Bull. Min. Res. Exp. (2019) 158: 141-164

Bulletin of the Mineral Research and Exploration

http://bulletin.mta.gov.tr

Mineralogy, petrography and origin of hydrothermal alteration in Eocene magmatites in Central Anatolia (Sivas-Turkey)

Zeynel BAŞIBÜYÜK[a*] and Hüseyin YALÇIN[b]

[a] *Ahi Evran Üniversitesi Mühendislik Mimarlık Fakültesi Jeoloji Mühendisliği Bölümü Kırşehir, orcid.org/0000-0003-2845-148X*
[b] *Cumhuriyet Üniversitesi Mühendislik Fakültesi Jeoloji Mühendisliği Bölümü Sivas, orcid.org/0000-0001-9539-281*

Research Article

Keywords:
Alteration zones and types, plutonic, volcanic, XRD, SEM.

Received Date: 16.11.2017
Accepted Date: 04.02.2018

ABSTRACT

Three different types of hydrothermal alterations have occurred in the Eocene magmatics of the northern part of Sivas-Turkey which include propylitic phyllic / sericitic and argillic. Hydrothermal alteration affected both Karataş volcanites and Kösedağ syenite. The clay formations are concentrated in two major zones; extending in NE-SW direction and intersecting both plutonic and volcanic rocks with circular opening cracks within the volcanics parallel to the plutonic-volcanic contact. Hypogene and supergene hydrothermal alteration products occurring on surface and/or near surface conditions represent the primary and secondary minerals that develop directly and mostly from feldspars with the mechanisms of neoformation and/or degradation. The hypogene minerals are formed in two stages of early (kaolinite, pyrophyllite, illite, I-S (illite-smectite), smectite, quartz and opal-CT) and late (barite, ore minerals, alunite, goyazite, jarosite, chlorite and C-S). Tourmaline, epidote and carbonates (calcite, dolomite, azurite and malachite) are considered as metasomatic and supergeneous minerals, respectively. The most common mineral paragenesis are kaolinite + quartz + goethite + goyazite or alunite, kaolinite + quartz + jarosite + feldspar ± goethite and/or goyazite in the argillic alteration zone, I-S + quartz + jarosite ± goethite ± feldspar as well as I-S + quartz + feldspar minerals in the sericitic alteration zone. Kaolinite (T) is mostly in the form of pseudohexagonal platies, I-S (R1, R3 as argillic alteration origins, $1M_d$, 2M1, 1M and R3 as sericitic alteration origins) forming fiber-acicular bundles parallel to each other.

1. Introduction

The reason why hydrothermal alterations that occur in magmatic rocks are important is not only for their scientific meaning but also the fact that they form important clay deposits that can be used as industrial raw materials. In the study area, there is a wide range of hydrothermal alteration zone (propylitic, phyllic/sericitic and argillic) that affects both Karataş volcanites and Kösedağ syenite. The argillic alteration zone contains kaolinite formations, which is an industrial raw material with a wide range of applications in the industry. In addition to the hydrothermal alteration of kaolinite, it can also form important deposits in sedimentary formations (Murray and Smith, 1973; Murray, 1988; Murray and Keller, 1993; Domínguez and Murray, 1995; 1997; Karakaya et al., 2001; Arslan et al., 2006; Cravero et al., 2010; Yıldız and Başaran, 2015; Ariana et al., 2016; Ünal Ercan et al., 2016). Turkey has many kaolinite deposits formed as a result of hydrothermal alteration (Gençoğlu et al., 1989; Yalçın, 1991; Şener and Gevrek, 2000; Karakaya-Çelik et al., 2001; Yalçın and Bozkaya, 2003; Ece and Nakagawa, 2003; Ece et al., 2003; Ece and Schroeder, 2007; Ece et al., 2008; Kadir and Akbulut, 2009; Kadir et al., 2011, 2014; Acarlıoğlu et al., 2013; Ece et al., 20013; Kadir and Erkoyun, 2013).The kaolinite formations in the study area show differences from sedimantary and metamorphic rocks-hosted other formations with respect to hydrotermal alteration variety and whole rock and clay mineral assemblages.

---

* *Corresponding author: Zeynel BAŞIBÜYÜK, zbasibuyuk@ahievran.edu.tr*
http://dx.doi.org/10.19111/bulletinofmre.461255

In order to better understand the mechanism of the hydrothermal alteration of the Eocene magmatics in the Sivas basin, it is necessary to look at the geological evolution of Anatolia and hence the area studied. The Central Anatolian region in which the study area is located consists of continental blocks separated from each other by ophiolitic suture zones. These tectonic belts are, from the north to the south, Pontide Continent, Intra-Pontide Suture, Sakarya Continent, Ankara-Yozgat-Erzincan Suture (Central Anatolian Metamorphites) and the Kırşehir Continent (Central Anatolian Metamorphics) (Figure 1), and the continental blocks developed as a result of Pan-African, Hercynian and Cimmerian orogenies and remained as the continental basement during the Neo-Tethyan evolution (Tüysüz, 1993).

The Neo-Tethys Ocean was opened by rifting of these continental bases along two lines in Lias, so that the Intra-Pontide and Ankara-Yozgat-Erzincan Ocean branches developed (Şengör and Yılmaz, 1981). At the beginning of the Late Cretaceous, a subduction started along the entire Pontide belt (Şengör and Yılmaz, 1981); in other words, the northern branch

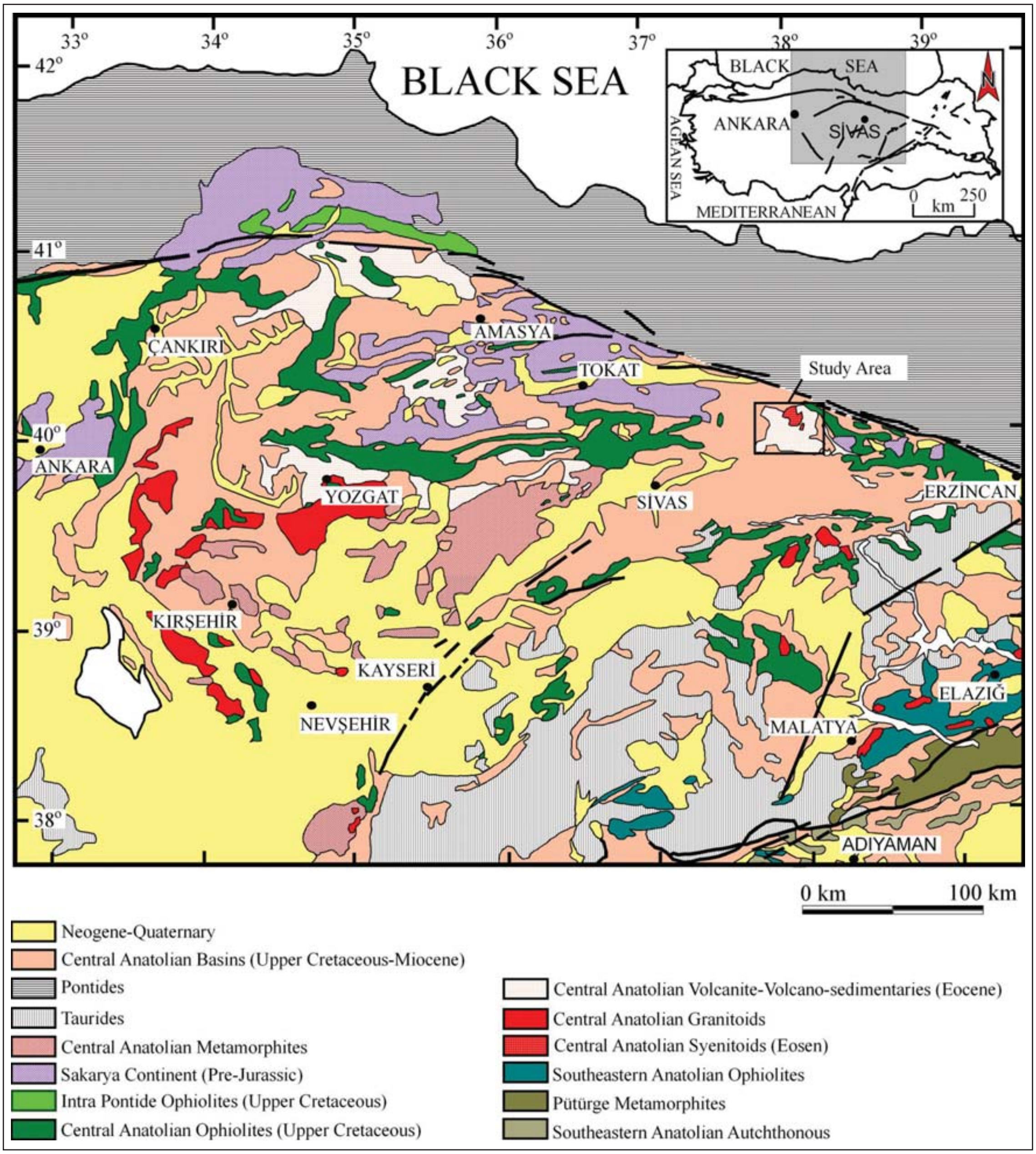

Figure 1- The regional geological map of the study area (Bingöl, 1989; Tüysüz, 1993; Göncüoğlu et al., 1997; Görür et al., 1998).

of Neo-Tethys began to subduct under the Pontide. During this period, the greatest ophiolitic nappes including Refahiye Complex, which is the oldest unit of the study area, was settled on Anatolide-Tauride continent (Şengör and Yılmaz, 1981, Göncüoğlu et al., 1997). In the Paleocene-Early Eocene, the northern branch of the Neo-Tethys was completely closed and the continent-continent collision (Şengör and Yılmaz, 1981) took place.

After the continent-continent collision, while the cold and high density oceanic crust is subducing into the asthenosphere producing a great force downward, the continental crust showed resistance to subduction and produce a stress effect in the bending zone (the subducting lithosphere and continental crust merging zone) (Davies and Blanckenburg, 1995). As a result, a thin opening occurred at the region where tension was effective, and the asthenosphere ascended into this opening, which continued until the oceanic crust had completely detached (Kusznir and Park, 1987, Davies and Blanckenburg, 1995). When previous researchers explain the geodynamic evolution of the study area and its immediate surroundings (Boztuğ and Jonckheere, 2007; Boztuğ et al., 2007), they claim that this phenomenon has created extensional tectonics in the region and caused horst and graben formation in the continental crust, lastly the Middle-Late basin was developed as a result of this. In the Middle-Late Eocene volcanism (Karataş volcanites) is derived from upper mantle at the syn- and/or post-collision and mostly contaminated by upper mantle continental crust and Kösedağ volcanites which is related with extensional regime and belong to same magmatic sequence of events with hot-hot contact. During the settlement of Kösedağ syenite, extensive hydrothermal alterations occurred in both plutonic and volcanic rocks that it intruded.

