Carpathian Journal of Earth and Environmental Sciences, February 2013, Vol. 8. No. 1, p. 5 - 18

MASS BALANCE OF SOIL EVOLUTION ON MT. ERENLER VOLCANIC MATERIALS IN CENTRAL ANATOLIA - A CASE STUDY

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Abstract: Mass-balance analysis was used to quantify elemental losses, gains and transformations for Soil developed on Mt Erenler andesitic rocks. Net losses of the main elements (Ca, Mg, K, Na, Fe, Al, and Si) by means of mass-balance calculations of the soils were examined with, selective dissolution analyses, X-ray diffraction and some chemical properties. These soils are characterized as medium- and fine-textured with low organic matter content. Bulk density was greater than 0.90 g cm^{-3} in all profiles. Selective extraction yielded the following relationship in all extractions: $Fe_d > Fe_o > Fe_p$. Additionally, in most horizons: $Al_p > Al_o > Al_{d.}$ According to selective dissolution analysis results and index values, noncrystalline minerals such as allophane, imogolite, and iron-humus complexes have not formed in these soils. Feldspar, cristobalite, and quartz were the most common primary minerals. Hematite, cummingtonite, and magnetite were also found in some profiles. X-ray diffraction indicated that kaolinite and illite were dominant minerals in the clay fraction; furthermore, a considerable amount of smectite was found in the clay fraction. Bulk density ratios of soils and bedrock as well as elemental concentrations referenced to Zr, were used to estimate strain and open-system mass-transport functions through the soil profiles. Estimated strains of the three soils indicated substantial volumetric changes during C horizon and saprolite formation. Dominant soil-forming processes include 1. desilication and loss of base cations and Al from the solum, 2. transformation of iron and aluminum from sand and silt-size fractions to secondary clay and crystalline Fe minerals. Silica represents the largest mass loss of any element from the system and varies from 27.14 to 107.38 kg m^{-2} Base cations represent only a small portion of the soil mass, but up to 34.3 % (5.44 kg m^{-2}. of the sodium present in the parent material is lost due to weathering and leaching. Our results imply that the rate of elemental mass-balance changes is determined by factors influencing its leaching (altitude, facing sites, topography, elevational gradient, slopes, and temperature) in the studied area.

Keywords: Mass balance; Chemical Weathering; Elemental losses; Soil forming.

1. INTRODUCTION

The factors controlling soil formation are essentially climate, bedrock, biology, topography and time. The reactions occurring during weathering of soil minerals are either physical microdivision or chemical dissolution, transformation, precipitation and ion exchange. It is thus important to understand how a soil is formed from bedrock and to examine how chemical or physical weathering influences the geochemical evolution of soils. Soil sequences can be classified based on a single variable if other conditions affecting soil development are subordinate or relatively constant. Commonly, the following sequences are differentiated: lithosequences (differences in parent mineralogy), climosequences (differences inprecipitation and or temperature), toposequences (lateral variations in slope and topography), chronosequences (effect of time on chemical weathering), and biosequences (variation in biota and its influence on chemical weathering). Soil sequences may give insight into the influence of a state factor on the weathering rates.

Chemical weathering of soils and rocks during pedogenesis is significant because it provides many essential elements for life and because it is coupled with the rise and fall of atmospheric CO_2. Soils show a wide range of variation in terms of time passing in their formation. During early pedogenesis, the chemical composition of a soil will be highly controlled by the composition of the geological parent material, whereas the chemical composition of mature soils strongly reflects the effects of the weathering environment.

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 time (Brimhall & Dietrich, 1987.) Mass-balance analysis of soils requires comparisons of bulk density, volume and chemical compositions between soil horizons and the parent material (Brimhall et al., 1991b). Based on these properties, a set of mass-balance equations is developed that determines soil deformation (strain) and open chemical system gins 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 (Brimhall et al., 1988, 1991a,b; Chadwick et al., 1990).

Rates of chemical losses typically are quantified by measuring solute concentrations and fluxes (Drever & Zobrist, 1992; Stonestrom, et al., 1998), or by determining the relative enrichment of a conservative constituent of the soil (April et al., 1986; Brimhall & Dietrich, 1987). Such a mass-balance approach requires well-defined timescales of landscape lowering, which are combined with the measured mass loss to calculate a rate of chemical weathering. Due to the need for a system with a well-defined timescale, mass balance approaches generally have been applied to non-eroding landforms whose age can be constrained, such as marine and fluvial terraces, as well as glacial moraines.

The purpose of this paper is to estimate volume change and elemental loss by quantify mass transfers during soil evolution in four soils derived from contrasting bedrock: senozoic mafic igneous material (andesite) near the Konya province, from central Anatolia. The specific objective of this paper is: to determine the net gains enrichments and losses depletions of the major soil forming elements Si, Al, Fe, Na, Ca, Mg and K that accompany weathering of volcanic materials.

2. MATERIALS AND METHODS

2.1. Theoretical background

Time-averaged leaching rates can be calculated if the age of the parent material and the initial volume of the weathered material are known. Long-term weathering rates are determined by comparing the chemistry and mineralogy of soil profiles of known age and the fresh source rock composition (April et al., 1986). Such calculations are based on enrichment/depletion factors determined using immobile element contents. Usually, weathering rates of such soils are derived by means of concentration profiles of immobile elements such as Ti or Zr. This method has been applied to several investigation areas on silicate host material (e.g., Langley-Turnbaugh & Bockheim, 1998; Nieuwenhuyse & van Breemen, 1997; White, 1995). This procedure has recently been revised by Egli & Fitze (2000).

Two important assumptions concerning elemental components are required in the mass balance calculations using immobile elements (White, 1995). The first involves the determination of the composition of the parent material. For soils developed in sites on bedrock, the potential errors are confined to local heterogeneities in bedrock composition. The estimate of the initial composition becomes more difficult when soils are developed on sedimentary parent materials such as alluvial terraces or loess deposits. For such deposits, the least weathered horizon in the soil profile is assumed to be the parent material. The second requirement is that weatherable elements must be rationed against an inert component *i*, present in both the parent material and the soil. Ti and Zr are considered to be almost immobile. Some investigations point out, however, that under certain circumstances these metals may also be slightly weathered (Nieuwenhuyse & van Breemen, 1997; Cornu et al., 1999). The derivation of mass-balance equations and their applications to pedologic processes are discussed in detail by Brimhall & Dietrich (1987), Brimhall et al., (1991a), Chadwick et al., (1990), Merritts et al., (1992) and Egli & Fitze (2000).

