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WEATHERING OF GRANITIC TILLS AND THE GENESIS OF A PODZOL

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ABSTRACT. The bulk chemistry, bulk mineralogy, and clay fraction of a podzolic soil from the Plastic Lake Watershed of central Ontario was examined. The relatively constant Zr/Ti ratio of incremental samples through the soil profile suggests it developed on a homogeneous parent material, thus allowing quantitative documentation of the changes in the chemical constituents. The quantitative data indicate that in the upper zone (Ae horizon) all minerals are subject to significant dissolution and that plagioclase is weathered congruently. The middle zone of the profile differs considerably: most chemical components (including Al) are leached in much lesser proportions than the upper zone, and Fe and Mg are accumulated. Vermiculite, hydroxy-interlayered vermiculite (HIV), and kaolinite dominate the <2 μm fraction of this zone. Bulk compositional and XRD evidence suggests that most, if not all HIV is the first alteration product of mica transformation and that the authigenic production of HIV is a significant process in the middle zone (B horizon). The genesis of this profile is not greatly affected by the chemical translocation of Al, which is currently thought to play a critical role in podzol genesis.

INTRODUCTION

Podzolic soils and the process of podzolization have been the subject of intense research for over 100 yrs (Lag, 1987). These soils occupy a large portion of the boreal forest zones of the northern hemisphere (Wilding, Smeck, and Hall, 1983) and are considered to form only under acidic conditions. Podzols are most often associated with a parent material low in base cations or weatherable minerals; hence these soils are unable to buffer incoming acidic solutions (McKeague, DeConinck, and Franzmeier, 1983). For these reasons, podzols have received considerable attention, especially with respect to acid rain studies (for example, Likens and others, 1977; Mazzarino, Heinrichs, and Folster, 1983; Paces, 1983; April, Newton, and Truettner Coles, 1986; Li and others, 1988). In addition, the deforestation of boreal forest zones may further deplete the nutrient status of podzols to the extent that subsequent reforestation may be hampered as a result of the depleted state of the soil (Chesworth and Marcias-Vasquez, 1985).

Podzols are characterized by an upper eluviated Ae horizon, middle podzolic B horizons which have significant accumulations of amorphous Fe, Al, and organic matter, and lower parent materials (McKeague, Ross, and Gamble, 1978). The most characteristic property ascribed to podzolic soils is the movement or "vertical separation" of Fe and Al between eluviated Ae horizons and podzolic B horizons. The factors affecting podzolization (climate, parent material, vegetation, relief, and time) are relatively well known (McKeague, Ross, and Gamble, 1978; McKeague, DeConinck, and Franzmeier, 1983). However, the process by which

podzolization occurs has been of considerable debate over the past decade. Theories have concentrated on the relative importance of humic substances or organic matter (and its associated organometallic complexes) versus amorphous or non-crystalline secondary phases as agents of the chemical transport of Al and Fe (for example, De Coninck, 1980; Farmer, 1982, 1984; Buurman and Van Reeuwijk, 1984; Chesworth and Marcias-Vasques, 1985).

Evaluation of the bulk chemistry and mineralogy by comparison of primary and secondary minerals in weathered horizons versus the lower, least weathered C horizons of a soil can provide a useful means by which the overall change in the soil profile can be examined, provided all horizons have a common parent material. Concern as to whether or not soil profiles can be proven to be homogeneous has resulted in relatively few detailed reports on bulk chemistry and mineralogy of soil profiles. Evans (1978, 1980) and Evans and Manley (1983) have applied bulk chemical techniques to podzolic soils in northern Ontario using both quartz and Zr as immobile components to which changes in chemistry could be compared. Santos, St. Arnaud, and Anderson (1986) used Zr/quartz ratios to document the losses of major elements in luvisolic profiles in Saskatchewan. Mazzarino, Heinrichs, and Folster (1983) and Folster (1985) have utilized similar methods to determine overall watershed weathering rates of soils in central Germany by bulk compositional methods using a geochemical balance sheet and quartz as a basis for comparison.

Many of the studies listed above rely on the quartz content or quartz content/immobile element ratio to determine the relative losses and gains of chemical constituents. However, even the use of quartz as an "immobile" phase has been challenged by results from recent dissolution studies; quartz may be subject to dissolution within the soil profile, primarily in zones rich in organic acids (Bennett and Siegel, 1987). The use of insoluble element ratios such as Zr and Ti as a test for homogeneity has been suggested (Chapman and Horn, 1968). If a given weathering or soil profile is composed of a uniform parent material, then the ratio of two insoluble components will remain constant through the profile regardless of the degree of weathering. The degree of variability of the ratio has been subject to considerable debate (Drees and Wilding, 1973; Evans, 1978). However, April, Newton, and Truettner Coles (1986), studying podzolic profiles in the Adirondack region in the United States, have used bulk compositional soil data to determine the relative gains and losses of the soil chemical constituents using Ti as a conservative element to which changes were compared. This approach is adopted here and further developed in an attempt better to understand processes affecting the formation of podzols.

This study of the Plastic Lake Watershed is part of a large project investigating the effects of acidic precipitation on forested catchments in central Ontario (Dillon, Reid, and de Grosbois, 1987). The effect of acid rain on soils is difficult to determine without a complete knowledge of the

reactions that govern the chemical changes in the profile and the resultant changes in mineralogy. In this study we investigate the bulk chemical and mineralogical trends of a soil profile originally homogeneous (as determined from "insoluble" constituents). In addition, the clay mineralogy of the profile has been determined, and this information, combined with bulk chemical trends, provides evidence for the processes governing chemical redistribution or podzolization.

METHODS

Site description.—The Plastic Lake Catchment is located south of Dorset, Ontario in the Muskoka-Haliburton region of central Ontario (fig. 1). Plastic Lake is typical of low ionic strength Precambrian Shield headwater lakes in central Ontario, most of which are sensitive to acidic precipitation (Dillon, Reid, and de Grosbois, 1987).

Approx 50 to 70 percent of the local bedrock is dominated by subvertically dipping granitic biotite gneisses. The remainder is hornblende-biotite amphibolite and minor crosscutting pegmatite veins. Bed-

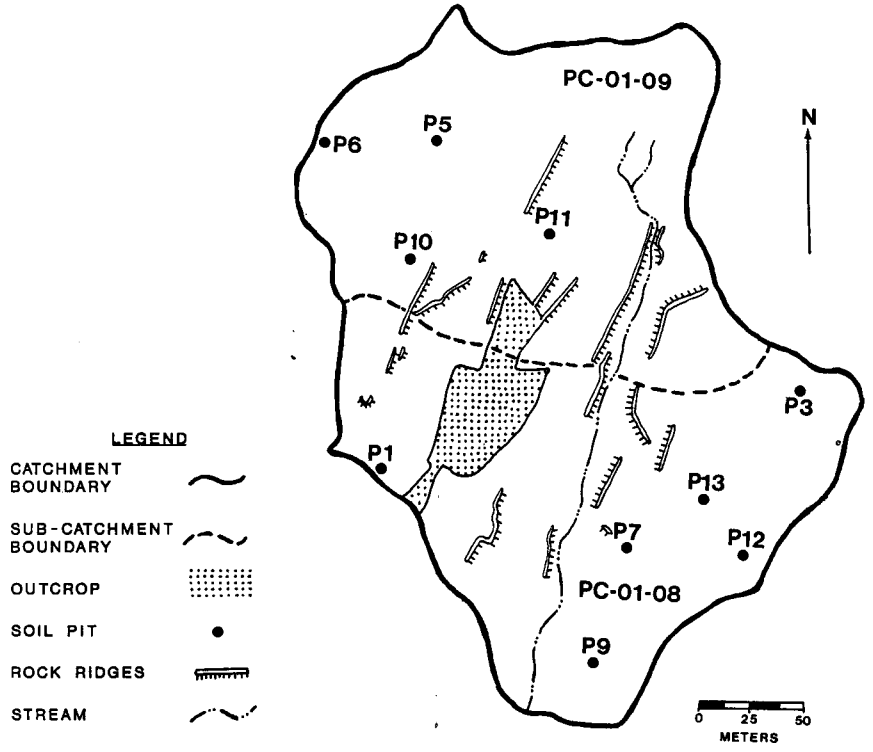


Fig. 1. Location of the P11 soil pit in Plastic Lake subcatchment, located at 45°11′N and 78°50′W.

rock outcrops comprise 5 to 10 percent of the 5.5 hectare study area and control the topographic expression of the catchment; local highs are composed mainly of granitic gneisses, and lows of amphibolite. The remainder of the catchment is covered with coarse-textured, weakly developed podzolic soils plus minor occurrences of gleysols in the poorly drained lowland areas; all soils are developed on thin sandy basal tills (Dillon, Reid, and de Grosbois, 1987). The soils of the catchment are generally < 0.5 m thick although the chosen study site P11 (fig. 1) is 1.2 m thick and is one of the deeper profiles of the catchment. The greater depth of this profile results from development on amphibolitic bedrock and the topographic location, which is in close proximity to the valley floor (very gently sloping). The soil mapping of the Plastic Lake catchment (Lozano, Vanderstar, and Parton, 1987) indicates the soils in the region of the P11 profile are ferro-humic podzols. According to the data presented by Lozano, Vanderstar, and Parton (1987), the podzolic B horizons of these soils meet the requirements of the U.S. System of Soil Classification as spodic horizons (McKeague, DeConinck, and Franzmeier, 1983). As our study did not concentrate on the chemical extractions required to classify properly these soils, we have not used horizon designations (for example, Ae, B, C) but the terms upper, middle, and lower zones which in our estimation roughly coincide with the Ae, Bhf, and Bf horizons respectively. Table 1 outlines some of the physical and chemical characteristics of the 7-5 profile (ferro-humic podzol) of Lozano, Vanderstar, and Parton (1987) and includes the horizon designations of the U.S. Soil Taxonomy system of classification.

Basal till comprises the parent material for these soils, and it was deposited during the final retreat of the Wisconsin Ice Sheet approx 10,000 yrs ago. The till is locally derived, as is evident by the dominance of angular stones of both gneissic and amphibolitic composition in the soils and local till deposits (Kirkwood, ms).

TABLE 1

Physical and chemical properties of the 7-5 profile in Plastic Lake, from Lozano, Vanderstar, and Parton (1987)

Horizon*	Depth	pH	Organic Carbon	Sand	Silt	Clay	Fe-p	Al-p	Fe-d	Al-d
	cm					%				
LFH (O)	7 - 0	3.9	37.0	--	--	--	0.04	0.07	0.24	0.09
Ae (E)	0 - 2	4.1	2.5	73	26	1	0.07	0.05	0.29	0.08
Bhf1 (Bs1)	2 - 32	4.8	10.0	61	24	15	4.60	2.60	4.50	2.80
Bhf2 (Bs2)	32 - 60	4.8	9.4	68	20	12	1.90	2.80	2.40	3.40
BC (BC)	60 - 75	4.9	2.9	71	22	7	0.58	1.20	0.98	1.40
R (R)										

*U.S. Soil Taxonomy horizon designations in brackets
-p Pyrophosphate extraction
-d Citrate-Bicarbonate-Dithionate extraction

As mentioned previously, the soils of the catchment are sandy and highly permeable. As the permeability is great, water transport within the profile is limited by the rainfall regime. In this region rainfall is neither frequent nor intense and results in very few periods when saturated conditions persist. The Plastic Lake Catchment experiences the highest flow and export conditions during the spring, but there is little or no flow in the late summer period (Wels, Cornett, and LaZerte, 1990). Such conditions are not favorable for the dominance of lateral flow within the catchment. In addition, lysimeter studies within the catchment further indicate that lateral transport is not significant.

Samples.—Undisturbed soil samples were collected from a soil pit 1.2 m deep, in 2.5 × 10 × 15 cm metal containers. These open-ended containers were pressed into the soil pit face to obtain a high density and volumetrically similar sample suite. Large stones (which did not fit the sampling boxes) were removed and retained for further analysis, and the sample box re-inserted at that level in the soil in the immediate vicinity.

Chemical analysis.—A portion of the air-dried <2 mm soil sample was crushed in a tungsten-carbide mill (30 sec) in preparation for XRF analysis. Analyses were performed on a Philips PW-1450 sequential wavelength dispersive spectrometer, and samples were prepared by fusion in lithium tetraborate after Norrish and Hutton (1969). The data for the P11 samples are presented in table 2. Mineralogical compositions of bedrock core, soil stones, and epoxy-impregnated bulk soil samples were determined using a JEOL JXA-8600 electron microprobe (4 wavelength dispersive spectrometers).

X-ray diffraction.—The mineralogy of the bulk soil samples was determined using X-ray diffraction (XRD) method. All samples (bulk and clay fractions) were analyzed on a Rigaku diffractometer using CoKα radiation utilizing a nickel filter, generated at 30 KV and 25 mA. The samples were analyzed under the following conditions: 2°2Θ per min, 1° divergent slit, 1° scatter slit, and a 0.3 mm receiving slit.

Clay mineralogical analyses were undertaken on bulk samples separated into 5 zones within the soil profile. We attempted to preserve the physical and chemical properties of these reactive fine-grained materials in the state that they exist in the profile by using a minimum of pretreatments. There was no removal of Fe oxides and cements, as there is no assurance that this treatment would not remove reactive hydroxy-Al interlayer or poorly crystallized material (Carstea, Harward, and Knox, 1970; Kunze and Dixon, 1986). The samples were pretreated with a 3 percent sodium hypochlorite digestion at 60°C to remove some of the organic matter. Dispersion of the bulk sample was achieved using probe-tip sonicator. The <2 μm and 2 to 20 μm fractions were removed by sedimentation. Separate portions of the sample were treated with 2N KCl and 2N $CaCl_2$ and washed a minimum of four times to remove excess salt and then freeze-dried. Fifty mg subsamples of both the Ca and K saturated samples were pipetted onto a glass slide and analyzed by XRD using the following conditions: Ca-54 percent relative humidity (RH),

TABLE 2

X-ray fluorescence data, bulk samples

SAMPLE	SiO2	TiO2	Al2O3	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	LOI	TOTAL	Zr
						wt.%							p.p.m.
P11- 0	69.05	0.53	14.11	3.65	0.07	1.44	3.04	3.56	2.51	0.13	1.66	99.73	261
P11- 1	69.86	0.54	13.98	3.68	0.07	1.18	3.12	3.64	2.63	0.13	1.61	100.44	299
P11- 2	70.06	0.51	13.94	3.65	0.07	1.32	3.10	3.44	2.63	0.14	1.46	100.32	282
P11- 3	70.61	0.48	14.23	3.41	0.06	1.04	2.94	3.07	2.68	0.12	1.25	99.89	289
P11- 5	72.38	0.36	14.26	2.46	0.04	0.91	2.69	2.78	2.66	0.08	1.59	100.23	146
P11- 7	69.60	0.52	13.96	3.64	0.06	1.22	3.04	3.45	2.42	0.13	1.61	99.65	256
P11- 9	68.06	0.66	14.31	4.54	0.08	1.45	3.30	3.50	2.45	0.12	1.68	100.13	302
P11-11	69.20	0.51	14.64	3.81	0.06	1.32	3.19	3.42	2.64	0.13	1.74	99.69	255
P11-13	64.91	1.04	13.77	6.96	0.11	1.50	3.45	3.74	2.31	0.16	2.53	100.50	672
P11-15	60.58	0.99	13.78	6.82	0.11	1.87	3.38	3.01	2.10	0.15	6.81	99.59	569
P11-17	59.45	0.77	13.96	6.11	0.09	2.52	3.69	2.56	2.10	0.14	8.52	99.91	397
P11-19	58.23	0.82	14.08	6.46	0.09	2.47	3.58	2.29	1.99	0.13	9.80	99.95	498
P11-21	57.53	0.81	14.12	6.68	0.08	2.47	3.53	2.39	2.11	0.13	10.94	100.45	422
P11-23	55.97	0.75	14.33	6.15	0.07	2.19	3.21	2.31	1.99	0.14	13.26	100.37	442
P11-25	56.21	0.73	14.56	6.03	0.07	2.27	3.16	2.37	2.05	0.13	12.83	100.41	465
P11-27	54.55	0.76	14.74	6.16	0.08	2.14	2.95	2.41	1.94	0.14	14.04	99.89	423
P11-29	52.32	0.75	13.93	7.06	0.07	2.09	2.70	2.11	1.79	0.15	17.11	99.70	453
P11-30	55.13	0.87	12.37	7.83	0.09	1.77	2.60	1.95	1.85	0.16	15.29	99.92	496
P11-31	64.37	1.04	10.29	5.89	0.08	2.14	2.97	1.74	1.93	0.09	9.29	99.83	580
P11-32	65.29	0.95	9.78	4.41	0.06	1.99	2.97	1.32	1.94	0.06	11.66	100.44	530
P11-33	62.87	0.89	9.22	3.99	0.05	2.03	2.79	1.19	1.85	0.06	15.27	100.22	535

Ca-glycolated (and Na glycerol for vermiculite identification where necessary), K-0 percent RH, K-300°C, and K-550°C.

INTERPRETATION

Al distribution in the profile.—The P11 soil profile is a relatively deep orthic ferro-humic podzol (Lozano, Vanderstar, and Parton, 1987). Lozano, Vanderstar, and Parton (1987) determined extractable Al (citrate-bicarbonate-dithionate extraction, CBD) for two similar profiles in the vicinity of the P11 profile, and their results are presented in figure 2. Additional data (organic carbon, CEC, et cetera.) used to classify these soils are reported by Lozano, Vanderstar, and Parton (1987). These podzols show maximum CBD extractable Al in the upper Bhf horizons,

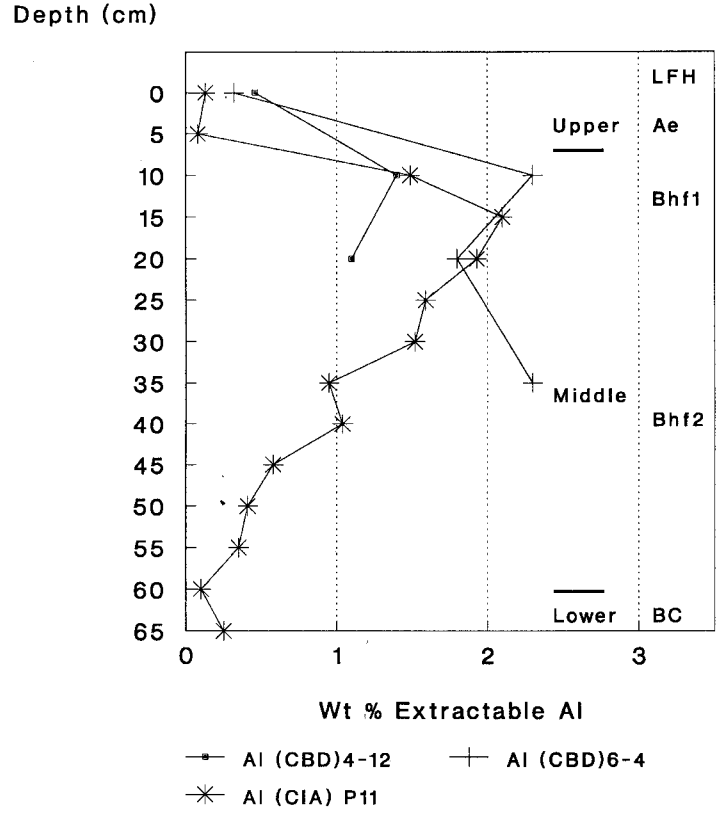


Fig. 2. Average extractable Al values for profiles 4-12 (⊟) and 6-4 (+) in the Plastic Lake Catchment (Lozano, Vanderstar, and Párton, 1987). Also included is the Al associated with secondary products as calculated from the CIA values (*) for P11 (see text). The horizontal lines indicate the delineation of the upper, middle, and lower zones in the P11 profile (terminology used subsequently for all P11 figures).

indicating that Al liberated by weathering reactions in the upper horizons is retained by secondary phases within the same range. The possible sources of Al from this extraction include Al associated with organic complexes, free oxides, and non-crystalline and amorphous phases (McKeague, DeConinck, and Franzmeier, 1983) and Al associated with hydroxy-interlayers (Jackson, Lim, and Zelazny, 1986).

A different analytical approach, the chemical index of alteration (CIA), provides additional insight into Al behavior in the profile (Nesbitt and Young, 1984). In this method all forms of Al are considered, including primary minerals, secondary minerals, and Al associated with colloids, gels, and organic complexes. The intent is to determine the degree of weathering that a soil has undergone by evaluating its CIA value. It reflects the degree of weathering of primary minerals and the extent to which Al is redeposited as secondary phases. The CIA is calculated on a molar basis and is defined as (Nesbitt and Young, 1984):

$$\mathrm{CIA} = [\mathrm{Al_2O_3}/(\mathrm{Al_2O_3} + \mathrm{CaO^*} + \mathrm{Na_2O} + \mathrm{K_2O})] \times 100 \qquad (1)$$

$\mathrm{CaO^*}$ indicates the Ca supplied by the silicate fraction of the sample; corrections are necessary if carbonates or apatite are present (Nesbitt and Young, 1984). The procedure is simple and rapid and requires only one analytical step to obtain the data necessary to evaluate the chemical distribution (and re-distribution) of Al within soil profiles.

All feldspar minerals have a CIA value of 50, whereas biotites have values ranging from 50 to 55. Feldspar minerals, quartz, and biotite are by far the most abundant minerals of the parent till and derived soils; consequently the parent till had a CIA value near 50. All granitic and felsic volcanic rocks have CIA values in the range 45 to 55, demonstrating the preponderance of the feldspars in these rocks. In contrast, calcic amphiboles and pyroxenes have CIA values ranging between 0 and 35; gabbros, basalts, and amphibolites, which contain these mafic minerals in abundance, accordingly have CIA values of 35 to 45.

The secondary minerals illite and smectite have CIA values ranging from 75 to 85, whereas aluminosilicates such as kaolinite, imogolite, and gibbsite have values very close to 100. Average shales (Pettijohn, 1975), which contain abundant clay minerals, have CIA values of 65 to 80. Thus there is an obvious separation of clay minerals and shales on one hand and primary igneous and metamorphic rocks on the other, according to their CIA values. CIA can thus be used as a sensitive proxy indicator of mineralogy and a measure of the proportion of primary and secondary phases in soil samples.

The average composition of the Earth's crust is dominated by feldspar minerals (Shaw and others, 1967; Nesbitt and Young, 1984); it follows that the average CIA value for the upper crust is approx 50. Shaw and others (1967) have tabulated the average composition of the Precambrian Shield, and the CIA calculated from these data is 52. Nesbitt and Young (1982) demonstrated that CIA values for Pleistocene tills from the Matachewan area (bedrock is Precambrian Shield gneisses and granites)

also have values of 52. The variation in CIA with SiO_2 values of bedrock core samples from the Plastic Lake catchment are presented in figure 3. As expected the amphibolitic samples have lower CIA values and SiO_2 contents than the granite gneisses.

The CIA values for the Plastic Lake P11 soil profile are presented in figure 4. Three zones are outlined by the CIA trend: the lower, middle, and upper. The CIA values at the base of the profile are near 50, as expected for unweathered till derived from local Precambrian Shield corroborating observations of stone lithology and angularity (site description). The values increase well above 50 in the middle zone and indicate the comparative abundance of aluminous secondary products. The upper zone has CIA values near 50, which are similar to those of the lower zone indicating a dearth of aluminous secondary products in this zone.

Interpretation of CIA and implications. The CIA of the lower zone (fig. 4) is near 50, indicating relatively unaltered tills dominated by feldspar minerals. The constancy of the CIA values within this zone suggests that the primary minerals remain relatively unaffected by reaction with soil solutions. Furthermore, significant amounts of Al have not been deposited in this zone, as CIA values would be much greater than 50.

Samples from the middle zone show the most significant departure (CIA up to 58) from the unweathered samples of the lower zone. The only means by which CIA values can rise above 50 is to increase the

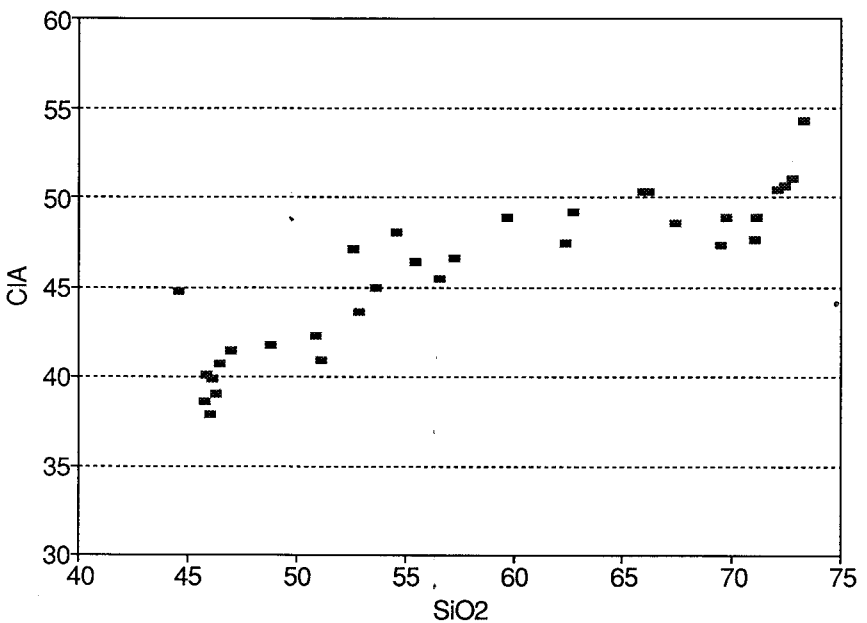


Fig. 3. SiO_2 content of the Plastic Lake bedrock core samples plotted against CIA values.