2. Geology

The Upper Cretaceous-Paleocene aged Refahiye complex composed of peridotite and serpentinites (Figure 2) is the oldest unit in the region (Yılmaz

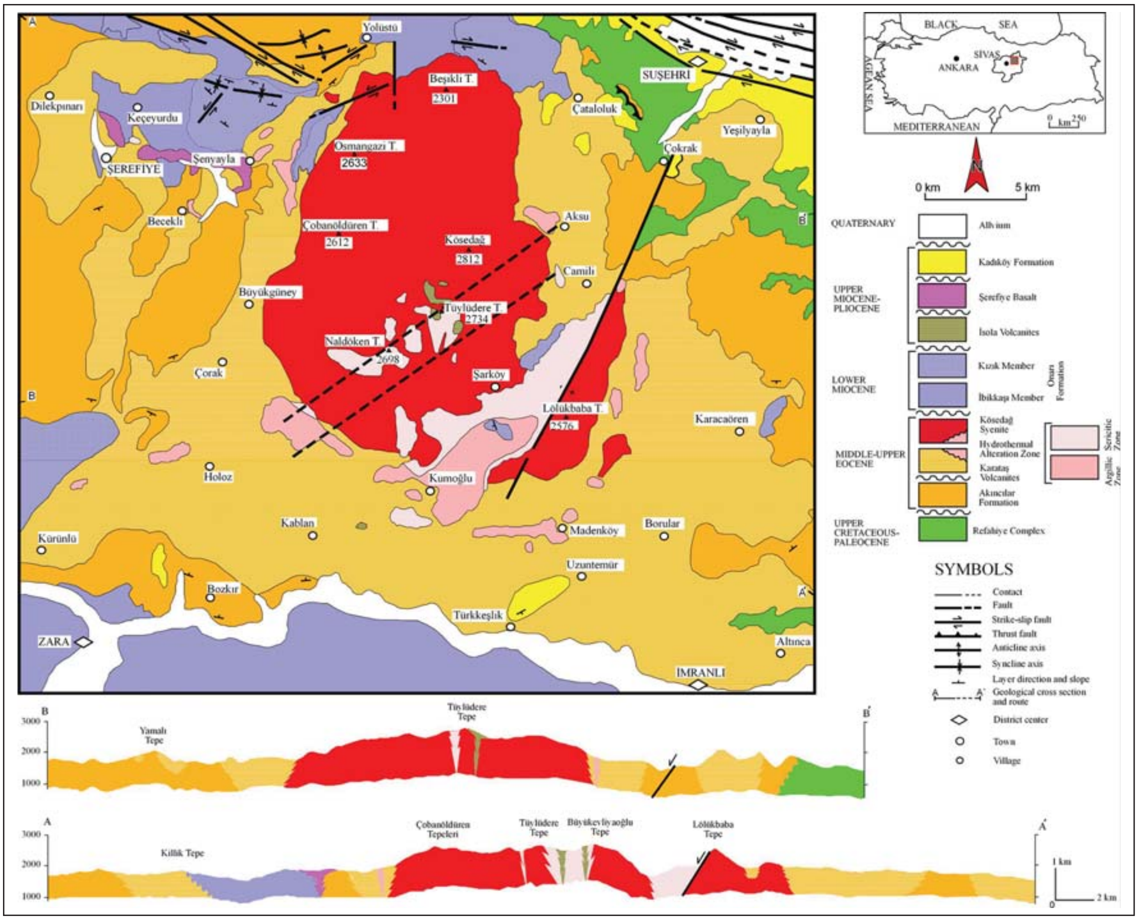

Figure 2- Geological map of the study area (Kalkancı, 1974; Yılmaz et al., 1985; Uysal et al., 1995; Başıbüyük, 2006).

et al., 1985). The Eocene magmatism in which the hydrothermal alteration occurred begins with Akıncılar formation with pyroclastic products. It continues with basaltic-trachytic lava flows belonging to Karataş volcanites, and ends up with Kösedağ syenite in shallow depths with hot-hot contact relation with alkaline feldspar syenite, syenite and quartz alkaline feldspar syenite, and partly monzonitic composition.

Plutonics with alkaline character, large scale upper continental crustal contamination and fractional crystallization of the upper mantle material, representing syn- or post-collisional plate magmatism, were found as 42 ± 4 m.a. for quartz syenite and 37 ± 2.6 m.a. for pegmatitic biotite syenite by previous researchers by analyzing Rb-Sr age determination (Kalkancı, 1974, 1978). The evaporation age of Kösedağ Syenite is determined with single zircon ^{207}Pb/^{206}Pb method as 52.1 ± 6.4 m.a. (Boztuğ et al., 2007). Hydrothermal alteration affected only Karataş volcanites and Kösedağ syenite. The age of the alteration was found to be 38.0 ± 0.9 million years with K/Ar radiometric dating from the alunite mineral (Başıbüyük, 2006). The clay formations are concentrated in two major zones. One of them is circle-shaped extending fractures in volcanics which are parallel to plutonic-volcanic contact. The second one is the zone that intersecting both NE-SW trending plutonics and volcanics. The age of alteration and the situation of the zones suggest that the alteration has occurred in the pegmatitic phase of the plutonic intrusion. Three types of hydrothermal alteration, propylitic, phyllic/serizitic and argillic, were distinguished in Kösedağ syenite and Karataş volcanites (Başıbüyük et al., 2007). Hydrothermal alteration levels are usually observed in zones of several km^2 (up to 30 km^2).

3. Material and Methods

376 samples were taken from the field studies in order to determine mineralogy of the alteration. 337 samples which are prepared in Cumhuriyet University Geological Engineering Department Thin Section Laboratory are studied to determine the rock-forming components and their textural features. 3 samples from altered levels are studied in Scanning Electron Microscope in Turkish Petroleum Cooperation in order to specify their textural relations and origin of clay minerals.

X-ray diffraction (XRD) analyzes were carried out with Rigaku DMAX IIIC model X-ray diffractometer to determine the polymorphic changes in the minerals and whole rock mineralogical compositions and clay size components of the submicroscopic rocks so small that they could not be studied with Optical microscope (OM) (XRD-TK: 356 samples, XRD-KF 283 samples). The whole rock and clay-size components (<2 mm) of the samples are defined with these analyzes and the semi-quantitative percentages are calculated based on the external standard method (Brindley, 1980). When determining the polytypes of pure or near pure kaolinite, illite, chlorite and pyrophyllite minerals, the identifier peaks which are suggested by Bailey (1980, 1988) and Fawcett et al. (1989) are used (kaolinite 4, chlorite 3, illite 2, pyrophyllite 1 sample). An alunite sample formed in the argillic alteration zone for K-Ar dating, with the aim of determining the age of the hydrothermal alteration, is analyzed in Activation Laboratories Ltd. (Actlabs) in Canada.

4. Research and Findings

4.1. Field Observations

4.1.1. Propylitic Alteration

Its distribution is very small and developed only in a few-meter zone within the volcanics at the plutonic-volcanic contact (Figure 3a). The plutonic rocks are observed in pinky skin colour, and they have very fine grain and holocrystalline texture, and the volcanic rocks are found in grayish light green with porphyritic texture.

4.1.2. Sericitic (Phyllic) Alteration

Such alterations have been extensively developed in Kösedağ syenite and rarely in Karataş volcanites. Its spread in the volcanics is not very much and observed as telescoping levels in the argillic alteration (Figure 3b). The outer appearance of the altered zones is light greenish yellowish color, soft and crumbly, and their thickness reaches up to 10 m.

Serizitic alteration has a very wide spread in syenites. It is characterized by a white-yellow-light brown appearance (Figure 3c). Sericitic alterations in the syenites includes NE-SW trending parallel barites with 0.15-1 m thick, light gray and black colored tourmaline veins rarely intersecting each others with 0.05-20 cm thick, yellowish red colored Fe-oxide coating levels, and orange-red colored oxidations (goethite) and sulphatization (jarosite) which are developed through fractures (Figure 3d).

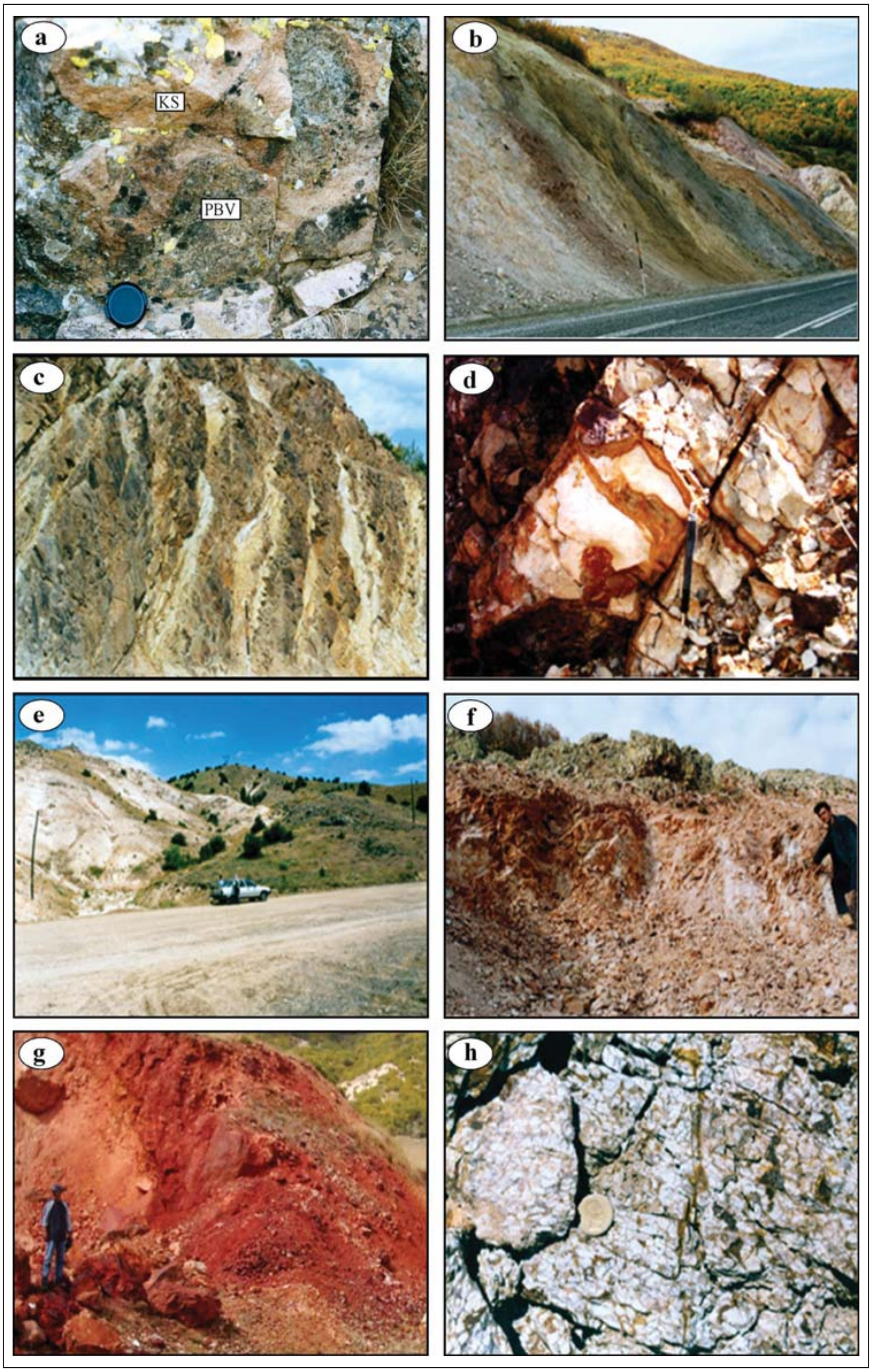

Figure 3- Field photographs of different hydrothermal alterations in the study area, a) Volcanic-plutonic contact in which propylitic alteration developed (KS=Kösedağ syenite, PBV=Propylitic altered volcanics), b) White argillic and green-yellow sericitic alteration zones within the volcanics, c) Lİght Brown-yellow sericitic alteration zone within the syenites, d) Oxidation (goethite) and sulphatization (jarosite) types of alterations developed within the cracks of sericitic alteration zones from syenites, e) Argillic alteration-volcanic contact observed within the Karataş volcanites, f) Silica hat observed at the upper part of argillic alteration in the volcanics, g) White argillic and green-yellow sericitic alteration zones within the volcanics, h) Argillic alteration with relic porphyritic texture in the volcanics.

4.1.3. Argillic Alteration

It is the most widespread and widest alteration zone in the region. It is usually observed in volcanics (Figure 3e); In syenites it is very small in amount and it is found in the sericitic alteration zone. Considering the topographic distributions, brecciated silica flats (Figure 3f) and iron oxides (Figure 3g) are represented in the upper sections with kaolinitic levels below this zone. They are not differentiated with clear boundaries. In some of these, rich levels of alunitic other clay minerals (illite, I-S and smectite) are in the form of telescoping zones.

In the field its yellowish-white appearance is characteristic. The kaolinites in the alteration zone is dominant and contain mostly cracks and fracture planes originating from the primary rock, and Fe-oxides are observed on the surfaces in very thin plasters. In argillic alteration which is developed from porhyritic textured volcanic rocks, porphyritic texture is not dissapeared. Feldspar phenocrystals turned into white color and matrix is turned into light brown kaolinite minerals (Figure 3h). In altered levels rarely 1-2 m wide unaltered rough and nodular levels which belong to primary rock are found.

4.2. Optical Microscopic Studies

4.2.1. Propylitic Alteration

It has been observed that biotitization, chloritization, sericitization, opacification (pyrite), carbonatization, epidotization and Fe-oxidation types of alteration develop in the microfractures and matrix of the propylitic altered andesites and also within the fine-grained matrix (Figure 4a-b).

4.2.2. Sericitic (Phyllic) Alteration

As a result of OM analysis coarse grained fibrous calcedonic quartz, very fine grained muscovite (illite, I-S) and in little quantity barite, tourmaline, kaolinite, smectite, chlorite, jarosite, goethite, pyrite and topaz minerals are defined in sericitic alteration zone of syenites.

In feldspar minerals, completely sericitization (sometimes coarse ~ 100 µm), argillization, rarely kaolinization, and silicification (fine-coarse-grained quartz) are observed (Figure 4c-d). As for mafic minerals, they are entirely iron oxidized within the microfractures in brecciated levels are observed to be filled with iron oxide formations (hematite, goethite) and brown-greenish jarosite.

