This is seen in the significant differences that exist even between duplicate analyses of the 100cm sample (sequence 99, Table 4.10) in spite of their superimposition in fig. 4.7 where the derived soil and fresh rock form a relatively straight line which passes through the origin. Slight deviation towards the Zr axis gives higher Zr enrichment factors and would imply removal of Ti relative to Zr and vice versa if they deviate towards the Ti axis.

In sequences, where the fresh rock plot deviates significantly from the weathering trend [sequences 132 and 139 (fig. 4.7)] it indicates non-representative sampling of fresh rock. In these instances concentration factors of the 30 and 10 cm levels relative to the deepest sampled soil level show better correspondence (Tables 4.7-4.10); The closer correspondence Ti with Nb than of Ti and Zr (relative the 100 cm level), is compatible with earlier observations (section 4.4.1). Both correlation indices and trace element : Ti ratios were calculated mostly for the upper 100 cms of soil. Not surprisingly, concentration factors of sequences that had uniform plots of trace elements : Ti ratios [sequence 71 and 147, fig. 4.4 F; sequences 16 and 100, fig. 4.4 I] have above average correspondence [sequence 71, Table 4.9; sequences 16 and 100, Table 4.10]. Analytical error (Appendix 1) is significant for Zr (+10%) as against TiO_2 (+1%) and may partially account for the fractional increase in Zr concentration factors. However the remaining excess is significant since it denotes loss of Ti and Nb from the sequence relative to Zr.

These observations suggest the fact that the 100cm level has acted as pseudo parent especially to the 30cm level and to the 10cm level in many instances. This is a realistic possibility, since with progressive development of a soil mantle that shields the fresh rock from the surface, alteration of the underlying soil mantle is more likely to be the route source for even more surficial levels.

In sequence 145 (fig. 4.6A and Table 4.7) good correspondence between Zr and Ti concentration factors occurs only in level 103 (plot 06) when the fresh rock is considered as parent. Hence the concentration factors mimic the split level trend for this sequence in fig. 4.6A.

As a result of the poor correspondence between Ti and Zr concentration factors for most of the screened and selected sequences from section 4.4.2 mass balances have been calculated only for segments of sequences and one complete sequence using parent rock (Table 4.11). The 100cm level was used as starting material wherever good correspondence between the concentration factors was obtained (Table 4.12). Ti was chosen as the index element purely because analytical error is less for Ti relative to Zr. To show the variance that results when a large difference exists between the concentration factors mass balances were calculated for sequence 145 with fresh rock as starting material using both concentration factors (Table 4.11) Table 4.13 gives mass balances of sequences that have lost Ti relative to Zr. Na and P results may not be reliable since they were analysed using XRF techniques, for which as Appendix 1 shows, percent error is high. Amounts of starting rock mass given in Tables 4.11-4.12 may not be representative where Ti concentration factors are less than 1, since it implies dilution and yields a starting rock mass of less than 100 grams.

4.5.1 Results

A point that stands out in sharp contrast in the wet zone sequences (Table 4.11, sequences 145 and 123) is the amount of alkali and alkali element removal (90 - 100%) that has taken place from the fresh rock to form the weathered residue immediately above. However this is to be expected in a region that results in the production of kaolin and gibbsite as secondary minerals directly from the fresh rock. Rb, Al and Fe are enriched. Fe is relatively more enriched in sequence 123.

In the dry zone profile that withstood the screening, - sequence 99, progressive loss of most elements is observed towards the surface. Percentage loss of Na and Ca is surprisingly high, (80-90%). Rb and K(30-50%) are the most resistant of the alkali and alkaline earth elements and fall in the same category of Fe and Al, followed by Sr and Mg (55-70%). The mass balances hence quantify the commonly held view of the high resistance k-spar as opposed to plagioclase and other ferromagnesium minerals.

Well defined trends are not clear in mass changes calculated using the deepest available soil layer as parent (Table 4.12). Nevertheless, in the dry zone regardless of the extent of change, depletion of elements including Al and Fe characterise the change from 100cm to the surface. Sequences that comprised geochemically similar levels - sequences 16 and 100, (dry zone) show little change. In the wet zone sequences, where the surface 10 and or 30 cm levels plotted closer to the origin than the 100 cm level indicating dilution of Ti and Zr, in figs. 4.6 A- C, {sequence 49, no.51 (30cm); sequence 112 no.73 (30cm); 112a no.76 (30cm); sequence 71 }, enrichment of Si is common (Table 4.12) as are other elements, though no simple pattern emerges among the latter. In these instances concentration factors are less than 1, hence the starting soil masses are less than 100g. Abnormally high enrichment values for alkali and alkaline earth

Table 4.11. Percent Mass Change of Selected Sequences with Parent Material as Starting Material

Wet Zone	Rb	Sr	Y	Zr	Nb	Si	Ti	Al	Fe	Mn	Pb	Ca	Na	K	P	Starting Rock Mass (g)
14510 ¹	-32.3	-98.0	-88.7	0	-62.4	-77.4	-60.6	-61.7	-64.3	-93.8	-99.3	-99.69	-99.47	-82.17	-80.7	443
14530	-17.7	-96.3	-79.4	0	-45.1	-62.8	-60.7	-31.6	-16.6	-96.3	-99.1	-99.96	-99.81	-82.67	-76.5	243
145100	-22.2	-96.5	-80.5	1	-61.1	-74.4	-58.8	-25.5	-.3	-96.5	-99.1	-99.96	-99.82	-83.62	-80.5	257
145202	-50.0	-95.5	-75.0	0	-83.3	-63.7	-66.8	82.4	-54.7	-93.2	-98.6	-99.95	-99.76	-64.74	-50.0	200
145103	7.7	-95.1	-73.1	0	-28.2	-59.2	-2.4	9.0	9.9	-90.2	-96.5	-98.50	-99.75	-94.33	-23.1	186
145fr ^a																
14510 ²	72.4	-94.8	-71.3	154.5	-4.2	-42.5	.3	-2.6	-9.2	-84.3	-98.3	-99.2	-98.6	-54.6	-50.7	174
14530	110.5	-90.4	-47.4	155.6	40.4	-4.8	.5	74.9	113.3	-90.4	-97.6	-99.9	-99.5	-55.7	-39.9	95
145100	88.7	-91.4	-52.8	142.6	-5.7	-37.8	.2	80.8	141.8	-91.4	-97.9	-99.9	-99.6	-60.3	-52.8	106
145202	51.5	-86.2	-24.2	203.0	-49.5	10.0	.7	452.7	37.3	-79.3	-95.7	-99.9	-99.3	67.5	51.5	66
145103	10.5	-95.0	-72.4	2.6	-26.3	-58.2	.1	11.8	12.7	-89.9	-96.4	-98.5	-99.7	-94.2	-21.1	181
145fr ^a																
123100	-89.2	-98.7	-82.0	0	-27.9	-52.2	-5.2	-.9	42.3	-64.0	-92.9	-97.94	-98.93	-96.43	-7.3	185
123200	-86.3	-96.3	-82.9	0	-48.7	-50.7	-15.6	-20.3	16.3	-48.7	-93.3	-98.40	-97.96	-93.22	-56.0	195
123fr ^a																
Dry Zone																
9910	-29.4	-56.4	-73.5	0	-32.7	-64.3	-2.7	-59.2	-49.5	-34.3	-71.6	-81.8	-81.8	-55.1	-70.2	274
9920	-8.8	-54.3	-59.2	0	-24.7	-32.6	-1.7	-46.6	-40.9	-38.8	-74.4	-82.6	-90.0	-40.2	-72.2	163
99100a	-2.6	-57.4	-53.9	0	-22.0	-18.5	-13.3	-36.0	-31.9	-71.0	-62.9	-85.1	-82.0	-41.8	-67.0	138
99100	-5.5	-55.6	-48.9	0	-18.9	-24.1	-3.5	-28.3	-19.5	-57.8	-66.5	-84.1	-82.6	-34.2	-74.4	142
99fr ^a																

1 Using Zr as index element
 2 Using Ti as index element
 * Parent material

elements, in the surface 10 cms, eg. laterite sequence 145 (Table 4.1) leads to pronounced changes in Table 4.12, and may indicate addition from plant matter.

In the laterite sequence 145, (Table 4.12) enrichment of Fe in the 100cm level relative to the surface and underlying level is observed in the mass changes as is enrichment of Al in the underlying level (no. 05), reflecting the zonation of Fe and Al mentioned before. While enrichment of Si in the 30 cm level (no. 03) may associate with quartz, detected mineralogically and suggested by increase in sandiness in particle size analysis, the higher abundance in the underlying level (no. 05) may be linked with kaolin. Hence the dilution of Ti factors in levels nos. 03 and 05 may result from accumulation of quartz in the upper level and Al in the underlying level. To connect the upper levels to level no. 6, a marked enrichment of Zr and consequent loss of Ti should have to take place between levels 06 and 05-02. Whether such massive loss of Ti can take place is a question that remains unresolved in this case study. The extent of element fractionation taking place during this stage of lateritisation can however be judged, from the red and yellow segments in hand sample from sequence 148. To replace the yellow matrix massive influx of Fe, Al and Mg must be involved (Table 4.12, - mass change of red segment relative to yellow) resulting in Zr and Si dilution in the red segments. Replacement of kaolin by hematite in the red mottles within the kaolinitic matrix in the deeper soft laterite has been observed in SEM studies (Muller and Bocquir, 1986; Ambrosi and Nahon, 1986). The Fe is considered to be generated by the destruction of the iron crust at the surface by highly undersaturated, (and hence aggressive waters) and transported to lower horizons. Continued replacement of the yellow kaolin matrix at the base of the upper iron crust generates the iron crust itself according to Ambrosi and Nahon, (1986), that in turn breaks up into nodular iron gravel and quartz at the surface. Does the massive enrichment of Zr and Si calculated relative to Ti in the red segments imply the break up of the red segments to give the

uppermost 100cm level as Ambrosi and Nahon (1986) hypothesised ? Secondly how much Ti can be judged to have moved? If the explanation given by Ambrosi and Nahon is correct then suggested trends from mass balance calculations (Table 4.12) are compatible with the deduction made from correlation indices in section 4.4.2 regards the 'process related' origin of the successive levels of these laterite sequences. The chemical dichotomy that exists between the soft laterite and the upper surface levels is hardly cause for surprise then. The negative correlation between Fe-Al and enrichment of Fe observed in the upper zone in the successive horizon couplet of Fe and Al enrichment is explained by this mechanism. Enrichment of Zr will continue, which is possibly reflected in the concentration factor of 4.43 for Zr in the top soil, the good correlation index between Zr and Si and the negative correlation between Zr and Ti (Table 4.6).

Table 4.12. Mass Balances of Selected Sequences with Deepest Soil Level as Starting Material

Max Zone	Nb	Sc	Y	Zr	Nb	Si	Ti	Al	Fe	Mn	Mg	Ca	Mn	K	P	Starting Soil Mass (g)
02-14510	-8.6	-39.1	-39.1	4.9	1.5	-7.4	0	-46.1	-62.5	82.7	-20.1	813.7	204.56	14.2	4.4	144
03-14530	11.3	11.3	11.3	5.1	48.4	52.6	0	-3.5	-12.0	11.3	11.3	11.3	11.3	11.3	27.2	90
04-145100*																
05-145202	-20.1	59.8	59.8	24.3	-46.7	76.0	0	204.2	-43.5	139.7	99.8	59.8	59.8	319.6	219.7	62
06-145103	-41.5	-41.5	-41.5	-57.7	-21.9	-32.7	0	-38.2	-53.4	17.1	68.3	1656.6	-41.45	-85.4	67.3	170
33-14810	-24.2	0	19.1	9.3	-11.0	-11.4	0	-30.3	-44.1	13.7	-63.4	0	0	-16.6	-24.2	132
34-14830	-15.9	0	-28.0	.3	2.3	-22.3	0	-22.9	.8	26.1	-6.1	0	0	-7.5	380.3	119
35-148101*																
36-148100	-3.6	0	4.5	3.5	9.1	6.7	0	.9	4.0	4.5	-4.2	0	0	-6.0	19.4	208
37-148100*																
38-148100*	-46.0	-94.2	-61.4	-26.3	12.4	-43.6	0	8.4	513.6	363.2	148.1	0	0	-80.0	39.0	86
33-14810	56.1	0	200.5	166.8	11.8	238.5	0	-25.9	-25.5	2.5	-56.0	0	0	200.5	59.4	73
34-14830	73.1	0	81.7	144.9	28.5	196.9	0	-18.0	34.1	13.6	12.8	0	0	233.2	909.7	66
35-148101	105.9	0	152.2	144.2	25.6	282.3	0	6.3	33.1	-9.9	20.1	0	0	260.3	110.2	54
36-148100	88.3	0	163.6	152.8	36.9	307.9	0	7.2	38.4	-5.9	15.1	0	0	238.9	151.1	53
38-148100*																
39-15310	-44.9	0	20.1	19.7	7.2	-50.8	0	-50.3	8.1	120.3	93.5	781.0	0	-31.2	10.1	182
40-15330	-44.6	0	31.0	11.4	7.9	-46.5	0	-37.2	-9.1	66.2	49.3	786.6	0	-10.0	10.8	180
41-153301	-45.4	0	28.5	9.3	5.9	-47.5	0	-54.0	-11.3	90.3	45.5	606.9	0	-18.4	17.8	137
42-153100*																
43-153600	-58.2	0	-.3	42.6	3.9	-26.3	0	-39.3	10.8	9.7	-28.9	192.4	0	-63.4	-51.3	85
44-153600*	-.8	0	188.6	277.3	23.8	-28.6	0	39.7	300.2	193.9	265.4	1193.2	0	-70.6	-56.8	114
50-4910	-29.6	-29.6	111.2	-5.3	-29.6	-32.7	0	-14.8	-35.9	76.0	158.1	-29.6	-29.6	15.6	-12.0	142
51-49040	-15.1	27.4	27.4	-7.8	-36.3	47.7	0	-7.0	-24.9	27.4	176.0	27.4	27.4	9.2	-4.5	79
52-49100*																
75-11210	2.8	-16.7	-1.3	-10.2	1.1	23.2	0	-6.9	18.3	-32.5	26.8	-14.8	-80.6	-.6	16.7	86
76-11230*																
73-11230*	129.3	-27.6	14.6	-9.8	72.0	143.7	0	60.4	29.8	129.3	384.0	81.5	19.9	58.6	205.7	44
74-112100*																
7110	23.5	23.5	-17.7	-1.8	-50.6	27.4	0	11.0	29.0	143.0	-1.8	126.4	270.5	105.8	116.1	81
7130	18.5	-21.0	-60.5	3.3	-5.2	17.4	0	14.0	33.2	75.8	-.4	18.5	18.5	18.5	58.0	84
7180*																

* Sample used as parent material with Ti as index element
 1 Sequential numbering correlated with Figs. 4.6 A-C and Fig. 4.7
 2 Mass change of upper 100cm relative to the red
 3 Mass change of red segments relative to the yellow

Table 4.13 gives mass changes of type 2 sequences characterised by negative to near vertical slopes of Ti vs. Zr plots (section 4.4.2) that are for the first time reported in literature. Depletion of Ti was considered to have taken place to give such weathering trends by the physical process of eluviation or wind erosion of amorphous Ti oxides together with other clay sized particles leading to enrichment of Zr, since this enrichment occurs in both climatic zones. Enrichment of Zr, Si and Mn is common in the mass changes of these profiles (Table 4.13). Al, Fe and P show enrichment as well as depletion. Of particular note is the uniformity in amounts either lost or gained, of these elements compared to continuous gain of Zr in increasingly large amounts towards the surface levels. Hence relative to Zr, Al, Fe and P have also been mobilised. The alkali and alkaline earths are depleted.