Mass-balance calculations and especially the calculation of time-averaged weathering rates of soil profiles or soil horizons are usually made by the following equations. Volumetric changes that occur during pedogenesis are determined by adopting the classical definition of strain, (Brimhall & Dietrich, 1987)

$$\varepsilon_{i,w} = \frac{\Delta z_w}{\Delta z} - 1 \tag{1}$$

with Δz as the columnar height (m) of a representative elementary volume of protore ‘p’ and Δz_w is the weathered equivalent height (m) ‘w’. The calculation of the open-system mass transport function t is defined by (Chadwick et al., 1990)

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

with *Cj.p* as the concentration of element *j* in protolith (kg/t), *Cj.w* as the concentration of element *j* in the weathered product (kg/t), and with ρ_p and ρ_w being the bulk density (t/m^3) of the prolithe and weathered soil, respectively. With *n* soil layers the calculation of changes in mass of element *j* is given by (Egli & Fitze, 2000).

$$m_{j,\text{flux}(z_w)} = \sum_{a=1}^{n} C_{j,p}\,\rho_p \left(\frac{1}{\varepsilon_{i,w}+1}\right)\tau_{j,w}\,\Delta z_w \qquad (3)$$

Zirconium was selected as the immobile element for calculating volume changes (strain). Zirconium and titanium have been used as immobile indices because they are generally stable in soil environments (Marshall & Haseman, 1942; Brimhall & Dietrich, 1987; Harden, 1988; Chadwick et al., 1990; Brimhall et al., 1991a,b; Merritts et al., 1992). Although the above equations provide a tool for estimating elemental loss or gain of a profile, the mass balance equations have several critical assumptions. First, the elemental contents in both rocks and soils should be relatively homogeneous or variation should be quantifiable. Replications help increase precision of mean and variance estimates. Second, since the calculations are highly dependent on immobile elemental concentrations, the reference element should be resistant to chemical dissolution.

2.2. Site description

The study was performed on Mount Erenler in central Anatolia, about 55 km west of the city of Konya, between 37°54'56"N and 37°33'22"N and between 32°11'06"E and 31°51'16"E. The study area is situated north of the middle Toros Mountains zone. Long-term records show that the mean annual precipitation is 379.38 mm and the total evaporation is 1226.4 mm. According to the Konya meteorological station, the mean annual temperature is 11.5°C and the mean annual soil temperature at 50 cm is 12.5°C (D.M.I., 1994). The research area has a semiarid Mediterranean climate with low humidity, according to the De Martonne-Bottman rainless index formula (Akman, 1990). Soil moisture and temperature regimes are xeric and mesic, respectively, according to the climate data (Soil Survey Staff, 1999). The study area comprises different stratigraphic and structural formations. The oldest formation in the area is the Kızıloren formation, which consists of dolomites and dolomitic limestone from the late Triassic early Jurassic. All of these units were overlaid unconformably by late Miocene-early Pliocene Erenler volcanic materials. The volcano was mapped as Kızıloren ignimbrite, tuff, andesite, trachyandesite, and Erenkaya ignimbrite, with andesite being the most common formation in the area. The volcanic materials in the study area were derived from continental crust and products of old subduction related volcanism (Kurt et al., 2005).

2.3. Sampling and analysis

For the study, 4 representative soil profiles were chosen, and disturbed and undisturbed soil samples were taken from the horizons after their macro morphological identification was completed. Soil samples were dried, gently crushed with a wooden roller, and sieved to 2 mm. Visible roots, stubble, and coarse fragments were removed and stored in plastic bags for use.

Soil pH was measured potentiometrically, both in a 1:2.5 soil water (w/v) suspension and 0.01 N KCl with a glass electrode. Organic matter in the soils was determined using the Walkley and Black wet digestion method (Van Lagen, 1993). Particle size distribution was determined by the hydrometer method after removal of organic matter using H_2O_2 and stirring in a sodium hexametaphosphate solution (Bouyoucos, 1951). Bulk density (BD) was determined by weighing soil cores after drying for 24 h at 105°C (Blake & Hartge, 1986). The amount of carbonate in the soil was measured with a Scheibler calcimeter (USDA, 2004). Selective dissolution of Fe, Al, and Si was conducted by the ammonium oxalate, dithionite-citrate bicarbonate (DCB), and sodium pyrophosphate extraction methods and their amounts were measured by ASS (USDA, 2004). Cations were designated by subscripts o, d, and p for the respective methods. Element pools in the soil (Ca, Mg, K, Na, Fe, Al, Si, and Zr) were determined by fusion with lithium metaborate ($LiBO_2$) and dilution in a HNO_3- HF procedure (Chao and Sanzolone 1992), and the contents were measured by inductively coupled argon plasma (ICP). All procedures were replicated 3 times for each soil sample, and means were reported. XRD analysis was also performed on powdered samples as randomly oriented powder mounts with a Shimadzu XRD-6000 with a Cu anticathode and K filter (40 kV, 35 mA). Diffractometric analysis of the pulverized saprolite and rock samples was carried out in the 2-40° 2θ range (Jackson, 1979). The clay fraction (<2 μm) was obtained from the soil after destruction of organic matter with dilute and Na-acetate-buffered H_2O_2 (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 15° 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. IR - spectra were recorded over the range of 4000 to 400 cm^{-1} of pellets made with 1 mg of samples and 250 mg of KBr previously heated to 150°C (White & Roth 1986).

3. RESULTS

3.1. Physical and chemical properties

The studied soils were situated on a steep slope and composed of andesitic materials. Horizon differentiation was poor. The solum depth ranged from 20 to 102 cm. The studied profiles were well drained. From the profile description, it is apparent that distinct soil horizons are lacking, with the exception of a weakly defined A (in profiles 1 and 2) and cambic B (in profiles 3 and 4). In general, the upper mineral horizons were characterized by high organic matter content (1.41%-5.95%). According the results the soils studied developed on volcanic material, but cannot be classified according to Soil taxonomy as Andisol because of the profiles don't fully meet all the requirements. As a result, the soils developed at Mt. Erenler cannot be classified as Andisols. According to soil taxonomy, profiles 1 and 2 are classified as Entisols because they have no diagnostic surface or subsoil horizons except for ochrik epipedon, therefore they are classified as Orthent because they have no other suborder properties of Entisols. Kurt et al., (2002) report that parent material contains <3% volcanic glass, this value does not satisfy the requirements of vitric or andic subgroups for other orders. Therefore profiles1 and 2 are Xerorthents in the great group of Entisols because of a xeric moisture regime, and the soils are in the subgroup of Lithic Xerorthents because they have lithic contact within 50 cm. Profiles 3 and 4 are classified as Inceptisols because they have a mollic and cambic horizon within 10 cm of the mineral soil surface; they are classified as Humic Haploxerept because they have a xeric moisture regime and mollic epipedon and have no properties of the Xerept suborder.