4.2.3. Argillic Alteration

OM investigations have identified the silisic, alunitic and oxydic subzones as intergrown levels within this alteration zone. Quartz, goethite, goyazite, alunite, hematite, pyrite, jarosite, opal-CT, barite and other clay minerals are also accompanied by varying abundances of kaolinite in these parts. In the totally altered volcanic rocks, the initial porphyritic texture has not completely disappeared and can be observed as a residue (Figure 4e-f).

Feldspars can only be identified from their shapes in completely kaolinitized specimens. In addition, microlites accompanying Fe-oxidation in the matrix appear to be completely transformed into kaolinite minerals (Figure 4g). The kaolinite booklets that replace feldspar phenocrysts can be easily recognized in the optical microscope with cross polarized light by first serie colours of interference and shapes. The kaolinite minerals developed from the feldspar minerals are observed to be overlaid as large booklets reaching 50-100 µm in size (Fig. 4h). Only 4 samples of pyrophyllite minerals were identified from the altered parts; they are usually fine-grained and developed from the matrix. Pyrophyllites with yellowish-gray interference colors are accompanied by clusters of kaolinite minerals.

4.3. XRD Studies

4.1.2. Sericitic (Phyllic) Alteration

Feldspar, quartz, clay, biotite, hematite, jarosite, goethite, tourmaline, goyazite, hornblende, pyroxene, pyrite, calcite, dolomite and barite minerals were determined as the result of the XRD-WR analyzes of samples taken from altered plutonic rocks (Figure 5) In clay mineral content increasing samples, the amount of quartz mineral is also increasing. The most common mineral paragenesis is clay + quartz + jarosit ± goethite ± feldspar and clay + quartz + feldspar.

The common clay mineral paragenesis in the sericitic alteration zone are composed of I-S + chlorite, illite + I-S + chlorite + C-S, pure I-S, I-S + kaolinite and illite + smectite + kaolinite associations (Figure 6).

The illite or smectite ratio (Moore and Reynolds, 1997) in the I-S from the most common clay minerals

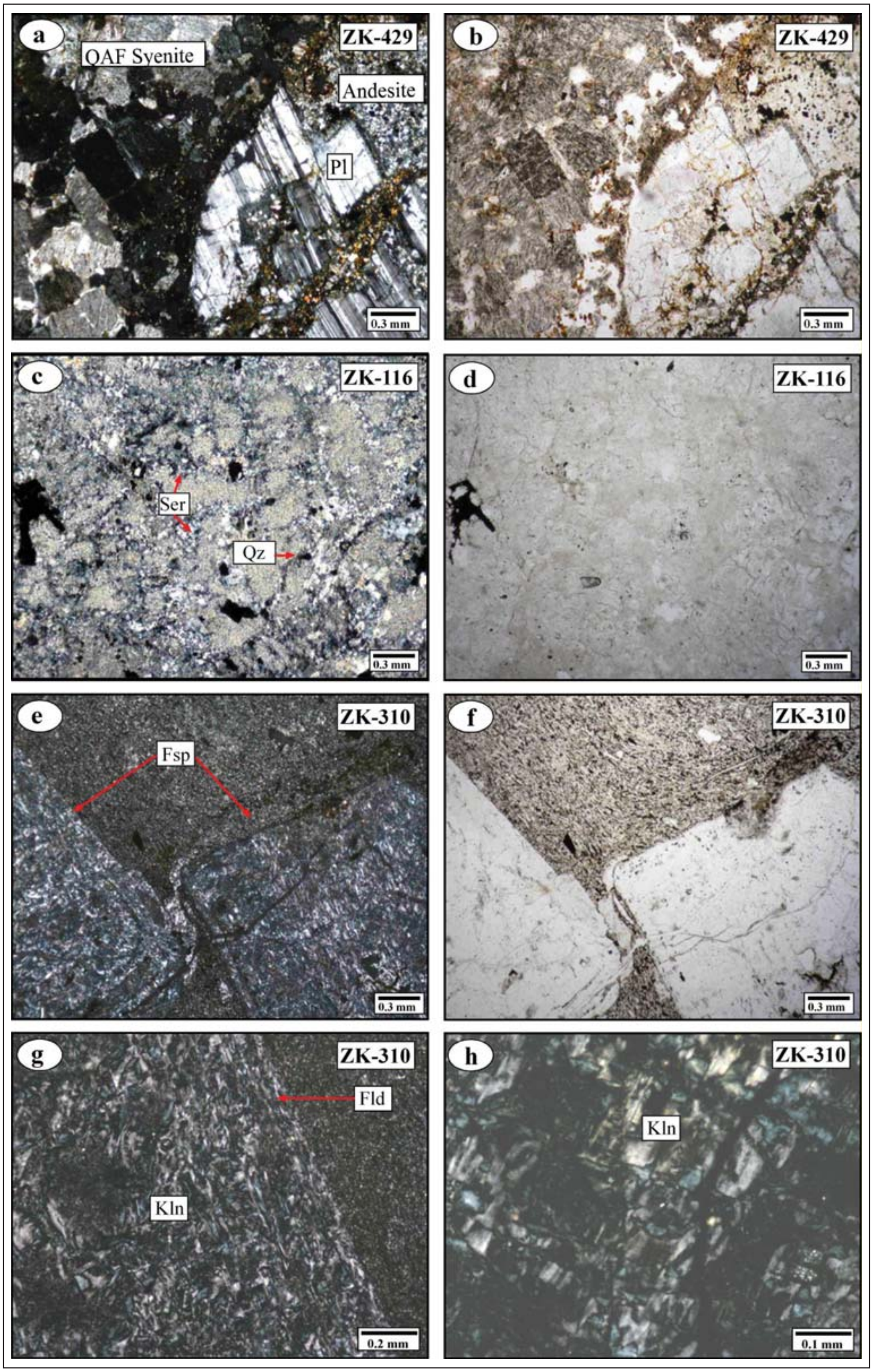

Figure 4- Thin-section images of the propylitic, sericitic/phyllic and argillic alteration zones in the study area (a-c-e=crossed polarized light, b-d-f=plane polarized light), a-b) Epidotization and Fe-oxidation in the propylitic altered volcanics within the Kösedağ syenite-Karataş volcanites contact (Pl=Plagioclase, QAF=Quartz alkali feldspar), c-d) Completely sericitization in feldspars and fine-grained quartzs in the sericitic/phyllic alteration zone within the Kösedağ syenite, (Ser=Sericite, Qz=Quartz), e-f-g-h) Relic porphyritic texture, completely kaolinitization in feldspar and matrix in the argillic alteration zone within the Karataş volcanites, (Fsp=Feldspar, Kln=Kaolinite).

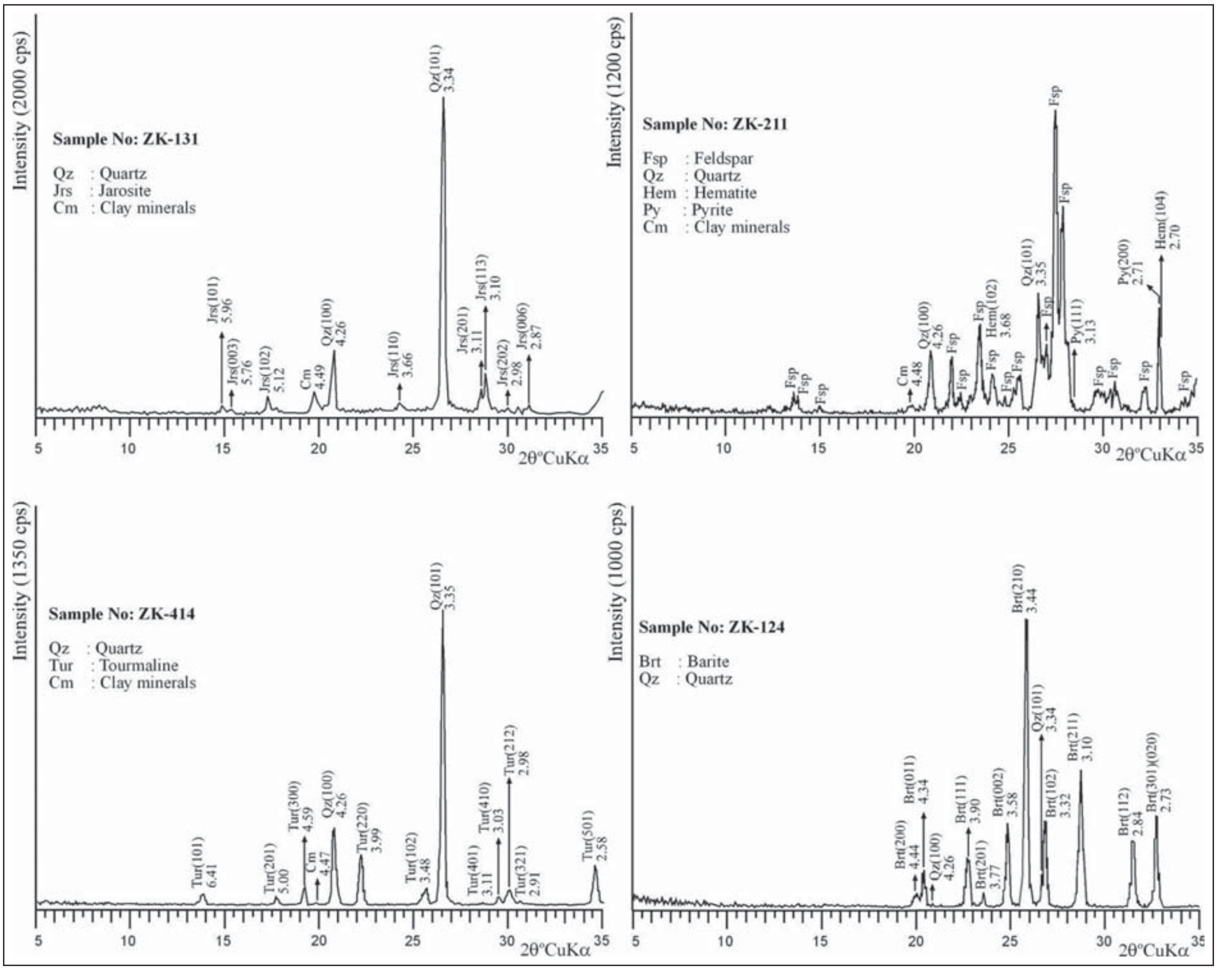

Figure 5- XRD-WR diffractograms of samples in the sericitic alteration zones in the study area..

in this alteration zone was calculated in 24 samples with illite content ranging from 84 to 95 % (smectite content 5 to 16 %), type of arrangement is observed as R=3 (Başıbüyük et al., 2010). In addition, it was determined that I-S had dioctahedral composition as a result of $d_{(060)}$ measurements of 11 pure or near-pure samples (Table 1).

As a result of the analysis of two polytype samples which prepared from pure I-S with illite high component, the illite in the I-S mineral is determined as type of 1Md+2M1+1M. In the XRD diffractogram of illite polytypes given in figure 7 as d (A˚) peaks, 3.88, 3.73, 3.49, 3.20, 2.98, 2.86, 2.79 and 2.58 peaks for 2M1; 4.34, 3.64, 3.07, 2.91 and 2.68 peaks for 1M, and the humpback between 2θ° 22-34 for 1Md are distictive.

It was observed that the $d_{(060)}$ measurement from one smectite and two C-S samples in the alteration zone had dioctahedral and trioctahedral compositions, respectively (Table 2). The chlorite content in C-S is in the range of 50-52 % (smectite content 48-50 %) and the arrangement type is determined as R=1.

4.3.2. Argillic Alteration

According to the order of abundance, quartz, goyazite, goethite, feldspar, alunite, jarosite, hematite, pyrite, calcite, opal-cristobalite/trydimite, biotite, dolomite, tourmaline and barite are determined by XRD-WR investigations, from samples taken from the argillic alteration zone.

The most common paragenesis minerals are formed of clay + quartz + goethite + goyazite, clay + quartz + alunite + goethite and clay + quartz + jarosite + feldspar + goethite and/or goyazite (Figure 8). Carbonate minerals (calcite and dolomite) are less likely to be found in high alteration grade, and opal-

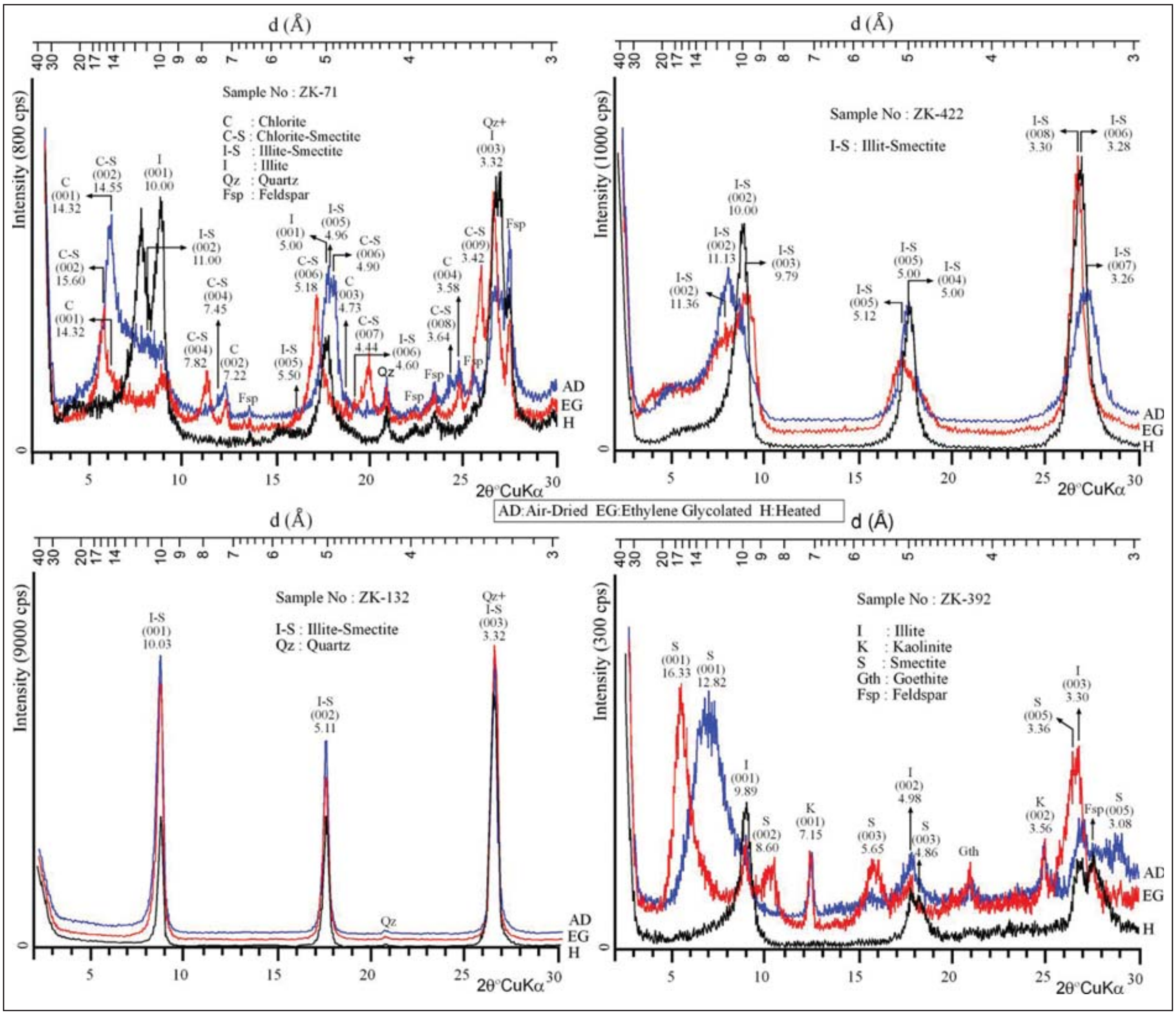

Figure 6- XRD-CF diffractograms of samples in the sericitic/phyllic alteration zones in the study area.

CT and barite are rarely present in the totally altered rocks.

As a result of the XRD analyzes of the samples taken from the alteration zone, it was observed that the clay fraction is consisted of kaolinite, I-S, smectite, illite, C-S, chlorite and pyrophyllite minerals (Figure 9). In the samples taken from the argillic alteration zone, kaolinite is very common and in most cases clay fractions are formed alone, whereas chlorite and C-S minerals are very common in rocks with less aleration. In this alteration zone only C-V mineral was observed in one specimen. The most common clay mineral associations in the altered samples are kaolinite + smectite + I-S ± illite, kaolinite + smectite and kaolinite + I-S ± illite, and pyrophyllite accompanies kaolinite in five samples.

The most common clay mineral in the alteration zone is kaolinite. It is found in 197 of 218 samples. 95 of them are clay fraction alone. As a result of polytype investigations made from four kaolinite samples, it was determined that all of them were T (triclinic)-type (Collins and Catlow, 1991) (Figure 10). Unlike monoclinic types (Toraya et al., 1980), d (A °), which is distinctive for T-polytype; 2.75, 2.34, 2.19, 1.99, 1.84 and 1.54 peaks were determined. Crystallinity measurements are performed from unoriented 7 samples (Hinckley, 1963). Hinckley Crystallization Index values were determined as 3 kaolinite samples (Sayın, 1987) with an index value between 1.30 and 1.0 as medium and lower than 1.0 as poorly crystallized (Table 3).

Another clay mineral, I-S, which is commonly observed in the zone of the argillic alteration zone, is

Table 1- The $d_{(060)}$ values and illite or smectite ratio and ordering type of the I-S minerals in the sericitic alteration zones of Kösedağ syenite.

Sample no	$d_{(060)}$ Å	Description	I %	S %	Type of ordering
ZK-52	1.498	Dioctahedral	88	12	R=3
ZK-63			93	07	R=3
ZK-64			93	07	R=3
ZK-116	1.495	Dioctahedral	92	08	R=3
ZK-117	1.497	Dioctahedral	86	14	R=3
ZK-118	1.497	Dioctahedral	90	10	R=3
ZK-122	1.497	Dioctahedral	88	12	R=3
ZK-125	1.498	Dioctahedral	84	16	R=3
ZK-126	1.498	Dioctahedral	84	16	R=3
ZK-131	1.497	Dioctahedral	85	15	R=3
ZK-132			93	07	R=3
ZK-133			94	06	R=3
ZK-136	1.498	Dioctahedral	90	10	R=3
ZK-212			92	08	R=3
ZK-334			94	06	R=3
ZK-387			94	06	R=3
ZK-390			94	06	R=3
ZK-394			92	08	R=3
ZK-395			92	08	R=3
ZK-396			92	08	R=3
ZK-397			87	13	R=3
ZK-412			95	05	R=3
ZK-416	1.494	Dioctahedral	84	16	R=3
ZK-422	1.496	Dioctahedral	86	14	R=3

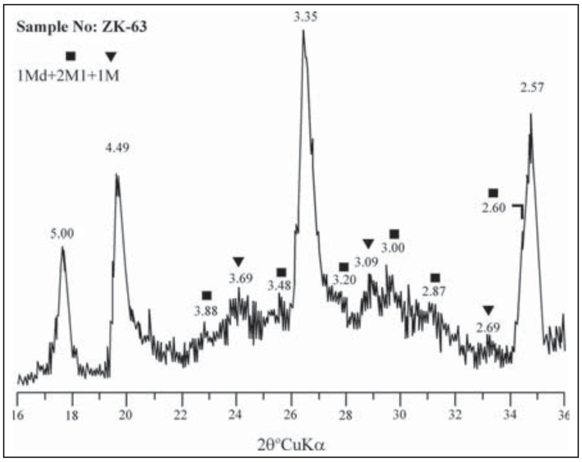

Figure 7- XRD diffractogram of illite polytypes in the sericitic alteration samples.

found in about one third of the samples and is usually observed together with kaolinite, smectite and illite. The illite or smectite ratio (Moore and Reynolds, 1997) in I-S, which was determined to have dioctahedral composition as a result of $d_{(060)}$ measurements made from 6 samples, was calculated for 21 altered volcanic rocks (illite content 54-91 %, smectite content 9-46). Arrangement types are determined as R=1 in 17 samples, R=3 in 4 samples (Table 4). The percentage of illites vary from 54 to 88 % in the case of the R=1 arrangement type, and from 84 to 91 % in the case of the R=3 arrangement type. In other words, as the degree of ordering increases the amount of illite increases.

Table 2- The $d_{(060)}$ values and chlorite or smectite ratio and ordering type of the smectite and C-S minerals in the sericitic alteration zones of Kösedağ syenite.

Sample no	Rock type	Mineral	$d_{(060)}$ Å	Description	C %	S %	Type of ordering
ZK-392	Altered quartz alkaline feldspar syenite	Smectite	1.497	Dioctahedral	0	100	
ZK-57	Quartz alkaline feldspar syenite	C-S	1.543	Trioctahedral	50	50	R=1
ZK-388	Altered granite	C-S			52	48	R=1

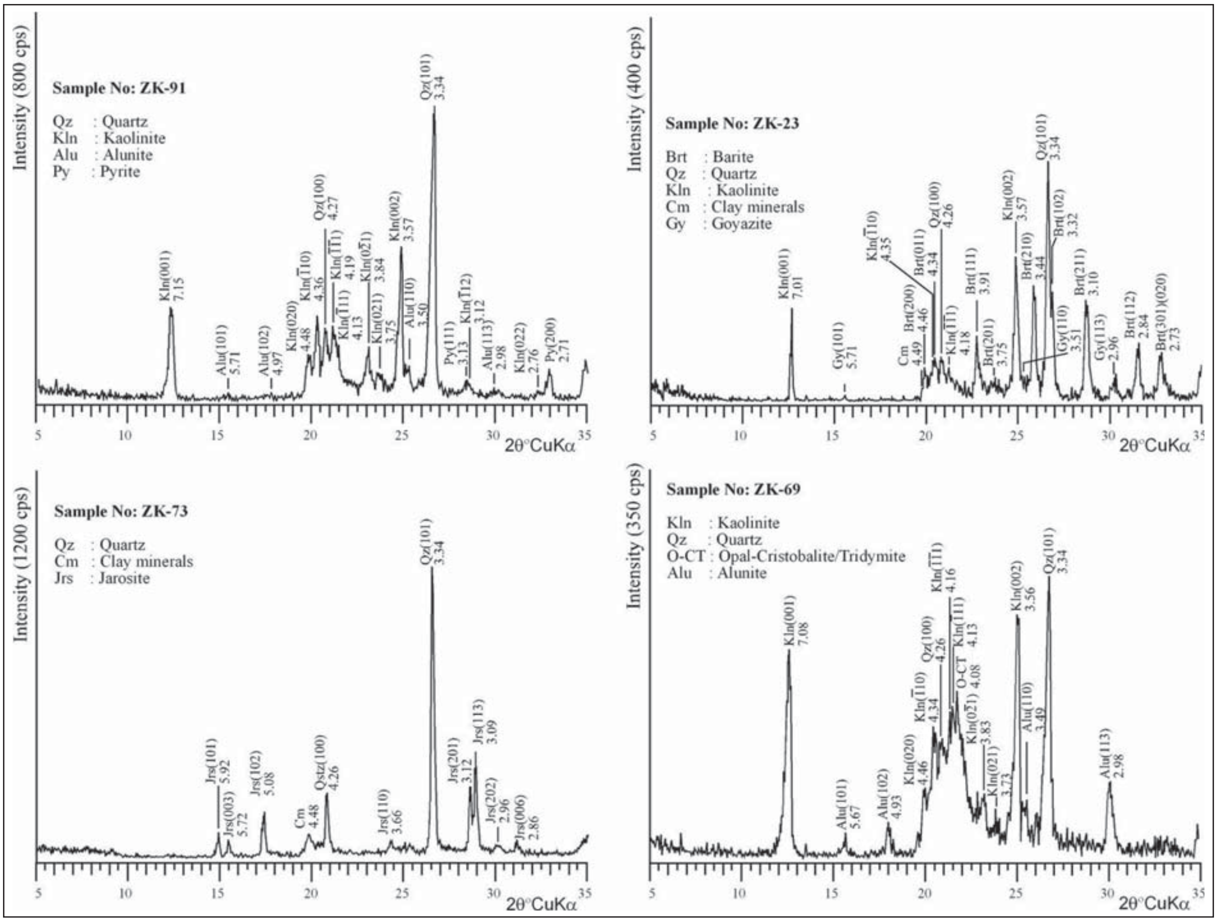

Figure 8- XRD-WR diffractograms of the argillic alteration zones in the study area.

The smectites in the alteration zone were found to have dioctahedral character as a result of $d_{(060)}$ measurements, and the illite content varied between 0 and 7 % (Table 5). The percentage chlorite and smectite content of C-S in this zone are calculated by using 3 samples. Its chlorite content is determined as 48-59 %, smectite content is found to be 2θ° 41-52. Arrangement type is determined as R=1 (Moore and Reynolds, 1997).

As a result of the $d_{(060)}$ measurements made on the two samples, it was found that C-S had trioctahedral composition (Table 6). The chlorite content of the C-S minerals in the andesites, which have not been too much altered, are higher than those of altered ones

Chlorites are one of the least observed clay minerals in the alteration zone, but they are present in 9 samples and are usually observed in less altered volcanics. They are mostly found with C-S and illite. However, kaolinite in two samples, smectite and I-S in three samples are accompanied by this mineral. The unit-cell compositions of the chlorites in the altered andesite samples, calculated from XRD data (Brown and Brindley, 1980; Chagnon and Desjardins, 1991), are given in table 7 and named as brunsvigite (Foster, 1962), (Figure 11). As a result of the polymorphism analysis of one sample, it was determined that chlorite has IIb polytope (Figure 12).

Pyrophyllite mineral is the least found clay mineral in the argillic alteration zone. It asociated with kaolinite and it formed of 57-71 % in three samples and 8-9 % in two samples of clay fractions. As a result of the polytype studies (Brindley and Wardle, 1970), d (A°); 3.76, 3.49, 3.17, 2.95, 2.75, 2.54, 2.34 and 1.89 peaks were observed. So it is differentiated from monoclinic-type and concluded that it has 1Tc polytype (Figure 13).

4.4. SEM Studies

Scanning electron microscope (SEM) studies were carried out involving Energy-dispersive X-ray

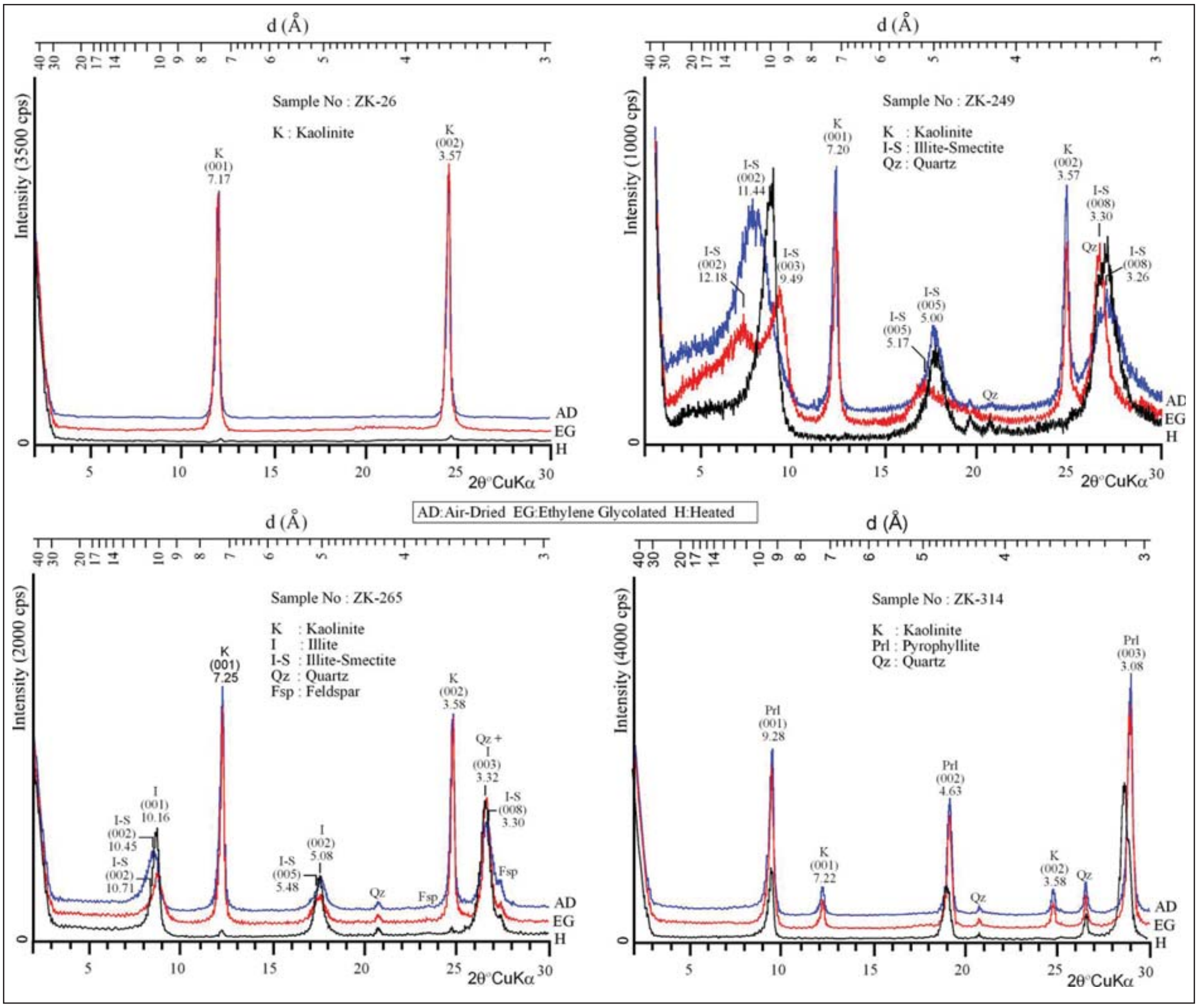

Figure 9- XRD-CF diffractograms of the argillic alteration zones in the study area.

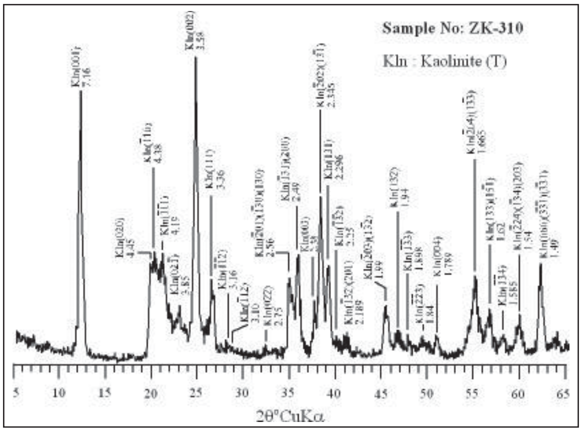

Figure 10- XRD diffractogram of kaolinite polytype in the argillic alteration zone of altered volcanic rocks.

spectroscopy (EDS) from three samples (ZK-169, ZK-314B, ZK-325) in the argillic alteration zone.

In the altered volcanic rock sample (ZK-169), I-S minerals are seen besides the anhedral kaolinite plates (Figure 14a). I-S minerals form fibrous-acicular bundles with 1 to 5 μm length which are partly parallel to each others. Jarosites often form single, rarely combined crystals. Trigonal-rombohedral jarosites with approximately equal dimension are similar to hexahedra and 1-2 μm in size (Figure 14b). The EDS spectra of the matrix of this example rich in jarosite and I-S show that semi-quantitative chemical composition on the anhydrous oxygen base varies between (%) Si 69.48-11.12, K 4.00-9.23 and Fe 26.52-79.65. These elements reflect the mineralogical composition of the rock, in other words to a large extent, a mixture of quartz, jarosite and Fe-oxide/hydroxide.

Table 3- Hinckley Crystallization Index values of kaolinite minerals in altered samples of Karataş volcanites.

Sample no	ZK-25	ZK-26	ZK-27	ZK-36	ZK-42/B	ZK-42/C	ZK-310
Hinckley K.İ.D.	1.10	1.22	0.71	0.96	1.15	0.78	0.73

Table 4- The $d_{(060)}$ values, illite or smectite ratio and ordering type of I-S minerals in the altered samples of the argillic alteration zones of Karataş volcanites.

Sample no	d(060) Å	Description	% I	% S	Type of ordering
ZK-41			61	39	R=1
ZK-50			76	24	R=1
ZK-73			67	33	R=1
ZK-74	1.500	Dioctahedral	84	16	R=3
ZK-75	1.495	Dioctahedral	69	31	R=1
ZK-149	1.494	Dioctahedral	88	12	R=1
ZK-159	1.500	Dioctahedral	84	16	R=3
ZK-161	1.496	Dioctahedral	74	26	R=1
ZK-223			64	36	R=1
ZK-225			67	33	R=1
ZK-227			54	46	R=1
ZK-228			61	39	R=1
ZK-229			74	26	R=1
ZK-233			78	22	R=1
ZK-234			74	26	R=1
ZK-249	1.497	Dioctahedral	74	26	R=1
ZK-258			91	09	R=3
ZK-265			91	09	R=3
ZK-283			76	24	R=1
ZK-322			66	34	R=1
ZK-377			70	30	R=1

Table 5- The $d_{(060)}$ values of the smectites in the altered samples in the argillic alteration zones of Karataş volcanites.

Sample no	d(060) Å	Description	I %	S %
ZK-177	1.501	Dioctahedral	7	93
ZK-188	1.500	Dioctahedral	2	98
ZK-297	1.499	Dioctahedral	2	98
ZK-329	1.494	Dioctahedral	0	100
ZK-359	1.491	Dioctahedral	0	100
ZK-410	1.500	Dioctahedral	2	98
ZK-417	1.496	Dioctahedral	0	100

In the SEM examinations of the altered volcanic sample (ZK-314B) consisting of clay (pyrophyllite and kaolinite), quartz and goyazite, platy pyrophyllite-kaolinite sheets are observed (Figure 14c). These minerals do not have typical morphologies and stacked up on top of each others; pyrophyllite is thicker and has angular edges, whereas kaolinite is composed of thinner and bended lamellas. The thickness of pyrophyllite ranges from 0.2 to 0.5 μm and the length varies from 3 to 5 μm. The morphological

Table 6- The $d_{(060)}$ values, illite or smectite ratio and ordering type of C-S minerals in the altered samples of the argillic alteration zones of Karataş volcanites.

Sample no	Rock type	$d_{(060)}$ Å	Description	C %	S %	Type of ordering
ZK-82	Andesite	1.538	Trioctahedral	59	41	R=1
ZK-172	Altered andesite	1.529	Trioctahedral	48	52	R=1
ZK-383	Alterered volcanic			52	48	R=1

Table 7- (002)/(001) and (004)/(003) peak intensity ratios and the octahedral Fe contents in the talc and brucite sheets of the chlorites in the argillic alteration zones of Karataş volcanites (B&B=Brown and Brindley, 1980; C&D=Chagnon and Desjardins, 1991).

Sample	$d_{(001)}$	Al^{IV}	(003)/ (001)	002+004/ 001+003	(002)/ (001)	(004)/ (003)	Fe^{+2} Talc		Fe^{+2} Brusite		SFe^{+2}			Mg
							B&B	C&D	B&B	C&D	B&B	C&D	Ort.	
ZK-258	14.25	1.04	1.00	2.36	2.68	2.04	2.3	1.3	1.9	1.1	4.2	2.4	3.3	1.66
ZK-259	14.23	1.10	0.86	2.32	2.54	2.07	2.2	1.3	1.9	1.1	4.1	2.4	3.3	1.60

characteristics of pyrophyllite are similar to the occurrences from hydrothermal alteration of volcanic material in Japan (Sudo et al., 1981); however, it differs from those of Pütürge (Malatya) in that it is smaller in size than the pyrophyllites formed by the hydrothermal alteration of the kyanites (Bozkaya et al., 2007).

In addition, pyrophyllite-kaolinite plates were observed, enclosing a material with a round amorphous-gel appearance (Figure 14d). The semi-quantitative chemical composition from EDS spectra of pyrophyllite and amorphous silicon-aluminum material were determined on the anhydrous oxygen base of pyrophyllite as (%) Si 74.23, Al 25.77. The chemical composition of the gel material (Si 74.01, Al 25.99) is almost identical to pyrophyllite. This is an important indicator of primarily kaolinite and/or pyrophyllite formation, followed by development of an aluminum-silica gel in the alteration process.

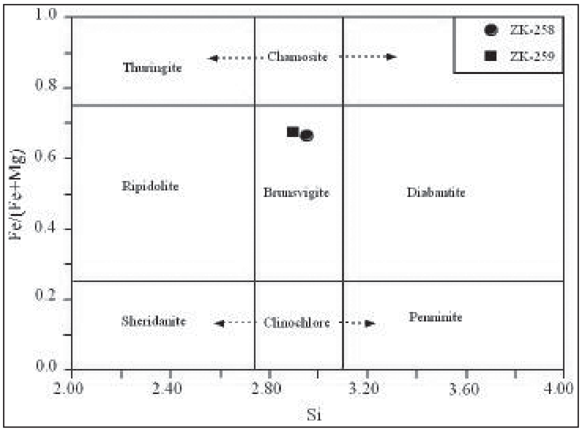

Figure 11- The settings on the Si^{IV} and octahedral Fe/(Fe+Mg) diagram of the chlorites in the altered andesites of the argillic alteration zone from Karataş volcanites (Foster, 1962).

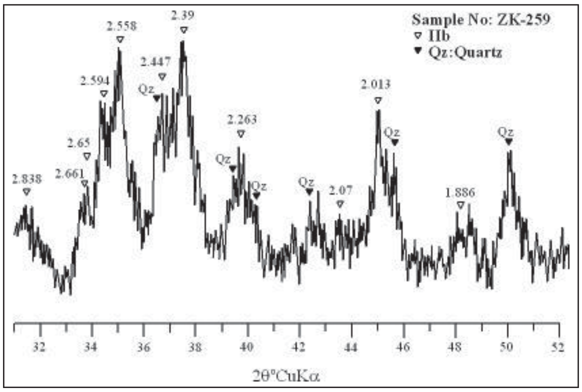

Figure 12- XRD diffractogram of chlorite polytype in the altered volcanic rocks in the argillic alteration zone from Karataş volcanites.

Fine-grained kaolinite plates are observed in the altered volcanic sample (ZK-325) containing quartz, clay (kaolinite), alunite and goyazite (Figure 14e). Equant kaolinite sheets are usually 1 to 5 µm in size, and their edges are not uniform. The thickness of kaolinite sheets are around 0.1 µm.

Alunites are found in micropores in the form of rhombohedral single and combined crystals, similar to hexaeder, with pseudohexagonal kaolinite plates about 2 µm in diameter (Figure 14f). Alunites are represented by euhedral crystals with a length of 5-10 µm. As a result of the EDS spectra and semi-quantitative chemical analyzes of this rock, the chemical composition (%) on the basis of anhydrous oxygen was determined as Si 61.15 and Al 38.85

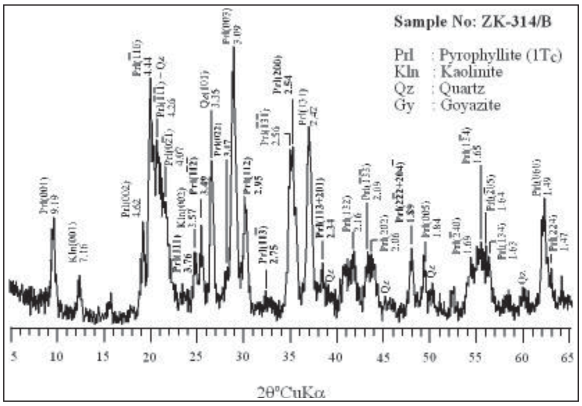

Figure 13- XRD diffractogram of 1Tc polytype of pyrophyllite in the altered volcanic rocks in the argillic alteration zone from Karataş volcanites.

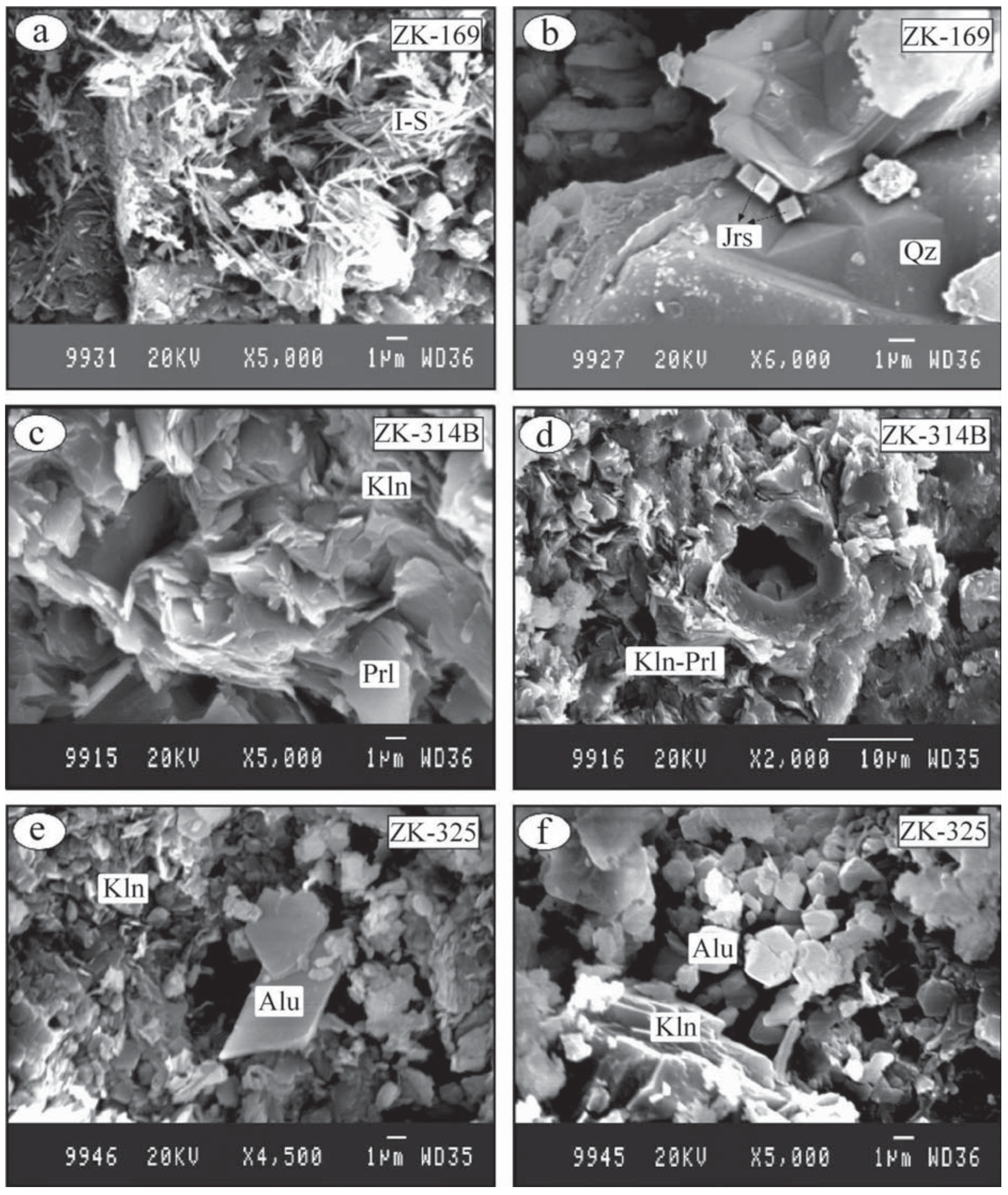

Figure 14- SEM microphotographs of samples in the argillic alteration zone (Qz=Quartz, Jrs=Jarosite, Prl=Pyrophyllite, Kln=Kaolinite, Alu=Alunite), a) Fibrous/acicular I-S minerals, b) Jarosite on euhedral quartz, c) Lamella of large pyrophyllite and thin kaolinite, d) Pyrophyllite-kaolinite plates developed from AlSi-gel, e) Weakly stacked euhedral kaolinite, and alunite minerals, f) Euhedral alunite minerals.

for kaolinite. Then percent values obtained for the groundmass (Si 19.92, Al 29.89, S 33.36, K 8.95, P 7.88) indicate the existence of minerals with silicate, sulphate and phosphate. The fact that kaolinite and pyrophyllite have weakly stacked texture indicates that the aqueous Al-silicate minerals are formed on the surface and/or near-surface conditions and they show a large similarity to those derived from the same type of rocks in literature (Keller, 1976, Gençoğlu et al., 1989; Yalçın, 1991).

5. The Formation and Origin of Hydrothermal Alteration Minerals

The formation of the minerals determined in the sericitic (phyllic) and argillic alteration levels in the Karataş volcanites and Kösedağ syenite are discussed below:

The formation of kaolinite and pyrophyllite which is found in studied area is discussed as follows. Liquid inclusion studies on quartz in the investigated area have determined that the solutions have a homogenization temperature ranging from 182-389 °C and a salinity equivalent to 2.8-10.5 NaCl (Efe and Gökçe, 1999). Pyrophyllite is a mineral which is stable at 275-350 °C in the Al_2O_3-SiO_2-H_2O system (Evans and Guggenheim, 1988). However, according to the same authors; when water is diluted with other components such as CH_4 and CO_2, the temperature of pyrophyllite formation can be reduced to lower values. In addition, silica-saturated fluids can cause pyrophyllite instead of kaolinite during hydrothermal alteration of silicates at low temperatures of up to 100°C (Hemley et al., 1980; Berman, 1988).

In this study, the presence of common silica, sulphur (alunite, jarosite, pyrite) and arsenic (goyazite) minerals from hydrothermal alteration and/or neoformation minerals; the fluids are rich in H_4SiO_4 and SO_2; but it is poor in terms of CO_2. Also; kaolinites are associated with other clay minerals (illite, I-S, smectite) and pyrophyllite is not widely developed, suggesting that the temperature of the solutions causing the alteration of the magmatics and/or the occurences of the neoformation minerals in the study area may be quite low.

Kaolinite is formed from both phenocrysts/microlites of feldspar, and the alteration of volcanic glass. Kaolinite-pyrophyllite sheets developed from aluminum-silica gel are observed in EDS investigations and SEM photographs taken from altered volcanic sample (ZK-314B). This fact suggests that an intermediate stage has happened (Yalçın and Bozkaya, 2003):

(Volcanic glass → Hydrous Al-silica gel → Kaolinite)

$4SiO_2.2Al_2O_3 + 14H_2O \rightarrow 2Al_2(OH)_6.4Si(OH) \rightarrow Al_4[Si_4O_{10}](OH)_8 + 10H_2O$

(Sanidine/Orthoclase → Hydrous Al-silica gel → Kaolinite + Quartz

$4KAlSi_3O_8 + 28H_2O + 4H^+ \rightarrow 2Al_2(OH)_6.12Si(OH)_4 + 4K^+ \rightarrow Al_4[Si_4O_{10}](OH)_8 + 8SiO_2 + 4K^+ + 26H_2O$

(Plagioclase → Hydrous Al-silica gel → Kaolinite)

$2(Na,Ca)Al_2Si_2O_8 + 12H_2O + 4H^+ \rightarrow 2Al_2(OH)_6.4Si(OH)_4$ ® $Al_4[Si_4O_{10}](OH)_8 + 10H_2O + 2(Na^+,Ca^{+2})$

(Feldspar → Kaolinite)

$2(Na,K,Ca)Al_2Si_2O_8 + 2H_2O + 4H^+ \rightarrow Al_4[Si_4O_{10}](OH)_8 + 2(Na^+,K^+,Ca^{+2})$

Excess silica during feldspar minerals transforming into kaolinite, Ca^{+2} and Na^+ from plagiclase, K^+ from sanidine/orthoclase are used in the formation of calcedonic quartz and other clay minerals, respectively. The low ratio of Si/Al in the system led to the formation of kaolinite, but pyrophyllite synthesis could only take place when this ratio rises rarely:

(Volcanic glass → Hydrous Al-silica gel → Pyrophyllite)

$4SiO_2.Al_2O_3 + 11H_2O \rightarrow Al_2(OH)_6.4Si(OH)_4 \rightarrow Al_2[Si_4O_{10}](OH)_2 + 10H_2O$

(Sanidine/Orthoclase → Hydrous Al-silica gel → Pyrophyllite + Quartz)

$2KAlSi_3O_8 + 14H_2O + 2H^+ \rightarrow Al_2(OH)_6.6Si(OH)_4 + 2K^+ \rightarrow Al_2[Si_4O_{10}](OH)_2 + 2SiO_2 + 2K^+ + 14H_2O$

It is thought that Na^+, K^+, Ca^{+2}, Mg^{+2} and Fe^{+2} cations, which are not used in the formation of kaolinites formed by the alteration of volcanic glass and/or feldspar, lead to the formation of illite/muscovite (sericite), I-S and/or smectites (Yalçın and Gümüşer, 2000 , Yalçın and Bozkaya, 2003, Yalçın et al., 2005):

(Volcanic glass → Hydrous Al-Silica gel → Illite/Muscovite)

$3SiO_2.2Al_2O_3 + 12H_2O \rightarrow 2Al_2(OH)_6.3Si(OH)_4 + K^+ \rightarrow KAl_3(Si_3AlO_{10})(OH)_2 + 10H_2O + 2OH^-$

(Sanidine/Orthoclase → Illite/Muscovite)

$4KAlSi_3O_8 + 6H^+ \rightarrow KAl_3(Si_3AlO_{10})(OH)_2 + 9SiO_2 + 2H_2O + 3K^+$

(Volcanic glass → Hydrous Al-silica gel → I-S)

$6SiO_2.3Al_2O_3.Na_2O.K_2O + 19H_2O + 4H^+ \rightarrow 6Al(OH)_3.6Si(OH)_4 \rightarrow KNaAl_4[Al_2Si_6O_{20}](OH)_4 + 18OH^-$

(Sanidine/Orthoclase → I-S + Quartz)

$6KAlSi_3O_8 + Na^+ + 4H_2O \rightarrow KNaAl_4[Al_2Si_6O_{20}](OH)_4 + 12SiO_2 + 5K^+ + 4OH^-$

(Plagioclase → I-S)

$3(Na,Ca)Al_2Si_2O_8 + 2H_2O + K^+ + 2H^+ \rightarrow KNaAl_4[Al_2Si_6O_{20}](OH)_4 + 2(Na^+,Ca^{+2}) + 2OH^-$

(Volcanic glass → Hydrous CaMgAl-silicate gel → Smectite)

$8SiO_2.3Al_2O_3.MgO.Na_2O.CaO + 25H_2O \rightarrow Na_2O.CaO.MgO.6Al(OH)_3.8Si(OH)_4 \rightarrow$

$NaCa(MgAl_5)[Si_8O_{20}](OH)_4.H_2O + 16H_2O + 12OH^- + Na^+ + Al^{+3}$

(Plagioclase → Smectite)

$5(Na,Ca)Al_2Si_2O_8 + 6Si(OH)_4 + 2Mg^{+2} + 2H^+ \rightarrow 2NaCa(MgAl_5)[Si_8O_{20}](OH)_4.2H_2O + 3(Na^+,Ca^{+2}) + 14OH^-$

OM studies indicate that chlorite and C-S have developed as a consequence of the alteration of biotite and/or volcanic glass (Yalçın et al., 2005):

(Volcanic glass → Hydrous MgFeAl-silicate gel → Chlorite)

$7SiO_2.Al_2O_3.2MgO.2FeO + 24OH^- + 10H^+ \rightarrow 9MgO.2FeO.2Al(OH)_3.7Si(OH)_4 \rightarrow Mg_9Fe_2Al[AlSi_7O_{20}](OH)_{16} + 9H_2O$

(Volcanic glass → Hydrous MgFeAl-silicate gel → Chlorite)

$7SiO_2.Al_2O_3.7MgO.FeO + 11H_2O + 12H^+ \rightarrow 7MgO.FeO.2Al(OH)_3.7Si(OH)_4 \rightarrow Mg_7FeAl[AlSi_7O_{20}](OH)_{12} + 4H_2 + 14H^+$

Jarosite is a secondary mineral that occurs in the conditions of superficial conditions in arid climates (Duda and Rejl, 1990). Jarosite in the study field are mostly accompanied by goethite. Here, it is possible that it can be occured by the Fe-containing minerals (pyrite, magnetite etc.) and/or biotite alteration, as well as the synthesis of solution according to the data obtained from the SEM examinations. Here, K which is released by the alteration of volcanic glass, sanidine/orthoclase and/or biotite, is also needed and is formulated as follows (Yalçın and Bozkaya, 2003; Yalçın et al., 2005):

(Biotite → Jarosite)

$KFe_3[AlSi_3O_{10}](OH)_2 + 2SO_2 + 4H_2O \rightarrow [(KFe_3(SO_4)_2(OH)_6] + 3SiO_2 + Al^{+3} + 4H^+$

(Biotite + Magnetite → Jarosite + Goethite)

$KFe_3[AlSi_3O_{10}](OH)_2 + Fe_3O_4 + 2SO_2 + 9H_2O \rightarrow [(KFe_3(SO_4)_2(OH)_6] + 3FeO(OH)_2 + 3SiO_2 + Al^{+3} + 8H^+$

(Pyrite → Jarosite)

$3FeS_2 + 22H_2O + K^+ \rightarrow [(KFe_3(SO_4)_2(OH)_6] + 4SO_2 + 38H^+$

(Ions → Jarosite)

$K^+ + 3Fe^{+3} + 2SO_2 + 10H_2O \rightarrow [(KFe_3(SO_4)_2(OH)_6] + 14H^+$

The other sulfate mineral observed in the study area is alunite and it can be suggested that jarosite has a similar formation mechanism. However, here, instead of Fe, Al has to enter the structure and this cation must be provided especially during the kaolinization (Yalçın and Bozkaya, 2003):

(Sanidine → Alunite + Quartz)

$KAl_3Si_3O_8 + 2SO_2 + 8H_2O \rightarrow KAl_3(SO_4)_2(OH)_6] + 3SiO_2 + 10H^+$

(Ions → Alunite)

$K^+ + 3Al^{+3} + 2SO_2 + 10H_2O \rightarrow [(KAl_3(SO_4)_2(OH)_6] + 14H^+$

Goyazite has a general formula of $[(Sr,Ca,Ba)Al_3[(P,As)O_4]_2(OH)_5.H_2O]$, and it is member of the krandallite group. A similar formation of jarosite and alunite for this mineral is possible:

(Feldspar → Goyazite + Quartz)

$3(SrCaBa)Al_2Si_2O_8 + 2P^{+5} + 2As^{+6} + 16H_2O \rightarrow$

$2[(SrCaBa)Al_3[(P,As)O_4]_2(OH)_5H_2O] + 6SiO_2 + (Sr^{+2},Ca^{+2},Ba^{+2}) + 18H^+$

(Ions → Goyazite)

$(Sr^{+2},Ca^{+2},Ba^{+2}) + 2P^{+5} + 2As^{+5} + 3Al^{+3} + 10H_2O \rightarrow [(Sr,Ca,Ba)Al_3[(P,As)O_4]_2(OH)_5.H_2O] + 14H^+$

In barite neomineralization observed in fractures of syenites and kaolinites, Ba, which is released during kaolinization, is the most important source:

Feldspar → Barite + Quartz)

$(Ca,Ba)Al_2Si_2O_8 + SO_2 + 2H^+ \rightarrow BaSO_4 + 2SiO_2 + 2Al^{+3} + Ca^{+2} + 2OH^-$

Consequently, the type of clay mineral (kaolinite, I-S or/and smectite) in argillic zone formed by hydrothermal alteration of volcanic material is seemed to be controlled by folowing parameters (Bohor and Triplehorn, 1993; Gündoğdu et al., 1996; Yalçın and Bozkaya, 2003): pH of hydrothermal solutions (kaolinite if acidic, I-S and smectite in medium-basic), salinity and/or alkalinity of hydrothermal solutions (kaolinite in low salinity, I-S and smectite in high salinity), degree of leaching in open and closed system (kaolinite in open system, I-S and smectite in closed system), silica saturation (kaolinite in high, I-S and smectite in low), activities of ions (H^+, H_4SiO_4, $[Al(OH)_4]$ etc.) and water (kaolinite in high activity, I-S and smectite in less), dissolution speed and quantity (kaolinite in high, I-S and smectite in low) and also composition of volcanic material (kaolinite if Fe and/or Mg, K, Na and Ca are poor, I-S and smectite if rich), alkali cation ratios (for kaolinite Na/K=0, for smectite 0.5, for I-S K/Na=1).

6. Formation Model of Kaolinite Deposits

It has been observed that a pyroclastic material, which is concentrated at intervals from the lowest levels of the Middle-Upper Eocene Akıncılar formation to the upper parts, is observed. At the highest levels, it passes to Karataş volcanites with agglomeratic level. A volcanic activity starting from Middle Eocene in the region continued until the end of Eocene in the form of lava flows. The composition of magma forming these volcanics is differentiated by fractional crystallization. Before Karataş volcanites have yet not completely cooled, the syenites have settled by ascending up to shallow depths with hot-hot contact (Figure 15a).

In the solidification of syenite and the volcanics around it, fractures and cracks were formed by the increase of the pressure of the volatile components in the pluton, and along these weak zones hydrothermal solutions formed alteration zones of interaction with magmatics (Figure 15b-c). As a result of the field observations, altough there is no definite zoning distinction of hydrothermal alteration types; in the main alteration zone (Kumoğlu Village) starting from unaltered syenites, sericitic and argillic + sericitic altered syenites; argillic + sericitic and argillic altered volcanics can be followed. In the volcanics, compared with the syenites, the reason for the argillic alteration zones are wider and also types of hydrothermal alteration are different; volcanics are finer grained (volcanic glass and microlites in the matrix) than syenites so it interacts with hydrothermal fluids faster.

These alteration zones are concentrated in the volcanics surrounding the plutonics and in two main zones with NE-SW trending where cut the pluton. In the main alteration zones, argillic, sericitic and propylitic and Fe-Pb-Zn ± Cu ± Mo-ore minerals were developed (Efe and Gökçe, 1999). Considering the environment and mechanism occured minerals, two different origins can be suggested (Esquevin, 1956; Millot, 1970). First is hydrothermal neoformation (direct formation from solution) and the other is hydrothermal degradation (the negative alteration of previously formed minerals in solid-solid phase). The boundary between mechanisms in the evolution of the minerals is not certain and neoformation mechanism can develop after degradation. Based on this classification; tourmaline, barite, ore minerals, quartz, opal-CT, alunite, goyazite, jarosite, calcite, dolomite, azurite and malachite were formed by neoformation; chlorite and C-S by degradation; and epidote, kaolinite, pyrophyllite, illite, I-S and smectite by both neoformation and degradation mechanisms. Considering only the environment, these minerals are secondary; when the mechanism is considered, it can be stated that the neoformation minerals are primary and the degradation minerals are secondary.

According to types of hydrothermal alteration (hypogen, metasomatism, supergene); barite, ore minerals, quartz, opal-CT, alunite, goyazite, jarosite from neoformation minerals; chlorite and C-S from degradation minerals; kaolinite, pyrophyllite, illite, I-S and smectite minerals formed by both neoformation and degradation mechanism are hypogene. As to carbonate minerals such as calcite, dolomite, azurite and malachite from other neoformation minerals, they are supergene. Tourmaline and epidote are thought to be metasomatic minerals. According to their mineral assemblages, textural properties, and macroscopic

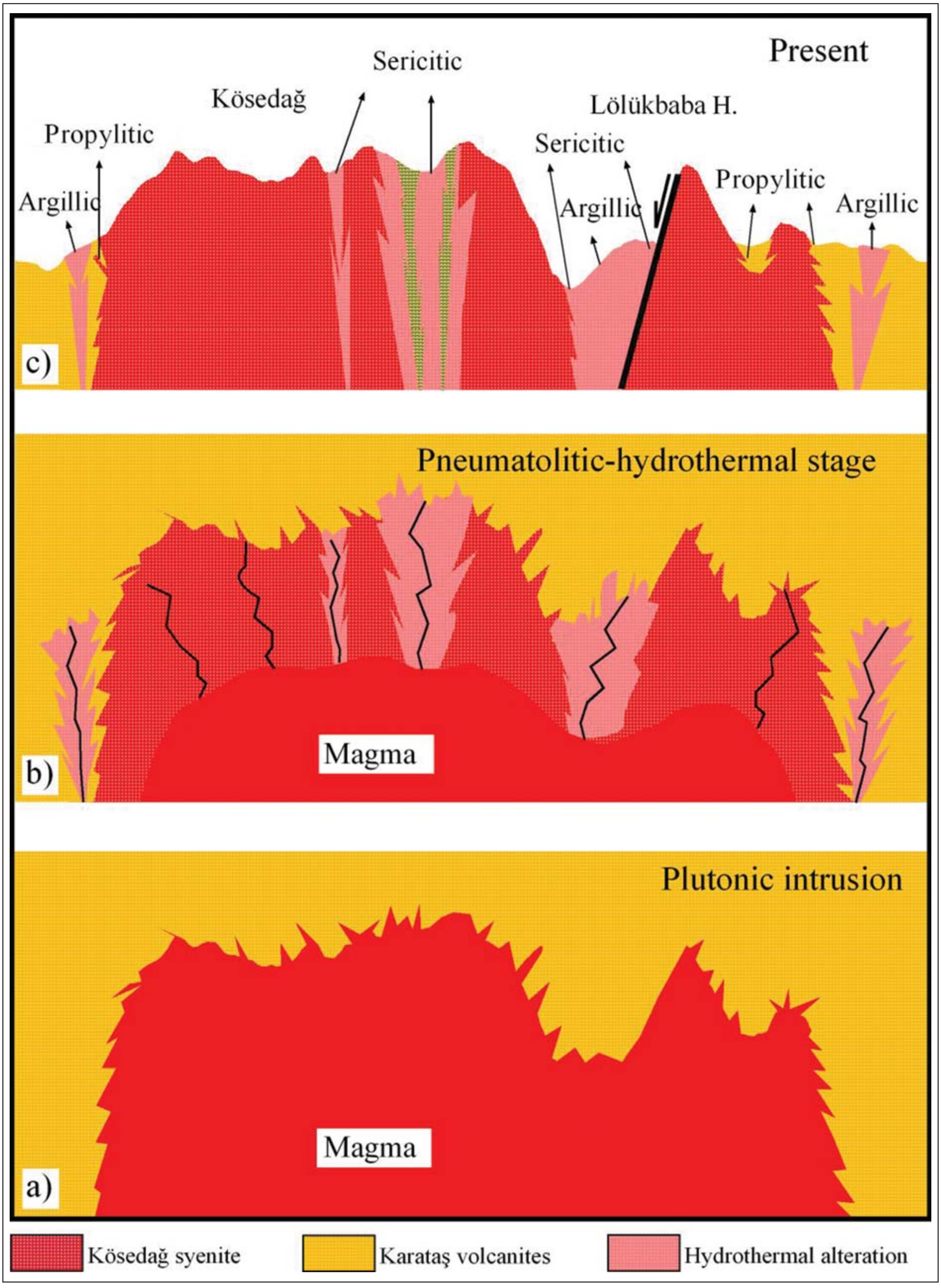

Figure 15- Hydrothermal alteration evolution model in Kösedağ syenite and volcanics, a) Upper shallow depth of Kösedağ pluton and intrusion into Karataş volcanites, b) Hydrothermal phase, c) Present location of magmatic and alteration products.

positions, hypogeneous hydrothermal minerals can be divided into two groups as early and late stages minerals. Of these, kaolinite, pyrophyllite, illite, I-S, smectite, quartz and opal-CT are early-; barite, ore minerals, alunite, goyazite, jarosite, chlorite and C-S are late-stage minerals.

7. Conclusions

The conclusions obtained from the lithological and mineralogical studies of the Kösedağ syenite and Karataş volcanites, where the hydrothermal alterations of the propylitic, phyllic/sericitic and argillic alteration in the study area develop, are presented below:

Upper Cretaceous-Paleocene Refahiye Complex is represented by serpentinized ultramafic rocks; Akıncılar formation of Middle-Late Eocene aged marine magmatism by clastic-volcanoclastic; Karataş volcanites the of Middle-Upper Eocene by of basaltic trachyandesite-trachyandesite volcanics in compositon; Kösedağ syenite of the Middle-Upper Eocene by quartz alkaline feldspar syenite. The Akıncilar formation was found to have widespread volcanosedimentary character; in other words, the unit reflects the first signs of the volcanism in region in the form of pyroclastics. In the region lava flows (Karataş volcanites) followed the agglomerate products of the magmatism for a short time, and then plutonics (Kösedağ syenite) intruded the lavas at shallow depths with hot-hot contact before they totally cooled.

Hydrothermal alteration affected only Middle-Upper Eocene Karataş volcanites and Kösedağ syenite. The age of the alteration was found to be 38.0 ± 0.9 million years as a result of K/Ar radiometric age dating from alunite mineral. The alteration zones are concentrated in two major zones. One of them is circle-shaped extending fractures in volcanics which are parallel to plutonic-volcanic contact. The second one is the zone that cutting both NE-SW trending plutonics and volcanics. The system that brings the alterations, solidification of syenite by the placement of Karataş volcanites into syenite with hot-hot contact before it cooled, the formation of the crack and fractures as a result of the increase of the pressure of the volatile components in the pluton and the interaction of hyrdrothermal solutions with magmatics through these weak zones. According to the syenites around volcanics, the reason for the argillic alteration zones is wider and the type of hydrothermal alteration is different; volcanics are finer grained than syenites (volcanic glass and microlites in the matrix) and interacted with hydrothermal fluids faster.

Although kaolinite occurrences are observed in both Kösedağ syenite and Karataş volcanites, the kaolinite deposit formations that can be operated have developed only in the argillic alteration zone of Karataş volcanites; it has been revealed that the region has an important potential for kaolinitic industrial raw materials. Hydrothermal altered levels are usually observed in a few km^2 zones; only the extent of the alteration zone observed in Gemin Beli is about 30 km^2. Kaolinite deposits with no sharp boundaries contain rich in iron oxide, alunite and other clay minerals (mostly I-S), and its upper parts are covered by a silica cap. As a result of the hydrothermal alteration, enrichment of ore minerals has occured in addition to clay minerals. In the contact of Kösedağ syenite and Karataş volcanites and generally within the plutonics perpendicular to dominant alteration trend, vein type of Pb-Zn deposits which are related to NW-SE-oriented fracture systems are observed. In Kösedağ syenite there are tourmaline-quartz (between a few mm and about 20 cm) and barite veins (0.3-1 m) in altered levels.

As a result of hydrothermal alteration, diferentiated as propylitic, phyllic/sericitic and argillic types, starting from Kösedağ syenite and Karataş volcanites, phyllosilicate/clay minerals (kaolinite, illite, smectite, chlorite, I-S, C-S and pyrophyllite), oxides and hydroxides (hematite, goethite), sulfides (galenite, sphalerite, pyrite, calcopyrite, molybdenite, covellite), carbonates (calcite, dolomite, malachite, azurite), sulphates (barite, alunite, jarosite), phosphate (goyazite), quartz and opal-CT minerals are formed. The most common hydrothermal mineral paragenesis in the Karataş volcanites, where argillic alteration is observed, are clay + quartz + goethite + goyazite, clay + quartz + alunite + goethite and clay + quartz + jarosite + feldspar + goethite and/or goyazite.

The kaolinite minerals formed by the alteration of volcanics in the argillic zone show moderate to poor crystallinity values according to the Hinckley Crystallization Indices. I-S minerals with volcanic origin are in dioctahedral composition and their illite content ranges from 54 to 91 % (smectite content 9 to 46 %). Smectites are dioctahedral; C-S minerals are trioctahedral and 48-59 % chlorite (41-52 % smectite) in content. Kaolinite has T (triclinic), pyrophyllite $1T_c$ and chlorite IIb polytope.

The most common mineral paragenesis are clay + quartz + jarosit ± goethite ± feldspar and clay + quartz + feldspar in the rocks formed by alteration of Kösedağ syenite. Illite or smectite contents in the I-S minerals from the altered products of the plutonics range from 84 to 95 % and from 5 to 16 %. I-S minerals have dioctahedral composition and 1Md + 2M1 + 1M polytype. The chlorite or smectite content of C-S minerals with trioctahedral composition in the rocks formed by alteration of the Kösedağ syenite is in the range of 50-52 % or 48-50 %. As for smectites, they are dioctahedral composition.

Field observations, OM and SEM studies show that hypogene and supergene hydrothermal alteration products are represented by the primary and secondary minerals formed directly or mostly from feldspars by neoformation and/or degradation mechanisms. Hypogene minerals are formed in two stages: early (kaolinite, pyrophyllite, illite, I-S, smectite, quartz and opal-CT) and late stage (barite ore minerals, alunite, goyazite, jarosite, chlorite and C-S). Tourmaline and epidote are considered as metasomatic and carbonates (calcite, dolomite, azurite and malachite) as supergene minerals. In other words, all of these minerals have formed in the surface and/or near-surface conditions.

The fluids forming the hydrothermal alteration have the salinity of 2.8-10.5 % NaCl and a homogenization temperature of 182-389 ° C. The presence of common silica, sulphur (alunite, jarosite, pyrite) and arsenic (goyazite) minerals from hydrothermal alteration and/or neoforming minerals indicate that the solutions rich in in H_4SiO_4 and SO_2 but poor in CO_2. Furthermore, the fact that clay minerals (illite, I-S, smectite) accompanying kaolinite, and low development of pyrophyllite, consider that solutions that cause alteration in the magmatics and/or occurence of neoformation minerals, have low temperature values. Kaolinite-pyrophyllite platies from aluminum-silica gel are observed in EDS investigations and SEM photographs. This fact suggests that an intermediate stage has happened.

The cations Na^+, K^+, Ca^{+2}, Mg^{+2} and Fe^{+2} which are not used in the structure of kaolinites from hydrothermal alteration of volcanic glass and/or feldspars lead the occurences of other clay minerals such as illite/muscovite, I-S and/or smectite. The low ratio of Si/Al in the system has caused the formation of kaolinite; pyrophyllite synthesis is occured in cases where this ratio rarely increases.

Jarosite in the field of study are mostly accompanied by goethite. It has been concluded that this mineral can be formed from Fe-containing minerals (pyrite, magnetite etc.) and/or biotite alteration, or it is possible to synthesize from solution in the light of the data from SEM. There is also a need for K, which is released by the decomposition of volcanic glass, sanidine/orthoclase and/or biotite.The alunite mineral has also a similar formation mechanism like jarosite, in which Al instead of Fe enters the structure and this cation must be provided from sanidine especially during the kaolinization.

Goyazite from a member of the krandallite group has a general formula of $[(Sr,Ca,Ba)Al_3[(P,As)O_4]_2(OH)_5.H_2O]$ and it is found with kaolinites. It seems that a similar formation as jarosite and alunite is possible for this mineral. Ba is the most important source released during kaolinization in the barite neomineralization within the fractures of the syenites and kaolinites,

The type of clay minerals (kaolinite, I-S or/and smectite) in argillic zone formed by hydrothermal alteration of volcanic material is seemed to be controlled by folowing parameters: pH of hydrothermal solutions (kaolinite if acidic, I-S and smectite in medium-basic), salinity and/or alkalinity of hydrothermal solutions (kaolinite in low, I-S and smectite in high), degree of leaching in open and closed systems (kaolinite in open, I-S and smectite in closed), silica saturation (kaolinite in high, I-S and smectite in low), activity of ions (H^+, $H_4SiO_4^{-4}$, $[Al(OH)_4]^-$ etc.) and water (kaolinite in high, I-S and smectite in less), dissolution speed and quantity of volcanic material (kaolinite in high, I-S and smectite in low), composition of volcanic material (kaolinite if Fe and/or Mg, K, Na and Ca are poor, I-S and smectite if rich), alkali cation ratios (for kaolinite Na/K=0, for smectite 0.5, for I-S K/Na=1).

References

Acarlioğlu, S., Kadir, S., Abdioğlu, E., Arslan, M. 2013. Epithermal-alteration geology, mineralogy and geochemistry of Eocene volcanic rocks in the Hasandağ (Giresun) area, eastern Pontides, NE Turkey. Neues Jahrbuch für Mineralogie Abhandlungen, 190, 79-99.

Ariana, Z., Par ,W., Mario, B., Vladimir, M. 2016. Geological, mineralogical and chemical characterization of Devonian kaolinite-bearing sediments for further applications in the ceramic (tiles) industry in La Paz, Bolivia. Environ Earth Sci, 75:546, 1-15.

Arslan, M., Kadir, S., Abdioğlu, E., Kolaylı, H. 2006. Origin and formation of kaolinite minerals in saprolite of Tertiary alkaline volcanic rocks, Eastern Pontides, NE Turkey. Clay Minerals, 41(2), 597-617.

Başıbüyük, Z. 2006. Eosen volkaniklerinin hidrotermal alterasyon mineralojisi-petrografisi ve jeokimyası: Zara-İmranlı-Suşehri-Şerefiye Dörtgeni'nden bir örnek (Sivas Kuzeydoğusu, İç-Doğu Anadolu, Türkiye). Doktora Tezi, C.Ü. Fen Bil. Enst. Sivas, 269s.

Başıbüyük, Z., Yalçın, H., Bozkaya, Ö. 2007. Eosen yaşlı Kösedağ magmatiklerinin hidrotermal alterasyonla ilişkili kil mineralojisi (Sivas Kuzeydoğusu). 13. Ulusal Kil 2007 Sempozyumu, Süleyman Demirel Üniversitesi, Isparta, 12-14 Eylül, Bildiriler Kitabı, s. 44-64.

Başıbüyük, Z., Yalçın, H., Bozkaya, Ö. 2010. Zara-Suşehri (KD Sivas) Yöresi Magmatik Kayaçlarında Hidrotermal Karışıkı Tabakalı İllit-Smektit Oluşumları. IV. Ulusal Jeokimya Sempozyumu, 26-28 Mayıs, Elazığ, Bildiriler ve Özetler Kitabı, s.29-30.

Bailey, S. W. 1988. X-ray diffraction identification of the polytypes of mica, serpentine, and chlorite. Clays and Clay Minerals, 36(3), 193-213.

Berman, R.G. 1988, Internally-consistent thermodynamic data for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2: Journal of Petrology, v. 29, p. 445-522.

Bingöl, E. 1989. 1/2.000.000 ölçekli Türkiye Jeoloji Haritası. Maden Tetkik ve Arama Genel Müdürlüğü Yayını, Ankara.

Bohor, B.F., Triplehorn, D.M. 1993. Tonsteins: Altered volcanic ash layers in coal bearing sequences. Geological Society of America, Special Paper, 285, 44 pp.

Bozkaya, Ö., Yalçın, H., Başıbüyük, Z., