

Araştırma Makalesi

www.ziraat.selcuk.edu.tr/ojs Selçuk Üniversitesi Selçuk Tarım ve Gıda Bilimleri Dergisi 25 (3): (2011) 86-95 ISSN:1309-0550

Orta Anadolu'da Karaman Karadağ Andezitik Materyali Üzerinde Oluşan Toprakların Mineralojik Yönden Değerlendirilmesi

Hasan Hüseyin ÖZAYTEKIN1,2, Saim KARAKAPLAN2

1 Selçuk Üniversitesi, Ziraat Fakültesi, Toprak Bilimi ve Bitki Besleme Bölümü, Konya/Türkiye

(Geliş Tarihi: 26.04.2011, Kabul Tarihi:08.06.2011)

Özet

Bu çalışmada yarı kurak iklim şartlarında Karadağ üzerinde oluşan toprakların mineralojik özelliklerinin incelenmiştir. Bu amaçla açılan horizonlarda morfolojik tanımlamalar yapıldıktan sonra horizon esasına göre örnekler alınarak mineralojik analizler ile mineralojik analizleri desteklemek için bazı kimyasal analizler yapılmıştır. Çalışma alanındaki topraklarda allofan, imogolit ve Fe humus kompleksleri gibi amorf mineraller saptanmamıştır. Amorf formda Al humus kompleksleri ve az miktarda da ferrihidrite bulunmuştur. Kristalize demir mineralleri diğer minerallerden daha bol, en yaygın primer mineraller olarak ise feldispat ve kuvars tespit edilmiştir. Ayrıca profillerde hematit de saptanmıştır. X ışınları difraktogramlarına göre kaolinit ve illit kil fraksiyonunda dominant mineraller olarak bulunmuştur. Ayrıca önemli miktarda klorit smektit ara tabakalı kil mineralleri de saptanmıştır. Kısa yağışlı dönem uzun kuru sezon ile karakterize edilen yerel iklimsel koşullar, düşük yıkanmaya neden olarak toprak oluşumunun yavaşlamasına neden olmuş, bu da toprak solüsyonunda Si konsantrasyonunu artırarak kaolinit ve illit gibi kristalize kil minerallerinin oluşumuna sebep olmuştur. Dolayısıyla ana materyal kaynaklı yüksek Si ve Al konsantrasyonu topraklarda allofan gibi zayıf kristalize olmuş minerallerin oluşumu engellenmiştir.

Anahtar kelimeler: Andisol, volkanik materyal, toprak oluşumu, toprak mineralojisi, Karadağ

Mineralogical Assessment of Soils Developed on Andesitic Materials at Mt. Karadag, Karaman from Central Anatolia

Abstract

This study the mineralogical characteristics of, the soils from Mt. Karadag, whose climate is semi-arid were investigated. For this purpose, samples were taken from the horizons after their macromorphological identifications were completed in all profiles and analysis for mineralogical properties was carried out. these soils lacked non-crystalline minerals like allophane, imogolite, and iron humus complexes. The only noncrystalline minerals that are present are, in great quantities, Al-humus complexes and, in small quantities, ferrihydrite. Crystallized Fe minerals were higher than the other Fe minerals. Feldspar and quartz were more common primer minerals. Hematite was also found in the profiles. X-ray diffraction indicates kaolinite and illite were dominant minerals in clay fractions. Furthermore, a considerable amount of chlorite-smectite interstrafied mineral was found to occur in the clay fraction. The local climate; which, due to its short wet season and extended dry season, experiences a lower degree of leaching that prevents rapid soil genesis, causes an increase in Si concentrations in the soil solution, and favors neogenesis of crystalline clays such as kaolinite and illite, thereby consuming a large amount of Al and Si derived from the parent material as opposed to poorly crystalline colloidal constituents such as allophone.

Key Words: Andisols, Volcanic Material, Soil Formation, Soil Classification, Mountain Karadag, Karaman

Introduction

Soil that forms in volcanic ejecta develops unique characteristics that are referred to as andic soil properties and they are classified as a special soil type, such as Andosols (FAO UNESCO, 1988) or Andisols (soil survey staff, 1999). The unique properties of Andisols include their low bulk density and high water retention ability, with water infiltration and hydraulic conductivity resembling very silty soils (Wada, 1985). Previous studies clearly indicate that, in addition to parent material, climatic conditions are an important factor in weathering since climate determines the weathering product of volcanic materials and, therefore, the type of non-crystalline minerals that will be formed. In these conditions the age of the soil and presence or absence of a marked dry season are the most important factors in the mineral evaluation of Andisols. At this point the fact that non-crystalline mineral formation is the result of oversaturation of soil solution with Si, Al, and Fe, which control soil solution concentration, makes the influence of climate on the characteristics of volcanic soils easily understood.In the semi-arid region of central Anatolia, the weathering products from volcanic materials are quite different from those in humid climates, and soil formation is not yet clearly

² Sorumlu Yazar: hhuseyin@selcuk.edu.tr

understood in this environment. Our aim was to identify the mineralogical properties, as well as to define the weathering processes and pedogenetic products of soils forming on the volcanic material of Mt. Karadag