Some chemical and physical properties of the 4 profiles are shown in Tables 1. All soils followed the general trend of having the highest organic matter content on the surface. Organic matter content ranged from 0.0% to 5.95% and declined rapidly with depth. BD values of the soils ranged from 1.23 to 2.11 g cm–3, with surface horizons generally having lower BD values than subsurface soils. The lower BD values of the surface soils were attributed to the relatively higher organic matter content of the surface soils. The $CaCO_3$ content was close to detection limits and ranged from to 0% to 0.6%. The texture of the soils was sandy clay loam and clayey (profile 3). Sand content ranged from 20.9% to 70.9%, silt content from 5.7% to 31.7%, and clay from 20.6% to 55.4%. With the exception of profile 3, all profiles had high sand content, but clay concentrations generally increased with depth. Soil pH (H_2O) values ranged from 4.17 to 6.70, with no regular distribution. Soil pH (KCl) values were consistently less than pH (H_2O) values.

The results of selective dissolution analysis are given in Table 2. Si_o content was less than 0.2% in all horizons, ranging from 0.0379% to 0.1737%. Si_o values increased with depth in profile 1, but no trend was observed in the other profiles. Al_o and Fe_o values ranged from 0.0891% to 0.4776% and from 0.050% to 0.636%, respectively. The highest Al_o and Fe_o values were observed in the deeper horizons of profile 3. Fe_p and Al_p values ranged from 0.0010% to 0.104% and from 0.08154% to 1.4664%, respectively. DCB affected crystallized materials more than the other extracts. In the studied profiles, Fed ranged from 0.420% to 1.973%, and Al_d ranged from 0.0757% to 0.2387%. Fe_d decreased with depth, whereas Al_d showed no trend with depth.

3.2. Total contents

The composition of the investigated material clearly reflects its andesitic character. Concentrations of the measured elemental oxides are shown in table 3. All soils contained much SiO_2, Al_2O_3, and Fe_2O_3. The SiO_2 concentration rose to 68.09%. Al_2O_3 values ranged from 15.02% to 27.84% and tended to increase with depth. The highest Fe_2O_3 value was observed in profile 3 as 9.92%. CaO values were higher in the surface than the subsoil. MgO values ranged from 0.52% to 0.98% and showed no important differences among the horizons. The small amount of MgO was due to the lack of biotite. Al concentration correlated with clay distribution in the soils ($r = 0.724$, $P < 0.01$). 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 0.65% to 3.03% and from 0.18% to 3.28%, respectively. K_2O and Na_2O values correlated with the presence of feldspar, the most common mineral in andesitic rock.

Table 1. Some physical and chemical properties of studied profiles

Pedon	Horizon	Depth (cm)	pH$_{(H2O)}$ (1/2,5)	pH$_{(KCL}$ (1/2,5)	Sand (%)	Clay (%)	Silt (%)	Bulk Density (g cm^{-3})	Organic matter (%)	CaCO$_3$ (%)
I	A1	0-12	6.44	5.81	60.8	22.6	16.6	1.49	2.87	0.3
	A2	12-32	6.34	5.75	68.8	20.6	10.6	1.44	2.31	0.6
	Cr1	21-47	6.21	5.54	65.0	25.4	9.6	2.01	0.77	-
	Cr2	+47	6.70	5.49	70.9	23.4	5.7	1.86	-	-
II	Ah	0-3	6.15	5.94	48.8	24.6	26.6	1.37	4.97	0.5
	A	3-15	6.13	5.48	48.8	32.6	18.6	1.37	1.93	0.2
	AC	15-20	5.99	5.42	44.8	36.6	18.6	1.28	1.43	0.3
	Cr	+20	6.18	5.38	52.9	27.4	19.7	1.80	0.0	0.0
III	Ah	0-10	6.13	5.97	35.4	42.9	21.7	1.36	5.95	0.3
	A	10-29	6.08	5.71	33.4	48.6	18.0	1.40	3.06	0.2
	Bw1	29-57	5.90	5.06	28.4	50.6	21.0	1.43	0.44	0.2
	Bw2	57-79	5.70	4.80	34.8	42.6	22.6	1.23	0.24	0.2
	Cr1	79-116	5.08	4.24	20.9	55.4	23.7	1.47	0.26	0.0
	Cr2	116-179	4.17	3.17	40.9	27.4	31.7	1.31	0.0	0.0
	Cr3	+179	4.65	2.86	24.9	51.5	23.6	1.53	0.0	0.0
IV	A1	0-16	6.19	5.96	65.1	21.6	13.3	1.53	1.41	0.3
	A2	16-40	6.28	5.65	59.4	23.6	17.0	1.59	0.81	0.1
	Bw1	40-70	6.17	5.84	68.4	23.6	8.0	1.50	0.01	0.2
	Bw2	70-102	6.23	5.54	69.4	22.6	8.0	1.55	0.0	0.0
	Cr1	102-130	6.35	5.51	60.6	29.4	10.0	1.82	0.0	0.0
	Cr2	+130	6.07	5.49	68.7	23.5	7.8	2.11	0.0	0.0

Table 2. Selective dissolution analyses of <2 mm of soils of studied soils (%).

Pedon	Horizon	Fe$_d$	Fe$_o$	Fe$_p$	Al$_d$	Al$_o$	Al$_p$	Si$_o$
I	A1	1.227	0.167	0.039	0.149	0.089	0.838	0.050
	A2	1.074	0.089	0.061	0.103	0.137	0.875	0.052
	Cr1	1.198	0.077	0.031	0.155	0.174	0.839	0.051
	Cr2	1.213	0.050	0.032	0.150	0.127	0.931	0.061
II	Ah	1.406	0.165	0.040	0.164	0.204	1.221	0.102
	A	1.664	0.214	0.039	0.206	0.251	1.036	0.066
	AC	1.140	0.157	0.032	0.157	0.263	1.466	0.077
	Cr	1.422	0.084	0.020	0.158	0.161	1.159	0.096
III	Ah	1.689	0.449	0.089	0.171	0.254	0.859	0.098
	A	1.973	0.599	0.105	0.239	0.353	0.900	0.114
	Bw1	1.964	0.636	0.063	0.224	0.478	0.939	0.174
	Bw2	1.739	0.530	0.071	0.168	0.468	1.026	0.089
	Crt1	1.378	0.194	0.001	0.154	0.354	0.821	0.064
	Crt2	1.352	0.123	0.059	0.115	0.264	0.923	0.064
	Crt3	1.399	0.191	0.003	0.195	0.251	0.815	0.065
IV	A1	1.053	0.091	0.038	0.076	0.168	0.842	0.046
	A2	1.275	0.127	0.041	0.119	0.126	1.018	0.056
	Bw1	1.162	0.128	0.051	0.102	0.118	0.900	0.058
	Bw2	0.983	0.178	0.021	0.137	0.156	0.890	0.038
	Cr1	0.420	0.101	0.036	0.089	0.124	0.912	0.046
	Cr2	0.661	0.051	0.030	0.121	0.111	1.026	0.050