The three sequences 131, 142 and 153 that had dual trends in figs. 4.7 and 4.6 B,C have dual mass change trends as well. Levels that had a positive slope [sequence 153, upper levels nos. 39-42 ; sequence 142 no. 88 - 100cm level and sequence 131 no. 31 - lowest level 131wr] are depleted in Si, whereas the remaining levels that connect to fresh rock with a negative slope are markedly enriched in Zr and Si. This feature of Zr and Si enrichment is common to the highly weathered laterite sequences discussed previously when Ti is assumed immobile. The cause of the noted enrichment could be as noted above, the result of loss of Ti associated mainly with the physical process of eluviation. In the laterite sequences additional loss could also result through a chemical process within its low pH environment as pointed out by Craig and Loughnan (1964).

The process of lateritisation eludes quantification in spite of the effort spent on it. Massive movement of Fe and Al is undeniable but meaningful quantification revolves around the issue of Ti mobility or immobility both by physical and chemical processes

Table 4.13. Percent Mass Change of Sequences Influenced by Pronounced Translocation of Elements Including Ti

	Rb	Sr	Y	Zr	Nb	Si	Ti	Al	Fe	Mn	Mg	Ca	Mn	K	P
63-14110	-10.9	-28.2	14.6	82.0	-23.6	26.8	0	33.5	15.3	22.2	-65.7	-63.7	-94.0	-26.5	-54.3
64-6130	-21.1	-31.6	18.3	53.1	-60.6	41.5	0	30.9	18.5	26.2	-67.4	-66.9	-61.7	-28.8	-61.3
65-61100	-26.7	-29.8	10.0	16.5	-26.7	20.7	0	39.2	15.5	10.0	-41.2	-56.1	-58.6	-25.1	-70.0
66-61100															
63-6110	21.5	2.2	4.2	56.3	4.2	13.4	-0	4.1	-2	11.1	-41.7	-17.3	-85.5	-1.9	28.9
64-6130	7.5	-2.6	7.5	31.4	-46.2	17.3	-0	3.9	2.6	14.7	-44.6	-24.6	-7.4	4.9	29.0
65-61100 ^a															
69-6310	14.9	88.8	-42.5	53.2	14.9	22.3	0	-5	2.8	5.6	51.0	90.6	107.3	89.0	27.6
70-6330	11.9	3.9	11.9	41.8	-62.7	27.5	0	-14.6	6.6	8.3	3.4	14.9	20.6	19.9	6.3
71-63100 ^a															
17-11510	-37.6	-56.5	-54.9	193.0	-9.9	28.2	0	-37.6	-46.1	28.8	-91.7	-93.5	-76.5	-56.1	-71.8
18-11530	-27.6	-51.3	17.6	213.7	-52.9	27.4	0	-20.1	-32.8	61.3	-87.4	-87.7	-61.8	-50.9	-58.8
19-115100	-29.7	-52.7	-54.3	212.4	37.1	22.9	0	-21.3	-35.7	30.6	-84.6	-85.0	-62.4	-52.5	-54.3
20-11510 ^a															
86-14210	46.4	46.4	46.4	89.2	-51.2	75.9	0	-4.1	17.4	143.9	6.2	379.1	46.4	17.1	67.3
87-14230	-5.7	25.8	88.7	39.3	25.8	40.1	0	1.8	13.1	109.6	-14.8	48.7	25.8	2.7	43.8
88-142100 ^a															
86-14210	116.4	-63.9	-56.7	85.5	-45.9	21.8	0	-18.6	3.7	-45.9	-68.0	8.2	-86.5	-52.8	8.2
87-14230	39.5	-69.0	-44.2	37.2	39.5	-3.0	0	-13.6	-1	-53.5	-74.3	-53.5	-88.4	-58.6	-7.0
88-142100	47.8	-75.4	-70.4	-1.4	10.9	-30.8	0	-15.1	-11.7	-77.8	-69.9	-75.4	-90.8	-59.7	-35.3
89-14200 ^a															
39-15310	-96.2	-99.9	-57.0	1.0	54.6	-31.8	0	-29.0	-7.1	-80.7	-74.5	-97.1	-99.9	-99.2	-6.0
40-15330	-96.2	-99.9	-53.2	-6.0	55.5	-26.0	0	-31.2	-22.0	-85.4	-80.5	-97.1	-99.9	-97.7	-5.4
41-153301	-96.3	-99.9	-54.0	-7.8	52.6	-27.3	0	-34.4	-20.8	-83.3	-80.9	-97.7	-99.9	-97.9	-5
42-153100	-93.1	-99.9	-64.2	-15.6	44.1	-38.5	0	-42.8	-14.1	-91.2	-86.8	-99.7	-99.9	-97.4	-14.7
43-153600	-97.1	-99.9	-64.3	20.3	49.7	2.0	0	-13.3	-4.9	-90.4	-90.6	-99.0	-99.9	-99.1	-58.4
44-153600 ^a	-93.1	-99.9	3.2	218.4	78.4	-1.2	0	99.5	243.7	-74.3	-51.9	-95.8	-99.9	-99.2	-33.8
45-1500 ^a															
Dry Zone															
9010	5.3	-16.9	57.9	26.2	-64.9	8.6	0	9.8	2.2	110.5	-64.5	-11.0	-52.0	-17.0	43.5
92-9030	-28.2	-32.0	176.9	204.1	-32.5	4.6	0	-6	-19.0	3.8	-59.5	-31.2	-48.1	-30.8	-41.3
93-90100	-2.8	-7.9	87.5	76.5	-58.3	-32.9	0	-19.9	-9	25.0	-42.6	-27.0	-43.9	-4.7	-9.1
94-900 ^a															
28-13110	-16.1	2.3	16.3	375.2	.9	17.4	0	18.9	15.2	236.5	-46.0	-40.5	-30.1	7.1	-56.9
29-13130	-12.5	5.6	10.1	451.7	11.5	33.2	0	23.9	35.1	147.8	-48.3	-47.1	-42.3	9.0	-52.4
29-131301	-12.1	4.8	13.5	457.9	14.9	35.9	0	27.9	36.9	137.1	-54.2	-44.8	-41.5	13.8	-50.9
30-131100	-38.1	4.7	6.1	189.0	-7.8	20.5	0	25.7	45.4	-17.7	-41.1	-39.2	-71.6	-8.3	-73.4
31-13110	-42.4	-20.5	44.8	-4.0	-4.0	-38.4	0	-18.0	11.2	-7.6	-9.7	-39.7	-27.3	-39.2	-63.1
32-13110 ^a															

¹ Sequential numbers that correspond to sample plots in Figs. 4.6 (A-C) and Fig. 4.7
^a Sample used as parent material with Ti as index element

and lack of detailed sampling and site specific information limits further understanding.

4.6 Discussion

Several lines of evidence had to be used to unravel the geochemistry of the sampled soils, because of their complex origins. Of these, Zr vs. Ti plots and concentration factors proved to be the most useful in understanding some of the complexity in addition to explaining other plots. Statistical correlation indices and element to Ti ratios provided valuable insight into the nature of mineral chemistry and transformations taking place between the wet and dry zone sequences. The complexity originates from two sources: heterogeneous parent material, and superimposition of physical processes on chemical weathering. Geochemical differentiation of the two weathering processes was shown to be possible by Kronberg and Nesbitt (1981), and was simulated in figs. 2.2 A and B (Chapter two), in this study. As discussed in section 2.6.1, geochemical trends from fresh rock towards gibbsite and trends from fresh rock towards quartz were taken to indicate chemical and physical weathering respectively. It can be seen from figs. 2.2 A and B that most of the sequences inclusive of type two sequences show a trend towards gibbsite with increasing depth, i.e. the level at 100 cms is richer in Al than the surficial levels; conversely the surficial levels are relatively enriched in Si. Since the weathering front proceeds downwards, if chemical weathering were alone responsible, Al should be increasingly concentrated towards the surface. Hence relative surficial enrichment of Si must imply physical removal of Al bearing particles. The Nesbitt and Kronberg diagram differentiates between physical and chemical weathering in terms of Al and Si contents and in retrospect once more reveals Al mobility in most of the sequences. The Zr vs. Ti plots (figs. 4.6 A-C and 4.7) indicate that Ti can be removed as well, and is substantiated by mass balance calculations which show converse enrichment of Zr and Si towards the surface in

such sequences, demonstrated geochemically for the first time using Ti vs. Zr plots in this study. A physical process is most likely the cause since sequences in both climatic zones developed on flat-lying as well as hilly terrains are affected. Definite isolation of the cause for such loss is not possible at present. However, it is possible that intense periods of rain provide a flushing-out mechanism for these amorphous particles which for an unknown cause may be developed more abundantly in these affected sequences. Most of the sequences affected had hb-bt gneisses as precursor material excepting sequence 115 which had developed on a unique parent type - calc gneiss.

Several aspects remain to be resolved. These are : the possible uses of the well recognised Ti - Nb correlations that are supported by equality between Ti and Nb concentration factors relative to the 100cm level; the geochemistry of Mg, in the laterites, and the nature of the change that takes place during the transition from weathered to highly weathered soils that precedence of Mg over K implies; the detailed implications regarding mineral chemistry and composition that changes in the depletion orders of K-Na normalised to Ti, signify. The dry zone depletion order relative to crustal abundances, ie. $K < Na < Ca < Mg$, is identical to that which obtains when these elements are normalised to Ti. They correspond to the well known order of mineral resistance to weathering. The complex ordering found in wet zone sequences may result from dissimilarity of precursor rock types and from the absence of primary residue minerals in silt fractions of some sequences. Detailed mineralogy of the heavy minerals inclusive of trace element associations in clays and heavy minerals and additional soil solution chemistry is required to understand these aspects.

A further addition to the explanations given for the high average values obtained for the coefficient of variation (section 4.2) is that which obtains from grouping soil levels of different parent rock origin into one sequence as in sequence 123. The contribution to the variation of having had uneven level intervals is illustrated by

sequence 99. As shown, differing quantities of rock, not always in progressively increasing amounts have led to each level, hence there was bound to be significant variation in abundances.

As a result of the rigorous screening undertaken, few sequences remain that can be used for quantifying change. This screening is necessary however, if false conclusions are to be avoided. Interpretation of Ti vs. Zr in terms of delineating genetic horizons and soil forming processes is introduced for the first time in this study and it amply demonstrates the need for such preliminary study. The use of Zr/Ti ratio plots perform the same function, but as noted, they can remain constant across stratigraphic discontinuities (Norton and Hall, 1988). Literature abounds in examples of mass balance calculations performed without adequate initial investigation. A case in point is the work done on Venezuelan Bauxite, (Schorin and Puchelt, 1987) that calculates mass balances for a single profile assuming that the sequences are genetically linked to the underlying 'source' diabase. A simple plot of the Ti and Zr values show a complete disarray of the successive plots of horizons indicating that massive changes have taken place in the Ti and Zr abundances as a result of dilution of Ti, or the premise that the diabase was parent to the whole profile is invalid. Hence the quantitative estimate of changes given are totally groundless. This points out the need for highly detailed sampling, detailed mineralogical studies and accuracy of analyses for such work especially in a geologically complex terrain subject to prolific rainfall and consequent intense weathering, where, as this study shows assumption of even Ti immobility becomes highly suspect. Hence it should be stressed that the mass balance tool cannot be applied indiscriminately in this environment without extensive preliminary ground work. Pit sampling where fresh rock is available at the base is not sufficient. A detailed knowledge of the geology of the site extended if necessary with drill core is required.

4.6.1 Relevance of Mass Balance Calculations to Agriculture

One of the primary aims of this study was to quantify the loss of elements during weathering, for which sequences with little or no physical movement of relatively immobile elements was sought. However sequences that have not been subject to fractionation of Ti relative to Zr through physical processes appear to be rare in this tropical terrain. Though element fractionation is part of the process of weathering, the effects on Ti were not expected. This demonstrable loss of Ti together with Al and Fe as possibly amorphous particles from surficial layers, is of particular concern to agriculture, since soil fertility depends on cation exchange sites made available by clay minerals.

Nonetheless mass balance calculations from the few sequences and segments available give an indication in quantitative terms of the extent of rock undergoing weathering to produce tropical soils. In the example of the dry zone sequence 99, a reduction of 48 % and 64% rock mass has taken place to produce the upper 100 cm, and the 100 cm level respectively. In the wet zone laterite sample 145, the corresponding value for the level above fresh rock is 68% (Table 4.11). More significant however is the loss of bio-essential elements Ca, Mg, K and Na. K is the most resistant, whereas of the other 3 elements less than 5% remains from the original rock in the wet zone.

The results obtained, especially the near complete removal of bio-essential elements during weathering, as quantified in this chapter are cause for much concern when dealing with the concept of rock-fertiliser application in these terrains subject to rapid weathering in spite of the reassurance that Sri Lankan soils are not as weathered as the Amazon soils. Results obtained from the wet zone do not cause as much surprise, as those from the dry zone characterised by the presence of residual primary minerals, where up to 90% of these requisite elements are seen to be removed. The

presence of primary minerals and smectite leaves no room for complacency with regard to the better quality of these soils compared to wet zone soils. In review however, these results are in concert with the presence of kaolin, into which primary minerals, and even more alarmingly, smectite deteriorate, even in this relatively dry zone (Plates 2 and 3). It is possible that analysis of more samples may provide contrary results, but it is unlikely, when the implications of the presence of kaolin in the majority of dry zone soils is taken into account. The challenge these soils present to the concept of rock-fertiliser, to promote its wide use over traditional fertiliser, would be to determine if feasible means exist to fix the cations released from its weathering into the soil. An in-built buffering action is required so as to prevent further soil deterioration especially in the intensely cultivated west and south west wet zone lowland laterite soils and dry zone soils where fresh rock outcrop is sparse. The danger of soil quality deterioration towards Amazon type soils is a very real threat especially in the wet zone lowlands.

Chapter V

Concluding Remarks

5.1 Weathering Dynamics

This study provides a good illustration and furthers our understanding of the manner by which the 'climate factor', recognised in soil science, provides overall dominance in soil mineral formation. The type of secondary mineral formed during weathering is shown to be mainly controlled by the rate of rainfall percolating through a weathering mantle, since it reflects directly on the concentration of dissolved elements in the resulting soil solution. It proves the important corollary that soil mineralogy in different climatic regions differs, not because of differing chemical reactions, that take place in their respective climatic regions during weathering but because of the rate of element concentration taking place in soil solution as a result of rainfall that, in turn, controls the type of mineral precipitating out of solution. Thus in regions of abundant, evenly distributed rainfall as in the wet zone of Sri Lanka, only the most structurally simple and insoluble of minerals form and persist in soils i.e. oxides, oxyhydroxides and kaolinite. The important contribution to our understanding is the fact that these secondary minerals need not be the extreme 'end product' of a series of secondary weathering reaction products as theorised by Jackson (1962), but the first and only minerals to be formed in regions of 'intense' weathering as in the tropics. Illustrations of the universality of chemical reactions taking place, independent of climate type, is shown in sequences that contain rare amounts of secondary minerals incompatible with 'the climatic type,' which occur however, where locally appropriate micro environments in terms of soil solutions had prevailed. The occurrence of gibbsite in a sequence (no. 104) taken from the dry zone, in direct contact with a primary feldspar which is otherwise incompatible with the dominant clay mineral smectite in the

sequence, is an example.