Materials and Methods

Site description

Anatolia, about 20 km northwest of Karaman province, 100μ) were separated by bromoform (density 2.89 at 20° at 37°15'07"–37°29'22" N latitude and 33°01'12"– C) and observed in glass slides with a polarizing 33°15'28" E longitude. The topography is flat, but Mt. microscope Volcanic glass content from the coarse silt Karadag, which is a volcano, spoils this landform and is plus sand fraction (0,02-2,00 mm) were also observed in the highest point at 2,228 m in the study area. Long-term glass slides with a polarizing microscope (Erkan, 1994; records show that mean annual precipitation is 340.1 Tinsley, 1974). mm, total evaporation is 1312.8 mm, mean annual temperature is 11.5º C, and mean annual soil temperature at 50 cm is 13.8º C (DMI 1994). Annual precipitation is irregular. Most precipitation falls in the winter months, with no rain during the summer. The research area has the same terrestrial climate as central Anatolia. Soil moisture and temperature regimes are xeric and mesic, respectively, according to the climate data (Soil Survey Staff 1999).

Quaternary and old Middle Anatolian volcanics and lie alone. Each specimen was studied at magnifications in parallel with the inner belt of the Taurus Mountains. This volcanism, which was active from the middle Miocene to the end of the quaternary period, contains lacustrine and alluvial deposits and covers the sedimentary deposits in a disharmonic manner. These volcanics cover a 300 km² area around Karadag. Karadag is mainly formed of volcanic dome and volcanic dome flows, tuff, lava debris in the form of pele, and volcanic mud flows. The first magmatic activity in the area can be seen in the upper Pliocene and continues until the Quaternary period. The age of the oldest magmatic unit has been determined as 3.2 million years (Işık, 1994).

Sampling and analysis

For the study, three pedons were selected and described as representative soil types of the region. Disturbed and undisturbed soil samples were taken from the horizons for mineralogical, and chemical analyses. 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 later use.

performed on a Shimadzu XRD-6000 with a Cu increased with depth in Profile 1 and decreased in anticathode and K filter (40 kV, 35 mA). The samples Profile 3, but no trend was observed in Profile 2. Al_c were in the form of powder for the saprolite and rock and Fe_o values ranged from 0.051% to 0.182% and from samples and isolated mineral phases or oriented 0.026% to 0.352%, respectively. The highest Al_o and preparation for the clay fraction. For the latter, different Fe_0 values were observed in Profile 3. Fe_p and Al_p pre-treatments were used: Mg saturation with and values were very low and ranged from 0.000% to without ethylene glycol (EG) solution and K saturation 0.142% and from 0.084% to 1.201%, respectively. Fe_p followed by heating to 550° C. XRD diffractograms and Al_p values were very low compared with those of were taken using a diffractometer in the 2[°] to 15[°] 2θ other Andisols because of the very low organic matter

range. Minerals were identified by their diagnostic XRD spacing. Diffractometric analysis of the pulverized saprolite and rock samples, meanwhile, was carried out in the 2° to 40° 2θ range (Jackson 1979). Minerals and relative abundance were identified and evaluated by their XRD spacing and relative peak intensities in the XRD diagram.

The study was conducted on Mt. Karadag in central Heavy and light minerals from the sand fraction (50–

Karadag's volcanics are classified as Neogene proved superior to a coating of either carbon or gold Fourier Transform Infrared Analysis (FTIR) was only performed on the <2µ fractions. 1 mg of each sample. Infrared spectra were recorded with a spectrometer (Perkin Elmer universal ATR probe) in the 4000–400 $cm⁻¹$ wavelength range with 1 $cm⁻¹$ resolution. Selected saprolite specimens were also studied under a scanning electron microscope (SEM). The samples were mounted onto aluminum stubs and coated first with carbon and then with gold. This double coating ranging from 250 to 20,000.

> Some chemical properties were also determined to confirm the mineralogical properties such as Soil pH was measured potentiometrically, both in a 1:2.5 soil/water (w/v) suspension and in 0.01 N CaCl₂ with a glass electrode (U.S. Salinity Lab Staff 1954). pH in NaF was determined in 1 N NaF at soil/liquid ratio of 1/50 in a similar way (Soil Survey Laboratory Methods Manual 2004). Phosphate retention capacity was measured according to the Soil Survey Laboratory Methods Manual. Short-range order constituents were characterized by selective chemical dissolution. Dark ammonium oxalate, dithionitecitrate bicarbonate (DCB), and sodium pyrophosphate-extractable Si, Al, and Fe were determined according to the Soil Survey Laboratory Methods Manual and through the use of an AAS for quantification. Cations were designated by subscripts o, d, and p for the respective methods.