3.3. Mineralogical properties

X-ray diffractograms of selected samples are shown in figures 1 and 2. No distinct differences in clay mineral distribution with depth were observed, and pedons from all geomorphic surfaces had similar mineral components. In the clay fraction, 3 intense peaks with weak and masked signals were observed. The Mg-saturated clay exhibited 3 intense peaks at 1.4-1.5 nm, 1.0 nm, and 0.72-0.73 nm. The reflection at 0.72 nm disappeared at 550°C. Glycolation expanded part of the peak, with a shoulder at about 1.6-1.7 nm, and the same peak closed to 1.2-1.4 nm after K saturation at 20°C. At 550°C, however, an ill-defined diffraction band between 1.0 and 1.1 nm was observed, indicating the presence of smectite with illite and kaolinite. X-ray diffraction (XRD) patterns of powdered samples indicated the presence of cristobalite, feldspars, and quartz. The feldspars were mostly plagioclases. In addition, soils contained minor amounts of hematite, cummingtonite, and magnetite.

IR spectra were taken from some horizons to identify the mineralogical composition of the studied soils. The IR spectra of the clay samples are given in Figure 3. The IR spectra of the soil showed 6 principal peaks at 779-791, 1032-1034, 1614-1638, 2360-2363, 3623-3627, and 3699-3702 cm^{-1}. In the IR spectra, OH peaks of H were observed as a structurally large band at 3100-3500 cm^{-1}. The bent vibration peaks belonging to H were found at 1636 cm^{-1}, and a Si-C single vibration band was present at 790 cm^{-1}.

3.4. Mass balance calculations: collapse, dilatation

The behavior of seven elements was evaluated for this study, and the data for these elements (Si, Al, Fe, Ca, Mg, K and Na) are presented here. These elements were selected because of their abundance in the soils 93% of total elemental composition expresses as oxides (Langley-Turnbaugh & Bockheim, 1998) and their significance in soil formation. 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 are calculated according to Eqs. (1)–(3). Chemical composition and bulk density of the parent material were assumed to be best described by the Cr horizon of soil profile. Zirconium was selected as the immobile element for calculating volume changes (strain). Zirconium and titanium have been used as immobile indices because they are generally stable in soil environments (Marshall & Haseman, 1942; Brimhall & Dietrich, 1987; Harden, 1988; Chadwick et al., 1990; Brimhall et al., 1991a,b; Merritts et al.,1992.) The open-system mass transport functions (τ) are listed against depth for each soil and element in table 4.

Generally, negative values, and thus, losses of elements are observed in the profiles except Profile 3 for Ca, Mg, Na and K. In generally negative strain was found top soil although presence of high organic matter content of top soil. Positive values are mainly due to the presence of organic matter and the formation of (bio)pores (Egli et al., 2001).

The measured losses along the soil sequence and with respect to the whole soil profile were for Si in range of 27.14-107.38 $kg.m^{-2}$ for Al 11.90-99.75, for

Table 3. Geochemical characteristics (total analysis of the bulk material including soil skeleton and fine earth) of the investigated soils

Pedon	Horizon	Depth	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	ZrO_2 (ppm)
I	A1	0-12	68.09	15.02	3.48	0.57	2.23	2.64	3.63	173
	A2	12-32	65.58	15.49	4.76	0.83	1.81	2.12	3.33	224
	Cr1	21-47	65.62	16.67	4.43	0.85	2.39	2.50	3.10	172
	Cr2	+47	66.92	15.80	4.26	0.85	2.40	2.68	3.34	170
II	Ah	0-3	55.95	18.62	7.19	0.89	2.19	2.00	2.63	231
	A	3-15	57.02	19.51	7.73	0.89	2.12	2.03	2.61	258
	AC	15-20	56.21	21.10	7.34	0.86	1.64	1.63	2.37	230
	Cr	+20	57.11	21.34	6.65	0.75	1.64	1.72	2.56	198
III	Ah	0-10	54.28	17.70	9.79	0.86	1.03	0.87	1.99	377
	A	10-29	54.88	19.63	9.92	0.98	0.98	0.95	2.09	333
	Bw1	29-57	53.86	21.94	9.06	0.97	0.78	0.79	1.87	280
	Bw2	57-79	52.47	23.65	9.27	0.86	0.52	0.52	1.32	279
	Cr1	79-116	50.49	27.84	7.61	0.63	0.18	0.18	0.65	247
	Cr2	116-179	52.07	26.11	8.19	0.54	0.11	0.29	0.81	254
	Cr3	+179	54.12	24.00	8.34	0.56	0.13	0.47	1.42	244
IV	A1	0-16	67.18	15.40	3.44	0.52	2.61	2.68	3.22	200
	A2	16-40	67.03	15.82	4.10	0.60	2.37	2.52	3.25	199
	Bw1	40-70	67.74	15.84	3.89	0.56	2.34	2.57	3.27	163
	Bw2	70-102	67.27	16.13	4.21	0.60	2.29	2.58	3.22	169
	Cr1	102-130	65.73	16.97	4.34	0.73	2.36	2.60	3.02	158
	Cr2	+130	66.45	16.85	3.54	0.63	3.31	3.28	2.86	146

Table 4. Mass transport functions (τ) for each element investigated with respect to the sites and soil depth

Site /horizons	Si	Al	Ca	Mg	Na	K	Fe
P1							
A1	0,038	-0,099	-0,067	-0,329	0,056	0,171	-0,214
A2	-0,225	-0,280	-0,413	-0,243	-0,343	-0,168	-0,167
Cr1	0	0	0	0	0	0	0
P2							
Ah	-0,160	-0,252	0,145	0,017	-0,003	-0,119	-0,073
A	-0,219	-0,284	0,045	-0,071	-0,076	-0,202	-0,090
AC	-0,136	-0,132	-0,122	0,007	-0,168	-0,187	-0,031
Cr	0	0	0	0	0	0	0
P3							
Ah	-0,304	-0,589	2,703	-0,117	2,127	0,981	-0,168
A	-0,203	-0,483	2,993	0,141	2,870	1,358	-0,044
Bw1	-0,061	-0,306	2,813	0,355	2,862	1,532	0,048
Bw2	-0,085	-0,252	1,542	0,201	1,542	0,787	0,072
Cr1	0	0	0	0	0	0	0
P4							
A1	-0,205	-0,294	-0,140	-0,446	-0,198	-0,171	-0,384
A2	-0,207	-0,275	-0,219	-0,361	-0,246	-0,163	-0,265
Bw1	-0,005	-0,099	-0,043	-0,259	-0,046	0,045	-0,135
Bw2	-0,045	-0,113	-0,094	-0,233	-0,074	-0,005	-0,095
Cr1	0	0	0	0	0	0	0

Ca 2,84-4,51, for Mg 0,08-3,49, for Na 0.36-5.44for K 0.68-4.07for Fe 0.46-13.46 kg.m^2. However for some elements such as Ca Na Mg and K slightly gain was found in profile 3.

