THE DEVELOPMENT OF A PODZOL USING STRATIGRAPHIC – AGE RELATIONSHIPS AND A MASS-BALANCE APPROACH

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INTRODUCTION

The notion that pedogenesis results largely from the alteration *in situ* of the regolith is widely accepted in the Earth sciences. An apparent consequence of this was the examination of the processes of pedogenesis in a vertical sense with particular attention directed to the upward and downward movement of soil constituents. In turn this led to the recognition of eluvial near-surface horizons (zone of depletion and sometimes bleached) and illuvial deeper horizons (zone of enrichment). This framework is enshrined in many introductory texts in soil science, ecology, geology and physical geography. Furthermore, the podzol soil type, with its characteristic bleached surface layer and pan, is often used to demonstrate this genetic style. One consequence of this thinking has been to assume that soil development operates within a closed system (e.g. Jersak *et al.* 1995) such that the eluvial and illuvial layers in a deposit form as a couplet, i.e. in one allostratigraphic unit, in which the two layers are of the same age. It is also purported that in a podzol and eluvial/illuvial horizons owe their origin to the input of organic molecules that are particularly active in complexing grain coatings and transporting the products downwards to produce an indurated layer (pan). Early researchers focussed on the role of humic and fulvic acids from litter in coniferous forests. This view is still widely portrayed in many texts even though the active organic molecules have been recognized for some time firstly as simple polyphenols (e.g. Bloomfield 1955 and Davies *et al.* 1964) and more recently as simple organic acids (Blasser 1994).

The coastal barrier systems along Australia's east coast appear to provide an exception to a simple closed system since thermoluminescence (TL) dating indicates that the bleached horizons are very much younger than the underlying pan (Nott *et al.* 1994). However, TL dating provides an age of the quartz sand grains and not necessarily podzol development. Furthermore, dated quartz is affected by mixing mechanisms such as bioturbation that results in grain turnover and re-exposure to sunlight (Humphreys *et al.* 1997). Any 'younging' trend towards the surface may represent the addition of new material on an aggrading surface and/or effective overturn. Hence, TL dating alone does not provide an appropriate discriminator of when podzolization commenced. Likewise, pedogenic studies on surficial materials that have not been adequately dated cannot properly address issues such as the initiation of, nor episodes of, podzolization. A partial resolution of this issue is to combine dating with mass-balance calculations and this provides the aim of this study.

MATERIALS AND METHODS

This study area is located adjacent to Middle Creek near Narrabeen, (Grid ref. 678383, Mona Vale 1:25,000 topographic sheet) and was selected following reconnaissance of podzol sites in upland settings in the neighbouring Deep Creek catchment and nearby West Head (Buchanan 1980, Buchanan & Humphreys 1980). A 3-dimensional stratigraphic approach was adopted to determine relationships between materials and pedogenic layers, and this involved > 30 pits, trenches and auger holes which were excavated/cored to the saprolitic clayey material and sandstone. Soil layer changes were assessed in the field following McDonald *et al.* (1990) and included thickness, colour, pH, texture, and gravel size and content. Additional data were obtained from one large pit (Pit 1) where the podzol had the thickest E horizon and strongest pan. Selection of the best representative layers was based on criteria outlined in Aitken (1990) and subsampled for the determination of bulk density and elemental analysis via XRF following the methodology of Norrish & Chappell (1977). These data were treated by mass-balance techniques developed by Brimhall *et al.* (1985) with the least mobile element selected via the 'graphical isocon method' (e.g. Moore 1998). Systematic dating of Pit 1 was achieved from a combination of ^{14}C of charcoal fragments from 2-5mm in size, AMS of fine charcoal and TL of 90-150 µm quartz grains.