What is not well known however is the mechanism by which secondary minerals form from soil solution. Several precursor clay mineral types have been identified by high resolution spectroscopy (Tazaki, 1987) but have as yet not been characterised. Knowledge of mechanistic pathways of mineral formation will be of immense help in artificially creating micro environments conducive to precipitating high cation exchange clay minerals, such as the smectite family of clay minerals. Recent observations of Al-Fe silicates in bacterial cell walls (Ferris et al., 1986) should provide leads in terms of possible catalysts, that may make artificial conversion of kaolinite to smectite possible under soil conditions.

5.2 Mineralogical and Geochemical Characterisation of the Soils of Sri Lanka

Results from this study uphold the basic mineralogical classification of Sri Lankan soils given by Herath and Grimshaw (1971). Minor modification of the dry zone clay mineral given as montmorillonite in the latter classification is suggested to encompass the existence of interstratified kaolin - smectite clays in these soils.

Sri Lankan wet zone soils are 10 - 1000 times enriched in K, Na, Mg and Ca compared to Amazon soils. However, geochemical calculations indicate that severe weathering occurs as a result of the enormous volume of water percolating through wet zone soils. Theoretically, 100% of the base cations, K, Na, Ca and Mg are removed from primary minerals such as feldspars as they weather and are replaced by kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and gibbsite ($\text{Al}(\text{OH})_3$). From mass balance calculations (Chapter 4), it would appear that at most 1% of these elements are retained within the soils. This study also identifies the movement of the relatively immobile elements Al and Fe through physical processes

in this weathering regime and reveals the extent of such movement, a fact hitherto not given sufficient credit to in studies of weathering in the tropics.

A clearer distinction in terms of geochemical characteristics between the wet and dry zone soils emerges from this study. Such a characterisation reinforces the need for individual assessments of chemical requirements for the two climatic zones in future fertiliser strategy for maintenance soil fertility. Clearly, the dry zone soils contain sufficient primary minerals that can act as a source of bio-essential nutrients. This is not true for the wet zone soils.

5.3 Evaluation of Crushed Rock as Fertiliser with Special Regard To Potassium

Nutrient elements, other than N, O, H and C are all rock derived including K which comprises one of the essential trio of primary nutrients (N, P, K). Ca and Mg which are major components of rocks, also figure as important secondary nutrients (Ca, Mg, S) in tropical plants as Table 5.1 illustrates. Fertiliser requirements can however vary considerably especially when improved fertiliser intensive seed varieties are used. For example Nagarajah (Handbook of Fertiliser, 1985-1986) states that rice yields of 5000 kg/ha remove 100 kg nitrogen, 18 kg phosphorus and 150 kg of potassium.

Table 5.2 provides an estimate of K, Ca, and Mg fertilizer recommendations for some tropical crops grown in Sri Lanka. Quantities of exchangeable K, Mg and Ca from analyses of exchangeable K, Ca and Mg as well as reserves of these elements from geochemical analyses of top soil (10cm) from the present study are also given.

The selection of crops gives an indication of the variance in fertiliser requirements among crops. Varieties of Rice and Tea cloned to provide high yields require very high inputs of fertiliser (compare

Table 5.1

(a) Nutrients Removed in Harvests of Common Tropical Crops¹

	Yield	Kg/ha				
		N	P	K	Ca	Mg
Maize (grain)	1121	17	3	3	0.2	1.1
Rice (paddy)	1121	13	3.6	3.9	0.9	1.6
Groundnut (kernal)	560	28	2.5	3	0.3	1.0
Cassava (tubers, 30 % D.M) ²	11210	25	3.3	65	6.0	-
Bananas (fruit, 30% D.M)	11210	25	4.6	62	0.7	-
Cocoa (beans)	560	11	1.1	25	-	-

(b) Nutrient Amounts in Some Tropical Cash Crops

Yield/ha equivalent to		Kg/ha		
		N	P	K
Oil palm	2.5 tons oil	162	30	194
Sugar Cane	88 tons of cane	45	25	121
Coconuts	1350 Kg dry copra	62	17	56
Bananas	45,000 Kg fruit	78	22	224
Rubber	1120 Kg dry rubber (Annual tree growth)	7 (78)	1 (11)	4 (34)

1 Cooke, (1967)

2 Dry Matter

Table 5.2 Nutrient Status of Crops, Fertiliser Recommendations, Nutrient Status of some Sri Lankan Soils and Nutrient Supply Capability of Crushed Rock.

(a)	Crop	Yield Kg/ha	Kg/ha							
			Amount of Nutrient Removed ¹			Amount of Nutrient Recommended ²				
			K	Mg	Ca	K	Mg	Ca	B	Zn
Rice	5000	150								
1. Wet Zone (3 - 3.5 month Transplanted Rice)						66				
2. Dry Zone ()						44				
Rubber	1120	4.7	1.1	.04						
Annual Tree Growth		34	17	22	16(Mn)	14(Fe)	2(B)			
(While tapping on virgin bark)					5(Zn)	1(Cu)				
							30	11		
Tea	1600	320								
	1600						83	16	0.4 5	
Oil Palm (22 yr. stand 148 palm/ha)										
Tree		250	230	220						
Roots		90	30	14						
Fruits		500	65	76						
Coconut (dry copra)	1350	56								
Coconut (173 palms per ha)							56	14		
(b)		Amount of Exchangeable Nutrient In Top 10 cm Soil			Amount of Nutrient In Reserve In Top 10 cm Soil			Percent Exchangeable of Total Reserve		
		Kg/ha			Tons/ha					
		K	Mg	Ca	K	Mg	Ca	K	Mg	Ca
1. Wet Zone and Intermediate										
Sequence 148		16	-	32	1.8	3.5	0.14	0.9	-	22
Sequence 153		117	14	196	1.7	15.7	2.3	7.1	0.1	8
Sequence 5 } 3		164	2	80						
Sequence 4 } 3		70	7	156						
Sequence 112		78	240	872	24.9	3.0	13.1	0.3	7.7	7
2. Dry Zone										
Sequence 88		390	1764	4400	58.7	36.5	28.7	0.7	5.0	15
Sequence 132		273	245	2148	88.9	5.7	13.6	0.3	4.0	16
Sequence 16		445	552	2908	44.5	19.5	47.9	1.0	2.9	6
Sequence 99		398	358	1712	72.7	8.1	17.0	0.6	4.0	10
(c) Amount of Exchangeable Nutrient Available after 12 months by Addition of Crushed Basalt (<.25 mm)										
At An Application Rate of : ⁴					Exchangeable Nutrient					
					Kg/ha					
					K	Mg	Ca			
Before Application (Soil Buffer)					120	240	1000			
100 tons/ha					n.a	400	1400			
200 tons/ha					n.a	480	1525			
300 tons/ha					200	520	1700			
Amount of Nutrient Element in 300 Tons of Crushed Basalt from Whole Rock Analysis					2490	12062	14286			
(d) Amount of Crushed Rock (<0.06 mm) Needed to Supply 100 Kg of Exchangeable K by some Sri Lankan rocks ⁵ :										
					Tons					
1. Quartzite, Marble					833					
2. Basic Charnockite, Microcline Granite					133					
3. Bt Gneiss					100					
4. Pink Granite					80					
5. Granulitic Gneiss					67					

1. Cooke (1967)
2. Handbook of Fertiliser Recommendations, Sri Lanka (1985-1986)
3. Moorman and Panabokke (1961)
4. Gillman (1980)
5. Nivas et al., (1987)

amounts of K removed by rice in Tables 5.1 and 5.2a). The recommended input of K (one of the primary bio-essential elements) in fertilisers for these crops averages 50 Kg/ha according to recommendations, and fall far below nutrient levels removed by the crops in the case of Rice and Tea (Table 5.2a). In the wet zone the amount of exchangeable K available in the top soil appears to be barely sufficient to provide an annual yield. However as with the dry zone soils the exchangeable K is less than 1 percent of the total reserve calculated assuming an average density of 2 g/cm^3 for the soils. While the reserves in the wet zone are an order of magnitude higher than that of the Amazon soils (Kronberg, 1976) it can be clearly seen that these reserves are an order of magnitude less than those of the dry zone soils which contain primary feldspars. In this context, the fact that the exchangeable reserve remains less than 1 percent in both climatic zones is noteworthy.

Gillman (1980) mixed crushed basalt with tropical Queensland soils at application rates of 100, 200 and 300 tons/ha, and increased the cation exchange capacity of the highly leached soils from 6 meq/100g (same range as those of the wet zone soils of Sri Lanka), to 14 meq/100g corresponding to the CEC of the dry zone soils at the highest application rate. Table 5.2 (c) shows the degree by which applications of crushed basalt raises exchangeable K, Mg and Ca. Apparently that the highest rate of application could raise the exchangeable cations of most of the wet zone soils other than the subgroup of laterite soils (sequence 148) to that of the dry zone soils.

In a similar experiment Nivas et al., (1987) measured the quantities of exchangeable K released by common rocks of Sri Lanka . Hb bt gneiss and granulitic gneiss provide 1.25 and 1.5 g Potassium per Kg of rock respectively. Table 5.2(d) gives an estimate of the amount of very fine crushed rock needed to yield 100Kg of exchangeable K. If the annual recommendations of K for the crops as indicated in

Table 5.3(a) were to be met by providing 50 Kg/ha of exchangeable K, half the amount of crushed rock given in Table 5.2 (d) has to be applied per hectare. For example in the case of coconut, if there are 173 palms per ha, each tree would receive 194 Kg of granilitic gneiss as against 0.1 Kg of Muriate of Potash, the commercial fertiliser. The magnitude of crushed rock needed to provide requisite amounts of elements compared to commercial fertilisers is and probably has been the major drawback to its commercial application. To this need be added the problems of spreading 50 tons of crushed rock per ha, in terms of man power, as well as that of problems that may arise due to mass scale erosion of the applied powdered rock and attendant problems of silting drainage systems.

5.4 The Agricultural Dilemma

The vulnerability of Sri Lanka's economy (resulting from economic dependence on agriculture) to the continued sustaining capability of her arable soils was pointed out in Chapter I. Its extent is exposed to a further degree, by the results of this study.

Simply stated, Foreign Trade, depends heavily on cash crops growing in the wet zone, that require copious rainfall, with such characteristics as high intensity and distribution throughout the year. Paradoxically, the very same rainfall that allows lush growth of vegetation, also results in continuous leaching of soil elements, thus creating a soil mineralogy low in its buffering capacity of bio-essential elements. It is the thoroughness of this removal, exemplified by the direct conversion of primary rock minerals to kaolin and gibbsite, both in the silt and clay fractions that is highlighted geochemically and mineralogically in this study, and requires further consideration, because of its agricultural significance.

These results force attention on the fact that continued maintenance of fertility in these soils under present day technology, demands continuous addition, in ever increasing amounts, of chemical fertiliser, most of which will invariably be leached. Unfortunately this will be true for rock powder too, though the rate of removal is likely to be far less due its lower solubility. Rock powder has the added advantage of supplying a greater range of elements than any chemical formula can. The results from this study should be considered together with the alarming development of widespread Mg deficiency and pockets of micro-nutrient deficiencies throughout the wet zone, that was reviewed in section 1.2. These findings advocate the introduction of rock powder with soluble chemical fertiliser as part of immediate government agricultural policy to delay further deterioration of soils. In the absence of a technique to transform kaolinite to smectite under soil conditions, a stop-gap proposal to mechanically introduce smectite with rock powder fertiliser, to absorb to some extent, elements released during fertiliser dissolution, may be feasible.

5.5 Recommendations for Further Study

Cost benefits of adding rock powder (containing smectite) as fertiliser, need to be established. Field studies to determine the rate of loss of smectite and rock powder in soils would form a natural extension of this study. Rate of loss of smectite and rock powder by dissolution could be monitored by X-ray diffraction as well as by monitoring soil solution chemistry. Such studies would be of benefit to determine ideal rock powder/smectite compositions required to maintain long range soil fertility and avoid element toxicity and environmental degradation. Soil erosion data needs to be developed in parallel with such a study.

Comparative studies of the annual variation in chemical composition of soil solutions from wet zone and dry zone soils are

urgently needed to complement this study, and obtain an in-depth understanding of the complexities of weathering taking place within an intensely seasonal environment as that brought on by the monsoons. The complexities were barely glimpsed by the present study through X-ray, electron microscope and ground water studies. This could help in understanding the conditions under which smectite forms in soils. This will lead to a better data base to judge if smectite could be made to form in wet zone soils by altering wet zone soil solutions in a cost effective manner. To be in step with the emerging trend noted with new agricultural technologies an environmental impact study is also necessary in order to make the use of rock powder admixed with smectite commercially viable.

Lappé (1986) summarises the research of several social economists who studied the tragic famine in Africa, when he says that "there is no country in the world in which the people could not feed themselves from their resources". By the same token, there is no reason why a country need be under-developed. Watts (1987) cites an example from the semi-arid Hausaland of Nigeria where traditional farming methods have been supporting large populations. Their success reveals their ability to cope with the vicissitudes of semiarid ecosystems by expert adaptation of farming practices to changing environmental conditions resulting from sound knowledge amassed through millenia of agronomic observation and experimentation. This example reinforces knowledge of the fact that economic success can be achieved from careful planning and utilisation of resources even where conditions conducive to success are at their poorest. Perhaps one of the distinctive qualities of developed countries is their capacity for far sighted planning, not their abundance of resources. An exemplary leaf can be taken from the far sighted development of agricultural policy projected towards the year 2000, by the U.S. Department of Agriculture.

Several seminars and workshops were sponsored by the U.S. Department of Agriculture during the years 1981 and 1982 (Canter,

1986) to determine from among emergent trends in agricultural production technologies, those most likely to be adopted commercially by the year 2000. In assessing their applicability, equal emphasis was given to their Environmental Impact, as for increase in efficiency in Land Use and Natural Resource Use. Eleven emergent Agricultural Production Technology clusters were singled out.

It is of educational value to digress and analyse these trends in technology, to once more assess their relevance to increasing tropical agricultural production. Of the 8 clusters pertaining to crop production technology, erosion control, soil management and waste utilisation ranked 4th among the following 8 emerging technological clusters:

- o genetic engineering (increase plant growth efficiency)
- o water management (including irrigation)
- o plant growth regulation (modifying physiological processes
chemically)
- o erosion control, soil management, and waste utilisation
- o enhancement of photosynthetic activity (increase yields by
maximising energy conversion)
- o plant pest control strategies
- o nitrogen fixation (small scale biological production of
nitrogen fertiliser)
- o multiple cropping

Nutrient Management technology per se is not considered as a main emergent agricultural technology division any longer. In fact soil-water-plant interaction in terms of critical water stress stages in

plant growth forms a subdivision of water management, within the emergent technologies compared to the non-subdivision status of developing improved chemical fertiliser, in the USDA study. Improving usage of waste as a form of organic fertiliser is the only predicted subdivision connected with fertiliser, considered to be part of the emergent technology. In fact Nutrient Management technology is predicted to be a major issue in Environment Quality Control rather than agricultural production technology. Methods of optimising nutrient application are ranked as more important avenues of study even within this category, compared to seeking out alternative sources of nutrients (organic fertiliser) or developing fertilisers with chemical inhibitors to delay nitrification and leaching. However, it is noted that assessment of Environmental Impact, a critical issue with future technology, was based on the Unger (1977) study, when rock powder application as an alternative fertiliser was in the processes of being developed in Brazil.