4. DISCUSSION

4.1. Physical and chemical properties

Nanzyo et al., (1993) explained that fresh ashes have a bulk density greater than 1.5 g cm^{-3}, and this value decreases with weathering and the development of soil porous structure thanks to the presence of noncrystalline materials and organic matter. All of the horizons of the studied profiles showed a bulk density greater than 0.9 g cm^{-3}, which is characteristic of Andisols. Bulk density is generally high because of high sand content, low weathering rates, and lack of smaller particle densities like allophane and imogolite, factors considered responsible for lower bulk density (Wada, 1989). The high (>2) values of bulk density were determined in the Cr horizons in profiles 1 and 4. Despite being the parent material, this horizon is relatively soft when wet. For this reason, it is designated as Cr with a higher bulk density. Organic matter concentrations were higher in the surface horizons and decreased with depth in all profiles. Organic matter content was relatively high compared with the arid regions of Turkey, but compared with other Andisols in the world, the organic matter content was very low. Low precipitation and a long dry season limited the organic matter level. The reasons for lower organic matter content include the lower clay content of the horizons and the lack of metal-humus complexes, indicating a lower content of Al_p and Fe_p. Most soils were weakly acidic, but some were moderately to strongly acidic (profile 3). The higher $pH_{(H2O)}$ values might be related to lower Al activity and lower organic matter content. The pH values (in most cases above 6.0) were relatively high considering the nature of the parent material and the absence of carbonates. Soil texture is generally described as sand, except in profile 3. Under climatic conditions of low precipitation and long dry seasons, the weathering process is not easily facilitated. Elevated concentrations of clay, especially in the B horizons, are the result of the transformation of primary minerals to clay minerals (Beckmann et al., 1974).

The high rate of change in clay content in the deeper soil may be due partly to the fact that clays can be formed from percolating solutions. Increased clay content in the cambic and C horizons of profile 3 showed that clays that are neoformation minerals could be inherited from the parent material. These clay minerals are formed by the alteration of feldspars to clay minerals. The XRD results confirmed the presence of clays in these horizons. The obtained kaolinite peaks in the power X-ray diffractograms verify the inheritance of this mineral from the parent material. Al, Fe, and Si values determined by selective dissolution analysis and index values of selective

Table 5. Index values of selective dissolution analysis of the studied soils.

Pedon	Horizon	Fe_o/Fe_d	Fe_d/Fe_t	Fe_p / Fe_o	Fe_p / Fe_d	$(Al_o-Al_p)/Si_o$	Al_p/Al_o
I	A1	0.136	0.503	0.23	0.03	-15.0	9.4
	A2	0.083	0.321	0.69	0.06	-14.2	6.4
	Cr1	0.064	0.386	0.40	0.03	-13.1	4.8
	Cr2	0.041	0.406	0.64	0.03	-13.2	7.3
II	Ah	0.117	0.280	0.24	0.03	-10.0	6.0
	A	0.129	0.307	0.18	0.02	-11.8	4.1
	AC	0.138	0.221	0.20	0.03	-15.6	5.6
	Cr	0.059	0.305	0.24	0.01	-10.4	7.2
III	Ah	0.266	0.246	0.20	0.05	-6.2	3.4
	A	0.304	0.283	0.17	0.05	-4.8	2.5
	Bw1	0.324	0.309	0.10	0.03	-2.7	2.0
	Bw2	0.305	0.268	0.13	0.04	-6.2	2.2
	Cr1	0.141	0.258	0.01	0.00	-7.3	2.3
	Cr2	0.091	0.236	0.48	0.04	-10.3	3.5
	Cr3	0.137	0.239	0.01	0.00	-8.7	3.2
IV	A1	0.086	0.436	0.41	0.04	-14.7	5.0
	A2	0.100	0.444	0.32	0.03	-16.0	8.1
	Bw1	0.110	0.424	0.40	0.04	-13.4	7.6
	Bw2	0.181	0.333	0.12	0.02	-19.3	5.7
	Cr1	0.240	0.136	0.36	0.09	-17.1	7.3
	Cr2	0.077	0.266	0.58	0.04	-18.5	9.3

dissolution analysis provide very important knowledge of the mineralogical composition of volcanic soils. According to Wada (1989), acid oxalate extracts the following: 1) aluminum (Al_o) from allophane, imogolite, allophane-like minerals, and Al-humus complexes; 2) iron (Fe_o) from ferrihydrite and Fe-humus complexes; and 3) silica (Si_o) from allophane and imogolite. Meanwhile, sodium dithionite citrate (DCB) extracts: 1) aluminum (Al_d) from allophane, Al-humus complexes, and noncrystalline oxides; and 2) iron (Fe_d) from ferrihydrite, crystalline oxides, and Fe-humus complexes. $Na_4S_2O_7$ extracts aluminum (Al_p) and iron (Fe_p) from organic complexes.

Some index values from selective dissolution analysis are given in table 5. The rather low Si_o, Al_o, and Fe_o values highlighted trace amounts or an absence of noncrystalline materials in the studied soils. The very small amount of Fe_o also indicates that Fe oxides are mainly crystallized. Pyrophosphate-extractable Al (Al_p) and Fe (Fe_d) provide the data for organometallic complex forms of Fe and Al. Al_p and Fe_p are very high in Andisols, but in the studied soils, these values were very low compared with those of other Andisols because of the very low organic matter content of the studied soils. Concentrations of Fe_o were consistently higher than concentrations of Fe_p. A low Fe_p-to-Fe_o ratio (<0.9 in all horizons) indicates that Fe-humus complexes are limited. A ratio of <0.42 in profile 3 suggests that the non- or poorly crystalline form of Fe is mainly ferrihydrite. Fe_d values were higher than the other fractions in the studied soils. Al_o was higher than Al_d in general, but in profiles 1 and 4, Al_d was higher than Al_o in some horizons. Fe_p/Fe_d values were quite small, as were Fe_o/Fe_d values, probably because crystalline Fe oxides were more abundant than ferrihydrite, and Al was present as Al-humus complexes. The rate of Al_p/Al_o was used to measure a characteristic of Andisols whereby an Al_p-to-Al_o ratio lower than 0.1 confirms the absolute presence of allophane. Al_p/Al_o values were higher than 0.1 in all profiles, indicating a lack of allophane and the existence of Al-humus complexes, as explained previously (Prado et al., 2007). The ratio of (Al_o – Al_p) to Si_o can be used to estimate allophane and imogolite formation in Andisols. This rate ranges from 1 to 2.5 in most Andisols; it is close to 1 in allophane-rich Andisols and close to 2 in imogolite-rich Andisols. The ratio of (Al_o – Al_p) to Si_o was outside the limits demonstrating the lack of allophane and imogolite in the studied soils and was negative in all profiles. Allophane formation was obstructed by inadequate desilication. Mass transport data of Si and Al confirm this finding.