Results

Mineralogy was determined through X-ray analysis horizons, ranging from 0.029% to 0.152%. Si_o values The results of the selective dissolution analysis are given in Table 1. Si_o content was less than 0.2% in all

content of the studied soils. The highest Fe_p and Al_p ranged from 0.26% to 1.43%, and Al_d ranged from values were found in Profile 1, which has the highest 0.054% to 0.167% . Fe_d decreased with depth in Profiles organic matter content indicating the relation of organic 2 and 3, whereas Al_d showed a decrease with depth in matter with Fe_p and Al_p . In the studied profiles, Fe_d Profiles 1 and 3.

Horizon	Depth	$\rm pH_{(H2O)}$ (1/2,5)	pH_{CaCl2} (1/2,5)	HCaCl ₂ . H ₂ O \overline{P}	$pH_{(NaF)}(1/50)$	\mathcal{C}° Phosphorous Retention ($\mathrm{Fe_{d}}(\boldsymbol{^{0}/_{0}})$	$\mathrm{Fe_{o}}(\%)$	$\mathrm{Fe_{p}}\left(\mathrm{^{9}/_{0}}\right)$	$\mathrm{Al}_\mathrm{d}\left(^{9}/_{0}\right)$	$\mathrm{Al}_{\mathrm{o}}(\mathrm{^{0}/_{0}})$	$\mathrm{Al_{p}}(\%)$	$\mathrm{Si}_\mathrm{o}(\mathrm{ ^{9}\!/\!\mathrm{o}})$	Al_0/Al_d	$\rm Al_p/Al_o$	$\rm Fe_{o}\!/\!Fe_{d}$	$(Al_o-Al_p)Si_0$
Profile I																	
A11	$0 - 16$	7,65	6,21	$-1,44$	7,94	19,2	1,34	0,074	0,142	0,167	0,182	1,201	0,098	1,09	6,6	0,06	$-10,4$
A12	16-48	7,61	5,89	$-1,72$	7,97	17,7	1,43	0,042	0,132	0,139	0,118	1,143	0,108	0.85	9,7	0,03	$-9,5$
R	$+48$	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Profile II																	
A1	$0 - 14$	7,45	6,41	1,04	8,07	8,6	0,50	0,324	0,010	0,097	0,083	0,870	0,079	0,85	10,5	0.65	$-10,0$
C1	14-45	7,44	7,08	0,36	8,17	14,0	0,53	0,135	0,017	0,135	0,131	0,862	0,152	0.97	6,6	0,25	$-4,8$
C ₂	45-76	7,53	7,03	$-0,50$	8,37	13.9	0,37	0,036	0,000	0,090	0,082	0,840	0,062	0,92	10,2	0,10	$-12,3$
C ₃	$+76$	7,63	7,13	-0.50	8,65	16,5	0,26	0,026	0,001	0,061	0,051	0,853	0,029	0,84	16.7	0,10	-28.1
Profile III																	
A1	$0 - 22$	7,70	6,90	-0.80	8,01	7,7	0,44	0,352	0,010	0,089	0,061	0,878	0,048	0.69	14,3	0,80	$-16,9$
C1	$22 - 51$	7,75	7,05	$-0,70$	8,12	9,9	0,40	0,299	0,000	0,064	0,084	0,929	0,044	1,32	11,0	0.75	-19.3
C ₂	$+51$	7,85	7,15	$-0,70$	8,05	8,6	0,37	0,283	0,001	0,054	0,067	0,897	0,031	1,24	13,4	0,77	$-26,7$
nd: not determined																	

Table 1. Some chemical properties of studied profiles

Table 2. Some heavy and light minerals distribution of soil studied (%)

consistently less than $pH_(H2O)$, and ΔpH ($pH_(CaCl2)$ $pH_(H2O)$) values ranged between - 0.36 (pedon 2) and soils. pH in NaF values ranged from 7.94 to 8.65, with values <9.5 in all soils, indicating lack of Al activity.

X-ray diffractions have been conducted on clay fractions and the whole soil (Fig. 1) body to determine mineralogical qualities in the profiles opened in the working area. Besides, infrared spectroscopy charts (Figure2) and SEM images (Figure 3) have been taken. Phyllosilicates of different amount and crystallization

 $pH_(H2O)$ is alkaline in all profiles, and soil $pH_(H2O)$ values degrees were found to have formed in all three profiles. ranged from 7.44 to 7.85, with no regular distribution. However, in spite of the low amount of amorphous Soil pH_(CaCl2) values ranged from 5.89 to 7.15, and were phase and also the high amount of clay in some 1.72 (pedon 1), indicating a net negative charge of the three profiles in 4 regions of the working area. Minerals horizons, weak and unclear signals have been taken from $2-13$ °20 areas. Similar peaks were observed in all with chloride-smectite intermediate layers, which have been seen as shoulders at 14.7–16.6 Å in the sample filled with Mg, which expands to $17.1-17.7$ Å with glycerol filling and which closes down to 14.0–14.2 Å with K filling, have been determined in the first region. Illite, with peaks between 9.9–10.3 Å, has been determined in all the applications in $2nd$ region, whereas chloride with peaks of 14.2 and 6.85 Å $(001$ and 002 reflections) has been determined in the $3rd$ region in the

samples filled with Mg and kaolinite, which shows contrary to clay minerals, more prominent peaks have mixed (heavy and light minerals are together) dust (2.53 Å) have been determined in the profiles. samples by means of an X-ray diffractometer. On the

peaks between 7.2–7.4 Å but gets lost at K+550 C° as been obtained in determination of minerals in thin sand has been determined in the $4th$ region. No significant sizes with x-rays in all horizons. Primary minerals such change has been observed with the depth in profiles. as quartz (3.38 Å) , biotite (3.20Å) , plagioclase (3.79 Å) , Diffractions in fine sand sizes have been obtained with orthoclase (2.66 Å) , hornblende (3.04 Å) , and hematite

Fig.1. X-ray diffractograms of selected samples (D+Kl) chlorite-smectite interstratified, (I); Illite, (K); Kaolinite (F) Feldspar; (Q) Quartz; (H) hematite; (Cr) Cristoballite; (Ed) Edenite ; (Hn) Hornblende, *d*-values in Ǻ

Distribution of light and heavy minerals in horizons, meanwhile, the amount of light minerals in the A1 than 90% of Profile 1 is formed by light minerals; mineralogical composition. We can see that while

which have been obtained with the study conducted horizon of Profile 2 decreases to 75% but increases to using a polarized microscope technique, has been 98.5% in the C3 horizon of the same profile. The presented in Table 2. As has already been seen in Table amount of light minerals in A1, which corresponds to 2, the majority of the particles in sizes of thin sand (50– 95%, has decreased to 76.6% in C2. Irregular 100 μ) that were previously distinguished and distribution of the percentages of both the total heavy determined in gravimetric terms are formed by light minerals and singular heavy and light minerals with minerals. Light minerals decrease with depth in Profiles depth, especially in Profile 2 and Profile 3, indicates that 1 and 3 and increase with depth in Profile 2, while more the primary material does not have a uniform

feldspars of light minerals are in majority in Profile 1, heavy minerals, biotites are the most common minerals, quartz is the mineral in majority in solum. In Profile 2, together with opaque minerals, after hornblende. They quartz is in majority in A1 and C1 horizons while calcite have been observed as brownish green and reddish is in majority and its rate is increasing rapidly in C2 and brown upon microscopic examination. A small amount C3. In Profile 3, feldspars are in majority and are of chloride as dark green and brownish green has been followed by quartz. A small amount of calcite, encountered in solum, primary material, and parent rock meanwhile, is contained in C1 and C2. No volcanic in all the profiles. Chlorides have been distinguished glass has been encountered during the studies conducted from biotites with biotite minerals showing double with a polarized microscope on the profiles researched. diffraction and having a lower amount of relief. In Weathered minerals are at different weathering levels addition to hornblende, a small amount of actinolite and are mostly formed of feldspars. Change of heavy from the amphibole group of minerals has been minerals in profiles with depth is irregular and no determined to exist in the profiles. Apatite, which has meaningful changes of importance are observed. been determined in the parent rock of Profile 1, has not Hornblende is the densest mineral among the heavy been determined in solum. Trace amounts of apatite minerals found in all the researched profiles. It has have been determined in the primary materials of generally been observed in microscopic examinations as Profiles 2 and 3. Heavy minerals weathered in profiles prismatic parts with shapeless forms that are green or have attempted to be determined according to their brownish. Transformation into oxy-hornblende is colors, mineral relief, and dark area angle and shape observed in some hornblendes because of Fe measurements, but no certain determinations could be enrichment. A similar formation can be seen in biotite done. Generally speaking, weathered minerals consist of and oxy-biotites that have also formed. Among the augite, hornblende, biotite, and hipersten minerals.

Fig.2 Infrared spectra of clay samples. IR spectra (a) from) profile 1 (A1); (b,c) profile 2 (A1 and C1) respectively); (d) profile 3 (A);

images (Figure 3) have been taken to confirm the C single vibration band was present at 797 cm⁻¹. existing of amorphous materials. The IR spectra of the soil show six principal peaks, at 797, 911, 1000-1003, 1423-1482, 1622–1635, 2360–2363, and 3348-3392 cm-Al, Fe, and Si values determined by selective H was observed at 3348-3392 cm^{-1.} The bent vibration

Infrared spectroscopy charts (Figure 2) and SEM peaks belonging to H were found at 1636 cm⁻¹, and a Si-

Discussion

¹. In IR spectra as a large band structurally OH peaks of dissolution analysis give very important knowledge of

the mineralogical composition of volcanic soils. oxides were the most abundant mineral fraction. The Fe_p / Fe_d ratios were also showed that crystalline Fe - all profiles.

Selective dissolution analysis of Si, Al, and Fe were rate of Al_p / Al_o was used a characteristic of Andisols, used to indicate the presence of amorphous materials where Al_p / Al_o lower than 0.1 confirms the absolute like allophane and imogolite. The rather low Si_0 , Al_0 , presence of allophane. Al_p / Al_0 values were higher than and Fe_o values highlighted the absence of non- 0.1 in all profiles, indicating lack of allophane and crystalline materials in studied soils. Pyrophosphate-existence of Al - humus complexes, Besides, the ratio extractable Al (Al_p) and Fe (Fe_p) provide the data for $(Al_o - Al_p) / Si_o$ can be used to estimate allophane and organometallic complex forms of Fe and Al. AI_p and imogolite formation in Andisols. This rate ranges from Fe_p are very high in Andisols, but in the studied soils 1 to 2.5 in most Andisols, is close to 1 in allophane these values were very low. In all pedons, Al_0 / Al_d rich Andisols, and is close to 2 in imogolite - rich were higher (> 0.5), indicating that free (dithionite - Andisols. The rate of $(Al_0 - Al_p) / Si_0$ was outside the soluble) Al exists predominantly in non - or poorly limit, which demonstrates the lack of allophane and crystalline form. Fe_p / Fe_d values were very low. Small imogolite in the studied soils; indeed, it was negative in

Fig.3. SEM photograph of selected samples **(a)** from profile 1 (A1), laminar-skeletal fabric with face–face and face– edge unions between particles. Area is enlarged in **(b)**; **(c)** from profile 2 (A1); Field of clay particles (domains) with face– face unions. Area is enlarged in **(d)**; **(e)** from profile 3 (A1) fresh-broken surface. Skeletal fabric, mainly composed of sand- and silt-sized particles. Area is enlarged in **(f).**

Infrared spectra and SEM images were taken to confirm the presence of allophane and imogolite, but neither allophane nor imogolite were found in IR spectra (Fig. 2) and SEM (Fig. 3). Allophanes have four major IR absorption regions. The first region is at $3475-3500$ cm⁻¹ due to OH stretching vibrations of the Al-OH octahedral and SiOH tetrahedral groups and/or adsorbed water, called the functional group region. The second region, appearing at 1400 to 1440 cm^{-1} , is due to HOH deformation vibration of adsorbed water. The third region $(800-1400 \text{ cm}^{-1})$ is called the fingerprint, attributed to Al-OH and/or Si-O linkages (Wada, 1989). Allophane shows a single absorption band, while imogolite shows two absorption maxima at about 940–1000 cm^{-1} (Wada, 1989). Samples from Mt. Karadag did not show any absorption in regions 1, 2, and 3. The maxima in the $1630-1650$ cm⁻¹ and $600-800$ cm⁻¹ region are typical of metal-organo complexes and fillo silicates, respectively. The result of the infrared spectra of clay samples of the studied soils do not show usual features for allophane and imogolite in the spectrum, thereby indicating an absence of allophane and imogolite. These findings are in agreement with the SEM. Consequently, the extremely small amounts of Al_0 and Si_0 compared with Fe_d suggest that crystalline aluminosilicates with high charge density could be occurring through neoformation, consuming both Al and Fe released from weathered parent material. Very low values of Al_0 and Si_0 , in combination with low P retention values, showed that allophane formation was non existent. In the studied soils, low precipitation and a long dry season restricted the leaching of silica. Allophane formation was obstructed by inadequate release of Al due to low weathering rate, use of released Al by secondary clay minerals, and inadequate desilication. Parfitt and Kimple (1989) report 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 Moustakes et al. (2005), who found trace amounts of allophane on the island of Thera (Greece) under a xeric moisture regime.

Feldspar and quartz have been determined as primary minerals in soils. It has been determined in the analyses that feldspars are plagioclases. Plagioclases are the highest-content minerals in andesitic materials. Minerals with iron, such as hematite have also been determined in some profiles. Wada (1987) and Bigham et al. (2002) have stated that hematite is related to magnetite and maghemite and that magnetite can easily be composed of maghemite under forest vegetation and in the existence of organic substances; these mentioned minerals, along with gibbsite, are found in well-weathered volcanic ash soils in Hawaii. Hematite is a very common mineral in soils formed of volcanic ashes and it exists as a result of ferrous compounds' oxidation in the environment of a very hot explosion. Existence of hematite in the primary material being evaluated also explains this situation. Besides, red hematite seen in Profile 1 also proves its existence. Kaolinite and illite is the dominant type in the clay fraction of soils. Also, clays with chloride-smectite intermediate layers and a small amount of smectite clays have been found in the examples. However, amorphous clays such as allophone and imogolite halloysite have not been determined. Similar results stating that no allophone and halloysite were determined have been reported by Poulenard et al. (2003) while they were working on five Andosol profiles and determining minerals such as 2:1 and 2:1:1 types of smectite and chloride. Profiles containing kaolinite and illite most possibly show that feldspars directly transform into kaolinite or illite (hydro mica) because of mineral weathering. Microscopic work that has been done with a polarized microscope on a thin sand fraction also confirms that an amount of weathered minerals have slightly increased in horizon A2. The amount of feldspars are 85% in parent rock due to weathering while it decreases in solum and also decreases in A2 to 26%, while the amount of weathered light and heavy minerals increases. No significant changes have occurred in the amounts of minerals in depths. However, while kaolinite amount increases in some horizons with depth, the amount of clays with chloride-smectite intermediate layers, which give a plato-shaped diffraction and which are not wellcrystallized, has slightly increased. This situation seems to be related to weathered light minerals increasing with depth. Formation of a 2:1-type clay has occurred in very low amounts in the working area. This is because weathering rate has been low due to low amounts of rain. Chadwick et al. (2003) have reported that clay formation in lava flows aged 150,000–400,000 years with alkaline character could only occur with rainfall amounts greater than 1,400 mm per year. Clay content of a lower 2:1 type or with a chloride-smectite intermediate layer in the working area may be explained by this low amount of rainfall.

While kaolinite increases with depth in Profile 1, the amount of minerals with chloride-smectite intermediate layers that are not well-crystallized and that give plato-shaped diffractions has increased. This situation seems to be related to the amount of weathered light minerals increasing with depth. Some of the feldspars, which form the majority of weathered light minerals in the profile, have turned into kaolinite because of direct hydrothermal effects before pedogenesis while part of them have turned into kaolinite with hydrothermal effects lasting until the present or with the effect of climate oscillation with high amounts of rainfall, which increases the speed of chemical weathering. Microscopic work that has been done with a polarized microscope on a fine sand fraction also confirms that an amount of weathered light minerals has slightly increased in A2. Amount of feldspars are 85% in the parent rock due to weathering

while it decreases in solum and also decreases in A2 to 26% and the amount of weathered light and heavy minerals increases. This shows that the soil is in the development stage in mineralogical terms. Since this can be understood from the fine sand mineralogy of horizons and the parent rock, it can be seen from x-ray diffractions that biotite exists in the mentioned profile, which is rich in plagioclase, and that biotite transforms into hydro biotite (illite) in both layers. Besides, free Fe amount being relatively high in the A2 horizon indicates that biotite has been weathered and that part of the kaolinite is formed of biotite. Besides, this profile has an iron amount that is higher than other profiles, although the depth of the profile is shallow, and the higher free iron amount in A2 than in A1 indicates that weathering is relatively higher in this horizon. Therefore, it is seen that transformation of secondary minerals formed in that horizon into kaolinite occurred more frequently and, therefore, the relative amount of kaolinite increased. More weathered heavy minerals have been found in A2 in Profile 1 during the examinations done with a polarized microscope. The failure to find apatite in solum while it is determined to exist in parent rock in the profile results from the fact that apatite, which can easily weather, possibly leaves the environment by decomposing in a chemical environment. Hornblende and biotite feldspar amounts feldspars having been determined to be lower in solum than in the parent rock through the examinations done with a polarized microscope in the fine sand fraction indicates that the kaolinite is formed primarily of feldspars and part of it is formed of biotite. Kaolinization, as determined on the weathering surfaces of biotites through microscopic examinations, also supports this idea. Chloride, meanwhile, has been determined in both parent rock and solum in the profile. Dixon and Weed (1989) report that generally chlorides are formed of primary minerals in metamorphic and volcanic rocks or of hornblende, biotite, and transformation products of some other minerals with ferromagnesium. Çelik and Karakaya (1998) report that chlorides are formed partially as a product of dense hydrothermal alteration (pyrophyllitization) of andesites and basalts as well as epidote, alkaline feldspars, quartz, sericites, carbonate, and pyrite in a way to fill in the amygdales. Although there is not that much chloride in the studied soil, unlike some other clay minerals, when the soil contains chloride it plays an important role in the chemical environment. Chloride forming in the soil being studied is called pedogenic chloride and is different from the chloride that comes from the primary material. Pedogenic chloride is seen in soils that contain significant acid and alkaline, while it has a lithologic character in lime soil. Some amount of mineral with intermediate layers exists in the environment if the environment contains pedogenic chloride. As in all the researched profiles, hornblende and biotite from heavy minerals and feldspars from

light minerals are dominant. It is seen that chloride in clay fraction in solum forms with the weathering of minerals in question. Peaks in K-clay+550 Cº applications that are almost identical with peaks of 14.9 and 14.2 Å were determined in samples filled with MG in A1 and A2 in Profile 1; these peaks' not closing towards 10 Å and the fact that the range where these peaks are contained is plato-shaped indicates that some minerals with a chloride-smectite intermediate layer exist therein. Indeed, the peaks' being closer to 14 Å shows that there is a high amount of chloritization (Sayın, 1985). This formation is a pedogenic formation. Similar formations have been determined in other researched profiles. Ghabru and Ghoss (1983) also have reported that minerals with intermediate layers and pedogenic chloride have been formed of mica under humid conditions in a profile belonging to the Entisol group in India; weathering of mica has slowed down as we go deeper in the profiles and they considered that feldspars and mica have had a weak weathering within these soils. Even if the profile were shallow, the similar appearance of the minerals in solum and the significant changes in their respective amounts show that these soils are young; the fact that there are clay minerals in solum shows the weathering density of this soil. According to this it is seen that, being slight on the surface of the soil, the weathering is at a level to form clays with intermediate layers. Higher amounts of clay and free Fe content exist in A2 and the color is 10 YR in A1, whereas it is 2.5 YR in A2, indicate that A2 has a denser weathering. $Fe₂O₃$ amounts decreasing through the surface in the profile indicates that chlorides were decomposed and altered. Illite in the profile, which is contained in both horizons in an increased amount, has possibly occurred with the transformation of minerals containing K in the environment where chemical reactions existed. Illite's near-uniformity in the profile supports the idea that it is formed as a byproduct of feldspar decomposition, which is common in andesites. Fitzpatrick (1975) and Millot (1970) also have reported that feldspars form illites in conditions similar to those in the working environment. Basically, formation of illite mineral is not based on either washing conditions or results from the K element, which is contained in higher amounts within the environment. Determining chloride and illite in the profile under the light of data obtained with XRD indicates that biotite has newly chloridized as the parent rock is slowly decomposing.

Clay minerals similar to the ones in Profile 1 have also been found in Profile 2. Especially in the A1 horizon, no prominent peaks could be obtained in the X-ray fraction from samples filled with Mg. The Clay mineral and groups determined in this profile are kaolinite, illite, chloride, chloride with a smectite intermediate layer, and smectite. The amount of illite in this profile slightly increases with depth. This situation indicates that weathering in the profile occurs very slowly. Changeable K and total K, meanwhile, decreases with depth and is found in the smallest amount in C3. This results from the fact that K cations, which emerge since illite's physical decomposition decreases with depth, remain in low amounts and this situation draws attention as another data supporting slow decomposition. Increase in lime amount in the profile with depth, especially its reaching 31.74% in C3, has caused the smectite amount to slightly increase in that horizon. On the other hand, kaolinite partially decreases with depth and exists in higher amounts in southern horizons. This situation results from the fact that surface weathering is slightly more significant in the profile.

Indistinct peaks in x-ray diffractions obtained in Profile 3 makes qualitative and quantitative analyses difficult. While the profile contains illite and kaolinite as clay minerals, a very small amount of minerals with a chloride-smectite intermediate layer is also contained therein. A minimal difference has been observed in the profile in terms of clay minerals. The profile's formation on volcanic colluvial material has caused the clay minerals to form in a manner similar to that in Profile 1. However, pedogenetic events have occurred at a minimum level in the profile because of possible rainfall decrease with height, formation on relatively rough material carried by erosion, and not having enough time for pedogenesis. Moreover, the extremely low free Fe amount within the entire profile indicates that there is an almost homogenous distribution of kaolinite and illite in the profile and that pedogenic development is at a very low level. Having nearly the same $Fe₂O₃$ content in the whole profile indicates that there is no chloride weathering, contrary to Profile 1. This is another data supporting the idea that pedogenic development in the profile is at a very low level. Besides, the highest amount of feldspar among the light minerals has been determined in Profile 3 during the study made with a polarized microscope. No decomposed light minerals have been observed. This also supports the idea of weak weathering revealed with chemical and mineralogical analyses. The reason why the free Fe content in this profile is very low is the weak weathering of hornblende. A high percentage of hornblende has also been determined in this profile during examinations made with a polarized microscope in thin sand and, especially, weathered heavy minerals have not been observed out of the surface horizon. In light of all these data, it can be said that the kaolinite in the soil has not been transmitted with pedogenic processes in the soil but with the inheritance from the parent rock or the material carried away from Profile 1 or higher sections where the weathering occurs in a more advanced manner, that trioctahedral micas (biotite group) exist as illite clay mineral with a small amount of change, and accordingly, not enough time has elapsed for the minerals in the parent rock to

transform into clay minerals of another character by being completely weathered.

Distribution of volcanic glass in horizons, which have been obtained with the study conducted using a polarized microscope technique. No volcanic glass has been encountered during the studies conducted with a polarized microscope on the profiles researched.

In light of all these data, it can be seen that the clay minerals in the researched soils form as transformation and weathering products of the feldspar, which originates from the primary material and is determined in quite high amounts in andesitic materials, along with other heavy minerals, biotite and hornblende that exist therein in the first place. Profile depths being shallow, the soils' containing quite high amounts of sand fractions, and the profiles' having A-R or A-C horizons reveal that the time elapsing in current pedogenesis is short and indicates that weathering in the profiles is slow and primary material has a strong effect. No formation of allophone and imogolite has occurred since the low amount of rainfall and dry summer period limits the Si loss of soils. In particular, since clay mineral types in clay fractions in the horizons of profiles remain the same and only change the amount of dominant clay mineral, a very slight difference between the types and amounts of clay minerals in the horizons of the profile and amount and type of primary minerals being similar indicate that pedogenic differentiation occurs very slowly.

Conclusions

The studied soils are at an initial stage of development, and only the ochric horizon was found. Non-crystalline minerals such as allophane and imogolite have not formed in these soils because of a low rate of weathering, inadequate Si leaching as a result of low precipitation, and a long dry season. A considerable amount of Fe released from weathering of primary minerals is transformed to crystalline Feoxides, whereas free Al is present mainly in Al-humus complexes. The clay mineralogical assemblage was composed mainly of kaolinite, illite, interstratified chlorite-smectite, and chlorite. Smectite was present in trace amounts. Dominant primary minerals were plagioclase and quartz. Minor amounts of hematite were found. The local climate has a dry season, and the very small amount of precipitation negatively affects soil moisture. This particular combination of parent material and climate prevents rapid weathering; thus, the soils were still at an initial stage of development. Horizon differentiation was poor and parent material effect on soil properties was strong. Non-crystalline minerals were not formed in profiles. Also lack of volcanic glass of parent materials of soil studied prevents andic soil properties.

Acknowledgments: This study is a part of the Ph D. thesis by Hasan Hüseyin Özaytekin. The authors gratefully acknowledge the financial support of Selçuk University Scientific Research Project Funds, Project number: FB 98/106).

References

- Bigham, J.M., Fitzpatrick, R.W., Schulze, D.G., 2002. Iron Oxides. In: Dixon, J.B., Schulze, D.G. (Eds). Soil Mineralogy with Environmental Applications. SSSA Book Ser. No. vol. 7. *Soil Sci. Soc. Am.* , Madison, WI, pp. 323-366.
- Chadwick, O.A., Gavenda, R. T., Kelly, E.F., Ziegler, K., Olson, C.G., Elliott, W.C., Hendricks, D.M., 2003. The Impact of Climate on the Biogeochemical Functioning of Volcanic Soils. *Chemical Geology*, 202. 195-223.
- Çelik, M., Karakaya, N., 1998. Sistematik Mineraloji 1. Baskı ISBN: 975-96541-05
- Dixon, J.B., Weed, S.B., (Ed.), 1989. Minerals in Soil Environment. *Second Edition S.S.S.A.* Book Series No 1 Madison W1 USA 729-788
- DMI, (1994), Meteorological Bulletin. Turkish State Meteorological Service
- Erkan, Y., 1994. Kayaç Oluşturan Önemli Minerallerin Mikroskopta İncelenmesi
- FAO-UNESCO, 1988. Soil Map of the World 1:5 000 000. Volume V. Legend. UNESCO, Paris.
- FitzPatrick, E.A., 1975. Description and Preparation of Thin Sections for Soils. Üni. Of Aberdeen Handout Aberdeen
- Ghabru, S.K., Ghoss, S.K., 1983. Soil Mineralogy and Clay Mineral Formation in Low Hill Zone of Kangra, Himachal Pradesh. *International Journal of Tropical Agriculture* 1:4 285-298.
- Işık, F., 1994. Karadağ (Karaman) Civarının Jeolojisi Ve Mineralojik, Petrografik İncelemesi (Yüksek Lisans Tezi). *S.Ü. Fen Bilimleri Enstitüsü Jeoloji Müh. Ana Bilim Dalı* Konya.
- Jackson, M.L., 1979. Soil Chemical Analysis. Advanced Course. *Department of Soil Science University of Wisconsin*, Madison, Vis. 53706, 468-509
- Millot, G., 1970. Geology of Clays. *Springer-Verlag*. S : 84-133 Newyork.
- Moustakes, N.K., Georgoulias, F., 2005. Soils Developed on Volcanic Materials in the Island of Thera, Greece. *Geoderma* 129 125-138
- Parrfitt , R.L. , Kimble , J.M. , 1989. Conditions for Formation of Allophane in Soils. *Soc. Am. J.* 53.971-977.
- Poulenard, J., Podwojewski, P., Herbillon, A.J., 2003. Characteristics of Non Allophanic Andisols with Hydric Properties from the Ecuadorian Paramos. *Geoderma* 117, 267-281
- Sayın, M., 1985. Seyhan, Berdan Ve Göksu Ovaları Topraklarında Toplam Mineralojik Analiz Ve Kil Analiz Yöntemlerinin Karşılaştırılması. *TÜBİTAK Doğa Bilim Dergisi* D2 9. 3 S: 331-342.
- Soil Survey Laboratory Methods Manual 2004. United States Department of Agriculture Natural Resources Conservation Service, *Soil Survey Investigations Report* No. 42.
- Soil Survey Manual, 1993. Soil Survey Manual. *USDA Handbook* No 18
- Soil Survey Staff, 1999. Soil Taxonomy. A Basic System of Soil Classification For Making And Interpreting Soil Survey. *USDA Agriculture Handbook* No 436 Washington D.C.
- Tinsley, J., 1974. A Manual Experiments For Student of Soil Science, *Univ. of Aberdeen* S: 96-128.
- U.S. Salinity Lab. Staff, 1954. Diagnosis and Improvement of Saline and Alkali Soils. *Agricultural Handbook* No 60 USDA.
- Wada, K. 1985. Distinctive properties of Andosols. *Adv. Soil Sci*., **2**:173-229
- Wada, K., 1987. Minerals Formed and Mineral Formation from Volcanic Ash by Weathering. *Chemical Geology,* 60,17-28
- Wada, K., 1989. Allophane and Imogolite. in: Dixon, J.B., Weed, S.B. (Eds.), *Minerals in Soil Environment. Soil Sci. Soc. of America*, Madison, WI, Pp.1051-1087.