Analysis of the above emergent crop production trends projected towards the year 2000 in the West, appear to underscore a trend in distancing itself from further emphasis on chemical fertiliser by leaning towards manipulating crops to be more efficient bio-machines with higher capabilities of pest and weather resistance, and photosynthesis. Futuristic fertiliser research is considered to devolve on enhancing biological nitrogen fixation in soils in both leguminous and non-leguminous plants. These lines of research would undoubtedly reduce requirements of highly soluble nitrogen inputs as fertiliser. Hence, they will generally improve surface water quality, in addition to conserving non-renewable sources of energy. Therefore, these emergent technologies are likely to meet concerns regarding (1) shortages of energy, water and soil resources; and (2) deterioration of environmental quality due to pesticide and fertiliser usage and soil erosion (Canter, 1986).

Since cash crop farming in the tropics has been a fairly recent

development, sufficient time has not elapsed to formulate an agricultural tradition capable of sustainability (in concert with environmental conditions) as in traditional farming practices. Thus it is advisable that a study similar to that of the USDA, be conducted for the tropics, to map out the course of future agricultural technology, independently, since it is clear that a base line assumption of the fertility of tropical soils cannot be made as in the case of young temperate soils. Most particularly with tropical soils, nutrients removed must be returned, if sustained agricultural productivity is to be maintained. As an initial step, information available on obtaining agronomic productivity on a sustained basis - such as annual nutrient requirements of cash crops should be collated with knowledge of the available reservoir of such nutrients in soils. Results from this study concerning the nature of tropical weathering and the intensity of tropical leaching undoubtedly indicate that soil nutrient enhancement in its totality has to be a major division of emergent agricultural technology in the tropics, if Agriculture is to sustain the economies of these countries in some part, in the future as well. As Norman Hudson (1988) states, "it has taken nearly fifty years to realise how little of the North American experience is relevant in the very different conditions of the developing world". This statement applies in more than one way. In western countries soil fertility is maintained at an enormous cost to agriculture through the use of chemical fertiliser. To drastically reduce operational costs, western economies have also had to weed out small farmers. Intractable problems such as farm subsidies and small farm foreclosures riddle these economies. Developing countries cannot afford to follow this path since so much employment is generated through agriculture. Hence increased production must be obtained through other approaches. Application of rock powder to sustain soil fertility to curtail the need for increased use of chemical fertiliser presents a very attractive and practical alternative. A second round of mistakes simply cannot be afforded again by blindly transferring technology from the west.

APPENDIX 1
GEOCHEMICAL DATA FOR STANDARDS

Table 1-j. Comparison of XRF analyses at U.W.O Laboratories with Standard Analyses

Standard	Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	P ₂ O ₅	Na ₂ O	LOI	Total
sy-2	59.76	.13	11.85	6.23	.30	2.58	8.16	4.51	.40	3.69	1.50		99.11
sy-2	59.64	.13	11.95	6.27	.31	2.59	7.97	4.54	.39	3.97	1.50		99.27
sy-2	60.01	.13	11.85	6.26	.30	2.48	8.00	4.60	.39	4.42	1.50		99.94
sy-2	59.48	.12	11.82	6.30	.30	2.58	8.11	4.57	.39	3.70	1.50		98.87
sy-2	60.03	.13	11.87	6.24	.31	2.50	8.03	4.55	.37	3.68	1.50		99.21
sy-2	59.97	.12	11.90	6.26	.30	2.63	8.06	4.55	.39	3.93	1.50		99.61
sy-2	59.93	.12	11.78	6.28	.30	2.53	7.93	4.57	.38	3.91	1.50		99.23
sy-2	59.88	.11	11.80	6.26	.31	2.48	7.99	4.56	.37	5.19	1.50		100.46
sy-2	59.91	.12	11.89	6.26	.30	2.63	8.10	4.61	.39	3.86	1.50		99.57
mean	59.85	.12	11.86	6.26	.30	2.56	8.04	4.56	.39	4.04			99.47
(standard ¹ syenite-2:													
sy-2	60.10	.14	12.12	6.28	.32	2.70	7.98	4.48	.43	4.34			
s.d.	.19	.01	.05	.02	.01	.06	.07	.03	.01	.49			.49
error%	31	5.76	.45	.33	1.65	2.35	.93	.66	2.62	12.1			.49
mrg-1	38.75	3.84	8.02	18.04	.16	12.61	15.17	.22	.05	.41	1.89		99.16
mrg-1	38.94	3.68	8.08	17.98	.17	12.91	14.92	.19	.06	.62	1.89		99.44
mrg-1	38.85	3.80	8.08	18.03	.17	12.60	14.92	.21	.06	.40	1.89		99.01
mrg-1	38.80	3.81	8.16	17.98	.16	12.80	14.91	.21	.06	.73	1.89		99.51
mrg-1	38.93	3.77	8.02	18.06	.17	12.83	14.94	.20	.06	.35	1.89		99.22
mrg-1	39.11	3.75	8.09	18.01	.17	12.87	14.86	.20	.04	.53	1.89		99.53
mrg-1	38.80	3.76	8.13	18.13	.18	12.64	14.90	.20	.05	.06	1.89		98.74
mrg-1	38.84	3.75	8.05	18.06	.17	12.89	14.82	.17	.04	.34	1.89		99.02
mrg-1	38.81	3.81	8.03	17.94	.17	13.00	14.97	.21	.06	.80	1.89		99.70
mrg-1	38.81	3.82	8.10	17.97	.18	12.85	14.87	.19	.06	.14	1.89		98.88
mean	38.86	3.78	8.08	18.02	.17	12.8	14.93	.20	.05	.44			99.22
(standard ¹ gabbro-1:													
mrg-1	39.32	3.69	8.50	17.82	.17	13.49	14.77	.18	.06	.71			
s.d.	.11	.05	.05	.06	.01	.14	.10	.01	.01	.24			.32
error%	.27	1.24	.58	.31	3.88	1.07	.64	7.00	15.60	54.3			.32

¹ Geol. Survey Canada (1980); paper 80-14.

Detection limits for major oxides at U.W.O and X-ray Assay laboratories = 0.01%

Detection limits for trace elements at X-Ray Assay laboratories = 10 ppm

Detection limits for trace elements at U.W.O laboratory:

Ga Nb Sr Rb = 1 ppm

Y = 2 ppm

Ba = 3 ppm

Zr = 5 ppm

La = 10 ppm

APPENDIX 2

**SITE LOCATION DESCRIPTIONS OF SAMPLES
USED FOR DETAILED ANALYSIS**

Appendix 2

Site Location Descriptions of Samples Used For Detailed Analysis

These samples constitute a segment of the samples taken during the reconnaissance survey mentioned in section 2.5. Sample location is given in fig. 2.1. Plate 1 provides an indication of colour and gross texture.

1. Wet Zone

Sequence 148 was taken from a productive laterite pit in the mildly undulating coconut and rubber growing lowlands on the Panadura Horana road. Sampling was done within the unconsolidated gravelly yellowish brown atypical upper section of the sequence according to the sampling design. However an additional, >100cm sample was taken from the soft productive laterite zone consisting of vasicular red and yellow mottled laterite.

Sequence 153 was taken from a strikingly reddish yellow tea estate roadcut in Watawala which is located in the wettest (>5000mm) part of the country in the tea growing highlands. No fresh outcrop was available, hence a sample at greater depth than 10% cm, the 600 cm sample which contained decomposed rock fragments within a reddish-yellow matrix was taken in lieu. Even though sampled from the wettest part of the country, in contrast to sequence 148, this sequence contained many small rock fragments and was not a typical laterite. (Fresh outcrop is still available because of continuous uplift and exposure of fresh outcrop from erosion.)

ii. Intermediate Zone

Sequence 112 was located in the Narramaala coconut growing lowlands close to a granitic gneiss outcrop. The 100cm sample consisted of coarse quartz and feldspar aggregates welded together by kaolinitic material.

Sequence 61 (elevation ~300m) was located on the migmatitic base of an "arena" structure at Nugawela, in the coconut growing uplands close to kandy.

Sequence 88 was sampled from the reddish brown soils typically developed on dolomitic marble, located in the mildly undulating coconut growing uplands edge on the Matale-Dambulla road close to Naula.

iii. Dry Zone Lowlands

Sequence 99 was taken from an uncultivated reddish brown regosol at a road cut developed on a leucocratic migmatite/granitic precursor, along the Anuradhapura-Puttalam road, close to Anuradhapura.

Sequence 132 was sampled from an uncultivated immature brown to yellowish brown soil developed on a granitic migmatite underlying a forested grove on the Amparai-Siyabalanduwa road, close to Amparai. Sample 132 contained abundant grains of feldspar and quartz. Sample 132scf was from the topsoil of an adjoining sugarcane field, 3m away.

Sequence 16 was taken at the base of a migmatite outcrop within a sugar cane plantation on the Sevanagala-Suriyawewa road.

APPENDIX 3

**SOIL SEQUENCE INFORMATION
FROM MOORMAN AND PANABOKKE (1961)
USED FOR COMPARISON IN THIS STUDY**

Table 3-1. Soil Sequence Information used for Comparison in
the Present Study ¹

X Data	TOT CEC. (NH ₄ →Na)	BASE SAT %	Sequence	Rainfall (mm)	Rocktype
1	63.30	63	11	1775	Marble
2	65.50	71			
3	50.20	86			
4	12.70	77	1	1525	Mica Schist
5	14.40	51			
6	17.40	52			
7	18.40	53			
8	8.10	74			
9	9.40	73	2	1800	Acid Gneiss
10	8.20	55			
11	8.80	56			
12	7.30	59			
13	11.80	77	10	2200	Mica Gneiss
14	11	39			
15	10.70	41			
16	31.80	61	3	2050	Mica Schist
17	20	51			
18	16.40	31			
19	15.80	26			
20	13.50	20			
21	13.30	24			
22	34.30	13	6	2250	Colluvium over Gt Gn seperated by stone line
23	17.90	5			
24	15.50	5			
25	11.50	5			
26	18.90	49	9	2600	Mica Schist
27	7.60	57			
28	8.50	70			
29	15.50	4	5	3825	Bt schist & Gt Sil Schist
30	11	5			
31	11.90	4			
32	11.70	4			
33	10.10	20	4	3250	Gt Sil Schist
34	9	9			
35	9	7			
36	10.20	6			

1. Moorman and Panabokke (1961)

APPENDIX 4

MASS BALANCE CALCULATIONS: INITIAL STUDIES

Appendix 4

4-4 Mass Balance Calculations: Initial Studies

To successfully estimate mass changes during weathering, it is necessary to be as certain as possible regarding the choice of index elements in addition to making certain that the levels found in a sequence are indeed derived from the same precursor material, i.e. that they are genetically related. It is noted that mass balance calculations are a very popular tool used by geologists from the proliferation of its use in literature, however very few researchers screen their samples to determine that pre-requisites for meaningful calculations are present especially in soil studies, before hand.

Since quantifying abundance variations failed to provide sufficiently specific insight into the nature of element behaviour with respect to choosing immobile elements, element abundances normalised to Ti instead of Zr, assuming its relative immobility and greater analytical reliance as suggested by Nesbitt (1979), were plotted in figs. 4.2 to 4.4, to obtain an indication of their interrelations. This technique can be used, both to (i) identify elements that are geochemically affiliated, i.e. 'process related', and to (ii) identify mineral transformations. Depletion of an element towards the surface relative to Ti is indicated by an upward trend with depth, i.e. decreasing element/Ti ratios, whereas enrichment towards the surface will have an opposing trend. An element that has identical behavioural patterns with depth to Ti will be flat-lying. Identical behaviour to Ti implies that the elements are conserved as Ti is and thereby gets enriched with progressive weathering. Hence this method was used to search for the latter type of elements. Relative enrichment or depletion of elements can be gauged by the ratio value along the y axis. As elucidated by Nesbitt et al., (1980) the trends reflect mineral transformations during progressive weathering.

Progressive decrease of the maximum y axis value in figs. 4.2 A-E from dry to wet zone sequences (from 1.6 to 12.0) does point towards the enrichment of Ti and depletion of cations Mg - K, as expected with increasing weathering intensity. However these figures highlight more strongly than even fig. 4.1A did, (see section 4.2), the retention of Mg relative to all the other mobile cations within the most weathered sequences, the laterite sequences - 145 and 148 (fig 4.2 A). As pointed out earlier, this was observed to be true for the Amazon Bauxites when compared with the less weathered Amazon sequences (Kronberg, 1987, fig.4; Rinkus, 1987). Separate analyses of the yellow and red segments of laterite sequence 148, shows Mg to be enriched in the Fe - rich red segments, (fig. 4.2 A - sample no.11 compared to sample no.10). In contrast in the dry zone profiles (fig. 4.2 D-E) Mg shows the greatest depletion, more so than Na and Ca. K appears to be the least mobile of the four elements. Dominance of K over the other three elements is to be observed in the wet zone profiles that are less weathered in the sense that some primary minerals are retained in the silt fraction as in sequences 142 and 123 in fig.4.2 A ; sequences 61, and 115 in fig. 4.2 C. Intermediate zone sequences 112 and 88 (fig. 4.2 C) have major element patterns similar to the dry zone sequences.

All the dry zone sequences that derive from granitoid precursors have the same order of depletion, $K < Na < Ca < Mg$ (fig. 4.2 D,E) whereas, the less weathered sequences (excluding 145, 148 and 153) in the wet and intermediate zone rocks, show variation in the order of depletion, among Ca, Mg and Na.

Dry zone profiles show a relatively persistent downward trend of element:Ti ratios from fresh rock to the 30cm level with a slight upward trend at the 10cm level in some instances, compared to the absence of such a noticeable trend in the wet zone profiles. According to Table 4.1 in most of the dry zone profiles Ti abundances increase

at a greater pace towards the subsurface whereas the mobile element abundances decrease denoting depletion, excepting at the surface, where a local enrichment results thus accounting for the observed trend.

The changes with depth of the ratios to Ti of the resistate elements Al and Fe are plotted in figs. 4.3 A -C. Within the wet zone sequences (fig. 4.3A), significantly high variation of Al/Ti and Fe/Ti obtains in the deeper horizons of the laterites, (sequences 145 and 148) compared to the other wet zone sequences that appear to be relatively uniform at the scale chosen. Trends in the dry zone sequences (fig. 4.3C) appear to be less even for Al and Fe between sequences, though within a given sequence both Al and Fe show a downward (towards surface) depletion trend. Of the elements considered it appears that only Al and Fe co-vary with Ti in some of the wet zone profiles, including the upper zone of the laterite sequences; differing behavioural patterns between Al, Fe and Ti can be distinguished in the lower zones of the laterite sequences.

Uniformity, is once more noted as with Al and Fe ratios to Ti, in the Nb plots in some of the wet zone and most of the dry zone sequences, at the scale chosen (fig. 4.4 B,E and G). However, flat-lying plots for all four elements, Rb - Nb excluding Zr, are noted only in sequences 153, (fig.4.4 A,B), 88 and 147 (fig. 4.4 D) and 16 (fig.4.4 E). In addition Nb plots remain uniform within further sequences in which Zr plots are not (fig. 4.4 A,B: sequences 148 - upper 100cms; fig. 4.4 F-H: sequences 131, 99); overall uniformity of Nb plots is also more marked than for Zr. Exceptions where Zr is more uniform than Nb are observed for example, in fig. 4.4 A-C: sequences 145-upper 100cm, 49 and 71; fig. 4.4 H: sequences 99, 100. Of these, sequences 71, 16 and 100 show little within sequence chemical variation (Table 4.1, also figs. 4.2 A-E). Overall, the Zr plots are highly variable. These plots show that Al, Fe and Nb behave similarly to Ti in more sequences than does Ti and Zr, even though

Fig. 4.2 A-B. Changes in alkalis and alkaline earths relative to TiO_2 in Wet Zone sequences.