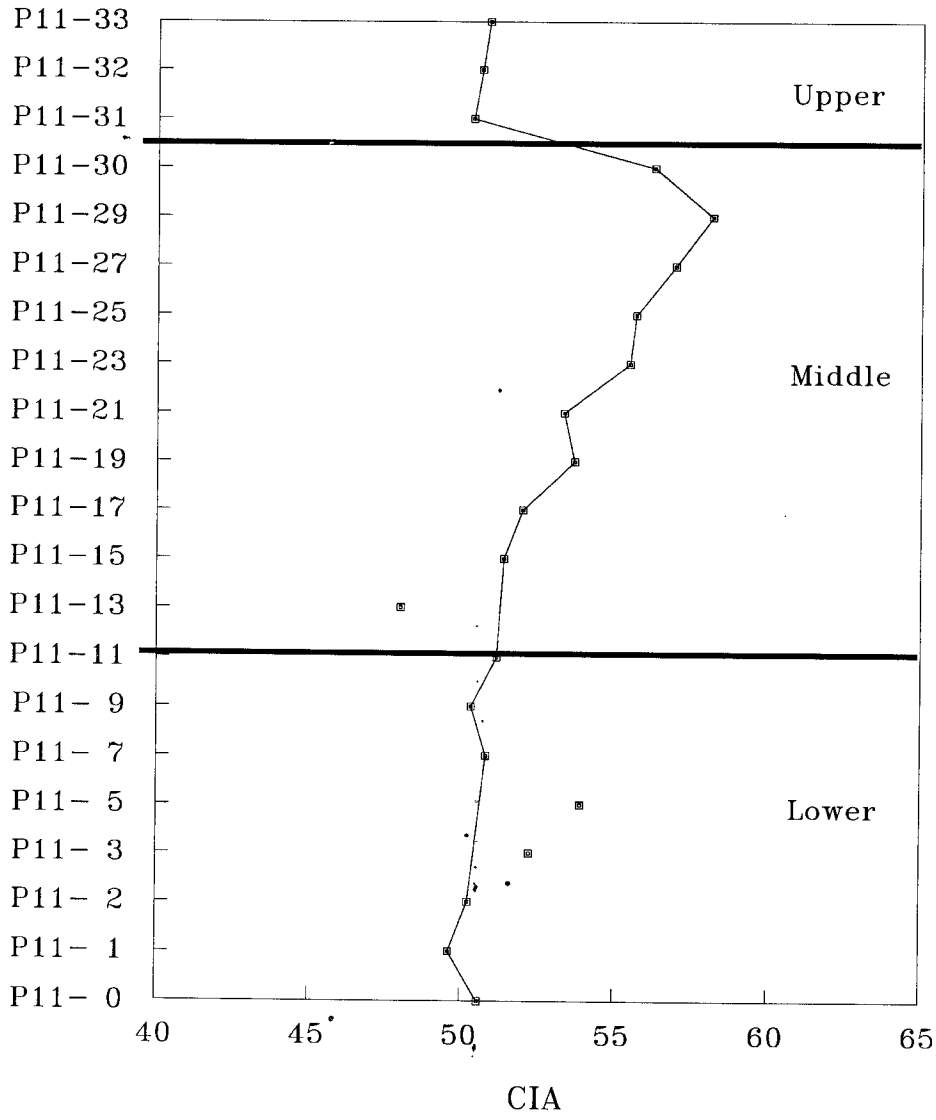


Fig. 4. Chemical index of alteration (CIA) plotted against depth (sample no.). Samples 3, 5, and 13 are omitted, and the reasons are discussed later in the text (Homogeneity of Samples Within the Profile).

amount of Al_2O_3 relative to CaO*, Na_2O, and K_2O. Increases in the CIA may result from the preferential removal of base cations and/or the introduction of Al to this zone.

In contrast to the middle zone, the upper zone CIA values approach feldspar values (50–51). The soils of this zone are subject to very aggres-

sive solutions (Manley, Chesworth, and Evans, 1987), and there is undoubtedly extensive reaction between solution and soil constituents. Nonetheless, CIA values are low, indicating there is no significant accumulation of aluminous weathering products. The best explanation of this phenomena is that the feldspars have dissolved congruently (stoichiometrically), and all constituents have been removed by solution. As a result, the CIA of the upper zone remains near 50, the value of the parent till. Stoichiometric dissolution of soil feldspars by acidic solutions has been demonstrated in the laboratory, and there is indirect evidence for stoichiometric dissolution of feldspars in the Ae horizon of other soils (Berner and Holdren, 1977, 1979). The bulk chemical data to be presented subsequently indicate that the most pronounced leaching of all the major chemical elements does occur within this zone, in accord with the classical interpretation of podzol formation based on extractable Al and Fe profiles. The use of the CIA supplements the information obtained from the extractions: it provides data regarding the major source of the Al (feldspars primarily) and valuable information about the nature of the reactions (stoichiometric dissolution of feldspars).

Comparison of Al-extractions with CIA data.—Extractable Al (CBD) which includes Al in organic complexes, exchange sites, hydroxy interlayer material, and non-crystalline and amorphous phases is at a maximum in the middle zone of the profile (Bhf horizon). The extractable Al data (fig. 2) mimic the CIA data in that both show maximum values within the upper B horizon or middle zone. The XRF data (table 2) for the P11 profile have been recast to facilitate a more direct comparison of the CIA results with the extractable Al of the two ferro-humic podzols. The amount of Al needed to increase any given sample's CIA value from 50 (parent material) to the observed values (holding Ca, K, and Na constant) is presented in figure 2, and this value represents Al associated with all secondary phases, including clay minerals, amorphous material, and organic complexes. It is, therefore, equivalent to extractable Al (by CBD) with the possible exception of Al tied up in the octahedral sheet of clay minerals. The calculated values are similar to those obtained by the CBD technique, and they fall within the range expected for Plastic Lake ferro-humic podzols. The similarity of the CIA calculated Al and CBD extractable Al values (in the upper 35 cm) suggests that the CBD extraction technique may extract all the Al associated with secondary products, including most of the hydroxy-interlayers in clay minerals (which will be discussed in subsequent sections).

Zr/Ti in bedrock.—Zr/Ti ratios for 32 samples of fresh bedrock from the Plastic Lake Catchment are plotted against SiO_2, Fe_2O_3, and CaO in figure 5A, B, and C respectively. These plots stress the chemical separation of amphibolitic bedrock ($SiO_2 < 52$ wt percent) and the granite gneisses ($SiO_2 > 62$ wt percent) on the basis of major element chemistry and Zr/Ti ratio. The amphibolites depleted in SiO_2 and enriched in Fe_2O_3 and CaO have low Zr/Ti ratios, whereas the granite gneisses are enriched in SiO_2, depleted in Fe_2O_3 and CaO, and have very high Zr/Ti ratios. This

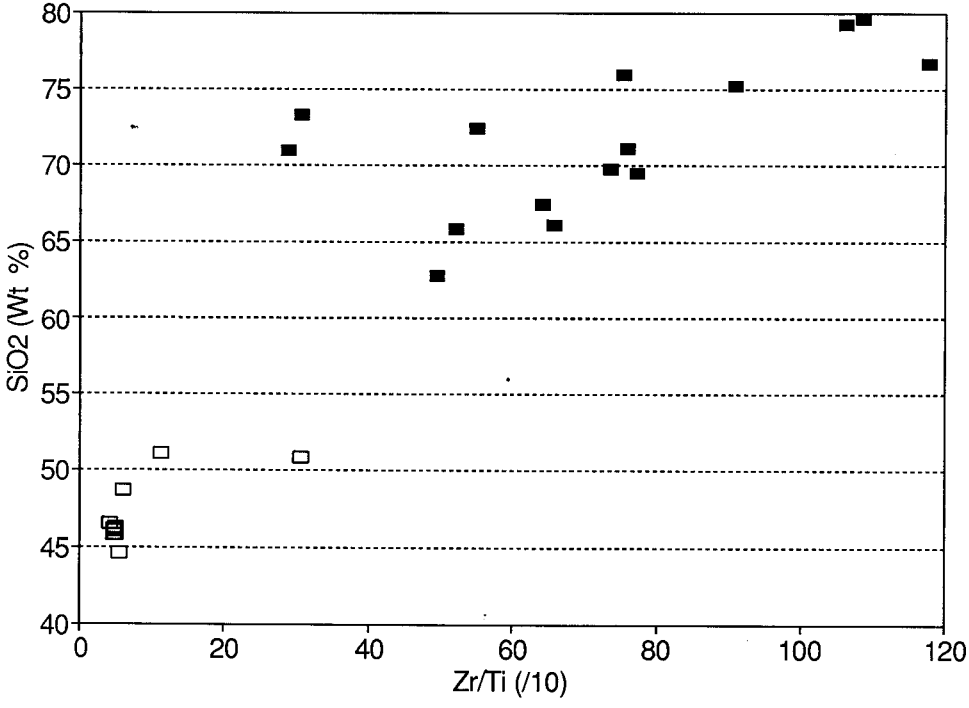
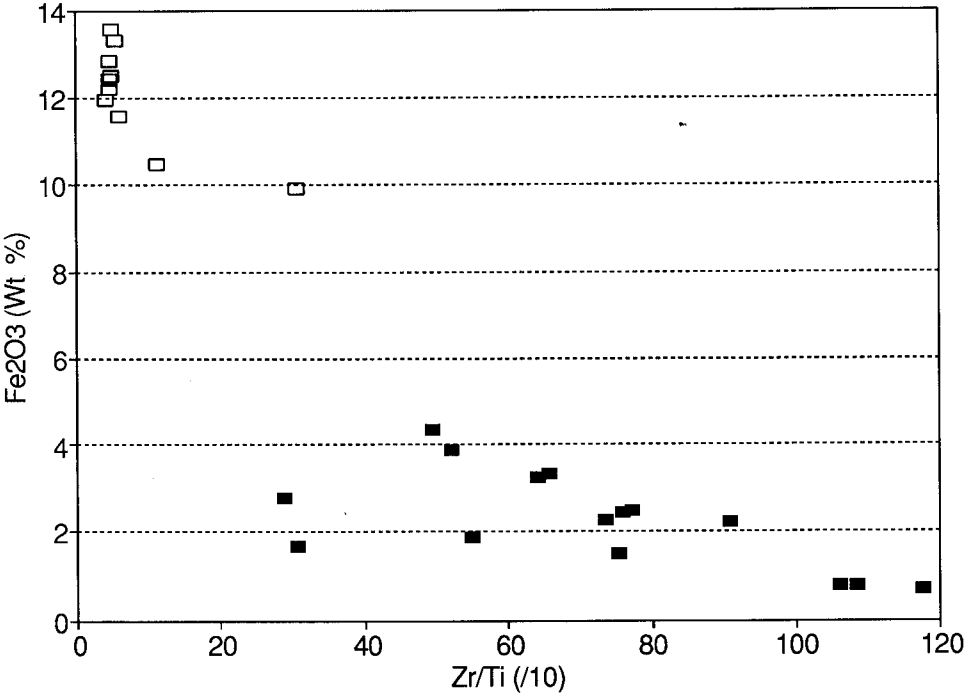


Fig. 5. Comparison of (A) SiO2, (B) Fe2O3, and (C) CaO major element contents and the Zr/Ti ratio for the Plastic Lake bedrock samples. Note the separation of points where (□) are amphibolites and (■) are granite gneisses.

relationship is expected in that basalts, from which amphibolites were derived, have high Ti but low Zr values, whereas granodiorites, granites, and their derivatives contain low concentrations of Ti and comparatively high concentrations of Zr. The bulk of Ti in amphibolites and granitic gneisses of the catchment resides in biotite, amphiboles, and oxides. Zr resides in zircon grains almost exclusively. The tills (parent to the Plastic Lake soils) are derived locally from bedrock, and a wide range of Zr/Ti values in soils of the Plastic Lake Catchment might be expected depending upon the proportion of amphibolites and siliceous gneisses incorporated into the parent till and upon the homogeneity of the till (that is, efficiency of mixing).

Zr/Ti of P11 soil samples.—Zr/Ti ratio and the percent change of this ratio with respect to the grand average Zr/Ti for P11 are shown in figure 6. Although there are fluctuations of up to 22 percent, there is no systematic change in the ratio within the profile. The ratio remains constant despite significant weathering of the profile as indicated by CIA values. This can result from only two processes: (1) the two elements are unaffected by weathering (within the accuracy of the XRF analyses), or



B.

Fig. 5. (continued)

(2) the elements are affected by weathering but are removed from the profile in the proportion equal to that found in the original material.

Ti is found primarily in biotite (now altered) but also in hornblende, Fe-Ti oxides, and rutile in the Plastic Lake soils. The weathering rates of these Ti-bearing minerals are extremely varied. Biotite is one of the most rapidly weathered phases (Garrels and Mackenzie, 1967; Nesbitt and Young, 1984; Velbel, 1984, 1985). Consequently, Ti is available to solution early in weathering. The susceptibility of hornblende is variable but weathers at a rate lower than that for plagioclase and biotite (Harriss and Adams, 1966; Nesbitt, Markovics, and Price, 1980; Wahlstrom, 1948), and in the P11 soil profile it is observed in highly weathered samples where all biotite has been altered to vermiculite. Ti oxides and hydroxides are sparingly soluble to insoluble even in acidic aqueous solutions (Baes and Mesmer, 1976). These oxides, for example, are classed as resistates (inert) in the sedimentary environment (Pettijohn, 1975). Zr is essentially restricted to zircon, which is virtually insoluble in aqueous solutions (Tole, 1985), and is also classified as a resistate in the sedimentary environment (Pettijohn, 1975).

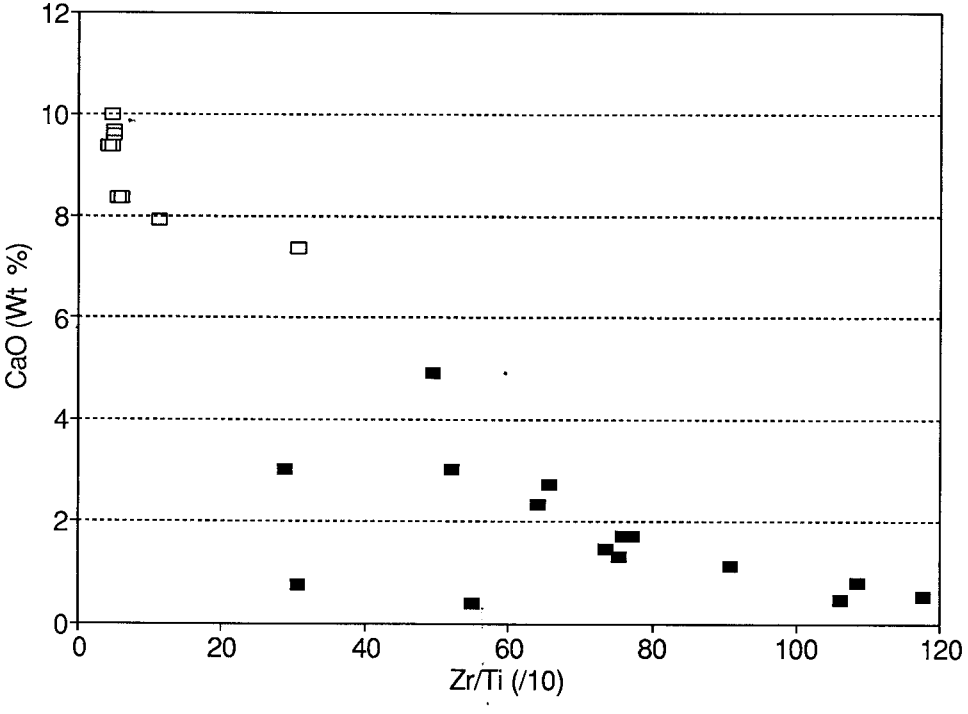


Fig. 5. (continued)

If Ti or Zr are removed from the soil, Ti will be removed first, and more rapidly, as a result of biotite weathering. Zr will be released much more slowly. Consequently, Zr/Ti values should increase as weathering proceeds (assuming that these elements are mobilized). However, the ratio does not change within the Plastic Lake soil profile (fig. 6), and we conclude that both Zr and Ti are effectively immobile in the P11 profile. Ti released from biotites and Zr released from zircons must be rapidly redeposited on the scale of our sampling (2.5 cm vertically). Bain (1976), examining podzolic soils in Scotland, determined the Ti content of bulk soils and clays and concluded that Ti released by weathering was incorporated into cryptocrystalline anatase, and that the concentration of this phase in the upper portion of the profile resulted from the removal of other chemical constituents. Banfield and Eggleton (1988) studied the products of biotite weathering using TEM, STEM, SEM, and microprobe analysis and also conclude that Ti is not mobile except on a microscale and is commonly redeposited in cracks and etch-pits in the biotite structure.

Physical transport or translocation of these immobile elements may produce variations in the Zr/Ti ratio. Zircons are dense and tend to be

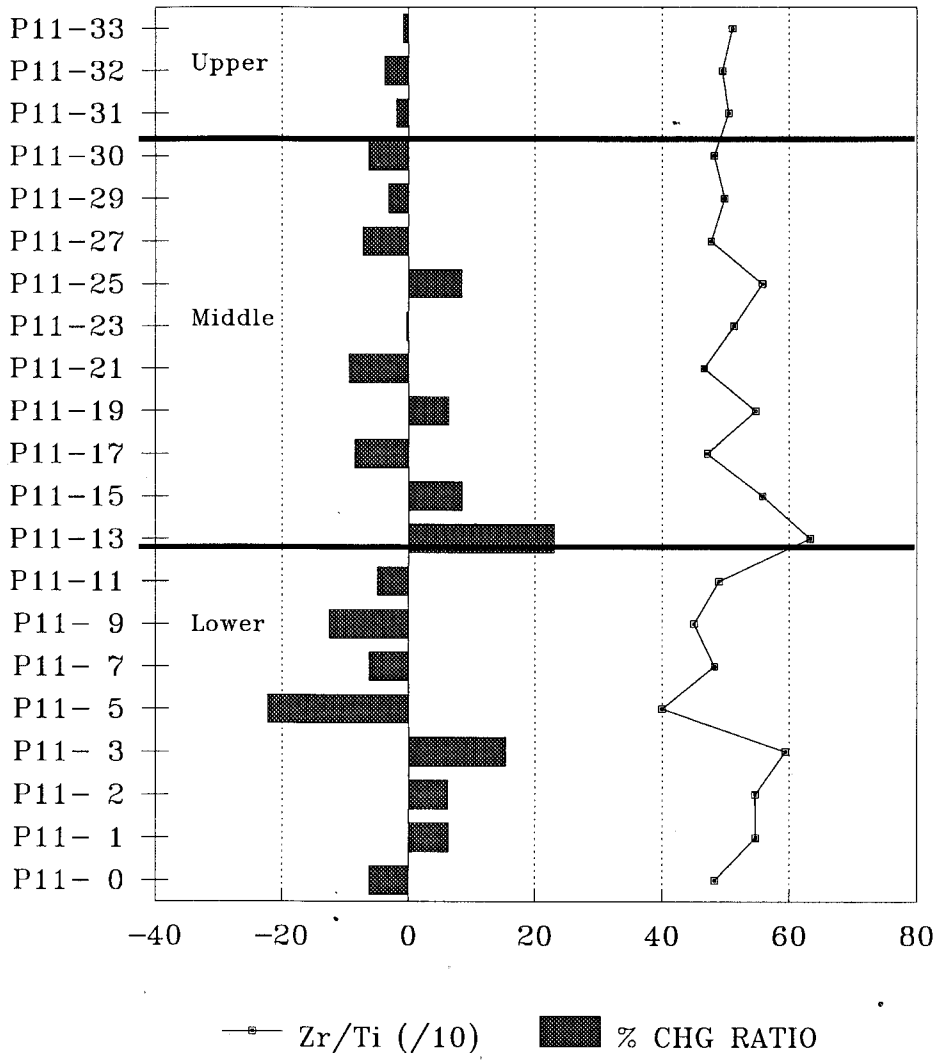


Fig. 6. Zi/Ti ratio and the percentage change of the ratio with respect to the average Zr/Ti value for the entire profile (plotted against depth).

retained in the heavy mineral suite of the soil. As a result of their density, zircons are not susceptible to transport in suspension by soil solutions. The weathering products of Ti (oxyhydroxides, such as cryptocrystalline anatase) may be dispersed in the colloidal or clay fraction of soils and, if so, may be transported in suspension by soil solutions. Such translocation of Ti-rich materials will be expressed by comparatively high values of the Zr/Ti ratio in the zone where Ti is removed and low values where Ti is

deposited. Translocation of Ti is not evident from the Zr/Ti ratio in figure 6; apparently, the produced Ti oxides and hydroxides remain at the site of weathering.

Homogeneity of samples within the profile.—Figure 5 indicates the Zr/Ti ratio for gneisses and amphibolites for the bedrock of the catchment. From the separation of the Zr/Ti ratio for both these bedrock types, it is evident that the Zr/Ti ratio may be shifted by differing proportions of each rock type. Evans (1978) has pointed out the difficulties in determining the degree to which samples may be variable but still be considered homogeneous. For the P11 samples (fig. 6), only samples P11-3, 5, and 13 show deviations >10 percent from the average ratio. The samples probably contain significantly different proportions of bedrock types. Samples 5 and 13 are also anomalous in other elements (discussed in the next section); consequently these samples (and P11-3) have been excluded from all subsequent calculations (and the CIA calculation presented earlier) as their initial composition probably differs from that of the other samples.

The compositional data indicate that the Zr and Ti are effectively immobile in the P11 soil profile and that the profile has been developed on relatively lithologically homogeneous parent material. The lowermost samples of the profile, which are the least weathered (CIA values near 50), can be taken as representative of the parent till composition. It is important to note that these samples do not represent unaltered till, and all the interpretations based on these samples as the parent material will likely be not as pronounced as those determined from completely unaltered material. Data for samples P11-1, 2, 7, and 9 (table 2) have been averaged to provide a representative composition for the parent material. Samples 3 and 5 were omitted from the average (and all subsequent calculations) due to their anomalous Zr/Ti values, as was sample P11-0 because many bottom samples (resting on bedrock) within the catchment may be affected by reaction with waters flowing along the till/bedrock interface (Kirkwood, ms).

BULK COMPOSITIONAL TRENDS

Zr and Ti.—The percent change of Zr and Ti with respect to the parent material is presented in figure 7. For each element the concentration remains relatively constant from the base of the profile to sample P11-11, indicating that the lower zone has had little material added or removed. In the middle and upper zones both Ti and Zr show marked (up to 100 percent) increases in concentration relative to the parent material. Enrichment of these immobile species can result only from the removal of reactive (labile) components. Within the upper zone, 50 percent of the original material must be removed to obtain a 100 percent increase in Ti and Zr. There is no indication for addition of material to this highly weathered zone, the zone most affected by aggressive soil solutions.

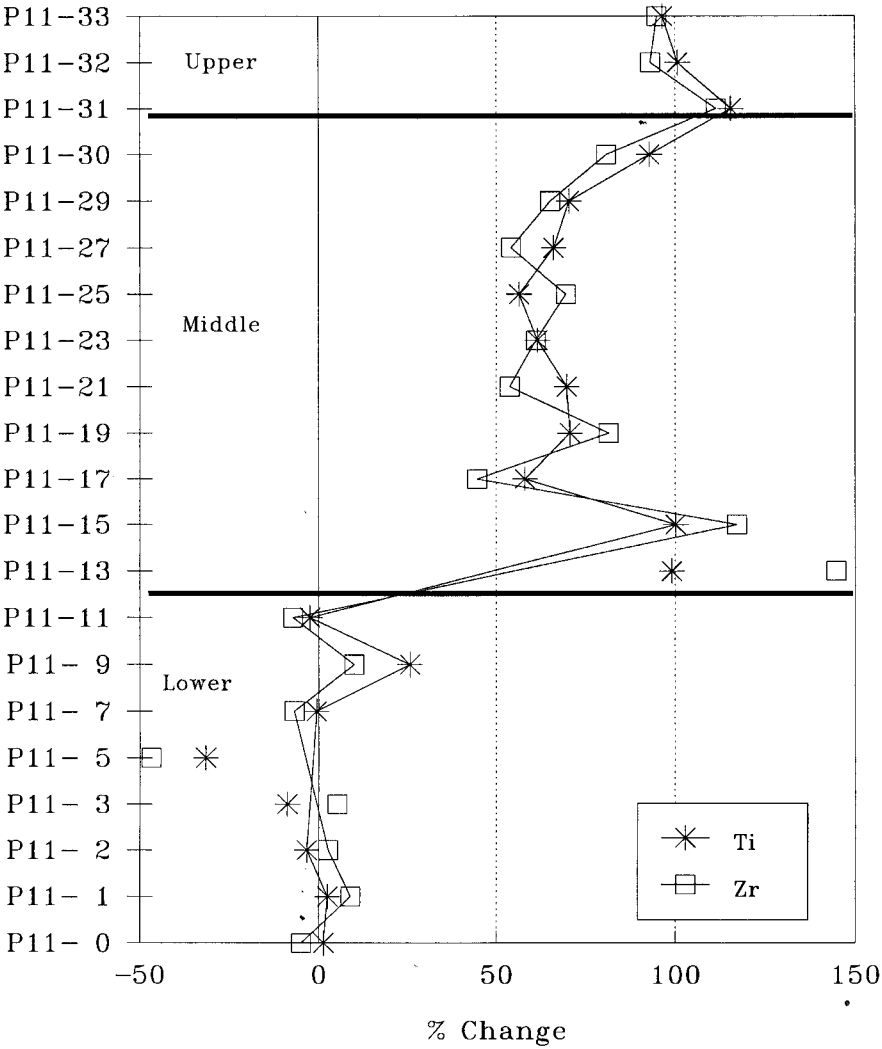


Fig. 7. Percent change of Ti(*) and Zr (□) with respect to their concentrations in the parent material, plotted against depth.

Within the middle zone Ti and Zr are enriched by approx 50 percent, indicating that a third of the original parent material has been removed by weathering. This value is a minimum because the addition of Al (as indicated by CIA trends), Fe, and Mg (discussed subsequently) has partially offset losses of labile constituents. Loss from the upper horizon (approx 50 percent) represents a maximum, thus total materials removed from the middle zone are probably between 33 and 50 percent.

The B horizon is a zone of accumulation of materials leached from the Ae, and the CIA trend demonstrates that in fact some Al-rich constituents accumulate in the B horizon. But the Zr and Ti data indicate that there is a net loss of material from the B horizon. In effect, the accumulation of Al, Fe, and Mg (discussed subsequently) is more than offset by the loss of other constituents from the B horizon.

There is one atypical sample, P11-15, which displays anomalously high Zr and Ti values, yet Zr/Ti is not anomalous. There is no obvious explanation for the values. Variations in grain size, however, were not noted in the field and are not obvious in the samples collected.

Major element chemistry.—Having ascertained that the P11 soil profile was developed on relatively homogeneous parent material of known composition, the gains and losses of chemical constituents throughout the soil profile can be quantified. The percent change for each element (Nesbitt, 1979) is,

$$\% \text{ change} = [(R_s - R_p)/R_p] \times 100 \quad (2)$$

where R_s represents the ratio of the concentration of the element to the Ti content (on a weight basis), and R_p is the same ratio in the parent material. Ti is chosen as the immobile element rather than Zr because the concentration of Ti is at the wt percent level within our samples, whereas Zr is present in much smaller quantities (ppm). As a result, Zr is more sensitive to incomplete mixing and shows greater intersample variation than Ti.

The percent changes of the major elements in the P11 soil profile are presented in figure 8A, B, and C. The variability of the elements from the lower zone is within 15 percent of the parent. Fluctuations about the average are approx 10 percent which is probably representative of the cumulative error associated with these results.

The major element trends demonstrate that there is little leaching or accumulation of major constituents in the lower zone, which is also indicated by CIA values and Zr and Ti concentrations. The choice of these samples to construct average parent material is well justified by these data. The middle zone is characterized by the depletion of the major elements (Na > Si & K > Ca & Al) and gains in Fe > Mg (fig. 8). The upper zone samples are the most highly depleted in major elements, indicating that all elements are leached in this zone of the profile. The order of susceptibility (or lability) is Na > Al > K > Si > Ca > Fe > Mg.

The Si and Al trends (fig. 8A) can be compared to evaluate their relative mobilities. The comparison is justified as the bulk of *labile* Si and Al resides in the feldspars. Furthermore, the CIA data suggest that feldspars dissolve congruently which should result in a sympathetic relationship between Al and Si losses from the profile. The Si profile (fig. 8A) indicates that Si is lost in a relatively constant proportion (40–50 percent) from the top of the profile to base of the middle zone. This relationship indicates that a significant amount of feldspar has dissolved from the upper and middle zones, and little has dissolved in the lower

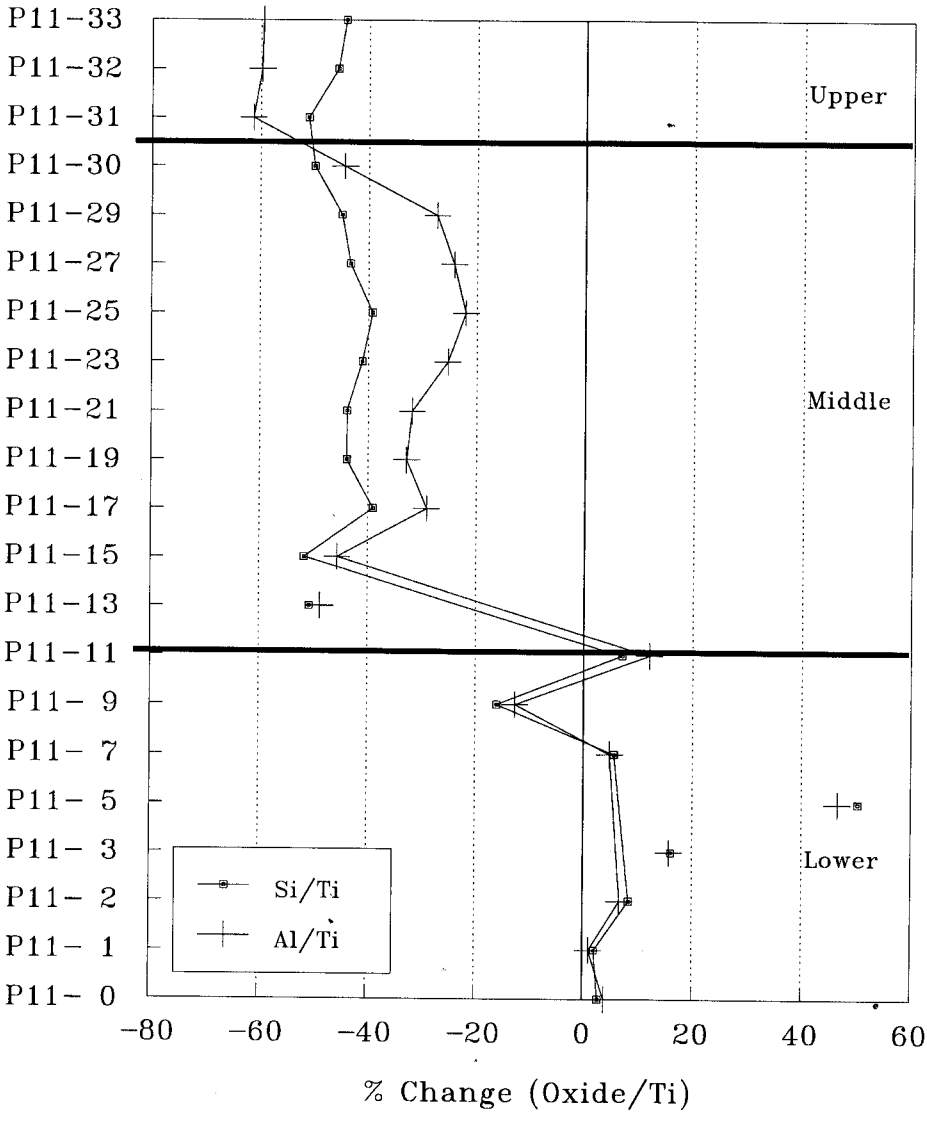
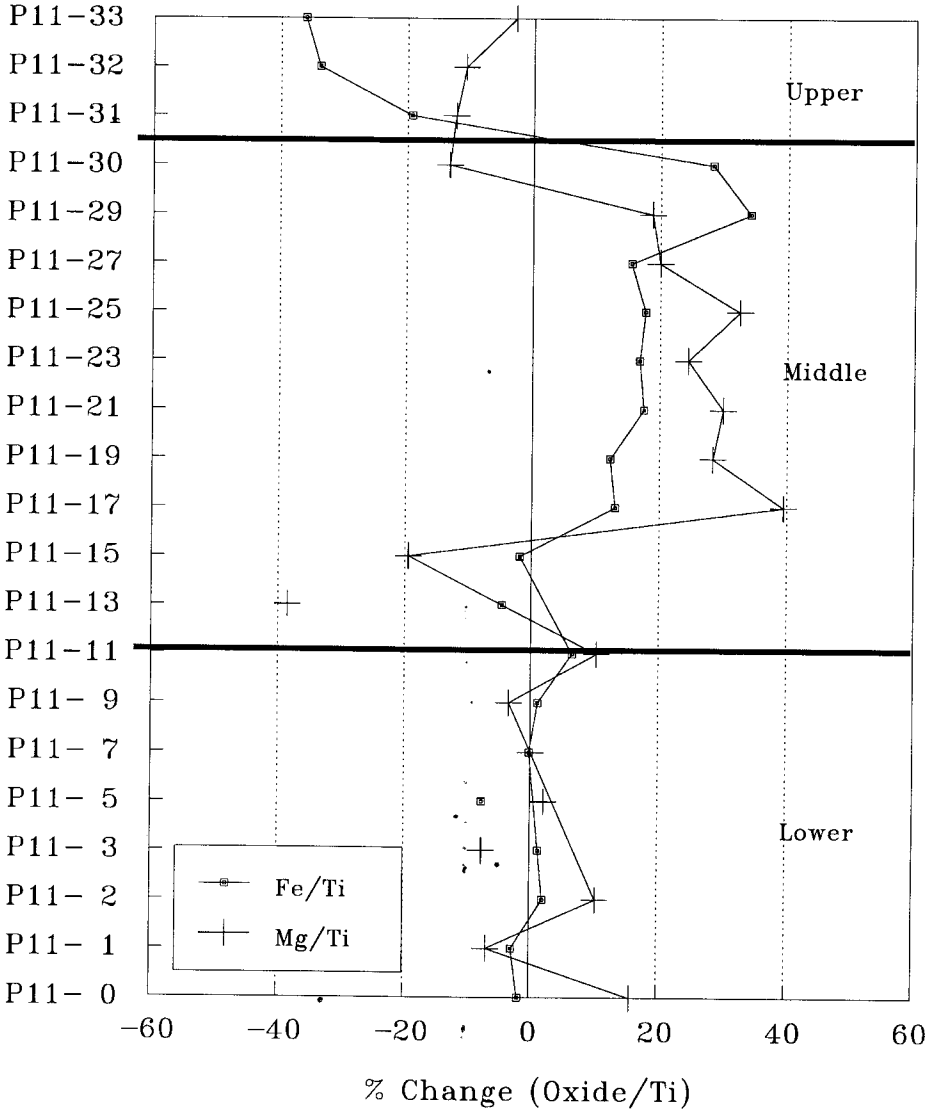


Fig. 8. Percent change of the major oxides relative to changes in TiO_2: (A) Si and Al, (B) Ca, Na, K, and (C) Fe and Mg.

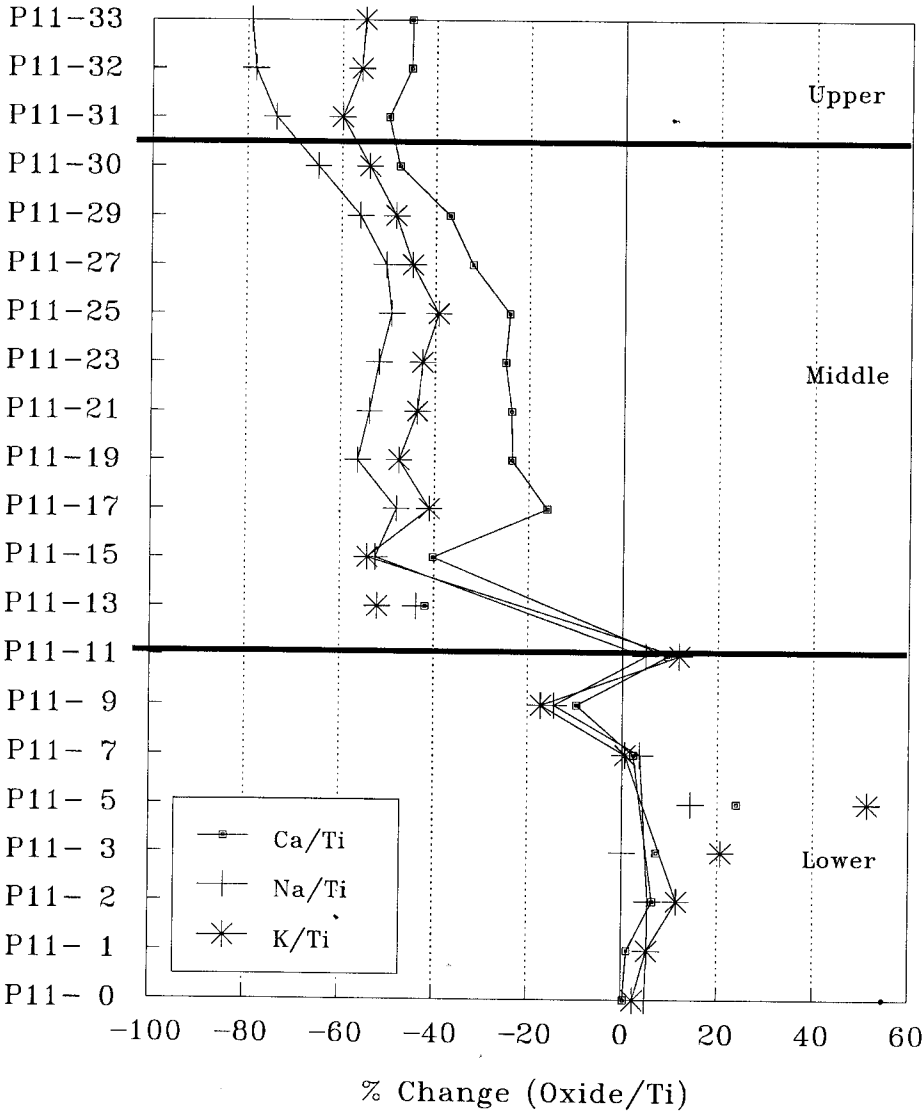
zone. There should be a similar sympathetic loss of Al if feldspar dissolution alone influences the losses in Al. In the upper zone Al has been strongly leached; its trend is similar to Si. Al loss, however, decreases dramatically to only 20 to 30 percent in the middle zone suggesting addition of some Al to this zone. Thus the behavior of Al and Si differs



B.

Fig. 8. (continued)

noticeably in the transition from the upper to middle zone and suggests that reactions other than feldspar dissolution affect Al in the profile. Apparently there is accumulation of secondary Al in the middle zone, as also indicated by the CIA data. However, it is important to stress that the middle zone, which includes the B horizon, is *not* a zone of *net* accumulation of Al.



C.

Fig. 8. (continued)

The percentage changes in Na, K, and Ca (fig. 8B) indicate that Na is more highly depleted than K and Ca in the upper zone. Na resides primarily in plagioclase, and little Na (supplied by weathering reactions) is adsorbed or exchanged onto clay minerals. The extreme depletion of Na is expected if the dissolution of plagioclase is the dominant reaction

occurring within this zone. K, supplied by the dissolution of biotite and K-feldspar, and Ca, from plagioclase and to a lesser extent hornblende, are also highly depleted (45–60 percent) and exhibit similar behavior, suggesting that the minerals of the upper zone are weathered in similar proportions.

The Na, K, and Ca profiles (fig. 8B) demonstrate similar behavior in the middle zone despite the fact that each element is supplied by different minerals. Ca, however, is less highly depleted in samples P11-25 to P11-17. It is probable that Ca is retained on exchange sites and/or reconstituted in secondary products. The relative similarity of these curves suggests that each of these minerals dissolves in similar proportions in the middle zone.

The enrichment of Fe and Mg provides the most conclusive evidence that authigenic secondary products are produced in the middle zone (fig. 8B). The formation of podzolic soils is most commonly associated with the addition of Fe and Al in podzolic B horizons and the importance of organic compounds in the transport of these constituents. However, Mg is not considered to be associated strongly with the organic fraction, and thus the increase in Mg content suggests that authigenic silicates (as opposed to the organic fraction) control the transport and deposition of Mg and possibly Fe and Al in the middle zone.

The quantity of Mg lost from the upper zone (fig. 8C) is not great enough to account for the quantity accumulated in the middle zone. The source of Mg is the upper zone, but there is also an additional source. The only other possible source is decaying organic material, which releases Mg to soil solutions in the uppermost region of the profile (LFH horizon). The chemical composition of the forest litter in the Plastic Lake catchment has been examined by Lozano (1987), and Mg represents a major inorganic component at approx half the concentration of K in the forest litter (0.1 wt percent). It is reasonable that the decomposition of the forest litter and the supply of Mg to the soil complicates the Mg concentrations in the upper and middle zones.

MINERALOGY AND MINERAL COMPOSITIONS

X-ray diffraction analyses of the bulk soil samples indicate quartz, plagioclase, K-feldspar, hornblende, and vermiculite are the major minerals of the Plastic Lake soils. Quartz and plagioclase dominate all samples. Microprobe analyses of fresh amphibolitic and granite gneiss bedrock samples indicate average plagioclase compositions of An_{34} (n = 5) and An_{24} (n = 6), respectively.

Amphibole is evident in all XRD patterns and thin sections and represents approx 8 to 15 percent of the bulk sample (XRD estimate). The microprobe analyses of amphibole (table 3) indicate the hornblende composition is intermediate between edenite and pargasite.

Although biotite is present in both the granite gneiss and amphibolite, it is much less abundant than quartz and feldspars; no trace of biotite is evident from bulk sample XRD patterns. A 10 Å mineral is observed in

TABLE 3

Microprobe compositions used to calculate mineral proportions in the Plastic Lake soils

Rock Type[1]	GNEISS			AMPHIBOLITE		SOIL		
Mineral	Bio.	Hnblde	Biot.	Bio/ Verm[2]	Verm.[3]	Verm[4]	HIV[5]	HIV[6]
No. Analyses	3	4	2	5	4	12	14	1
Tetrahedral Sites*								
Si	2.68	6.27	2.79	2.81	2.76	3.24	3.56	2.81
Al	1.31	1.73	1.21	1.19	1.24	0.76	0.44	1.19
sum(IV)	4.00	8.00	4.00	4.00	4.00	4.00	4.00	4.00
Octahedral Sites**								
Al	0.19	0.44	0.17	0.19	0.33	1.56	1.34	1.49
Ti	0.21	0.14	0.19	0.18	0.17			
Fe	1.46	2.03	1.19	1.19	1.00	0.24	0.28	0.25
Mg	0.83	2.45	1.16	1.16	1.16	0.20	0.37	0.26
Mn+Cr	0.01	0.04	0.00	0.01	0.00			
Sum(VI)	6.00	10.96	6.00	6.00	6.00	5.80	5.60	5.74
Exchange Sites (other sites for hornblende)***								
K	0.81	0.29	0.86	0.62	0.02			
Na	0.00	0.64	0.00	0.00	0.00			
Ca	0.00	1.93	0.00	0.01	0.00	0.20	0.13	0.40
Ba	0.01		0.01	0.00	0.00			
Mg	1.17		0.13	0.10	0.05			
Al				0.09	0.34	2.60	0.99	2.18
Sum(XII)	1.17		1.14	1.11	1.18	8.20	3.23	7.34
(OH) groups	2.00	2.00	2.00	2.00	2.00			
H2O(+)	1.00		0.66	2.10	4.88			

[1]Rock type from which the mineral was collected, the gneiss and amphibolite analyses are of fresh bedrock. Bio/verm and verm. grains are from the surface of a partially altered amphibolite stone in the B-horizon of Plastic Lake soil.

[2]Indicates a phase compositionally intermediate between biotite and vermiculite, not a mixed layer phase.

[3]Silt sized vermiculate from Plastic Lake.

[4]Soil Vermiculite after Kirkland and Hajek (1972)

[5]Average soil HIV composition from Karathanasis (1988).

[6]Modified Lucedale Ap HIV (Karathanasis, 1988, p. 1505), see text for further explanation.

*Calculated assuming 4 sites for micas and 8 sites for hornblende

**Calculated assuming maximum of 6 charges in octahedral sites. Al in octahedral sites calculated assuming Mg is leached from, not added to mica during weathering; therefore maximum Mg is that of biotite.

***Elements in excess of those needed to fill tetrahedral and octahedral sites are assumed to enter the 12-fold coordination of exchange sites.

XRD patterns of the fine fraction of some samples. Vermiculite is observed in the XRD patterns of most bulk samples, suggesting that biotite has largely altered to vermiculite (see next section). Microprobe analyses of sand and silt-sized vermiculites from the surface of amphibolitic stones

and vermiculite in the bulk soil are presented in table 3. A distinct compositional range exists from fresh biotite to K-deficient vermiculite. It is not possible to determine which composition (table 3) is representative of "average" vermiculite in the soils. Since biotite is altered, the electron microprobe analyses of K-deficient, silt-sized vermiculite are, therefore, considered to be representative of the vermiculite in this profile (table 3).

XRD studies demonstrate that the <2 μm fraction (following section) contains hydroxy-interlayered vermiculite (HIV). The small quantity of clays extracted and the mixtures of phases prevented the compositional analysis of this mineral. However, a composition is required for subsequent calculations, thus a derived composition was estimated. Karathanasis (1988) provides numerous analyses of HIV of minerals formed in mature soils of the southeastern United States, but these may not be representative of HIV in the younger Plastic Lake soils. EDX analyses (Kettlewell, ms) of HIV from soils developed on glacial deposits in the vicinity of Plastic Lake indicate the Si generally is low compared with values for the mature soils of Karathanasis (1988). The average tetrahedral or Si(IV) content of Plastic Lake biotites, biotite/vermiculite, and vermiculite is 2.79, 2.81, and 2.76 respectively (table 3). These data suggest that Si in tetrahedral sites is little affected by weathering. Velbel (1985) also observed that tetrahedral layers are unaffected during weathering of biotite to HIV. Assuming that HIV and vermiculite at Plastic Lake are genetically related (Douglas, 1977) and that tetrahedral occupation is not greatly affected by weathering, the HIV should also contain approx 2.8 Si atoms per half unit formula (table 3). We have modified the Lucedale (Ap) HIV composition of Karathanasis (1988) by substituting Al for Si in the tetrahedral positions (with charge compensation by substituting Ca in interlayer positions) to reduce the tetrahedrally co-ordinated Si to 2.8 atoms per half unit formula (see table 3).

Iron-oxides were not detected by XRD, although their presence is observed in thin section and as iron-staining in the soil pit. SEM/EDX analysis of mineral surfaces indicates that an iron-rich phase coats most mineral surfaces, especially in the middle-zone samples. The phase is most likely an iron oxyhydroxide; a goethite composition is assumed in the calculations that follow.

Calculated bulk mineralogy.—The proportions of minerals present in samples from throughout the profile are difficult to determine as mineral grains are coated with secondary products. Furthermore, modal analyses of the fine (clay) fraction are impossible as the individual phases cannot be identified microscopically. Mineral proportions and, most importantly, changes in the mineral proportions have been calculated using the bulk compositional data (XRF) and mineral compositions (electron microprobe) of individual samples from the profile. The analytical data are combined to construct a system of linear equations solved for the amount of minerals in the bulk samples. Calculation of modes (of minerals) involves solving a system of 7 linear equations one for each of the 7 major oxides of the soil. The 7 minerals considered in the mathematical solution

are quartz, plagioclase, K-feldspar, hornblende, vermiculite, goethite, and HIV, using the compositions discussed previously (see table 3). Solution of the equations is accomplished by routine matrix algebraic procedures (inversion and multiplication). This calculation is not just a normative mineral calculation, as the actual mineral compositions (with the exception of HIV) are used. The calculation has been applied to each sample from the P11 profile, and the cumulative mineral percentages are presented in figure 9.

Quartz and feldspars are the dominant minerals and account for approx 80 percent of the soil. Quartz constitutes about 30 percent of the lower zone samples, and its abundance does not change appreciably until the upper zone where it increases to more than 45 percent. Plagioclase is most plentiful in the lower zone (40 percent avg) and decreases continuously to lower values (<10 percent) in the upper zone. Hornblende comprises approx 6 to 10 percent of the lower zone, increasing to 15 percent in the upper zone. Vermiculite represents 7 percent of the minerals in the lower zone, increases in the middle zone to 15 percent, but then decreases markedly to 1 to 2 percent in the upper zone. HIV is insignificant in the lower zone but is present in appreciable quantities (up to 9 percent) in the middle and upper zones. Goethite, present in only small amounts, shows a slight increase in the middle zone (up to 5 percent).