RESULTS AND DISCUSSION

Stratigraphy

The podzol is developed in the distal end of a distinct sandy unit that commences from the base of a 5 m high sandstone bench. The proximal end consists of < 0.5 m thick gravelly (pebbles-cobbles) loamy sand. Gravel

In: Roach I.C. ed. 2002. *Regolith and Landscapes in Eastern Australia*. pp. 28-32. CRC LEME.

content and size decrease downslope and the unit thickens (> 1.5 m at Pit 1) over a distance of 90 m. The sandy unit overlies a distinct saprolitic clayier unit of sandy clay loam to sandy clay. In classic pedological terms the upslope part of the sequence provides typical texture contrast soils (TCSs) whereas the proximal end forms a deeper variety (cf. Paton *et al.* 1995). Hence, the podzol occurs within a distinct sandy allostratigraphic unit that, in turn, is the topsoil of a thick TCS. Podzol development, as expressed by thickness and whiteness of the E horizon in conjunction with the colour strength and induration of the pans, increases downslope as the deposit thickens and surface gradient declines. This may imply an internal drainage and microtopographic influence as discussed for similar sites near Narrabeen by Buchanan (1980).

Dating

Dating indicates that there are no substantial age inversions (Table 1). However, the range of ages suggests that the sandy allostratigraphic unit may consist of three sub units: up to 2,000-3,000 yrs for the 'A' and upper 'E' horizons; about 10,000 yrs for the bulk of the 'E' to the 'Bh' and 'Bhs'; and > 20,000 yrs from the base of the pan into the 'C' material. The existing age discrepancy of 8,000 years between the 'A' and the upper part of the 'E' over an interval of 5-10 cm remains to be resolved. The charcoal appears as a discrete lens but of limited lateral extent (1-2 m). Hence, it may represent a surface accumulation of charcoal. Such an accumulation could result from the burning of a tree or the localized deposit of a charcoal as occurs with sediment transport events after a fire. The charcoal was then either incorporated into the soil profile via bioturbation, i.e. the original charcoal was deposited on a surface higher than the present day level of charcoal or was emplaced on a lower surface that has since been buried. The available information does not permit resolution of this issue. The age determinations defined for the 'E' material at 45 cm and the 'B' material at 80-90 cm, overlap by one standard deviation indicating that they are probably part of the same deposit.

Table 1: Dating results for Pit 1.

Sample No.	Depth (cm)	Soil Layer	Dating Technique	Age (years B.P.)
Beta-94604	20-30	A base	Radio carbon	2,090 +/- 60.0
Beta-94605	30-40	E top	Radio carbon	2,770 +/- 60.0
W2181#	45	E	TL	10,600 +/- 0.7
Beta-099265	80-90	Bhs	AMS	9,890 +/- 50.0
Beta-108010	110	C	AMS	20,260 +/- 220.0
W2182#	117	C	TL	27,800 +/- 1.7
Beta-110147	150	C	AMS	35,950 +/- 390.0

Table 2: Summary of relevant major and trace element analysis results for soil layers in Pit 1.

	Depth (cm)	10	25	40	60	85	100	110	140
	Horizon	A1	A1	A2	A2	Bh	Bhs	C	C
Majors (wt. %)	SiO_2	97.08	98.44	98.18	98.22	90.79	90.06	94.10	94.75
	TiO_2	0.33	0.36	0.35	0.41	0.74	0.49	0.44	0.43
	Al_2O_3	0.58	0.17	0.14	0.13	4.29	5.98	2.82	2.28
	Fe_2O_3	0.22	0.08	0.04	0.05	2.21	1.75	0.75	0.61
Trace (ppm)	Ba	31	19	19	18	70	59	46	42
	Cr	9	6	5	10	26	27	19	16
	Nb	7	8	7	8	15	10	8	9
	Ni	23	14	5	6	9	24	7	6
	Pb	12	1	0	0	61	5	2	4
	Rb	3	2	1	2	20	21	14	14
	Sr	11	8	5	6	67	41	32	29
	Th	2	4	1	4	9	10	6	5
	U	0	0	0	1	2	2	3	2
	V	13	12	12	13	65	43	28	25
	Y	5	5	5	6	12	9	6	8
	Zn	9	3	3	1	4	5	5	3
	Zr	225	219	211	262	251	202	186	196

Elemental Variation in the Podzol Profile.