Fig. 4.2 C. Changes in alkalis and alkaline earths relative to TiO_2 in less weathered Wet and Intermediate Zone sequences.

Fig. 4.2 D-E. Changes in alkalis and alkaline earths relative to TiO_2 in Dry Zone sequences.

Sample depth increases to the right for each sequence.

FR = Fresh rock

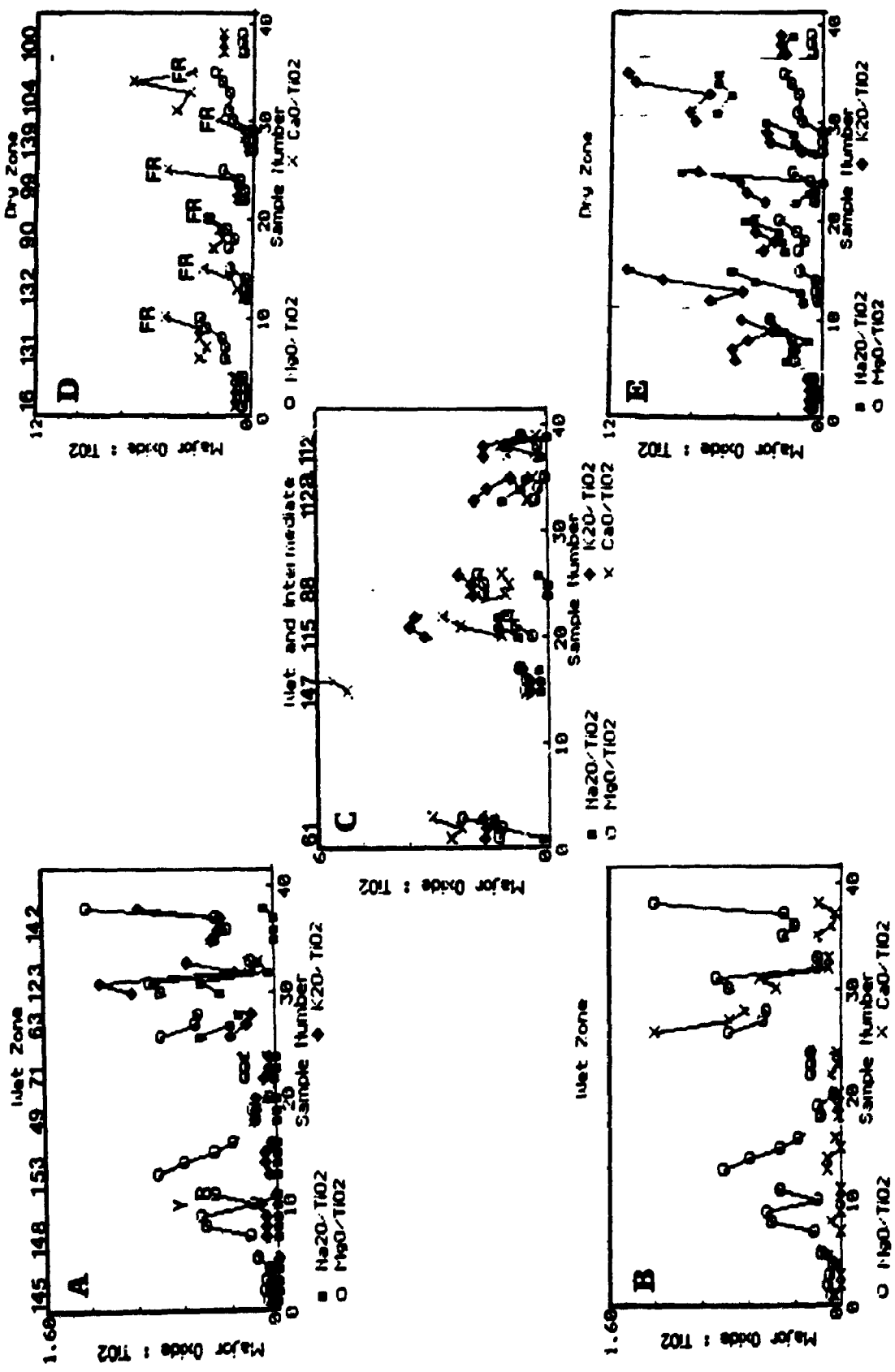


Fig. 4.3 A. Changes in aluminium(Al) and Iron(Fe) relative to TiO_2 in Wet Zone sequences.

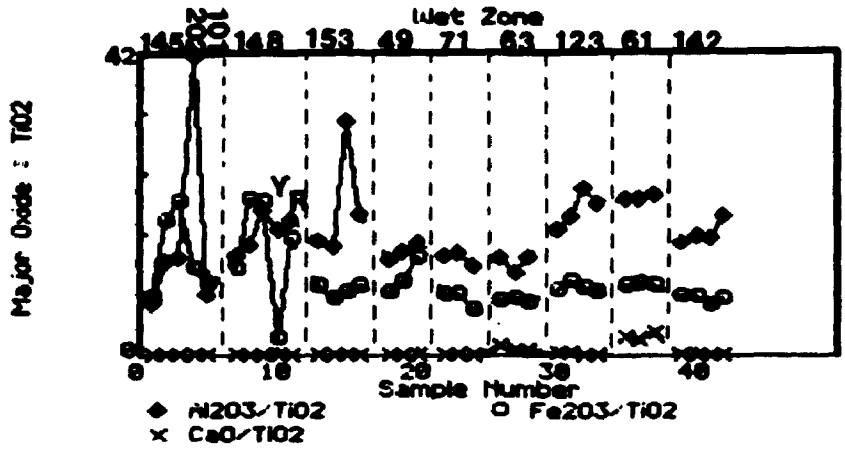
Fig. 4.3 B. Changes in aluminium(Al) and Iron(Fe) relative to TiO_2 in less weathered Wet and Intermediate Zone sequences.

Fig. 4.3 C. Changes in aluminium(Al) and Iron(Fe) relative to TiO_2 in Dry Zone sequences.

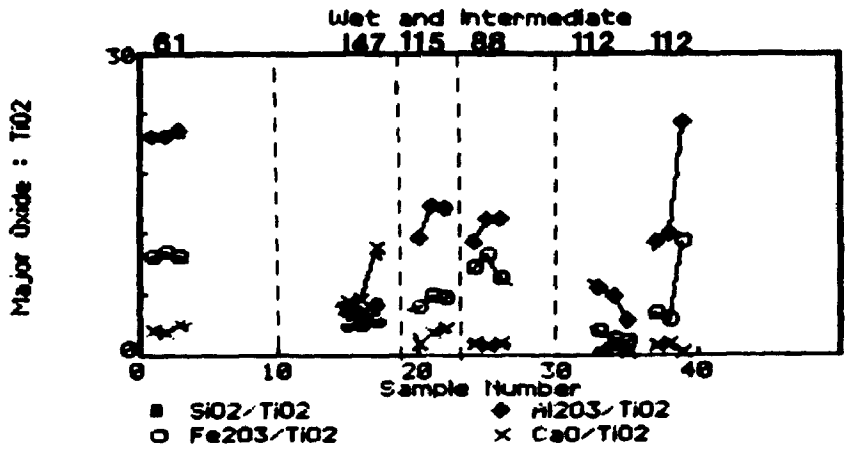
Sample depth increases to the right for each sequence.

FR = Fresh rock

(A)



(B)



(C)

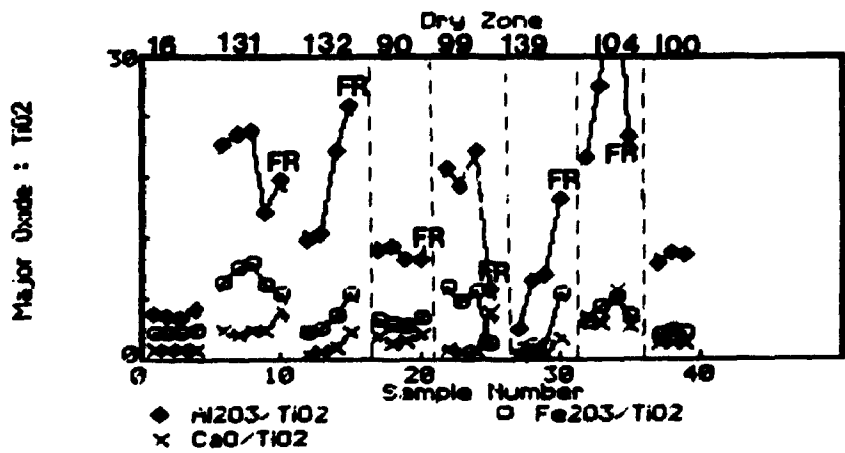


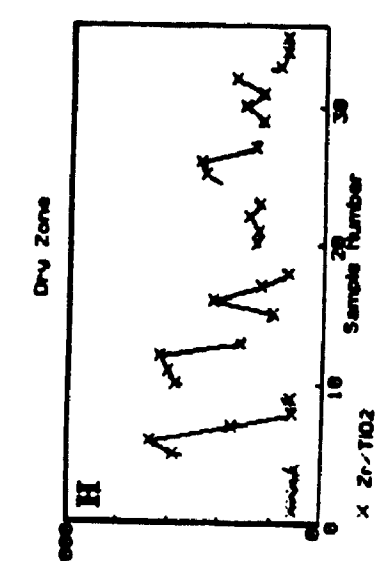
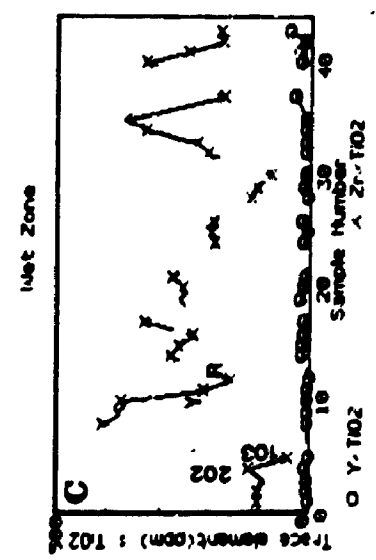
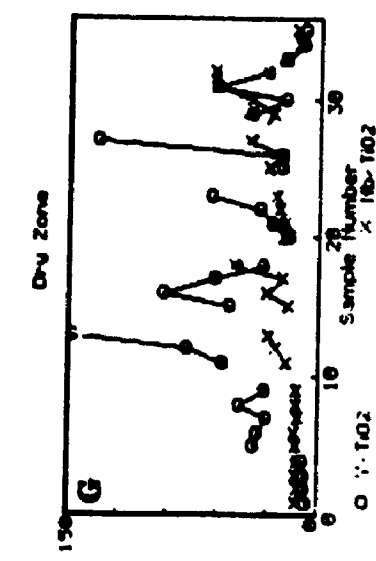
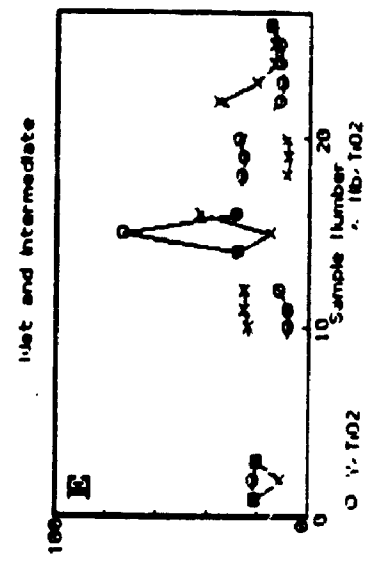
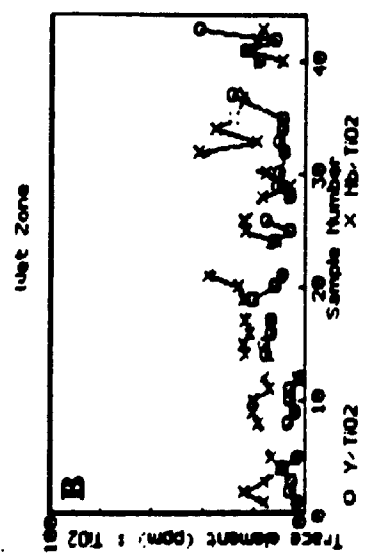
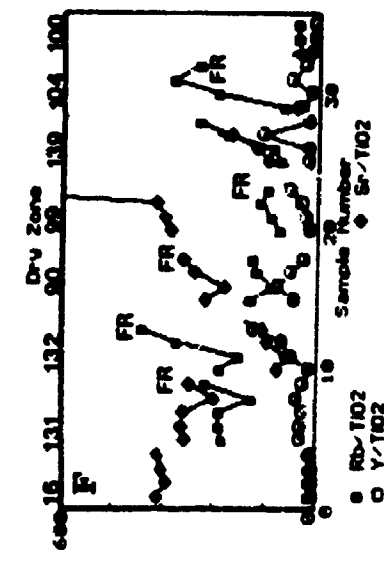
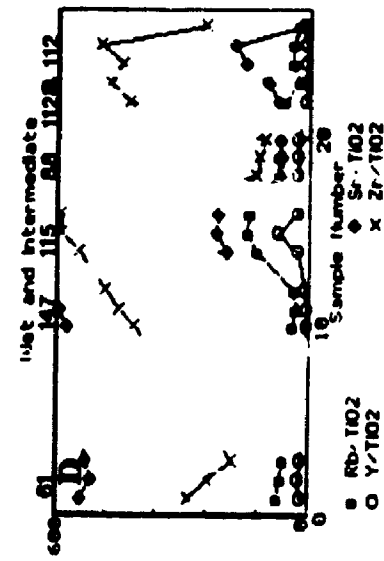
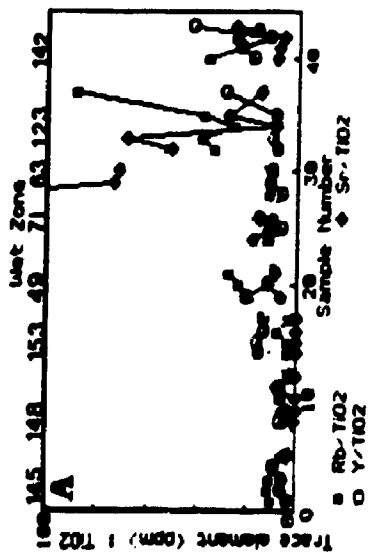
Fig. 4.4 A-C. Changes in trace elements relative to TiO_2 in Wet Zone sequences.

Fig. 4.4 D-E. Changes in trace elements relative to TiO_2 in less weathered Wet and Intermediate Zone sequences.

Fig. 4.4 F-H. Changes in trace elements relative to TiO_2 in Dry Zone sequences.

Sample depth increases to the right for each sequence.

FR = Fresh rock



uniform trends for Al and Fe in addition to the trace elements occurs only in sequence 16 (fig.4.2 C and figs. 4.4 F-H). Several combinations of uniformity between elements prevail when figs. 4.3 and 4.4 are considered. Few sequences however have depletion trends for all four trace elements excluding Zr. Exceptions are sequences 132, 99, and 139 (fig. 4.4 F,G).