Implications of calculated bulk mineralogy.—The accuracy of the calculated bulk mineralogy is constrained by the accuracy of the XRF analyses and mineral compositions used in the matrix calculation. Quartz, plagioclase, K-feldspar, amphibole, and goethite mineral compositions will not deviate significantly from the values determined by microprobe analyses. As these minerals comprise up to 85 percent of the profile mineralogy, the proportions indicated in figure 10 are considered to be reasonably accurate. Vermiculite abundance may be subject to deviations as a result of changing vermiculite composition throughout the profile and different mineral compositions among different size fractions. For example, some biotite remains in the <2 μm fraction of the lower zone samples (see next section); perhaps the composition of lower zone vermiculites differs from that of the most weathered upper zone. The HIV mineralogical composition is somewhat uncertain as the Plastic Lake HIV could not be isolated for analysis. These uncertainties are most evident in the upper zone where the proportion of vermiculite is low and that of HIV high. Bulk sample and <2 μm fraction XRD patterns suggest a small quantity vermiculite and still smaller amounts of HIV for this zone. The proportion of vermiculite in this zone most likely is higher (and the quantity of HIV lower) than indicated from the calculated mineralogy in figure 9.

In the highly weathered upper zone, quartz represents 50 percent of the cumulative mineralogy. Feldspars constitute 20 to 25 percent of the upper zone as opposed to 50 to 55 percent of the lower zone. Plagioclase is the most highly depleted primary mineral of the profile in this part of the profile. Its proportion of the cumulative mineralogy indicates a 65

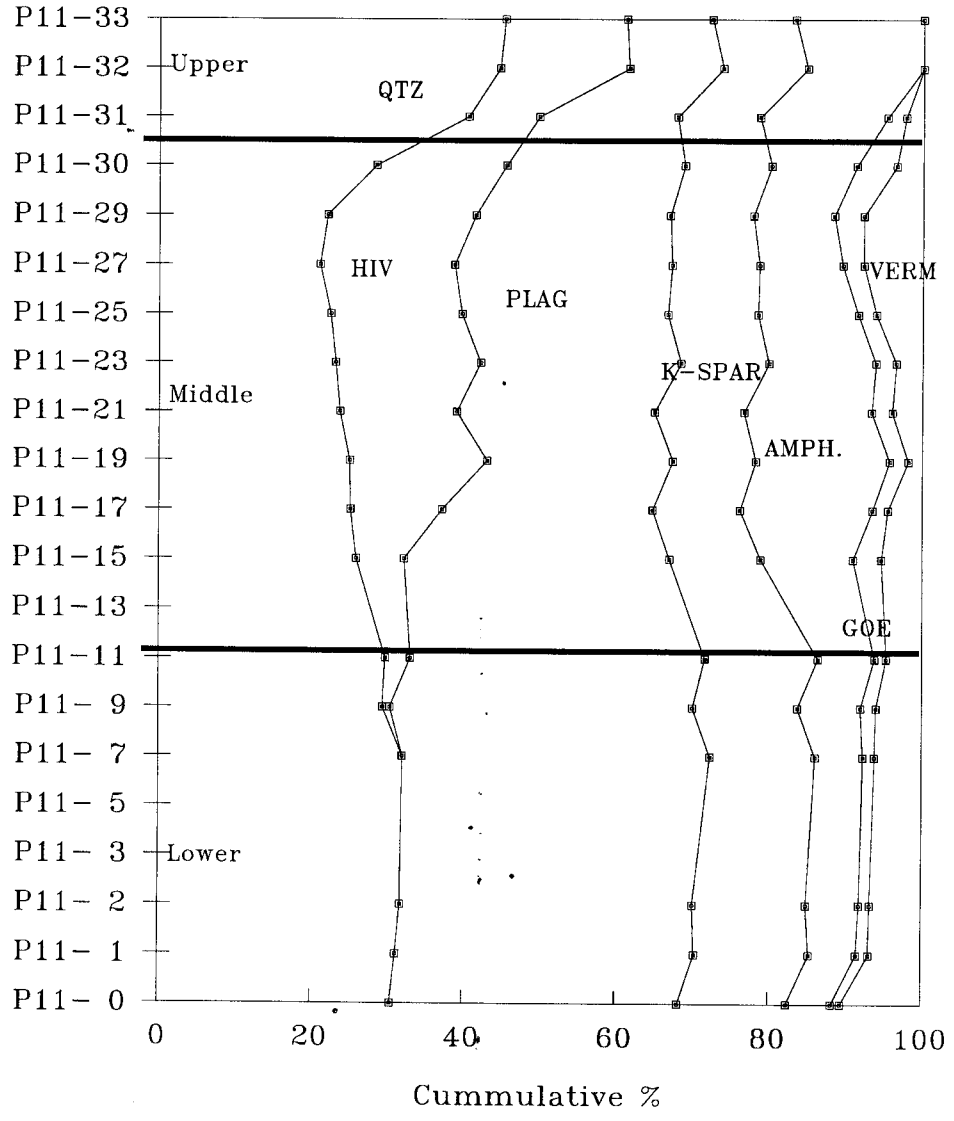


Fig. 9. Bulk mineralogy as determined by matrix calculation (see text). Labels: quartz (QTZ), plagioclase (PLAG), K-feldspar (K-SPAR), amphibole (AMPH), goethite (GOE), vermiculite (VERM).

percent loss in the upper zone relative to the parent (lower zone samples). K-feldspar decreases somewhat (22 percent) in the middle zone; its proportion remains constant throughout the upper zone. Apparently, K-feldspar is less susceptible to dissolution than plagioclase. The bulk of

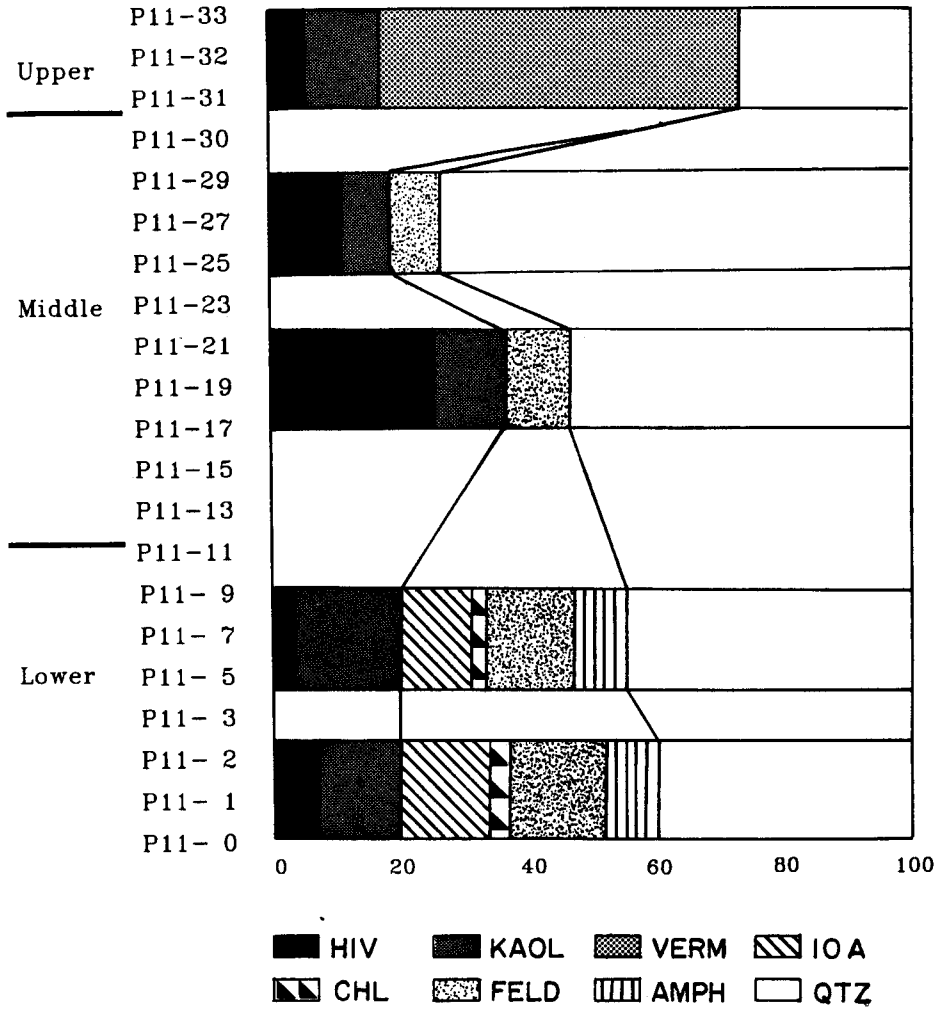


Fig. 10. Semi-quantitative proportions of the <2 μm mineralogy for each zone of the P11 profile (weighted peak height method used, see text). Zones are divided (solid vertical lines) into clay minerals, primary minerals, and quartz.

the decrease occurs near the base of the middle zone, comparable to the K trend indicated in figure 8B.

The calculated hornblende concentrations are affected significantly by chemical compositions selected for vermiculite. The increase in hornblende abundance is probably not as great as shown (fig. 9) and may result from changing vermiculite composition up the profile. Similar compositional difficulties arise with vermiculite in the upper zone. The

composition of vermiculite in the middle and lower zones is probably different from vermiculite of the upper zone, but the actual variation in vermiculite composition remains unknown and has not been included in the calculation.

The increased proportions of all secondary minerals (HIV, vermiculite, goethite) and depletion of the primary minerals, combined with the progressive increase in Zr and Ti, provide convincing evidence that significant mineral dissolution has occurred in the middle zone. These observations are also complementary to the information provided by CIA and bulk compositional data; although the calculated mineralogy also uses bulk compositional data, it uses independent mineral chemistry as derived from the electron microprobe. Bulk compositional data demonstrate the depletion of all mobile constituents, except Fe and Mg in the middle zone. This is evident from the calculated mineralogical trends, where there are shifts in the proportions of all the essential minerals (depletion of primary minerals, addition of secondary minerals) at the transition from the lower to middle zone (sample P11-11). The losses of feldspar, both plagioclase (up to 35 percent) and K-feldspar (22 percent), represent the bulk of the minerals dissolved in the middle zone.

MINERALOGY OF THE <2 μm FRACTION

The clay mineral fraction of the soils was separated and analyzed by XRD to determine the nature of the secondary products. The proportion of clay-sized material within these soils is low (1–13 percent). The P11 profile was divided into 5 sections from which the clay mineralogy was examined. The upper zone clay minerals were determined from samples P11-32 and 33. The middle zone was subdivided into two sections (P11-23 to P11-30 and P11-15 to P11-21). The lower zone is represented by samples P11-1 to 9; sample P11-0 (collected from the bedrock/soil interface), was also examined.

The five selected zones in the profile indicate that the clay fraction is dominated by quartz, vermiculite, hydroxy-interlayered vermiculite (HIV), kaolinite, illite, chlorite, plagioclase, K-feldspar, and hornblende (fig. 10). The relative abundance of each mineral was estimated using weighted peak heights following the approach of Biscaye (1965). Background subtracted peak heights were determined using the most intense diffraction of Ca-saturated ethylene glycol solvated samples for all minerals with the exception of chlorite. The proportion of chlorite was estimated using K-saturated samples after 550°C heating for 2 hrs. The weighting factors employed in this study were: (A) $\times 1$ for quartz, plagioclase, K-feldspar, hornblende, vermiculite, and HIV; (B) $\times 2$ for kaolinite; and (C) $\times 4$ for illite. It must be realized, however, that relative abundances calculated using this method are semi-quantitative at best.

Diffractograms for the lower zone sample are presented in figure 11. All identified clay minerals are evident in this example except for vermiculite. Vermiculite was identified only in the upper zone, using a Na-glycerol treatment in which the 14 Å diffraction maximum distinguished

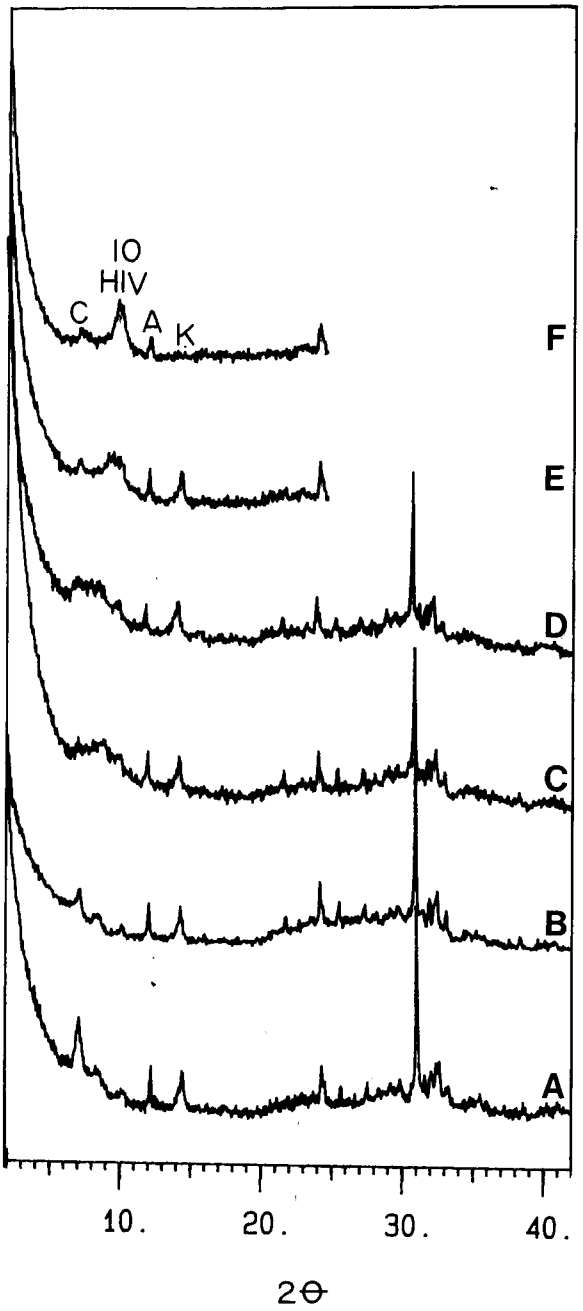


Fig. 11. Sample diffractogram of the <2 μm mineralogy of the Lower Zone for different environmental conditions: (A) Ca saturated, 54 percent relative humidity (RH); (B) Ca saturated, glycolated; (C) K saturated, 0 percent RH; (D) K saturated, 54 percent RH; (E) K saturated, 300°C heated; (F) K saturated, 550°C heated. On upper diffractogram the characteristic spacing of the clay mineral is listed: C-chlorite, 10 for the 10 Å mineral, A-amphibole, K-kaolinite.

it from smectite (MacEwan and Wilson, 1980). HIV was distinguished from vermiculite by K-saturated samples which did not collapse to 10 Å but retained spacings ranging from 11 to 13 Å and collapsed to 10 Å upon heating to 550°C. Kaolinite was also present in all clay separates and was identified by the collapse of the 7 Å peak during the 550°C heat treatment. The 10 Å mica (10 Å spacing with all treatments) and chlorite (persistent 14 Å peak) were identified only in the lower zone and P11-0 samples. The remainder of the <2 μm fraction is dominated by primary minerals (quartz, feldspar, hornblende, chlorite, 10 Å mica), reflecting the relative immaturity of the soil profile.

Upper zone.—The results presented earlier demonstrate removal and/or redistribution of major elements within a podzolic soil profile. Clay minerals are most abundant in the upper and middle zone; they are much less abundant in the lower zone where primary minerals and quartz are prevalent (fig. 10). Zr and Ti values for the upper zone (Ae horizon) indicate extreme leaching, with approx half the original material removed (dissolved). The <2 μm fraction is dominated by mica-derived vermiculite, but this fraction represents a very small proportion of the sample. The conclusion is evident from the CIA values of the upper zone which are very close to 50. The vermiculite, probably derived from primary biotite, contains no hydroxy interlayers and suggests conditions of extreme leaching (Douglas, 1977). No vermiculite peaks are evident in bulk sample XRD patterns, and we surmise that the intense leaching conditions have resulted in the dissolution and degradation of sand-sized vermiculite to clay-sized vermiculite. The dominance of vermiculite over HIV in Ae horizons of podzolic soils has also been documented in Japan (Hirai, Araki, and Kyuma, 1989) and in the Adirondack region of the United States (April, Truettner Coles, and Newton, 1986b).

Middle zone.—Quartz is more abundant than HIV, kaolinite, and plagioclase in the upper middle zone (fig. 10). It is not well cemented by iron-oxides and hence is easily extracted in the <2 μm fraction. HIV is the dominant clay mineral in the lower portion of the middle zone (fig. 10).

The CIA values indicate that the middle zone contains the greatest concentration of secondary products; bulk compositional data indicate notable gains in Fe for this zone (fig. 8). Fe gains in B horizons are characteristic of podzols and have been quantitatively determined (using other methods) by Evans and Manley (1983) and Santos, St. Arnaud, and Anderson (1986). Fe is likely supplied by dissolution of hornblende and mica-derived vermiculite (Banfield and Eggleton, 1988; Ghabru, St. Arnaud, and Mermut, 1990). As no XRD peaks were detected for an iron-rich phase in the bulk samples or <2 μm fraction, the phase is most likely amorphous and/or microcrystalline Fe oxides and oxyhydroxides or organically bound Fe. Johnson and McBride (1989) have used Mossbauer spectroscopy to identify "microcrystalline" goethite and ferrihydrite in Spodosols (podzols) in the absence of XRD peaks for these

minerals; such phases probably are also present in the Plastic Lake profile.

Bulk compositional data indicate that Mg accumulates in the middle zone or B horizon (fig. 8C). The pH of soil waters from these podzols is low, ranging from 4.3 to 5.1 (B. LaZerte, personal communication). The waters are also greatly undersaturated with respect to Mg-bearing hydroxides, oxides, and carbonates. These minerals cannot form in this environment; the only constituents likely to take up Mg in the middle zone are organic complexes and silicates (Mokwunye and Melsted, 1972). However, there is no evidence that Mg is adsorbed onto, or incorporated into, insoluble organic phases, especially in large quantities. By contrast, Mg is an essential element of many highly reactive clay minerals including montmorillonite, vermiculite, HIV, and chlorite; it is most likely that Mg is taken up by clay minerals in the middle zone. HIV, an authigenic phase (the term authigenic does not imply the process by which HIV forms), is the most abundant secondary product of this zone. Although HIV may have a precursor (that is, biotite, vermiculite), it probably has extracted Al, Mg, and Fe^{2+} and Fe^{3+} from soil solutions and incorporated them into the mineral structure. Velbel (1985) has also observed the extraction of Fe and Al from solution in the process of biotite weathering; however Mg was released from the reaction, and this difference may be related to original composition, degree of weathering (age), and weathering environment.

To our knowledge, excess Mg in B horizons of podzolic soils has not been quantified before and deserves further investigation. Ross and others (1982) have found anomalously high values of Mg in the B horizon of podzolic soils of New Brunswick. These high values were attributed to a Mg-rich octahedral sheet in the HIV forming from chlorite, as these soils were developed on a chlorite-mica schist. Losses in Mg have been reported for podzolic soils of northern Ontario (Evans and Manley, 1983) and for Adirondack Spodosols (podzols) (April, Newton, and Truetter Coles, 1986). Mg profiles generally are not documented in podzols, yet there they provide important evidence that HIV is an authigenic phase within the profile.

Although there is a net loss of Al within the middle zone (fig. 8A), the extent of leaching is low compared to the upper zone. Al may be preferentially retained in the middle zone as a result of HIV formation. Its presence (persistence) probably prevents interlayer Al from being easily and rapidly extracted from the horizon. The interlayer sites provide a ready environment for uptake of Al from the upper zone or Ae horizon. Some Al probably is also associated with non-crystalline secondary products such as imogolite and Si-Al or Al-Fe sols, gels, or oxyhydroxides (Eggleton, 1987; Farmer, 1982, 1984; Taylor, 1988).

Lower zone.—HIV and kaolinite are authigenic products formed in the lower zone of the P11 soil profile. A 10 Å mica is also present and probably is an altered biotite rather than illite. Unfortunately, the quantity of the 10 Å clay in the <2 μm fraction was too small to separate to

determine whether this mica is dioctahedral or trioctahedral. We predict that this 10 Å mica is trioctahedral (after biotite) as removal of K from the interlayer position and Si substitutions in the tetrahedral sheet of biotite would result in the retention of a 10 Å spacing.

Both HIV and vermiculite probably formed from the alteration of biotite. The predominance of HIV in all P11 zones and the identification of vermiculite only in the upper zone suggest that HIV is the primary alteration product of all biotite-derived secondary products. Harris and others (1988) have examined soil samples and found biotite weathering to HIV directly, with no apparent vermiculite intermediary.

The 14 Å chlorite present in the lower zone probably has been inherited from the parent material. Chlorite is observed in the thin sections of bedrock as a deuteric alteration product of biotite (Kirkwood, ms). However, the absence of a 14 Å peak in bulk bedrock samples indicates this mineral is present only in trace quantities. The relative instability of chlorite in acidic conditions (Lindsay, 1979; Kittrick, 1983) has resulted in its loss from the rest of the profile, with a small amount remaining in these least weathered samples. The presence of chlorite in these samples also suggests that a small quantity of the HIV in the other zones may have formed by the degradation of chlorite as discussed by Ross and others (1982), Proust, Emery, and Beaufort (1986), and Ghabru, Mermut, and St. Arnaud (1990).

IMPLICATIONS FOR PODZOL GENESIS

It is commonly believed that the mechanisms of podzol genesis are governed by the changing chemical distribution of Fe and Al in the Ae and B horizons. Methods commonly employed to test for the presence of Fe and Al use extractants, specific to amorphous, non-crystalline, and organically bound Fe and Al. In the present study, bulk chemical rather than extraction methods were used to examine quantitatively the changing chemistry of a weakly developed podzolic profile. Our study indicates that Fe is accumulated in the P11 middle zone or B horizon. We will not address the process by which this occurs. Al is depleted from this profile in both the upper and middle zones. The bulk compositional data prove that only a small quantity of Al is held up by the secondary products in this zone. McKeague, DeConinck, and Franzmeier (1983) propose that the most important weathering reaction in podzols (Spodosols) is the dissolution of ferromagnesian minerals; these minerals supply Si, Al, Ca, and Fe to the soil system. In addition, Duchaufour and Souchier (1978) suggest that one of the fundamental differences between brunisolic and podzolic soils is the ferromagnesian content of the parent material. The parent material for the P11 profile is not significantly Fe-rich. The dissolution of ferromagnesian minerals is not the most significant reaction when compared with the amount of feldspar weathered. The supply of Fe from the dissolution of both mica-derived vermiculites and hornblende is important to the development of podzolic soils, but dissolution

of feldspars is the most significant mineral dissolution reaction affecting the chemistry of the bulk soil.

The middle zone or B horizon is commonly referred to as a zone of net accumulation of organically-complexed and/or amorphous Al (McKeague, DeConinck, and Franzmeier, 1983). The maximum extractable Al for Plastic Lake soils (fig. 2) is in the upper reaches of the middle zone (Bhf). Bulk chemical analyses include all forms of Al in the samples, including that which is organically complexed. Al, however, shows a net loss in the middle zone (B-horizon) rather than the expected gain. Although some Al derived from weathering in the upper zone is retained by the middle zone to form secondary products, it is insufficient to counterbalance the loss of Al resulting from weathering of primary minerals, especially feldspars.

The amount of Al retained in the B horizon of a podzolic soil may be as dependent on the primary minerals of the parent material as on the weathering process. If, for example, large amounts of biotite are present in the parent material a significant quantity of HIV will be produced in the B horizon. Consequently, Al released from the Ae and uppermost B horizons may accumulate in significant quantities in HIV interlayer sites. However, if HIV is scarce (that is, little biotite in the parent material), Al from the surface horizons may be transported through the B horizon and not accumulated.

Wilson (1986) suggests that the Al chemistry of podzolic soil profiles appears to be controlled either by Al-hydroxy interlaying of expandable layer silicates or by production of amorphous or noncrystalline compounds such as proto-imogolite allophane. While amorphous and noncrystalline phases have not been specifically analyzed in the P11 profile, they are evident in the soil profile (preliminary SEM analyses). These compounds, however, are volumetrically unimportant compared with authigenically produced HIV. At most, 2.5 g Al/100 g sample (from extractable data, fig. 2) is distributed among the organic, amorphous, and clay mineral fraction.

The above observations also have implications with respect to recent concerns of the ability of low base status soils to buffer incoming inputs of anthropogenic acids. Much of the recent research has advocated the importance of silicate mineral weathering and, particularly, feldspars for proton neutralization (Katz, Bricker, and Kennedy, 1985; Velbel, 1985; Wilson, 1986; Giovanoli and others, 1988; Kirkwood and Nesbitt, 1991). Our study provides further evidence that in the acid P11 soils, feldspar weathering is by far the most important weathering and hence proton-consuming reaction.

CONCLUSIONS

Bulk chemistry and mineralogy of the P11 soil profile demonstrates that the genesis of this podzolic soil is governed primarily by the weathering of aluminosilicate minerals and to a lesser extent by weathering of ferromagnesian minerals. The upper zone is the most highly depleted in

primary minerals, and dissolution of these minerals (namely plagioclase) is the dominant process operative in this zone. The middle zone is not as highly weathered as the upper zone, and production of authigenic silicate phases and oxides is significant, as indicated by quantitative gains in Mg and Fe. Al, which is bound by secondary products in the middle zone, still shows a net loss within this zone and does not appear to play the most significant role in the genesis of the P11 soil profile.

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