The extremely small amounts of Al_o and Si_o compared with Fe_d suggest that crystalline aluminosilicates with high charge density could be occurring through neoformation, consuming both the Al and Fe released from the weathered parent material. Consequently, all selective dissolution analysis results and index values of selective dissolution analysis indicate that noncrystalline minerals such as allophane and imogolite have not formed in these soils.

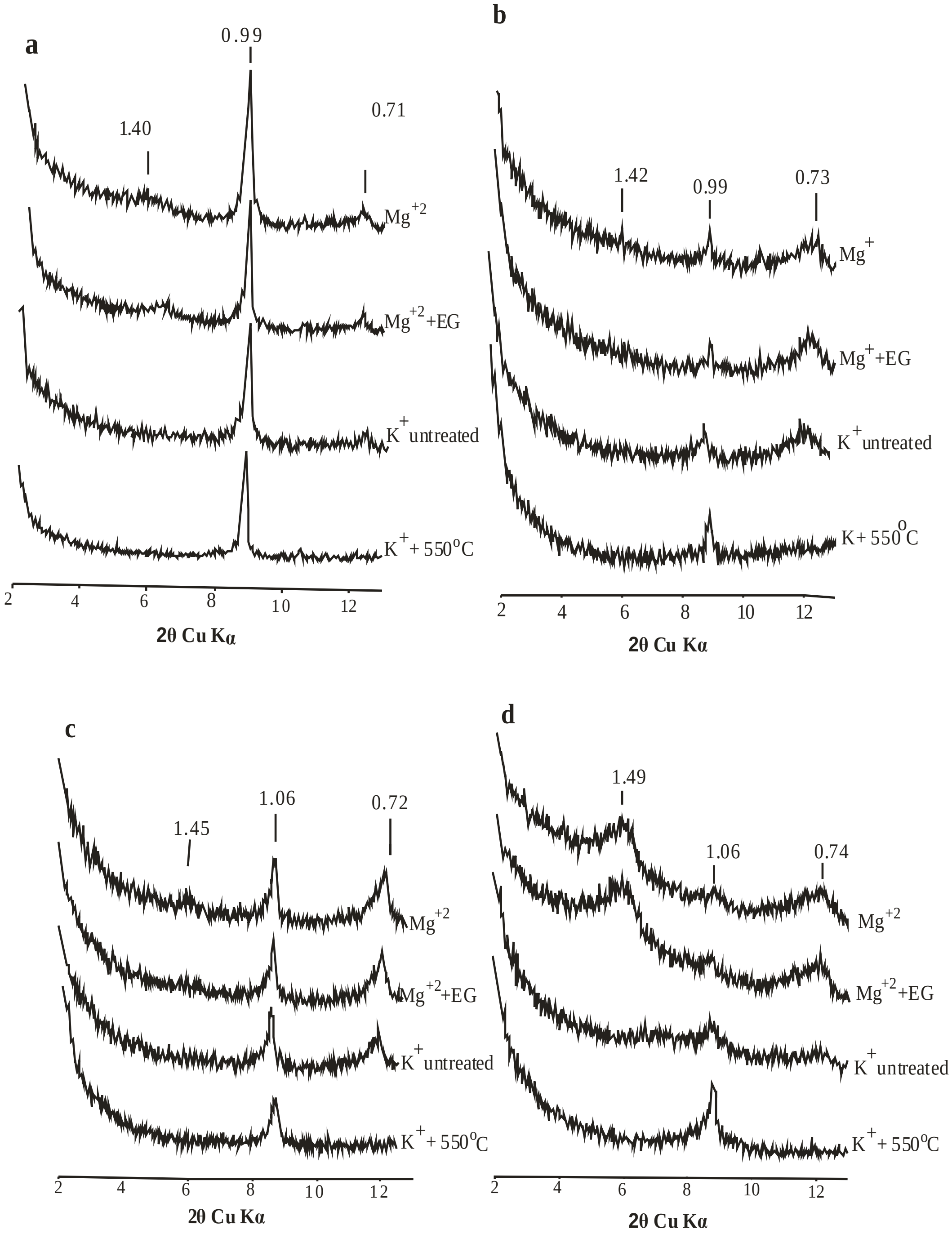

Figure 1. X-ray diffractograms of selected samples: (a)P1-A1; (b) P2-Ah; (c) P3-Ah1; (d)P4-A1 , *d*-values in nm

Parfitt & Kimble (1989) reported that allophanes are rarely found in soils under ustic, xeric, or aridic moisture regimes due to the restricted leaching of silica. A similar result was reported by Moustakas & Georgoulias (2005), who found trace amounts of allophane on the island of Thera (Greece) under a xeric moisture regime.

4.2. Mineralogical properties

The X-ray diffractograms showed only weak and often not very clear signals in the region of 2-15° 2θ. Results of the X-ray analysis are shown in Figures 1 and 2. As illustrated in figure 1, a wide range of phyllosilicates occurs, including 1:1 minerals (kaolinite) and various 2:1 minerals. Smectite is rare, occurring only in trace amounts. In our samples, peaks are mostly weak and poorly crystallized. In the studied soils, differences in composition between topsoil and subsoils are generally small. Illite is the dominant constituent of profile 1 and occurs in greater amounts higher in the surface. Kaolinite and smectite follow illite. XRD results for profiles 2 and 4 revealed the following relationship: kaolinite > illite > smectite.