The complex pattern of variation that changes between climatic zones for Mg - Na and the combinations of the relatively more resistant elements exhibiting uniform behaviour relative to Ti, appear to reflect soil mineralogy and changes in mineral composition within sequences more than process relations. For example the dominance of K indicates the persistence of relatively resistant k-feldspars as opposed to plagioclase feldspars, especially from the granitoid terrain of the dry zone (an observation found to be universal), whereas the higher Mg content in the laterites suggest a change in element association in minerals at this late stage of weathering when these primary minerals are no longer present. If the enrichment in the red segment of the laterites is used as an indicator Mg is possibly substituted for Fe in Fe oxides because of its close chemical affiliation to Fe, in addition to occurring in the 14\AA Al-hydroxy vermiculite and retained in secondary minerals. High variation of Si relative to Ti substantiates its mobile nature as discussed previously in section 4.2 as does the increasing variation of Al and Fe at depth in the laterite profiles.

The nonuniformity of most of the Zr plots is cause for concern since it implies lack simultaneous enrichment with Ti during weathering. Stated differently, the high variability of the Zr plots imply removal or addition of one element relative to the other. These observations also suggest that Ti and Nb possibly constitute a better choice as index elements for many of the sequences.

4.1.1 Brief summary of Methods of Investigation

Successive methods used to determine inter-element relationships were coefficients of variation analysis, element : Ti ratio analysis, cluster analysis and Spearman's rank coefficient analysis. Ti vs. Zr plots and enrichment factor analysis were used to seek out sequences with genetically related horizons (of common parent material).

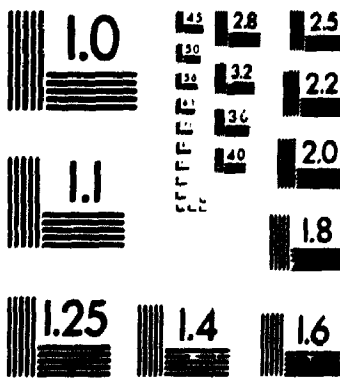
Coefficients of variation indicated that Ti and Zr were the most suitable immobile index elements to use for mass balance calculations. Plots of element : Ti were used to check this observation, to search for other alternatives and to note the behaviour of other elements relative to Ti. However plots of Zr:Ti which should be uniformly flat had both Zr and Ti been immobile during weathering were quite non-uniform. Hence an unbiased statistical analysis - Spearman's rank coefficient analysis - was carried out to check if other element associations that could be used as index elements were present. Results obtained validated the previous choice of Zr and Ti. Enrichment factor analysis further indicated that Zr and Ti were the least immobile by generally giving the highest enrichment factors among the elements. XY-plots of these two elements and enrichment factors were used for subsequent delineation of sequences developed on the same parent material prior to mass balance calculations.

Oxide analyses recalculated to dry weight (Table 4.1) were used in all calculations. (It should be noted that the detection limits for trace elements as reported in Appendix 1 vary between the two laboratories where the samples were analysed).

4

OF/DE

4



4-2 Check on Choice of Suitable Index Element with Statistical Methods

Since element to Ti ratio analysis and element variation analysis (section 4.3) provided conflicting information on the best choice of elements to use as index elements it was considered appropriate to use an unbiased statistical approach in order to check whether the choice of the pair Ti - Zr, constitute the best indicator for quantitative analysis and further evaluation of soil development, for all the sequences, especially because of the existence of a range both in climate and parent material within and from which the soil samples were collected.

High positive correlation between elements can be (i) process related, ie. can result from similar behaviour either depletion or enrichment from both physical and chemical processes, or, (ii) they can result from persistent association of an element pair within resistant minerals - Ti and Nb in rutile, for instance. An example of the former would be enrichment of Zr and Ti through the sequence even though the elements originate and reside in minerals drastically different from one another. Ti derived from ferromagnesian minerals and resistant minerals is transformed and retained in oxyhydroxides and persistent resistant minerals whereas Zr usually occurs in Zircon and remains in Zircon within the heavy mineral suite.

Because of this wide sample variation, samples were first clustered to obtain natural groupings among them prior to statistical correlation of the elements.

Two independent computation methods, CLUSTAN (Wishart, 1979) and SPSSx (1983) were used to produce cluster dendrograms in figs.4.5A and B. Both methods clearly indicate, that 2-3 natural groups exist even within the two major groups of soils belonging to the different

climatic zones. In the wet zone group, sequence 115 (calc gneiss), sequence 147 (beach sand with aragonite shells) and sequence 112, form a distinct cluster - Group 2 (figs. 4.5 A,B). The laterite sequences 145 and 148 and a few other highly weathered samples from other sequences form another cluster - Group 3 (ultra). The rest form the third large cluster. According to the cluster combine distance scale, Group (2) formed by sequences 115, 147 and 112 is very distinct from the other sequences. Hence it was decided to compute correlation matrices for Group 2 sequences separately from the others. A correlation matrix for Group 3 sequences were also calculated. In the dry zone group, a large distance separation exists between sequence 16, and the other clusters according to the SPSSX clustering program (fig.4.5C) whereas in the CLUSTAN dendogram, while sequence 16 is still considered as an outlier, it is grouped more closely to one of the remaining clusters (fig.4.5D). Once again the samples in the three clusters appear to be sufficiently unique for the two independent programmes to identify. Correlation matrices were calculated for the two major groups separately, exclusive of sequence 16.

Correlation matrices of the elements for the different groups are presented in Tables 4.6 - 4.9 and figs. 4.6 - 4.8, calculated using two computing techniques for comparison . The Spearman's Rank Correlation matrices were computed using SPSSX, and program BMDP (1983) calculated a simple distance matrix by considering the distance between successive pairs of elements as a means of judging inter-element relationships, which were subsequently displayed in the form of a dendogram (figs 4.6 - 4.8).

In the dendogram the first number next to each variable in a row is a measure of correlation between it and the first variable listed below it. The second number next to a variable in a row is a measure of correlation between it and the second variable down the line, and so on. Comparison with corresponding BMDP correlation matrices showed

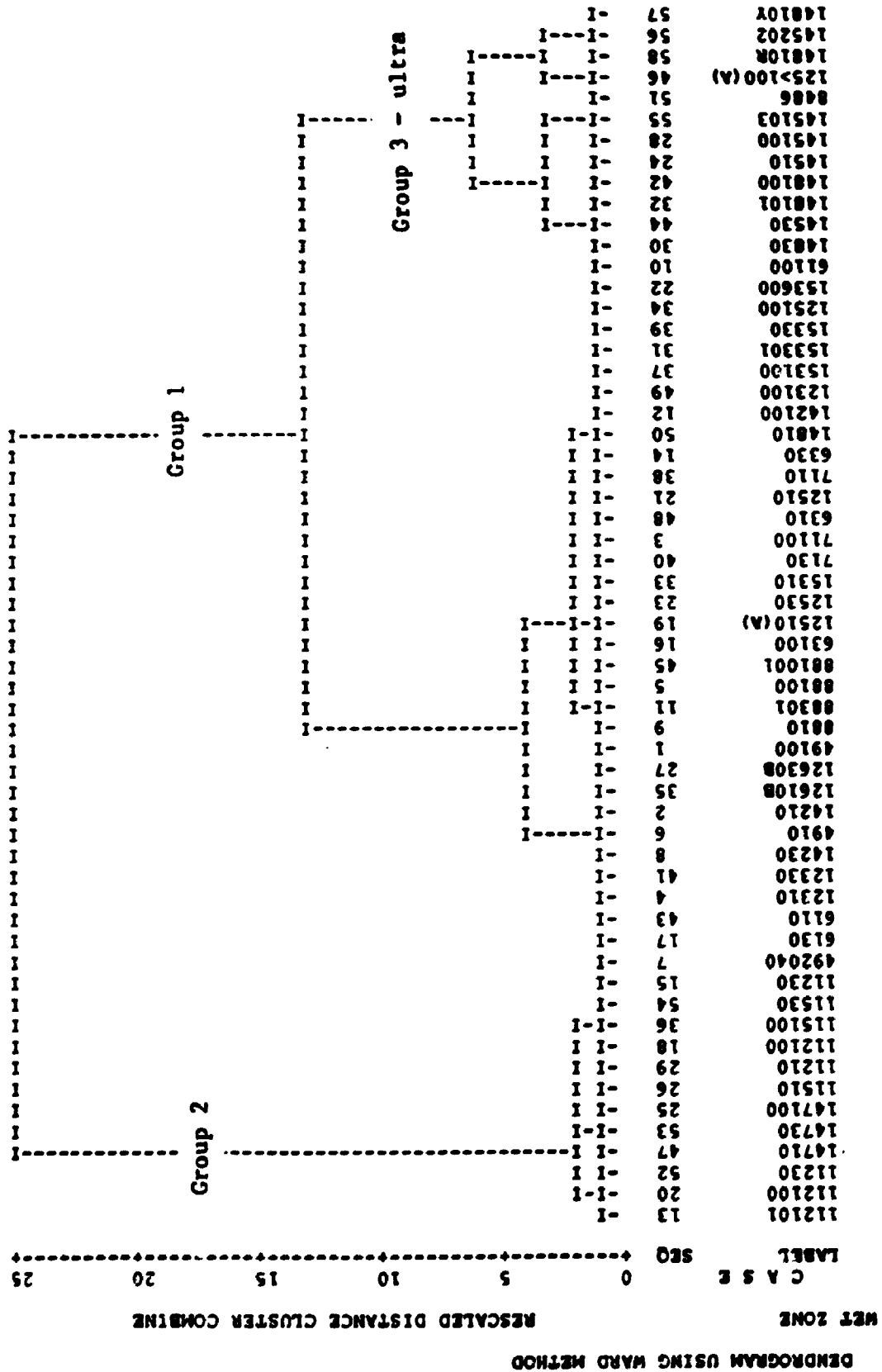


Fig. 4.5 A. Wet Zone cluster analysis (SPSSx).

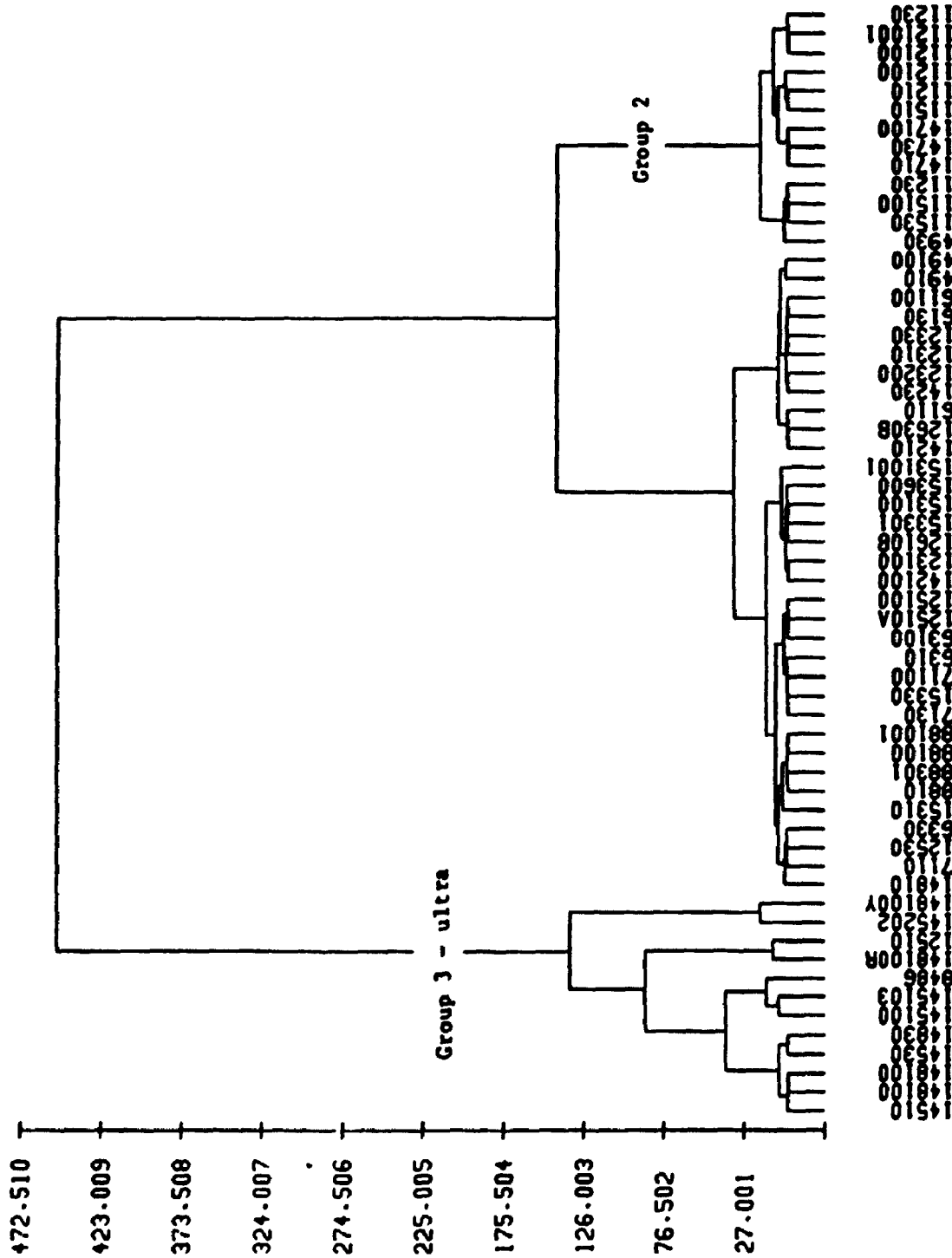


Fig. 4.5.B. Wet Zone cluster analysis (CLUSTAN).

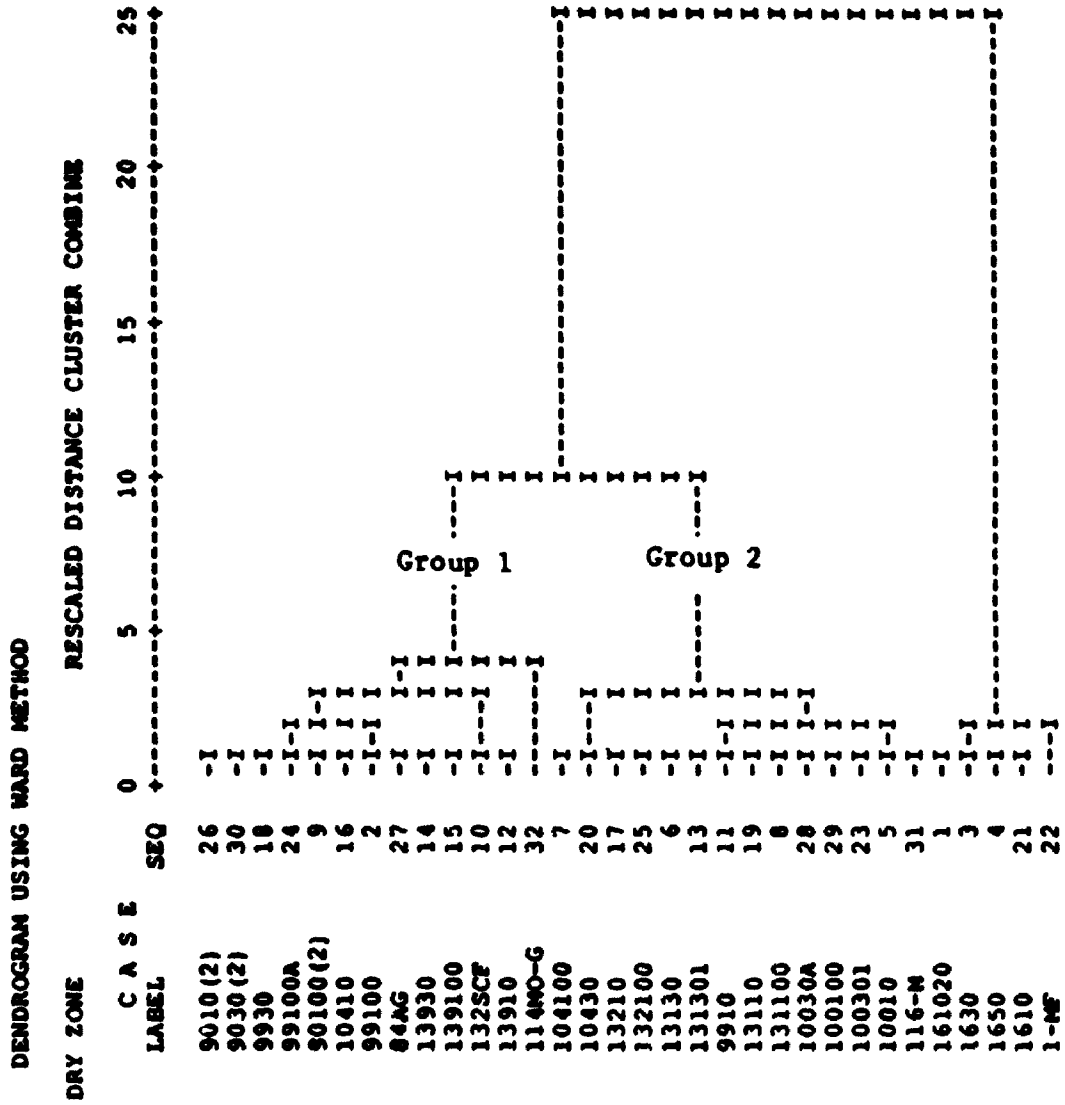


Fig. 4.5 C. Dry Zone cluster analysis (SPSSx).

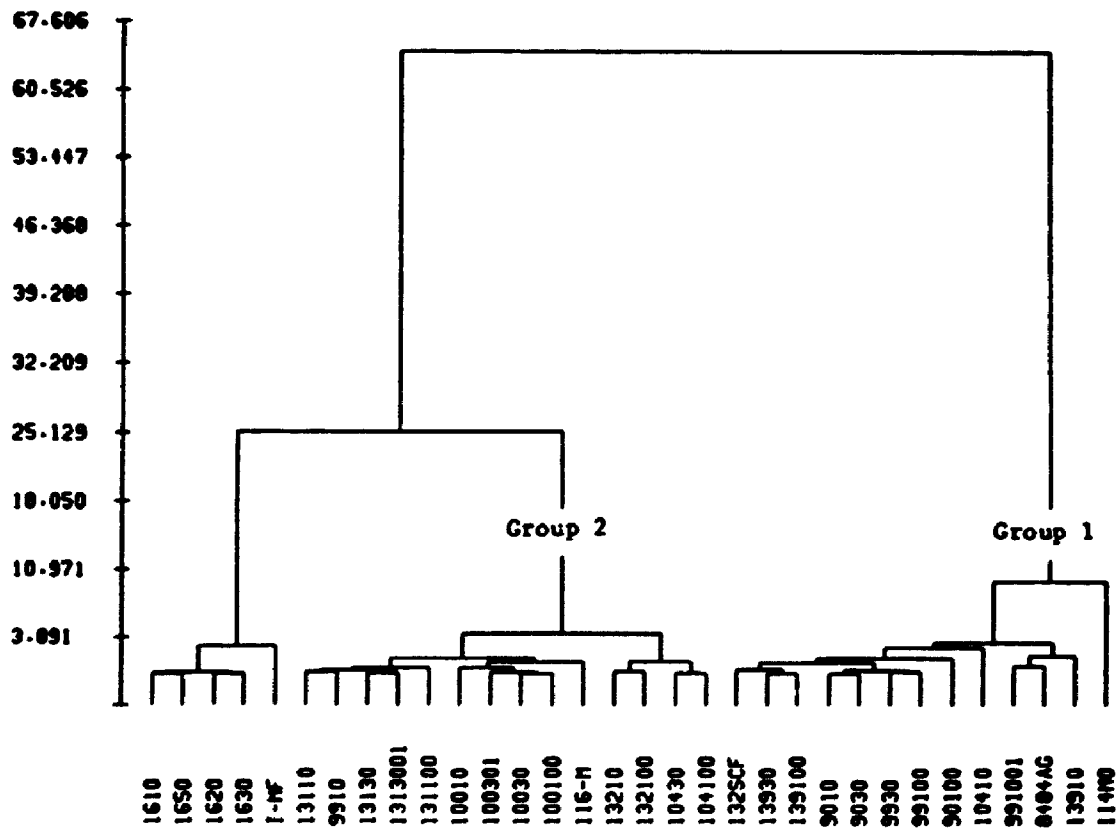


Fig. 4.5 D. Dry Zone cluster analysis (CLUSTAN).

that the two separate systems picked out most of the good correlations and trends, excepting that they did not coincide in the absolute figure of the correlations. A large discrepancy between the two systems was observed however in the dry zone Group.

When the wet and dry zone soil groups are considered individually (Table 4.6, figs. 4.6-4.7) strong correlations are obtained for Rb - K, Sr - Ca, in both zones; strong negative correlations obtain between Si and - Al, - Ti, - Fe, in both zones which was also pointed out in Chapter II. These correlations remain essentially the same when the zones are broken down to the group level. In the dry zone, Si is negatively correlated with Ca, Mg, and P as well, as opposed to the positive correlations found in the wet zone between these pairs. However these correlations change in strength and sign in some instances when the zones are broken down to group level. A strong correlation consistently seen in the dry zone as well as in Group 2 in the wet zone is that between Fe - Mg, and Ca - Mg (Tables 4.6 and 4.7; fig. 4.7) . Similarly, correlation between Fe, Al, Mg and Ca were deduced from the persistent downward depletion trends of these elements relative to Ti in figs. 4.3C and 4.2D.

In dry zone Group 1 sequences high positive correlations between Ti, Zr and Nb and negative correlations between Ti and the elements Al, Fe, and P which are unique to this group, exist (Table 4.10). The negative correlations between Zr and - Si, Al endorse the individuality of this group.

Some of the salient correlations relevant to the primary objective of the statistical analysis are summarised in Table 4.10. A high degree of index variability for a given pair is apparent among the groups. Ti and - Al, - Fe are positively correlated among one another in the wet zone where a more advanced stage of weathering prevails than in the dry zone. While Al - Fe are correlated in both zones, for the first time a negative correlation obtains between the

Table 4.6. Spearman Correlation indices for Wet and Dry Zone soils.

WET ZONE

SR	.7502**					
Y	.4506**	.3737*				
ZR	-.0395	-.0461	-.0299			
NB	-.1724	-.1655	-.1244	.3083*		
SI	.2680	.2758	.0595	.2198	-.3095*	
TI	-.1017	-.1174	.1148	.0177	.5401**	-.6762**
AL	-.4056**	-.3716*	.0177	-.1658	.3700*	-.7702**
FE	-.2929	-.4045**	-.1006	-.1690	.3598*	-.8832**
MN	.2821	.3315*	.4273**	-.3394*	-.2331	.0012
MG	.2964	.3422*	.4201**	-.1435	-.1302	-.2750
CA	.7010**	.8170**	.4011**	-.0637	-.2753	.3537*
NA	.6057**	.7942**	.2283	-.0720	-.2234	.3929*
K	.8789**	.7464**	.4607**	-.0425	-.3708*	.3893*
P	.1391	.1144	.0503	-.0604	.3506*	-.4140**

RB SR Y ZR NB SI

AL	.6033**							
FE	.6296**	.5999**						
MN	.0587	-.0536	-.0006					
MG	.1723	.1529	.1966	.4459**				
CA	-.1825	-.4448**	-.3858*	.4569**	.5760**			
NA	-.3146*	-.4000**	-.4261**	.3305*	.2628	.7802**		
K	-.2355	-.4481**	-.4871**	.3796*	.3848*	.7584**	.6902**	
P	.4235**	.3587*	.4589**	.2529	.3310*	.1428	.0077	-.0174

TI AL FE MN MG CA NA K

DRY ZONE

SR	-.3543							
Y	.2109	-.3365						
ZR	.5630**	-.1713	.4376*					
NB	-.2017	.1593	.2224	.3298				
SI	-.0029	-.6590**	.0143	-.2958	-.2156			
TI	-.2602	.3855	.1007	.4671*	.7460**	-.5577**		
AL	.0193	.5031*	.0637	.2040	.0712	-.8882**		
FE	-.2108	.4636*	-.0751	.0955	.0472	-.7629**		
MN	.1262	.2630	.3896	.5652**	.2831	-.5524**		
MG	-.3517	.5723**	-.2288	-.0999	.0927	-.7688**		
CA	-.3441	.7579**	-.2363	-.0715	.2027	-.8002**		
NA	-.0566	.5415**	.0371	.1335	.3877	-.4438*		
K	.7537**	-.0487	.0841	.5909**	-.0850	-.0511		
P	-.4688*	.6347**	-.1158	-.2134	.3386	-.5587**		

RB SR Y ZR NB SI

AL	.3747							
FE	.4459*	.7039**						
MN	.5195*	.3383	.4433*					
MG	.3920	.6746**	.8732**	.4133*				
CA	.4107*	.5964**	.6274**	.5027*	.8585**			
NA	.2866	.1948	-.0623	.3967	.1800	.6058**		
K	.0034	-.0264	-.3329	.1489	-.4840*	-.2645	.1987	
P	.4428*	.4474*	.4963*	.3972	.7051**	.7699**	.4929*	-.3757

TI AL FE MN MG CA NA K

* - SIGNIF. LE .01

** - SIGNIF. LE .001

Table 4.7. Spearman Correlation Indices for Dry Zone-Groups 1 and 2.

DRY ZONE - GROUP 1

SR	.2867					
Y	-.0624	.0086				
ZR	.7117*	.0390	.1526			
NB	.3000	-.2595	.1130	.7995**		
SI	-.4633	-.4039	-.0565	-.5604	-.4730	
TI	.5986	-.0836	-.1470	.8571**	.8880**	-.5824
AL	-.1076	.3984	-.1187	-.0385	-.1217	-.3736
FE	-.3145	.3343	-.3165	-.4011	-.2932	-.3132
MN	.4896	.1173	.4846	.4132	.3911	-.3829
MG	-.5746	-.1060	-.2264	-.6850*	-.4321	.1926
CA	-.1545	-.0585	.1413	-.1209	.1577	-.1154
NA	.5221	-.0251	.6056	.5557	.4709	-.2669
K	.9462**	.3984	-.1243	.7088*	.2407	-.4121
P	-.5014	-.1157	-.2261	-.7094*	-.4874	.2837

RB SR Y ZR NB SI

AL	-.1209								
FE	-.2527	.2967							
MN	.3691	-.5207	-.1074						
MG	-.5475	-.0440	.7290*	-.0745					
CA	-.0055	-.4725	.3846	.6446*	.6245				
NA	.3796	-.4044	-.4759	.8745**	-.3085	.4209			
K	.5604	-.0714	-.3242	.3251	-.6575*	-.3022	.3604		
P	-.5703	-.0974	.6426*	-.0335	.9694**	.6176	-.2382	-.6231	

TI AL FE MN MG CA NA K

DRY ZONE - GROUP 2

SR	-.7701**								
Y	.7143*	-.5066							
ZR	.7217*	-.6659*	.8297**						
NB	-.2414	.4178	.0179	-.2378					
SI	.0836	-.1077	-.2478	-.3099	.2800				
TI	-.4493	.5281	.0609	.0396	.3882	-.4290			
AL	.3608	-.2527	.4934	.5648	-.3711	-.7626**			
FE	-.1430	-.2088	-.0066	.2835	-.4445	-.7187*			
MN	.3363	-.1812	.4794	.6895*	-.1575	-.3050			
MG	-.4246	.1604	-.3496	-.1165	-.4378	-.6000			
CA	-.8713**	.7758**	-.5797	-.6571*	.1622	-.1912			
NA	-.3432	.5604	-.1903	-.4945	.5845	.3670			
K	.7236*	-.4928	.6722*	.5699	.0200	.1760			
P	-.5613	.7876**	-.2945	-.3760	.6693*	.1624			

RB SR Y ZR NB SI

AL	.1034								
FE	.1386	.5385							
MN	.3031	.3978	.2365						
MG	.2134	.2967	.8330**	.1834					
CA	.4246	-.3011	.1648	-.0884	.5648				
NA	.0572	-.6659*	-.6264*	-.3624	-.4637	.3626			
K	-.1344	.2486	-.3762	.3219	-.6095	-.7129*	-.1364		
P	.6671*	-.4383	-.4160	.0805	-.1535	.5384	.5851	-.2806	

TI AL FE MN MG CA NA K

* - SIGNIF. LE .01

** - SIGNIF. LE .001

Table 4.8. Spearman Correlation Indices for Wet Zone-Groups 1 and 2.

WET ZONE-GROUP 1

Y	.1510						
ZR	-.2282	-.0168					
NB	-.0337	.0170	.1944				
SI	.3579	.2694	.1616	-.2088			
TI	-.1455	.0435	.0503	.4975**	-.6019**		
AL	-.3481	.0211	-.1158	.2853	-.7427**	.5316**	
FE	-.3446	-.3151	-.0718	.3064	-.7503**	.5235**	
MM	.3017	.4976**	-.1916	.0905	-.0436	.2236	
MG	.1137	.2922	-.1023	-.0824	-.1955	.1254	
CA	.5753**	.3778*	-.2865	-.1074	.2580	-.0442	
K	-.8166**	.2451	-.1303	-.1796	.3313	-.1975	
P	.4569*	-.0026	-.0140	.2315	-.0302	.2336	

	RB	Y	ZR	NB	SI	TI	
FE	.3492						
MM	.1263	.0367					
MG	.1494	.0406	.5821**				
CA	-.2095	-.2660	.6454**	.6445**			
K	-.2469	-.4671*	.3998*	.4150*	.6558**		
P	-.0166	.0969	.5419**	.1913	.5362**	.4098*	
	AL	FE	MM	MG	CA	K	

* - SIGNIF. LE .01

** - SIGNIF. LE .001

- - - SPEARMAN CORRELATION COEFFICIENTS - - -

WET ZONE - GROUP 2

Y	.9160**						
ZR	-.0841	-.0723					
NB	.0378	-.0836	.7410**				
SI	-.6190*	-.6080*	-.1762	-.3166			
TI	.5868	.4526	.1342	.3732	-.8229**		
AL	.6863*	.7022*	-.2341	-.1150	-.8025**	.6488*	
FE	.6381*	.6264*	.0876	.2336	-.9133**	.7596**	
MM	.1746	.1989	-.7565**	-.7840**	-.0412	-.0304	
MG	.8347**	.6553*	-.0161	.2893	-.6720*	.7560**	
CA	.4290	.2329	.2770	.3810	-.1501	.3146	
K	.9419**	.9134**	-.1984	-.1833	-.5022	.4433	
P	.5621	.4287	.1574	.5190	-.8291**	.8687**	

	RB	Y	ZR	NB	SI	TI	
FE	.7750**						
MM	.4937	.1038					
MG	.5036	.6893*	-.0537				
CA	-.1679	.0607	-.4544	.6750*			
K	.6714*	.5143	.2791	.7000*	.3571		
P	.5229	.8338**	-.2133	.8158**	.3953	.3702	
	AL	FE	MM	MG	CA	K	

* - SIGNIF. LE .01

** - SIGNIF. LE .001

Table 4.9. Spearman Correlation indices for Wet Zone-laterite soils.