The compositional data (Table 2) were derived from XRF analysis and showed that, as expected, the most prominent major element in the quartz sand of the podzol is Silicon (Si), comprising more than 91.00 wt. % of all samples tested. Aluminium (Al) and Iron (Fe) are at low concentrations in the 'A$_1$' and 'A$_2$' layer materials but comprise the next highest concentrations, particularly in the accumulation zones of the 'Bh' and 'Bhs' horizons. A number of the other major elements also follow a similar trend but to a lessor extent, as concentrations are 0-1 wt. %. Many of the trace elements Ba, Cr, Ni, Pb, Rb, Sr, Th, Zn, V, appear to have been removed from the topsoil but are concentrated in the pan horizons too.

The Isocon Approach

The 'graphical isocon diagram' was applied to all major and trace elements to determine the least mobile within all horizons. It portrays a graphical representation of elemental mass changes due to alteration relative to a unit mass of unaltered material. The results provide a means of qualitative and semi quantitative assessment of changes in rock chemistry during alteration (Moore 1998) thereby making it easier to interpet histograms of element gains and losses, undertake mass-balance calculations (Gresens 1967), graphical interpretations (Grant 1986), and modified scaling techniques for displaying the data (Huston 1993). The change in mass of each element in relation to the isocon standard is defined by the Relative Elemental Mass Change Equation:

$$\Delta Me(\%) = 100\left(\left(Ce_w / m \times Ce_o\right) - 1\right) \qquad \text{(Equation 1)}$$

Where $\Delta Me(\%)$ = elemental mass change, Ce_w = concentration of an element in the weathered sample, m = slope of isocon line for a particular sample, Ce_o = concentration of an element in the least weathered sample which is taken to be the material at 140 cm depth.

In order for this procedure to be applicable, the immobile elements to be used for comparison between weathered and unweathered parent material must be established. This was based on examining general down-profile trends and selecting the least variable defined in this study by the lowest Coefficient of Variation (CV = standard deviation/mean x 100). This showed that the elements with the least variation were Zr, Ti, Nb, and Y (Table 3). All other elements had CVs > 50%. An identical result was obtained on very different soils on basaltic regolith by Moore (1998). Nevertheless, these four elements, though the least mobile, do display down profile variation and hence require further evaluation.

Table 3: Statistical data used for immobile element selection.

Element	Range	Mean	Std. Dev.	C of V (%)
Zr	160-599 ppm	209	31.70	15.2
Nb	1-15 ppm	8.90	2.33	26.2
TiO_2	0.33-0.74 wt%	0.44	0.12	27.3
Y	5-13 ppm	7.20	2.30	31.9

Mass-Balance relationships

The mass-balance equation (Brimhall *et al*. 1988, 1991, 1992) is used to determine gains and losses of elements between horizons/layers is written as:

$$\tau_{j,w} = \frac{100 m_j flux}{C_{j,p} \times \rho_p \times V_p} = \frac{\rho_w \times C_{j,w}}{\rho_p \times C_{j,p}} \times \left(\in_{i,w} + 1\right) - 1 \qquad \text{(Equation 2)}$$

Where $\tau_{j,w}$ = transport function describing mass loss from weathering (g/g^{-1}) or (wt %), $m_j$flux = mass flux of mineral weathered (g/cm^{-3}), $C_{j,p}$ = concentration of weatherable mineral or element in parent material (wt%), $C_{j,w}$ = concentration of weatherable mineral or element in the soil profile (wt%), ρ_p = density of protolith (g/cm^{-3}), ρ_w = density of weathered material (g/cm^{-3}), V_p = volume of soil sample (cm^3), $\in_{i,w}$ = volumetric strain (based on immobile element i) which is dimensionless.

Volumetric strain ($\in_{iw}$) is derived from the following equation:

$$\in_{i,w} = \frac{\rho_p \times C_{i,p}}{\rho_w \times C_{i,w}} - 1 \qquad \text{(Equation 2a)}$$

This is defined as volumetric changes that occur during pedogenesis, determined by using the classical definition of strain, $\in$: the ratio of volume change attributed to an alteration of initial volume (Chadwick *et al*. 1990). After the volumetric strain has been calculated, the mass-balance equation can be split into:

$$\tau_{j,w} = \frac{\rho_w \times C_{j,w}}{\rho_p \times C_{j,p}} \times \left(\in_{i,w} + 1\right) - 1 \qquad \text{(Equation 2b)}$$

$$m_j flux = \left(\rho_p \times V_p \times \frac{C_{j,p}}{100}\right) \times \tau_{j,w}$$

It is the transport function ($\tau_{j.w.}$) which is of interest in the present study.

Two protoliths (the assumed original parent material) were examined: (1) the 'C' material of the podzol at Pit 1, and (2) topsoil sampled from upslope since it was evident that the degree of bleaching and hence loss of Fe and Al decreased downslope in the sandy unit. The results of calculations demonstrate a net depletion of major elements from the 'A' and 'E' layers and net gains of these in the pans (B layers) though only the major cations of Fe and Al are shown here (Table 4). There was insufficient Al in the topsoil to account for the levels in the pans regardless of the protolith. This applies also for Fe in protolith-2 but not for protolith-1 where it is in balance. Clearly, the choice of protolith can exert a considerable influence on the interpretation. If protolith-2 is preferred the results demand either an additional source of Fe and Al such as from upslope and supplied by subsurface flow and/or from below and supplied via water table movement, or a much greater thickness of topsoil. The same applies for Al in protolith-1 but not for Fe. Indeed, the inconsistent results with protolith-1 indicate that 'C' material cannot be the original parent material of this soil!

Table 4: Mass-balance results at Pit 1 (+ = gains, - = loss).

Horizon	Depth(cm)	Protolith 1 (C material)		Protolith 2 (upslope A material)	
		ΔFe (g/cm^3)	ΔAl (g/cm^3)	ΔFe (g/cm^3)	ΔAl (g/cm^3)
A + E	0-80	-0.860	-0.749	-0.175	-0.825
Bh + Bhs	80-100	+0.861	+2.031	+0.681	+1.674
% change		100	+271	+389	+203

Pedogenesis

This study indicates a much more complex situation of podzol genesis than the possibilities posited in the Introduction. In the first instance the mass balance investigation does not support a closed system explanation. Secondly, age relationships are complex for the upper part of the 'B' is coeval with the 'E', ca. 10 ka, which is 3-5 times older than the 'A' but twice as young as the upper part of the 'C'. Hence, these results indicate that a 'period' of podzol development cannot be defined. *On one hand it is possible that the main characteristics of the podzol have developed in the last 10,000 years i.e. following the emplacement of the sand that has become the 'E' and possibly the 'A' horizons* with the pan positioned on an older Last Glacial Maximum surface*, i.e. the podzol is a Holocene feature. Such* an interpretation *is supported by the knowledge that* podzol profile expression can develop within short time frames as, for example, on mined coastal sands (e.g. Paton *et al.* 1976, Prosser & Roseby 1995). This interpretation clearly differs from the coastal barrier systems investigated by Nott *et al.* (1994). Alternatively, it is also possible that a podzol began forming much earlier since the pan is mostly developed in older material. However, this necessitates either the removal and subsequent re-emplacement of overlying sand (to become the A and E horizons) as per the Nott *et al.* (1994) explanation or the re-setting of the TL ages and the incorporation of younger charcoal via mixing mechanisms without adversely affecting podsol development. The important point to emerge from this study that no simple picture emerges despite the relatively detailed investigation.

CONCLUSION

Podzol genesis at the Narrabeen study site is much more complex than is implied from commonly acceptable explanations. Despite the detail of the investigation it has not been possible to resolve the timing of podzol development except in broad terms. It is also apparent that a closed bio-geochemical system is most unlikely on lower footslopes with a colluvial apron. This result probably applies to many other podzol settings too.

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