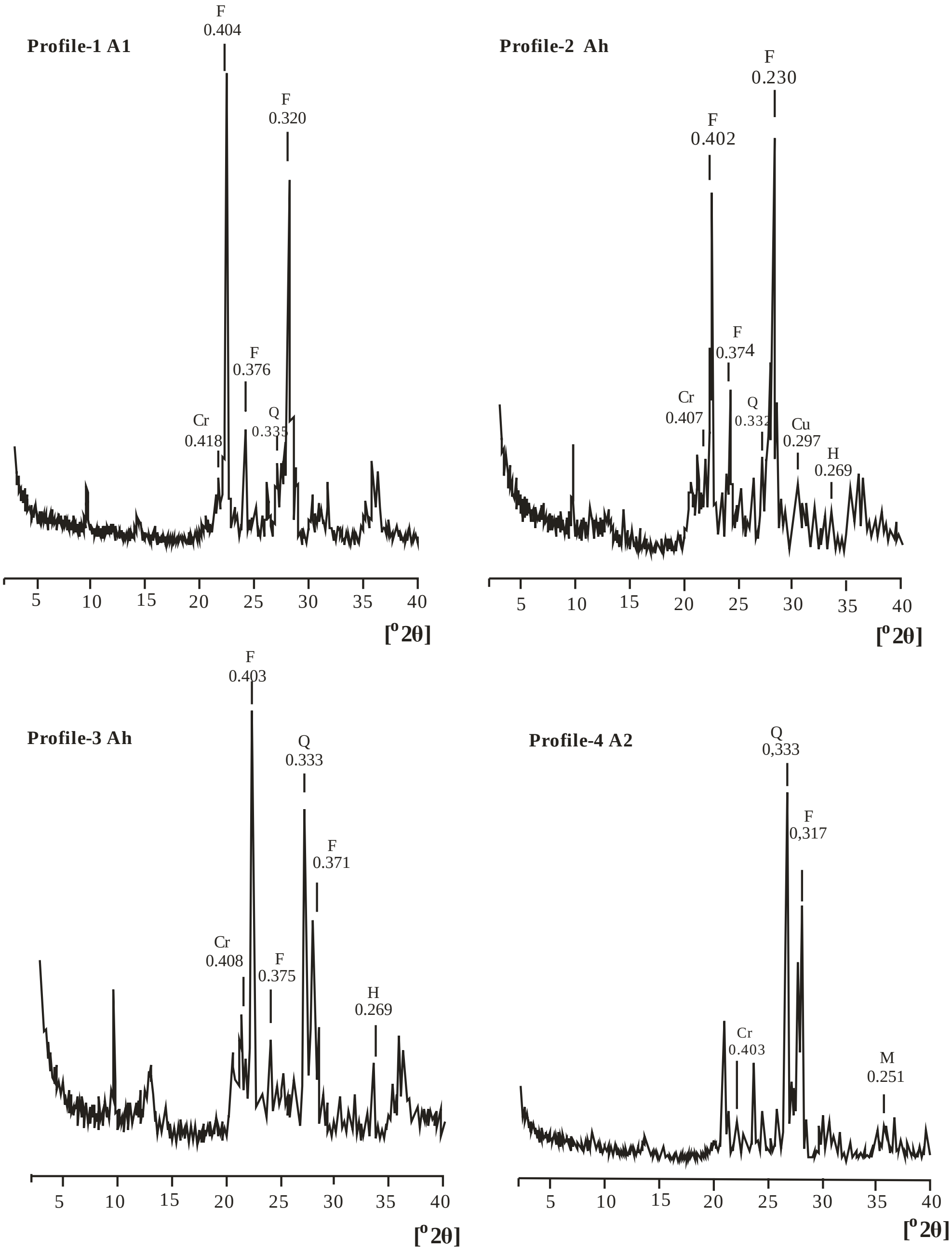

Figure 2. X-ray diffractograms of whole soils of representative horizons (F) Feldspar; (Q) Quartz; (H) hematite; (Cr) Cristoballite; (Cu) Cummingtonite; (M) Magnetite , *d*-values in nm

A similar distribution of clay minerals was observed in the Bw1 and Cr1 horizons of profile 3, but in the Ah horizon this trend changed to illite > kaolinite > smectite. Plagioclase, quartz, and cristobalite were the dominant primer minerals. Hematite was found in small amounts of sesquioxide in all profiles and is a common minor constituent of volcanic ash, especially from volcanoes that are very hot when erupting, leading to oxidation of iron compounds at high temperatures to produce hematite. The presence of hematite explains why these soils appear red, particularly during the dry season. The presence of crystalline Fe oxides is in agreement with the low Fe_o-to-Fe_d ratios, indicating that a considerable amount of Fe is released from the weathering of Fe-bearing minerals and transformed to crystalline Fe oxides.

The Fe_o-to-Fe_d ratio is related to the degree of crystallization of the Fe oxides, and it has been found that a low ratio indicates a weak degree of soil development (Schwertmann 1985; Vacca et al. 2003). Concentrations of Fe_o are consistently higher than Fe_p, indicated by Fe_p-to-Fe_o ratios of <0.42 in most horizons, suggesting that the non- or poorly crystalline form of Fe is mainly ferrihydrite. Magnetite (Fe_3O_4) was also found in some horizons.

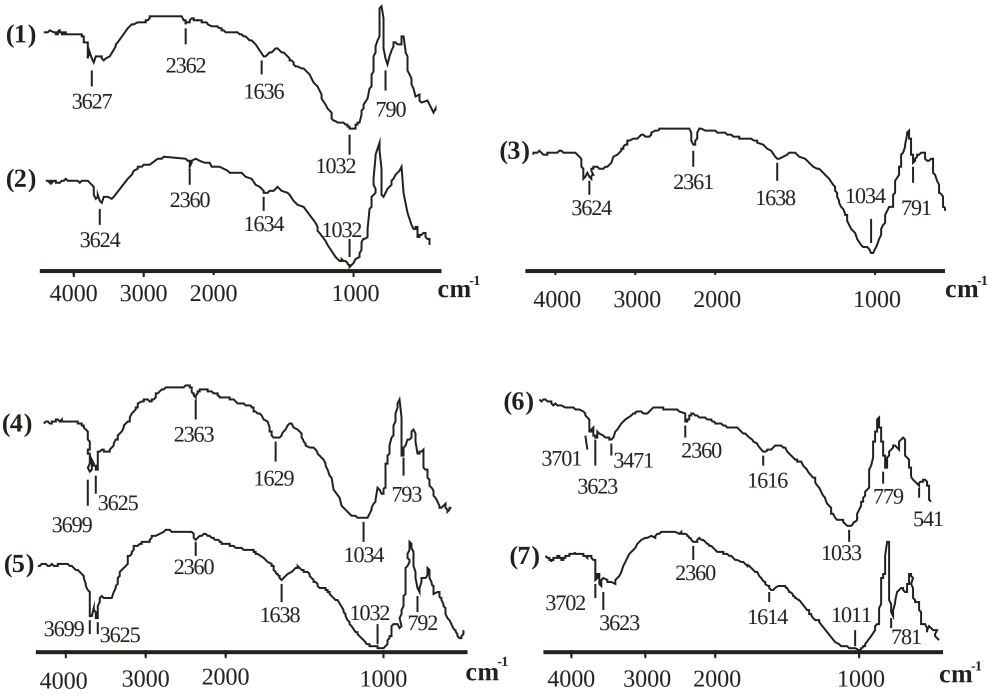

Figure 3. Infrared spectra of clay samples. Ir spectra from (1, 2) profile 1 (A1 and Cr1 respectively); (3) profile 2 (A); (4, 5) profile 3 (A and Bw1 respectively); (6, 7) profile 4 (A1 and Bw2 respectively)