GROUP-ULTRA

SR	.8041*							
Y	.5637	.8228**						
ZR	-.5430	-.4353	-.0335					
NB	.6606	.4951	.2443	-.2916				
SI	-.1996	-.2250	.2342	.6273	-.2050			
TI	.6359	.6016	.3680	-.3273	.8702**	-.3727		
AL	.1160	.4500	.1721	-.4727	-.0319	-.5545		
FE	.0511	-.2739	-.5209	-.3636	.2688	-.5818		
MN	.1154	-.1545	-.2525	-.2590	.2973	-.2119		
MG	-.7211*	-.7255*	-.6754	.4601	-.2032	.1139		
CA	.6983*	.3420	.0304	-.5683	.4923	-.3275		
NA	.8587**	.6032	.2947	-.7900*	.4853	-.3568		
K	.0606	.2924	.4273	.4201	-.2449	.4110		
P	.2465	-.0618	-.2103	-.3678	.0207	-.0414		
	RB	SR	Y	ZR	NB	SI		
AL	.3091							
FE	.2091	-.1091						
MN	.4097	-.0141	.1742					
MG	-.1595	-.0638	.1139	.1982				
CA	.4623	-.0867	.2697	.5288	-.2896			
NA	.4587	.1784	.1529	.3696	-.7151*	.7559*		
K	-.1827	.0776	-.8904**	-.1845	-.1648	-.1355	-.0768	
P	-.0782	-.2989	.0598	.4620	-.0484	.7989*	.4382	-.0300
	TI	AL	FE	MN	MG	CA	NA	K

* - SIGNIF. LE .01

** - SIGNIF. LE .001

pair in the ultra Group of the wet zone (the laterites) as observed in the Venezuelan bauxite profile (Schorin and Puchelt, 1987). In this group, surprisingly, Zr is correlated with Si.

The three elements Zr - Ti - Nb are well correlated only in Dry Zone Group 1 sequences where, as noted above other strong correlations prevail. Ti and Zr are well correlated only in this group. Ti - P - Nb are all three well correlated in dry zone Group 2. Ti is more positively correlated with Nb than Zr in most groups. Imasuen (1987) obtained the same high correlation between Ti - Nb ($r=.8$), -the highest for an element pair with Ti-, for Nigerian tropical soils, even though in that study no attempt had been made to calculate separate indices for soils sampled from three different climatic zones that coincide with those of this study. Strong correlation between Zr-Ti, was absent ($r=.57$) as was any correlation of equal magnitude between Ti and any of the elements common to this study, other than Nb. In the present study also, near zero correlations occur between Zr - Ti in all groups except in dry zone Group 1 sequences and in the most weathered laterite group (ultra) in the wet zone where it turns negative (Table 4.10).

In brief, the features that are pertinent are: the difference in type of well correlated element pairs between the two climatic zones, especially that of the Al- Ti- Fe association in the wet zone compared the strong correlation between Fe-Mg, Ca-Mg, Ti-Nb pairs in the dry zone; the greater number of strong correlation prevalent in dry zone Group 1 and wet zone Group 2, though different in type; the unique correlation in the laterite (ultra) group between Si-Zr, Al-Fe and Ti-Nb; and the lack of strong correlation between Zr-Ti.

The negative correlation between Fe and Al found only in the laterite group (Table 4.10 and fig.4.8) is likely both a reflection of the Fe and Al enrichment observed in successive zones as discussed in section 4.3 and also of their existence as two separate oxides at

Table 4.10 Correlation Indices of Selected Element Pairs

	Ti-Zr	Ti-Nb	Ti-Al	Ti-Fe	Ti-P	Zr-Nb	Zr-Si	Zr-Al	Al-Fe	Al-Nb	Nb-P
Dry Zone - Group 1	.8571 ¹	.8880	-.1209	-.2527	-.5703	.7995	-.5604	-.0385	.2967	-.1217	-.4674
Dry Zone - Group 2	.0396	.3882	.1034	.1386	.6671	-.2378	-.0399	.5648	.5385	-.3711	.6883
Dry Zone	.4671 (.4116) ²	.7460 (.7681)	.3747 (.3533)	.4459 (.6910)	.4428 (.8676)	.3298 (.6279)	-.2958 (-.0980)	.2040 (-.0727)	.7039 (.6894)	.0712 (-.0137)	.3386 (.4205)
Wet Zone	.0177 (.1452)	.5401 (.5468)	.6033 (.5907)	.6296 (.5217)	.4235 (.4364)	.3083 (.3410)	.2198 (.1723)	-.1658 (-.1665)	.6000 (.5585)	.3700 (.3533)	.3506 (.3605)
Wet Zone - Group 1	.0503	.4975	.5316	.5235	.2336	.1944	.1616	-.1158	.3492	.2853	.2315
Wet Zone - Group 2	.1342	.3732	.6488	.7996	.8687	.7410	-.1762	-.2341	.7750	-.1150	.5190
Wet Zone - Ultra	(-.2944)	(.8123)	(.0282)	(.0907)	(-.0092)	(-.1235)	(.6673)	(-.2495)	(-.4898)	(-.3915)	(-.0275)

1. Spearman's rank correlation indices

Dry Zone-Group 1: 99, 90, 139 (mainly)

2. BGP Distance correlation indices (within brackets)

-Group 2: 104, 100, 131 132

Wet Zone-Group 2: 112, 115, 147

-Ultra : 145, 146

this stage of weathering, in contrast to their association in primary minerals as in biotite that appears to be reflected in the high positive correlation between them in the dry zone. A similar process related relationship between Zr and Ti may be operative in the laterite sequences. The negative correlation between Zr-Ti in this group combined with the positive correlation between Zr-Si suggest that at this stage of weathering, these correlations result from the difference in physical processes acting on Zr and Ti (Nesbitt, H.W., 1987, pers. comm.). Zircon and quartz possibly accumulate in the upper 100cms, to give a quartz rich zone as observed in xrf results, because Ti, and even possibly Al and Fe bearing oxyhydroxides are likely elluviated or leached out, in these sequences where the pH in soils agitated in water is between 4-5.

On the other hand, the good correlations that are observed in dry zone Group 1 sequences where primary minerals are abundant, as well as the contrast in type of correlated pairs between the soils of the differing climatic zones that are marked by different mineralogical suites, seem to suggest that the indices reflect changes in mineralogy in terms of element associations in minerals more than process related associations caused by element enrichment or depletion as was expected from this study. For example the Ca - Mg association in the dry zone that is not observed in the wet zone Group 1 and ultra group is likely a reflection of their association in primary minerals that occur in the dry zone, which are absent in the two highly weathered wet zone groups. If behavioural associations were reflected then, since both these elements are lost during weathering they should still give high positive correlations in the wet zone. Similarly the positive correlation between Ti - Nb is likely a reflection of their association in a mineral that is resistant to weathering as it is prominent again in the laterite sequences (Table 4.10) even though a process related correlation cannot be ruled out. According to Wadehol (1978), the close association of Nb and Ti has long been recognised and a good correlation between Nb+Ta and Ti in rock forming minerals

as well as in bauxitic minerals, both residual and clay types, exist. Its geochemical behaviour is similar to Ti in that it occurs in ferromagnesium host minerals that release it during weathering to be absorbed onto clays, in addition to occurring in resistates such as Ti-minerals. A depletion order of $Si > Nb > Al = Fe$ is reported. Hence the near zero correlation between Ti - Zr which occurs in most of the Groups, is possibly a reflection of their preservation in separate minerals rather than being an indicator that the two elements are not enriched simultaneously during weathering. If this interpretation is correct then the use of the pair Ti-Zr in mass balance calculations is validated.

APPENDIX 5
COEFFICIENT OF VARIATION ANALYSIS

Appendix 5 Analysis of Variation Analysis

The coefficients of variation (=standard deviation/average * 100) were computed from xrf data of individual elements.

5.1. Variation of Si, Ti, Al and Fe

Low variability is observed in Table 4.5A for sequence 16 from the dry zone and sequences 71, 63, 123, 61, 147, 115, 88 derived from a spectrum of precursor materials in the wet zone. These wet zone samples in turn had relatively uniform enrichment/depletion patterns (Table 4.2A and B) and were not as depleted as the SW and W lowland samples, excepting sequence 71. Of this suite, sequences 71 and 147 were sampled from a river terrace and beach sand respectively where uniformity prevails as a result of good sorting. Samples 115 and 88 are derived from impure marble parent rock. Sequences 61 and 16 were sampled from a parent migmatite while 63 and 123 had charnockitic precursors. All excepting sequence 63 were under cultivation, (see Appendix 2).

Large differences are observed in the most weathered sequences, sequences 145, 148 and 153 on the whole especially when the variability calculated by taking into consideration, the upper 100 cms (145-3ss, 148-4ss) is compared with the sequence inclusive of deeper horizons (145-5ss, 148-6ss). This compares with the large variation noticeable in element abundances in xrf analyses (Table 4.1) in the lower levels compared to the upper levels of these sequences, the significance of which is discussed in section 4.3.

5.2 Bio-Essential Major Elements and Sr

The 4 major bio-essential elements, Mg,Ca, Na, and K show much

greater variation than the elements considered so far, as reflected by the higher mean values of the coefficients of variations (Table 4.5B). Very high mean variation of oxides (Ca=46) for example is correlated with wide ranges of geochemical status categories (fig. 4.1A) and the ordering of the mean values (Ca > Na > Mg > K) substantiates the trends observed in fig.4.1. to a remarkable degree. Extremely high variation within sequences, as in sequences 148, 145, for Ca values, sequences 88, 99 and 112 for Na values is correlated with excessive depletion and/or unusual enrichment of these elements in some of the horizons, especially the surface horizon (Table 4.1). In the instance of excessive Ca depletion sited above, close to the detection limit of the analytical technique (Table 4.1, sequence 145, for example) a difference of 0.14 between 3 samples with two at .01 abundance and the other at 0.15 wt % results in a coefficient of 143. Presence of approximately 4 such sequences, 148,145 and 125 have (Table 4.5B) resulted in high mean values. In addition instrumental errors would further increase variability at such low levels . In contrast in the dry zone samples where abundances are well above the detection limit of the analytical technique (Table 4.1) and the absolute value of the difference between samples far exceed the value sited above, the mean coefficient values are significantly lower .

Trace elements in both climatic zones have similar ranges of variation (Table 4.5B) with the exception of Sr. Variation of trace elements in the dry zone is of the same level of the alkalis and alkaline earths. Sr and Ba (where analysed) like Ca and Mg, have high variabilities, in the wet zone soils, (Table 4.5B), in concert with the wide range of abundances depicted in fig.4.1. As with Ca and Mg this results from sequences, for example 148, 125 and 112, where near complete removal of these elements coexists with levels with anomalous values in the highly weathered soils (see sequence 148, Table 4.1). Rb has a similar degree of variation as Al and Ti in the wet zone, in spite of being more depleted relative to crustal levels (fig. 4.1A).

APPENDIX 6

**POSSIBLE EVIDENCE OF AL AND FE FRACTIONATION
DURING LATERITISATION**

Appendix 6

Possible Evidence of Al and Fe Fractionation during Lateritisation

In sequence 148, strong fractionation of elements has taken place between the red verniform segments and yellow matrix (Table 4.1) at a hand sample scale. Sr, Y, Zr and K are enriched in the yellow matrix in addition to Si and Al while in the red segments Fe and Mg are noticeably abundant. In sequence 145 the upper 100cms have higher Fe and low Al contents compared to the lower level 145202 where Al exceeds Fe in abundance. This relative enrichment of Fe and Al in two successive zones is a commonly observed phenomenon, both in studies of Sri Lankan and other laterite profiles (Dahanayake, 1982; Schorin and Puchelt, 1986; Banergi, 1983; Craig and Loughnan, 1964). Correlation coefficients calculated by Schorin and Puchelt, (1986), give negative indices between Al-Fe. They explain the variation of Al through the profile as the result of congruent / incongruent dissolution of kaolinite depending on pH and silica activity. The negative correlation between Al-Fe is not addressed. Craig and Loughnan (1964), explained the distribution of Fe as resulting from redox changes associated with ground water saturation, however the anomalous coupled enrichment of Fe and Al in successive zones is not quite adequately explained by this mechanism alone.

SEM observations made by Muller and Bocquier, (1966) and Ambrosi and Nahon (1986) clearly indicate replacement of kaolin by hematite, within the red hematitic spots, red compacted verniform zones and the kaolinitic yellow matrix in the mottled clay and the upper soft iron crust layers in the profiles studied. The Fe is considered by Ambrosi and Nahon (1986) to be generated by the destruction of the iron crust at the surface and transported by highly desaturated, and hence aggressive waters to lower horizons. In this profile part of the Al

released as a result of the kaolinite replacement was accommodated by another generation of finely crystalline kaolinite, while part of it was deduced to have been transported out of the horizon from mass balance calculations. The negative correlation between Fe-Al and the enrichment of Fe observed in the upper zones is partially explained by this mechanism. Geochemical analyses of the complete profile have not been presented to check whether an Al rich zone existed at depth hence it is not possible to relate directly to the couplet of Fe-rich and Al-rich zones observed in the Sri Lankan profiles. Since profiles exist that do not show this phenomenon as well, it would appear that replacement of kaolinite by hematite by either congruent and or incongruent dissolution of kaolinite, are both possible depending on water activities and pH, resulting in variations observed between profiles. This would require further study involving soil solutions to explain all of the observations. However the fact that Fe and Al are relatively mobile in profiles undergoing intense weathering as in lateritic profiles is clearly brought out from both SEM and XRF analyses and hence are considered unlikely candidates as indices for mass balance calculations in this study.

APPENDIX 7

**CORRESPONDING USDA NOMENCLATURE
OF SRI LANKAN SOIL CLASSIFICATION**

Appendix 7

Corresponding USDA Nomenclature of Sri Lankan Soil Classification

Characterisation of the samples shows that the eight sequences studied in detail fall into five of the fourteen recognised Great Groups in Sri Lanka. According to Moorman and Panabokke (1961) these five Great Groups correspond to the suborders within the Ultisol, Alfisol and Inceptisol Orders of the U.S.D.A. 7th Approximation (1960). The five Great Groups and their corresponding 7th Approximation classification (within Brackets) in order of importance are:

1. Reddish Brown Earths (Rhodustalf great group/Ustalf Suborder/Alfisol Order).
2. Red Yellow Podzolic soils (Typochrult great group/Ochrult Suborder/Ultisol Order).
3. Reddish Brown Lateritic soils (Rhodochrult great group/ Ochrult Suborder/Ultisol Order).
4. Noncalcic Brown soils (Ultustalf great group/Ustalf Suborder/Alfisol Order).
5. Immature Brown Loams (Ustochrept great group/Ochrept Suborder/Inceptisol Order).

According to the U.S.D.A. classification, Ultisols are soils without a prominent highly base saturated Al horizon (mollic epipedon) shows distinct evidence of clay illuviation in the Bt horizon (argillic horizon) and has a base saturation of less than 35% in the Bt horizon; some weatherable minerals are present in the sand and silt fractions. Alfisols are similar to Ultisols except that their base

saturation in the Bt horizon is greater than 35%. Inceptisols are soils that have an A1 horizon which is not prominent (ochric epipedon) and that has a colour B horizon (cambic horizon) which shows no appreciable signs of clay illuviation. In Sri Lanka these soils have an appreciable amount of weatherable minerals in the sand and silt fractions.

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