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Effect of toposequences on geochemical mass balance and clay mineral formation in soils developed on basalt parent material under subhumid climate condition

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Four soil toposequences served as the basis to calculate the accumulation of soil organic matter, transformation of pedogenic Fe and Al and net losses of the main elements (Ca, Mg, K, Na, Fe, Al, Mn and Si) by means of mass-balance calculations. Elemental losses due to deglaciation and exposure to the weathering environment were calculated. These mass balance calculations indicate that extensive mineral weathering resulted in significant leaching losses of Si, major base cations, and Al (particularly from the upper horizons). Dominant duration identified with mass-balance analysis include desilication and loss of bases.

[**Keywords***:* Mass-balance, soil formation, toposequence, XRD of clay fraction]

Introduction

Soil Johnson and Watson-Stegner[1] indicated about the soil assessment model which can be distinguished between progressive and regressive pedogenesis. It has long been recognized that parent material and topographic position has a major influence on the mineralogical, morphological, physical and chemical properties of soils in local condition. With time, soil composition diverges progressively from that of the parent material under the influence of pedogenic processes determined by vegetation, topography and, in particular, climate[2].

For most pedological purpose, including the modeling of soil characteristics and variation, the most important feature of the parent material is considered its chemical composition. Physical properties such as texture or grain size are considered only secondary importance. The most useful criteria are silica (SiO_2) content and calcium-ferromagnesian (Ca-Fe-Mg) oxide content. These criteria allow parent material to be categorized in terms of their siliceous (high in silica, low calcium-ferromagnesian) or mafic (low in silica, high calcium-ferromagnesian) character[3].

Topographic positions or physiographical units have important role in soil formation and affects how water and energy were added to and was lost from soil systems. The systems could be open or close relative to the flow of water and energy. Dengiz & Baskan[4] indicated that soil formations were highly associated with topographic positions which influence on morphological and physico-chemical characteristics of the soils in local region. In their study, they found that young soils due to minimum soil formation and classified by taking into consideration of Soil Taxonomy[5] and FAO/ISRIC[6] as Entisol/Leptosol while, Inceptisols/Cambisol and Calcisol on plateau position had the greatest degree of pedogenesis that have cambic and calcic main subsurface diagnostic horizons. In addition to that, she significance of slope gradient, length of slope in meters, and slope aspect effect on soil physical, chemical and mineralogical properties has widely reported by many researchers such as authors[4,7,8 & 9]. In the upslope positions higher slope gradient is the main factor responsible for soil erosion and the loss of upper horizons following land degradation[10].

Birkeland[11] proposed that elements released by weathering may or may not be redistributed down-slope as a function of their mobility under constant or changing geochemical environments along the slope. The weathering rates of soils were derived from calculations of enrichment/depletion factors determined using immobile element contents. The derivation of mass-balance equations and their applications to pedologic processes were discussed in detail by authors[12&13] and revised[14]. Based on these properties, a set of mass-balance equations is developed that determines soil deformation (strain) and open chemical system gains and losses in the soil in relation to the parent material. An examination of soil mineralogy may be used to determine whether chemical differences in soils are caused by pedogenesis or differences in parent materials. Volumetric and mass changes during soil formation were evaluated by applying a mass conservation equation[12,13&15].

By taking into consideration of mass balance, geochemical and mineralogical data, the present study carried out a pedological evaluation aimed at identifying individual mineralogical and geochemical characteristics of Vertisols and Entisols with basaltic parent material and located on different topographies in order to understand the relationship between particular soils and the landscapes and ecosystems in which they function. Geochemical, mineralogical and other analytical characteristics are presented here in order to discuss their use in quantifying the maturity stages and mass balance.

Materials and Methods

This study was carried out on along transect settled between Bafra Plain and Canik mountain located approximately 20 km west of the Samsun province in the central Black Sea Region of Turkey (Figure 1). The study area is coordinated with 4594000-4598000N, 751000-758000E, (UTM/WGS 84 m).

The study area ranges from 10 m to 300 m in relief and includes four landscape positions (footslope, backslope, low and high land plateaus) representing changes in geomorphology, topographic gradient, parent material and soil characteristics. The underlying bedrock consists primarily of Quaternary-age basaltic colluvial deposits on the foot slope, low land plateau, and Mesozoic-age basalt and marl-limestone on the back slope and high land plateau.

The current climate in the region is semi-humid. Summers are warmer than winters (Avg. temperatures: July, 22.2^{o}C; January, 6.9^{o}C). The mean annual temperature, rainfall and evaporation are 13.6ºC, 764.3 mm and 726.7 mm, respectively. Soil temperature and water moisture regimes at the study site were classified according to the Soil Survey Staff5 as mesic and ustic, respectively. Physiographical, the area is comprised of four main units. The majority of the site consists of a slightly sloped (0.0-2.0%) low and high plateau and other units are hilly and moderately to severe sloped (3-20%). The study area is covered by dominantly pasture and forest land. Only small part of the agricultural land located on foot slope and low land plateau.

Based on the hypothesis that topography and parent material and also climate-vegetation cover might be the main controlling factor for mass balance in soil development, soils have been studied on along transect (crosswise from North to South direction) with representative four profiles (Figure 2). Morphological properties of these three profiles in the field were identified and sampled by genetic horizons and classified according to Soil Survey Staff[5&16]. Twenty four disturbed and undisturbed soil samples were taken to investigate for their physical, chemical and mineralogical properties at the laboratory. Soil samples were then air-dried and passed through a 2 mm sieve to prepare for laboratory analysis.