Consequently, the relatively lower degree of leaching in this semiarid climate with alternating dry and wet seasons is believed to cause higher Si contents (inadequate desilication) in soil solution and to limit allophane and imogolite formation. The small differences in clay mineral type and amount, similar content of primary minerals, high sand content in the profiles, and the existence of an A-C or A-Bw-C horizon arrangement indicate small pedogenetic differences.

Allophanes have 4 major IR absorption regions. No peaks were found in these regions in the studied soils, but 2 principal peaks appearing at 790 and 1636 cm^{-1} are characteristic of different forms of silicon dioxide and indicate the existence of amorphous silica. The maxima in the 1630-1650 cm^{-1} and 600-800 cm^{-1} region are typical of metal-organo complexes and phyllosilicates, respectively. The results of the infrared spectra of the clay samples of the studied soils did not show the usual features for allophane and imogolite in the spectrum, thereby indicating an absence of allophane and imogolite.

4.3. Mass balances

The open system mass transport functions (τ) were generally high in surface horizons and decrease with depth. The mass transfer profiles indicate that, there is substantial loss of silica from the soils at all depths with the exception of the profile 1 surface soil. Greater losses of silica occur at the soil surface (up to 30%) due to intense weathering and leaching, and losses decrease with depth. The anomalous value in the Profile 1 top soil is likely due to dust input resulting from atmospheric deposition. However, the positive mass flux may also be due to the inflow of silica rich water from higher area. Although desilication is one of the most dominant process in the soils but desilication has not been intense enough to result in the Si_o/Al_o ratios that characterize allophane and imogolite. Selective dissolution analysis and FTIR result confirm this finding.

All of the soils except Profile 3 have negative mass flux of sodium and the other base cations (CA, Mg, K) have patterns of gain and losses. This indicates a loss of base cations from the soil due to leaching. The positive strains are in some cases observed in surface horizons. The positive values are mainly due to the presence of organic matter that has a lover bulk density and lover concentrations of immobile element than mineral soil materials thus contributes to dilation (Egli et al., 2001). The gains of sodium in surface horizons of profile are likely due to atmospheric contributions. The overall decrease in sodium content of the soils is also due to the weathering of Na plagioclase dominant mineral supplying sodium to the soils. Due to the absence of amphiboles, pyroxene and apatite Na and K loses must be principally explained by changes in the albite and orthoclase content. The leaching of the potassium, iron and magnesium can be explained by the dissolution of the micas and the transformation of the biotites into hydroxy-interlayered smectite. These findings are in agreement with the XRD results. Plagioclase increasingly weathered with time and since sodium is not incorporated in to secondary clay minerals or strongly retained on exchange sites it is easily leached from the soil. Ca has slightly different behavior. The net losses of Ca seem in many cases to be minor if compared to Na in most cases. Also K is rather sensitive to early weathering processes at our investigation sites and is removed in its to about 20% of its initial content. Mg is only weathered to a substantial amount (maximum 45%) in the profile 4. Similar values (Mg losses in the E horizon of podzols from 73% to 86%. are also reported by Olsson & Melkerud (2000.) The higher Mg losses at the Profile 4 site are most presumably due to minor inhomogeneities in the geological substrate and thus the presence of more weatherable Fe–Mg phyllosilicates (Righi et al., 1999; Olsson & Melkerud, 2000) in profile 4.

A strong accumulation of Ca Mg Na and K in the all horizons of profile 3 can be recorded, which indicates bioaccumulation, due to nutrient cycling. The Profile 3 developed on the most covered area by different Pinus and *Quercus* forest (*Pinus binti Quercus occifera Pinus nigra*, *Quercus infectoria*, *Quercus cerris*, *Quercus libani*, *Cedrus libani*, *Abies cilicica*) and brushwood. Dilation of soils on profile 3 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 3 is confirming this result.

Mass transport data indicate that all profiles 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 lover leaching rates there.

Mass transport data indicate that all profiles have a negative mass flux of Fe. This indicates that some dissolved iron is leached from the profile. The iron and aluminum remaining in the profile are redistributed from sand to sesquioxides and clay-size fractions and from less stable to more stable clay minerals.

The calculation of losses was not for all soils equally successful. Some minor changes in the mineralogy (due to a slightly varying geology), such or aeolian additions might have led to some unexplained results (e.g. Table 4, positive values in the whole soil profile of the mass transfer function of Bases in profile 3). For all other components, almost no difference could be seen between the mineralogical properties of parent materials. Thus, the variation of the state factor parent material (Jenny, 1980) is of minor importance. The influence of aeolian contribution is nonetheless overshadowed by minor inhomogeneities in the geological substrate. The main differences may be also explained by differences climatic conditions resulted from of altitude, facing sites, topography, elevational gradient, slopes, temperature difference and the consequently different element leaching.

5. CONCLUSION

Soils formed on Mt Erenler provide an excellent opportunity to study elemental mass-balance changes. The dominant processes identified with mass-balance analysis include desilication and loss of bases. 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. This is primarily due to the weathering of plagioclase and K-feldspars and to a lesser degree quartz and amphiboles. Aluminum seems to exhibit a varying weathering behavior, with higher rates in the topsoil and a rather linear release with respect to the whole soil profile.

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.

A very simple relationship between the site properties and elements losses could be found. Our results imply that the rate of elemental mass-balance changes is determined by factors influencing its leaching (altitude, facing sites, topography, elevational gradient, slopes, 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.

ACKNOWLEDGMENTS:

This study was taken from a research project supported by TUBITAK (Scientific and Technological Research Council of Turkey, project no: TOVAG 108O302) and Selcuk University (S.U.) BAP Office (Coordinating Office of Scientific Research Projects, project no: 08201020 and a part of it was conducted as a master's thesis by Sıdıka Alp. The authors would like to

thank “the TUBITAK and S.U.-BAP staffs”.

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Received at: 05. 05. 2012
Revised at: 12. 09. 2012
Accepted for publication at: 12. 10. 2012
Publised online at: 16. 10. 2012