After soil samples were then air-dried and passed through a 2 mm sieve, particle size distribution was determined by the hydrometer method[17] after removal of organic matter with 30 % H_2O_2, of sulphate by leaching salts with distilled water, of carbonates with 1 M NaOAC at pH 5, and dispersion by agitating the

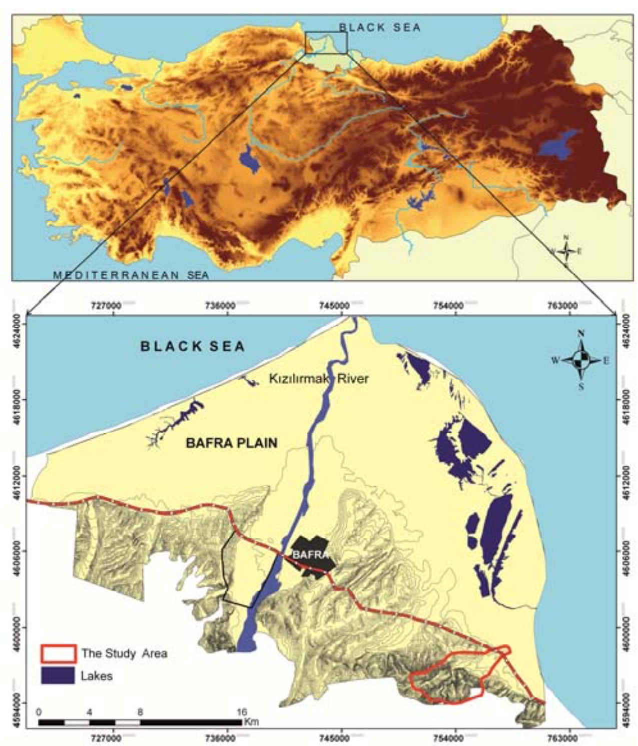

Fig. 1 — Location map of the study area

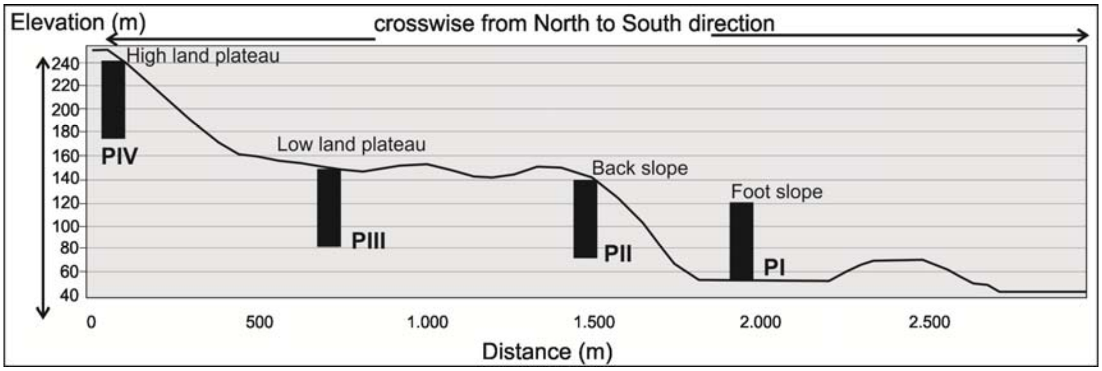

Fig. 2 — Transect of the four different soil profiles on the same parent material but different topographic positions.

sample in 10 ml of 40 % sodium hexametaphosphate (calgon)[18]. Bulk density[19] was determined from undisturbed samples. Organic matter and total nitrogen were determined in air-dry samples using the Walkley-Black wet digestion method[20]. pH, EC-electrical conductivity (of the saturation) by method of the Soil Survey Laboratuary[21]. Lime content by Scheibler calcimeter[16]. Exchangeble cations and cation exchange capacities (CEC) were measured using a 1 N NH4OAc (pH 7) method[21].

The clay fraction (<2 μm) was obtained from the soil after destruction of organic matter with dilute and Na-acetate-buffered H2O2 (pH 5), by dispersion with calgon and sedimentation in water. Oriented specimens on glass slides were analyzed by X-ray diffraction using Cu Kα radiation from 2° to 30° 2θ with steps of 0.02° 2θ at 2 s $step^{-1}$. The following treatments were performed: Mg saturation, ethylene glycol solvation (EG), and K saturation, followed by heating for 2 h at 550 °C. Minerals and relative abundance were identified by their diagnostic XRD spacing and evaluated by their XRD relative peak intensities in the XRD diagram[22].

Mass-balance models provide a means to account for the fate of elements during soil evolution by quantifying the additions, losses and transformations which occur over time12. Long-term weathering rates of soils were derived from the calculations of enrichment/depletion factors determined using immobile element content such as Ti, Zr or V[23]. In this study, Ti was used as an immobile element. Volumetric changes that occur during pedogenesis were determined by adopting the classical definition of strain, εi, w (C)[12].

$$\varepsilon_{i,w} = \frac{\Delta z_w}{\Delta z} - 1 \quad \dots (1)$$

with Δzw, is the weathered equivalent height (m), Δz, as the columnar height (m), positive value indicates enrichment, whereas negative values indicates depletation. The calculationof the open-system mass transport function (T)[13],

$$\tau_{j,w} = \left(\frac{\rho_w C_{j,w}}{\rho_p C_{j,p}}\left(\varepsilon_{i,w}+1\right)\right) - 1 \quad \dots (2)$$

Tjw, The calculation of the open-system mass transport function, Pw, being the bulk density of the weathered soil, Cjw, as the concentration of element in the weathered product, Cjp, as the concentration of element in protolith (e.g. unweathered parent material or bedrock) (kg.t-1), Pp, being the bulk density of the protolith (t. m-3)[14]

$$m_{j,flux(z_w)} = \sum_{i=1}^{n} C_{j,p}\rho_p\left(\frac{1}{\varepsilon_{i,w}+1}\right)\tau_{j,w}\Delta z_w \quad \dots (31)$$

Mj,flux(zw), with n soil layers the calculation of changes in mass of element j is given by Egli & Fitze14 ($g.cm^{-2}$), positive value indicates adding in the system, whereas negative values indicates loss in the system.

Total elemental analysis was performed on the fine-earth fraction of all soil samples. Oven-dried (70°C, 48 h) soil samples were dissolved using a mixture of lithium metaborate/tetraborate fusion and dilute nitric digestion[14]. Concentrations of total elemental composition were analyzed by ICP-emission spectrometry.

Results and Discussion

Field morphology and physical characterization data for representative four profiles are presented in Figure 2 and Table 1 & 2. Soils along transect in the study area show variation in terms of textural distribution, structural features, color and horizon depth. These differences represent the obvious effect of erosion, whereby surface soils have been carried from the back slope to the foot slope and low land

Table 1 — Morphological properties and classification (Soil Taxonomy-FAO/ISRIC) of profiles

Horizon	Depth (cm)	Color (dry)	Color (moisture)	Structure	Boundary	Special features
PI / Foot slope *(Typic Haplustert / Haplic Vertisol)*						
Ap	0-15	2.5Y 5/2	2.5Y 3/2	2mgr	as	cracks
Bss	15-66	10YR 5/3	10YR 4/3	2cpr	cw	slickenside
C	66+	10YR 5/4	10YR 4/3	mas	-	-
PII / Back slope *(Lithic Ustorthent / Eutric Regosol)*						
A	0-19	2.5Y 5/2	2.5Y 3/1	2fgr	cw	-
Cr	19+	2.5Y 5/3	2.5Y 3/3	mas	-	-
PIII / Low land plateau *(Typic Haplustert / Haplic Vertisol)*						
A	0-18	10YR 4/3	10YR 3/3	2cgr	cs	cracks
Bss	18-57	10YR 4/3	10YR 4/4	2msbk	cw	slickenside
Cr	57+	10YR 4/3	10YR 3/3	mas	-	-
PIV / High land plateau *(Typic Calciustert / Calcic Vertisol)*						
A	0-12	2.5Y 5/3	2.5Y 3/3	3mgr	as	cracks
Bss1	12-41	2.5Y 5/3	2.5Y 4/3	3mabk/2fsbk	cw	slickenside
Bss1	41-84	2.5Y 6/3	2.5Y 4/3	3mpr	ci	slickenside
2Ck	84+	5.0Y 8/1	5Y 8/2	mas	-	common carbonate nodules and micelles

Abbreviations: Boundary: a = abrupt; c = clear; g = gradual; d = diffuse; s = smooth; w = wavy; i = irregular Structure: 1 = weak; 2 = moderate; 3= strong; sg = single grain; mas = massive; vf = very fine; f = fine; m =medium; c = coarse; gr = granular; pr = prismatic; abk = angular blocky; sbk = subangular blocky.

Table 2 — Morphological properties and classification (Soil Taxonomy, 1999 and FAO/ISRIC, 2006) of profiles

Horizon	Depth (cm)	Color (dry)	Color (moisture)	Structure	Boundary	Special features
PI / Shoulder *(Lithic Ustorthent / Eutric Regosol)*						
A	0-16	2.5 Y 5/2	2.5 Y 3/2	2fgr	cs	-
Cr	16+	2.5 Y 3/3	2.5 Y 5/2	sg	-	-
PII / Low land plateau *(Typic Haplustert / Haplic Vertisol)*						
A	0-12	10 YR 5/3	10 YR 3/4	3mgr	cs	cracks
Bss1	12-48	10 YR 5/3	10 YR 4/3	2msbk	cw	slickenside
Bss2	48-89	10 YR 5/3	10 YR 3/2	3mpr	cw	slickenside
C	89+	10 YR 4/3	10 YR 3/2	mas	-	-
PIII / Backslope *(Lithic Ustorthent / Eutric Regosol)*						
Ap	0-24	2.5 Y 5/3	10 YR 3/2	2mgr	as	-
Cr	24+	2.5 Y 4/3	2.5 Y 4/3	sg	-	-
PIV / Footslope *(Typic Haplustert / Haplic Vertisol)*						
Ap	0-23	2.5 Y 5/2	2.5 Y 3/3	3mgr	as	cracks
Bss1	23-65	2.5 Y 5/3	2.5 Y 3/2	3mpr	cw	slickenside
Bss2	65-106	2.5 Y 5/2	2.5 Y 4/1	3cpr	cw	slickenside
C	106+	10 YR 6/1	10 YR 4/2	mas	-	-

Abbreviations: Boundary: a = abrupt; c = clear; g = gradual; d = diffuse; s = smooth; w = wavy; i = irregular Structure: 1 = weak; 2 = moderate; 3= strong; sg = single grain; mas = massive; vf = very fine; f = fine; m =medium; c = coarse; gr = granular; pr = prismatic; abk = angular blocky; sbk = subangular blocky.

plateau, their accumulation leading to progressively darker, deeper and finer-textured soils with decreases in elevation. Soil colour is closely related of some soil formation such as calcification process that reflect with high value of 2.5Y hue detected in 2Ck horizon of Profile IV, darkening progressively to reach a maximum value of 10YR on the low land plateau (PIII). Secondary $CaCO_3$ nodules and myceliums were also identified in the PIV, which apparently proofed the existence of carbonate leaching and accumulation. The accumulation of calcium carbonate in Profile IV and the slickenside features for all profiles except for the Profile II are indicative of pedological developments reflected in the variations in color, particle size distribution and surface horizon depth.

Profile II developed and located on back slope. Slope has been regarded as one of the most important factor that controls the pedogenic process on PII. Slope contributes to greater runoff, as well as to greater translocation of surface materials (organic matter, fine earth etc.) down slope through surface erosion and movement of soil. For all profiles included a strongly or moderately developed A horizon with a granular, angular, blocky structure; a strongly or moderately developed B horizon with a prismatic and angular blocky structure; and a C horizon with a massive or graded structure. While owing to loss of organic matter and fine texture, structural developing of backslope soils on surface horizon is weak, fine, granular (1fgr), back and foot slopes structure have 2fgr and 2mgr respectively in surface horizons. On the other hand, Profile I, III and IV included maximum structural formation and a strongly or moderately developed A horizon with a granular, angular, blocky structure; a strongly or moderately developed B horizon with a prismatic and angular blocky structure were observed Bss horizons. In addition it was determined C horizon with a massive or graded structure. According to Akamigbo & Asadu[24], along a toposequence the soils on the crest and back slope position could be more sandy than those on the lower catena. This was attributed to erosion effect which tends to wash off the surface soil horizons. Soil structure improved down the toposequences, as the surface horizons in the crest position were weakly structured and moderately structured in the valley bottom position. This could be due to increase in clay content and organic matter down the valley bottom catena.

The system of classifications employed in this study was those of the USDA Soil Taxonomy[5] and the FAO/UNESCO soil map of the world legend[6]. The basis of classification was the results of the morphological, physical and chemical characteristics of the soils. Accordingly, Profile I, III and IV were classified as Typic Haplustert, and Typic Calciustert. Soils in these profiles, located on footplain, low land plateau and high land plateau, were formed from a basalt parent material and contain an excessive amount of clay, as indicated by surface cracks ranging from 1-5 cm in width as well as intersecting slickensides and shiny pressure faces in the subsurface horizon, which also reflect a shrinking and swelling of the soil. The sub-horizons in these pedons include a layer more than 25 cm thick associated with slickensides and calcic horizons at a depth of 100 cm. These profiles were also classified as Haplic Vertisol and Calcic Vertisol[6].

Pedon II was classified as Lithic Ustorhent and Eatric Regosol. Slope was regarded as one of the most important factors controlling the pedogenic process in this pedon, which is located on a high backslope. Slope contributes to greater runoff, as well as to greater translocation of surface materials downslope through surface erosion and movement of soil. The horizon orders of the PII were defined to be A-C horizons. This means this profile has no diagnostic subsurface horizons and include lithic layer within 50 cm soil depth. Therefore, this soil can be defined as a young soil due to low pedogenetic development.

The major physical and chemical properties of the soils in each profiles in the study area are presented in Table 3 and Table 4. Properties in the different profiles varied as a result of a dynamic interaction among environmental factors including climate, parent material, land cover/land use and topography[25&26].

Solum depth ranged from 11-84 cm, particularly depending upon topographic position. Clay is dominant texture for all profiles except for PII with the highest clay content found in the Typic Calciustert and the highest sand content in the Lithic Ustorthent. The values of the bulk density ranged from 1.21-1.63 $g.cm^{-3}$ across the pedons of the toposequence. The least mean value of 1.59 $g.cm^{-3}$ was obtained from the back slope position. The foot slope and plateu flat lands have mean values of 1.32 $g.cm^{-3}$. The bulk density values were lowest in the surface or close the surface horizons and increased progressively with depth. Similar results have been reported by Göl & Dengiz[27]. Lower bulk density values related to organic matter and clay contents especially at the surface horizon.

Soil pH varies little across the toposequence. The pH of the soils was mostly moderately alkaline and there are no significant differences in the values of pH. Therefore base saturation is higher than 90 percentages. In addition, all profiles have slightly soluble with no significant differences among pedons. $CaCO_3$ content was close to the detection limit in all

Table 3 — Some physical and chemical properties of studied profiles

Horizon	Depth (cm)	$pH_{(H2O)}$ (1/2.5)	EC ($dS.cm^{-1}$)	$CaCO_3$ (%)	O.M (%)	Exchangeable Cations ($cmolc·kg^{-1}$)			CEC ($cmolc·kg^{-1}$)	B.D ($gr.cm^{-3}$)	P.S.D (%)			
						Na	K	Ca+Mg			C	Si	S	Class
PI / Foot slope *(Typic Haplustert / Haplic Vertisol)*														
Ap	0-15	8.28	0.26	0.79	2.21	0.36	0.36	42.97	43.70	1.28	58.3	20.0	21.7	C
Bss	15-66	8.12	0.18	1.26	0.67	0.47	0.32	42.58	43.37	1.21	61.8	25.6	12.6	C
C	66+	8.20	0.25	1.75	0.55	1.02	0.26	26.49	27.77	1.47	37.3	34.8	27.9	CL
PII / Back slope *(Lithic Ustorthent / Eutric Regosol)*														
A	0-19	6.94	0.35	0.09	1.54	28.70	0.35	0.43	27.92	1.56	22.0	21.8	56.2	SL
Cr	19+	7.01	0.20	0.29	0.87	17.66	0.54	0.12	17.00	1.63	14.6	9.3	76.1	LS
PIII / Low land plateau *(Typic Haplustert / Haplic Vertisol)*														
A	0-18	7.06	0.44	1.08	1.88	47.28	0.24	0.32	46.71	1.31	54.4	22.6	23.1	C
Bss	18-57	7.31	0.42	1.02	0.06	50.54	0.34	0.09	50.11	1.26	61.1	17.7	21.2	C
Cr	57+	7.01	0.51	0.39	0.57	40.54	0.58	0.09	39.87	1.28	57.5	22.6	19.9	C
PIV / High land plateau *(Typic Calciustert / Calcic Vertisol)*														
A	0-12	7.14	0.55	0.69	3.53	49.73	0.29	0.58	48.85	1.23	61.9	23.6	14.5	C
Bss1	12-41	7.70	0.54	0.98	1.78	44.57	0.27	0.31	43.98	1.31	49.9	27.7	12.5	C
Bss1	41-84	7.92	0.11	0.98	1.41	52.55	0.64	0.29	51.62	1.41	47.9	32.3	19.8	C
2Ck	84+	7.94	0.38	6.37	1.29	44.46	0.63	0.09	43.74	1.46	40.0	40.8	19.1	C

O.M: Organic matter, C.E.C: Cation exchange capacity, B.D: Bulk density, P.S.D: Particle size distribution, C: Clay, SL: Sand loam, LS: Loamy sand, CL: Clay loam

Table 4 — Geochemical characteristics (total analysis of the bulk material including soil skeleton and fine earth) of the investigated profiles

Horizon	Depthcm	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3
							(%)					
PI / Foot slope *(Typic Haplustert / Haplic Vertisol)*												
Ap	0-15	51.76	16.50	9.50	2.70	3.14	1.24	3.11	0.96	0.26	0.33	0.020
Bss	15-66	54.89	16.25	8.40	2.79	2.89	1.28	2.37	0.91	0.19	0.22	0.032
C	66+	53.35	16.48	8.55	3.04	3.47	1.29	2.20	0.88	0.17	0.22	0.026
PII / Back slope *(Lithic Ustorthent / Eutric Regosol)*												
A	0-19	46.04	17.10	11.36	5.03	5.84	1.24	3.09	0.86	0.44	0.17	0.009
Cr	19+	45.88	18.02	9.25	2.13	1.64	1.03	2.38	0.92	0.13	0.16	0.027
PIII / Low land plateau *(Typic Haplustert / Haplic Vertisol)*												
A	0-18	48.26	17.31	12.88	3.17	2.43	1.02	3.77	0.95	0.21	0.21	0.010
Bss	18-57	48.37	18.44	11.10	2.96	2.06	0.81	3.07	0.98	0.18	0.25	0.011
Cr	57+	51.03	17.11	10.67	2.61	1.99	1.08	3.80	1.13	0.19	0.29	0.014
PIV / High land plateau *(Typic Calciustert / Calcic Vertisol)*												
A	0-12	52.63	15.34	8.81	2.19	2.59	1.09	2.55	0.99	0.11	0.18	0.019
Bss1	12-41	56.14	15.96	8.60	1.89	1.79	1.06	2.36	1.00	0.05	0.15	0.023
Bss1	41-84	56.28	16.54	8.34	2.09	1.48	0.99	2.17	0.95	0.04	0.10	0.027
2Ck	84+	28.52	8.02	3.62	1.70	28.73	0.47	1.05	0.42	0.06	0.07	0.014

profiles, especially in surface horizons, and ranged from to 0.09 to 0.79%. Moreover, the calcium carbonate content was found even much higher in the horizons of Typic Calciustert (PIV) with carbonate accumulation (i.e. calcic horizons) (Table 3). All these profiles developed on basaltic parent material has calcium carbonate between 0.09%-6.37%. Lime in basaltic primer material is known to have 4 resources. These are: 1) basaltic lavas' taking some part of limy material under it into its body while flowing; 2) minerals in basalt, which include Ca, form $CaCO_3$ in the appropriate environment; 3) crystallization of hydrothermal waters, which are rich in lime, in foramens after the flow of basaltic lavas; and 4) recalcification with wind materials, including lime[28]. Similar to our findings, Aksoy[29] found a lime content of 2%-26% in soils on the Kayacik plains in Gaziantep, although the primer material in the area of their study was basalt. Soil CEC varied between 27.92 to 51.62 cmolc.kg^{-1}, with the highest CEC in the Typic Haplustert in which smectite was the predominant clay type, indicating the presence of stratified aluminosilicates with a high load intensity. The lowest CEC value was found in soil classified as Lithic Ustorthent. Ca and Mg were the dominant exchangeable cation for all profiles. For all soils, the organic matter is highest in the surface horizon and decreases sharply to its lowest level in the subsoil. In the study area, the reasons of the low level organic matter are attributable to rapid decomposition and mineralization of organic matter. Soil organic matter ranged from 0.55 to 3.53% in upper horizons.

Geochemical characteristics about total analysis for the concentration elemental oxides of bulk material including soil skeleton and fine earth in the investigated profiles were given in Table 4. All soils contained much SiO_2, Al_2O_3, and Fe_2O_3. The SiO_2 concentration rose to 56.28%. Al_2O_3 values ranged from 8.02% to 18.44% and tended to irregular distribution with depth. The highest Fe_2O_3 value was observed in PIII as 12.88% and all pedogenetic horizons have higher than 3% Fe_2O_3. Irmak et al.[30] indicated also that total Fe_2O_3 content of the basaltic soils was higher than other soils and changed between 4.36 and 6.70%. In addition, researchers reported that the total Al_2O_3 content of the basaltic soils was obtained relatively higher than other soils and changed between 4.92 and 8.72%. The high Al_2O_3 and Fe_2O_3 contents of the basaltic soils may be associated with the weathering of basalt rocks. CaO values were higher in the surface than the subsoil except for 2Ck which is not related basaltic material including calcification process. MgO values ranged from 1.70% to 5.03% and showed slightly significant differences among the horizons. The source of MgO and CaO is weathering process of labrador and bytownite mafic minerals in basalt rock. Other factors verifying this situation are the region's climate, the high Ca and Mg presence in the profiles and the high SiO_2/Al_2O_3 rates. In the studied soils, Al_2O_3 values were similar in solum and parent material as a result of the low weathering rate. K_2O and Na_2O values ranged from 1.05% to 3.07% and from 0.47% to 1.29%, respectively.

According to X-ray diffractograms (Figure 3a & b) of selected samples, no distinct differences in clay mineral distribution (except for PII) with depth were observed, and pedons from all geomorphic surfaces had similar mineral components. In the clay fraction, three intense peaks with weak and dirty signals were observed. The Mg-saturated clay exhibited three intense peaks at 1.42–1.60 nm, 1.0 nm, and 0.70– 0.74 nm. The reflection at 0.72 nm disappeared at 550°C. Glycolation expanded part of the 1.42–1.60 nm peak, with a shoulder at about 1.7–1.8 nm, and the same peak closed to 1.29-1.20 nm after K saturation at 20 °C, but at 550 °C, an illite-defined diffraction band between 1.0 and 1.1 nm was observed, indicating the presence of smectite, illite, and kaolinite. X-Ray diffraction analysis data showed that smectite was the dominant clay mineral in all the soils and followed by illite, kaolinite and vermiculite for PI, PIII and PIV. However, illite clay mineral was found common in PII. In addition, some primer minerals were also detected such as quarts, zeolite, Ca and K feldspars in some soil horizons in both depths. On the other hand, crystallization and amount of smectite exist much more in Bss horizon than that of surface soils (A horizon) of each profiles.

The pedological mass balance model is one of the best approaches in quantitative geochemistry in order to estimate chemical weathering and pedogenesis. The behaviors of eight elements were evaluated for this research and the values for these elements (Si, Al, Ca, Mg, Na, K, Mn and Fe) are presented in Table 5. Because of their abundance in the soils 93 % of total elemental composition expresses as oxides and their importance in soil formation process[31] these elements were selected in this study. Enrichment factor is a ratio of the chemical concentration of an element in the soil to its concentration in the parent material. The mass transport function is defined as the mass fraction of an element added or subtracted from the system during weathering relative to the mass of the element originally present in the parent material. Strain, mass fractions added to or subtracted from each horizon and loss or gain of elements during pedogenesis is calculated according to Eqn. (1)-(3). Chemical composition and bulk density of the parent material were assumed to be best described by the C horizon of soil profile[32]. Immobile elements are needed in order to calculate gains or losses of elements. Zirconium and titanium have been used as immobile indices because they are generally stable in soil

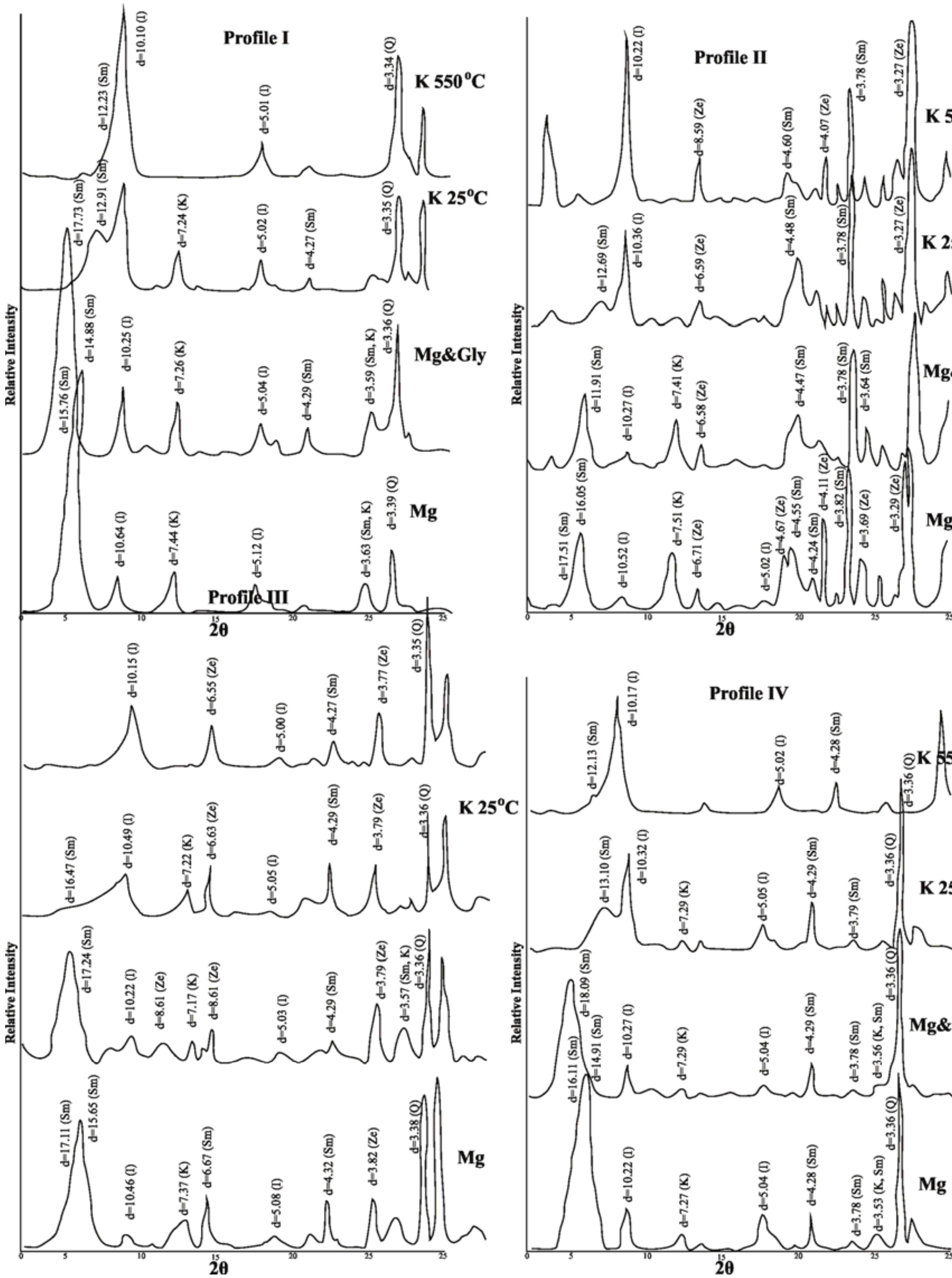

Fig. 3a — X-ray diffractograms of surface horizons for each profiles (Sm: Smectite, I: illite, K: kaolinite, Q: quartz, Ze:, zeolite, Ca and K feldspar)

environment[12,13,33&34]. Titanium was selected as the immobile element for calculating volume changes (strain). The open-system mass transport functions (τ) are listed against depth for each soil and element in Table 5. It was found that generally negative values and thus, losses of elements are observed in PI and PIV although presence of high organic matter content of top soil. On the other hand, PII and PIII have positive values which were high in surface horizons and decrease with depth. In this case, Egli et al.[35] indicated that positive values are mainly due to the presence of organic matter that has a lower bulk

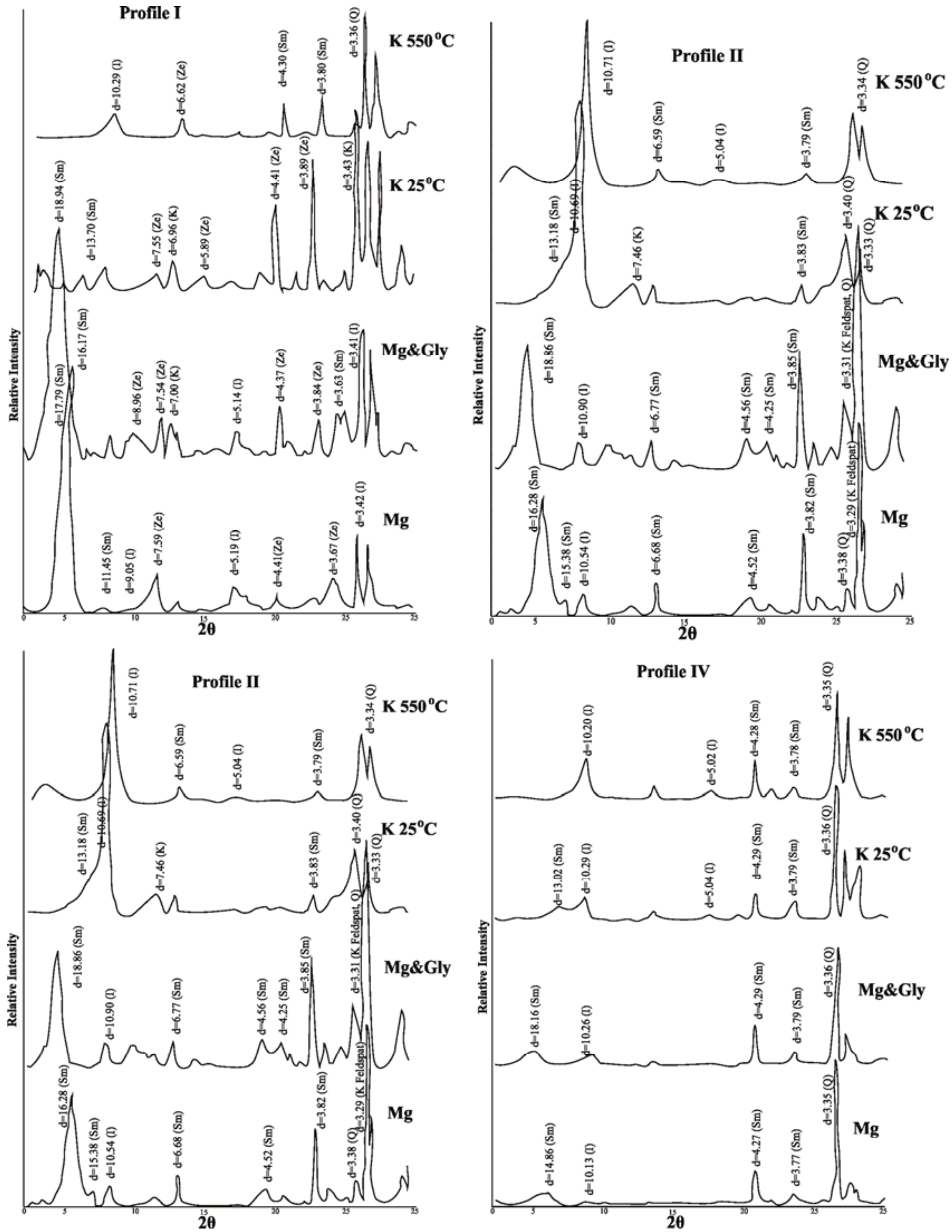

Fig. 3b — X-ray diffractograms of subsurface horizons for each profiles (Sm: Smectite, I: illite, K: kaolinite, Q: quartz, Ze:, zeolite, Ca and K feldspar)

density and lower concentrations of immobile elements than mineral soil material and thus contributes to dilatation. Additionally, the formation of (bio) pores, which is a main soil-forming process also in young soils (profile II-Lithic Ustorthent), contributes to positive strains.

The measured losses along the soil sequence and with respect to PI and PIV were for Si in range of 14.08-423.24, for Al 4.35-119.02, for Ca 0.92-426.35 for Mg 0.80-25.23, for Na 0.34-6.97 for K 0.58-15.58 for Fe 2.26-53.72 and for Mn 0.06-1.04 $kg.m^{-2}$ whereas, the measured gain along the soil sequence

Table 5 — Mass transport function values (τ) and mass losses/gains ($g.cm^{-2}$) for some elements of soil profile

Profiles	Horizon	Si		Al		Ca		Mg		Na		K		Fe		Mn	
		(τ)	M_{jflux}	(τ)	M_{jflux}	(τ)	M_{jflux}	(τ)	M_{jflux}	(τ)	M_{jflux}	(τ)	M_{jflux}	(τ)	M_{jflux}	(τ)	M_{jflux}
PI/Foot slope	*(Typic Haplustert / Haplic Vertisol)*																
	Ap	-0.11	12.36	-0.11	-3.82	-0.11	-0.80	-0.11	-0.70	-0.11	-0.30	-0.11	-0.51	-0.11	-1.98	-0.11	-0.05
	Bss	-0.01	-1.72	-0.01	-0.53	-0.01	-0.11	-0.01	-0.10	-0.01	-0.04	-0.01	-0.07	-0.01	-0.28	-0.01	-0.01
	C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	-	-14.08	-	-4.35	-	-0.92	-	-0.80	-	-0.34	-	-0.58	-	-2.26	-	-0.06
PII / Back slope	*(Lithic Ustorthent / Eutric Regosol)*																
	A	0.07	5.41	0.07	2.12	0.07	0.19	0.07	0.25	0.07	0.12	0.07	0.28	0.07	1.09	0.07	0.02
	Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	-	5.41	-	2.12	-	0.19	-	0.25	-	0.12	-	0.28	-	1.09	-	0.02
PIII/ Low land plateau	*(Typic Haplustert / Haplic Vertisol)*																
	A	0.12	12.64	0.12	4.24	0.12	0.49	0.12	0.65	0.12	0.27	0.12	0.94	0.12	2.64	0.12	0.07
	Bss	0.09	20.22	0.09	6.78	0.09	0.79	0.09	1.03	0.09	0.43	0.09	1.51	0.09	4.23	0.09	0.11
	Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	-	32.85	-	11.01	-	1.28	-	1.68	-	0.70	-	2.45	-	6.87	-	0.19
PIV/High land plateau	*(Typic Calciustert / Calcic Vertisol)*																
	A	-0.22	-21.54	-0.22	-6.06	-0.22	-21.70	-0.22	-1.28	-0.22	-0.36	-0.22	-0.79	-0.22	-2.73	-0.22	-0.05
	Bss1	-0.17	-44.69	-0.17	-12.57	-0.17	-45.02	-0.17	-2.66	-0.17	-0.74	-0.17	-1.65	-0.17	-5.67	-0.17	-0.11
	Bss2	-0.91	-357.00	-0.91	-100.39	-0.91	-359.63	-0.91	-21.28	-0.91	-5.88	-0.91	-13.14	-0.91	-45.31	-0.91	-0.88
	2Ck	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Total	-	-423.24	-	-119.02	-	-426.35	-	-25.23	-	-6.97	-	-15.58	-	-53.72	-	-1.04

and with respect to PII and PIII were for Si in range of 5.41-32.85, for Al 2.12-11.01, for Ca 0.19-1.28 for Mg 0.25-1.68, for Na 0.12-0.70 for K 0.28-2.45 for Fe 1.09-6.87 and for Mn 0.02-0.19 $kg.m^{-2}$.

Greater losses of silica occur at the soil surface due to intense weathering and leaching and losses decrease with depth in profiles (PI; C and PIV; 2Ck horizons). The anomalous value in the profiles gneiss top soil is likely due to dust input resulting from atmospheric deposition (PI; Ap and PIV; A horizon). However, the positive mass flux of the profile II and III may also be due to the inflow of silica rich water from higher area. PI and PIV have negative mass flux of K and the other base cations (Ca, Mg and Na). However, negative mass flux values, namely losses, were determined higher in profile PIV. This indicates a loss of base cations from the soil due to leaching.

Negative values for K and Fe in PI and PIV can be explained with leaching and transformation from biotite to smectite. Welch & Ullman[36] reported that negative values can be found for Ca due to weathering process of Ca- feldspars, labrador and bytownite that include high amount of calcium element. This case was also detected in PI and PIV. In addition, Berg & Banward[37] indicated that in the pH about at 7 weathering condition for anortite ($CaAl_2Si_2O_8$) which is one of the plagioclase minerals and mostly occupies in basaltic rocks, weathering process has more effect on dissolve of Si element when compared with Al. Therefore, this case can also be seen in this study by taking into consideration of pH range (6.94 and 8.25) in selected soils.

The positive strains are also observed in profile II and III which are placed at back slope and low land plateau. Sodium is very small amount in basaltic rock. So very small amount addition of these elements can be reason of gain. The positive values are mainly due to the inflow of Na rich water from higher area. Ca has a significantly different behavior. The net losses of Ca seem in many cases to be major if compared to Na. Mg is only weathered to a substantial amount in the Profile IV. Similar values (Mg losses in the E horizon of podzols from 73% to 86%) are also reported by Olsson & Melkerud[38]. The higher Mg losses at the Profile IV site are most presumably due to minor in homogeneities in the geological substrate and thus the presence of more weatherable Fe–Mg phyllosilicates[38&39] in Profile IV. A strong accumulation of Ca, Mg, Na and K in the all horizons of Profile IV can be recorded, which indicates bioaccumulation, due to nutrient cycling. The Profile IV developed on the most covered area by different

Pinus and Quercus forest and brushwood. Dilation of soils on Profile IV is also attributed to the biocyling of nutrients and organic matter, while soil collapse is due to the weathering and leaching of iron, aluminum and silica. High organic matter content of the Profile IV is confirming this result. Mass transport data indicate that profiles coded as PI and PIV have a negative mass flux of Al. This indicates a loss of Al from the soil due to leaching. Obviously weathering rates of Al are much faster in the top soil than those observed over the whole profile. The differences indicate that Al is quickly removed from the top soil and partially re-precieped in the lover horizons and therefore account for the lower leaching rates there. The same negative mass flux values for Fe and Mn were detected in these profiles.

The calculation of losses was not for all soils equally successful. Some minor changes in the mineralogy (due to a slightly varying geology, buried parent material), such or aeolian additions might have led to some unexplained results. The main differences may be also explained by differences vegetation or climatic conditions resulted from of altitude, facing sites, topography, elevational gradient, slopes, temperature difference and the consequently different element leaching.

Conclusions

In this research, features of pedogenic evolution of four soil profiles formed on topographically different position were detected by taking into consideration of mass balance, geochemical and mineralogical data of Vertisols (Typic Haplustert, Typic Calciustert) and Entisols (Lithic Ustorthent) with basaltic parent material in order to understand the relationship between particular soils and the landscapes and ecosystems in which they function. The results of the study showed a strong relationship between topography and some soil's morphological, mineralogical, physical and chemical characteristics. Soil depth, texture, structure and bulk density were found to improve downward with toposequence. Gravelly concretions were more in the back slope position whereas, low slope degrees positions include more clay content. Mass balance calculations indicate that extensive mineral weathering resulted in significant leaching losses of Si, major base cations, and Al (particularly from upper horizons). The dominant processes identified with mass-balance analysis include desilication and loss of bases. Generally, negative values, and thus, losses of elements become more frequent with increasing age of the soil. The open-system mass transport function $\tau_{j,w}$ suggests substantial losses in young soils. The older the soils the higher are these losses such as PIV. Gains and losses of the major soil forming elements (Si, Al, Fe) were also quantified relative to mineral transformations. Iron and aluminum are being redistributed from the sand and silt-size fractions to secondary clay and sesquioxide fractions. Whereas PI and PIV have a negative mass flux PII and PIII have positive strains. This study results imply that the rate of elemental mass-balance changes is determined by factors influencing its leaching (vegetation types, altitude, facing sites, topography, elevational gradient, slopes, and temperature). The results show that the site conditions of soil development have a much greater influence on elemental leaching and weathering than parent material in the soils studied.

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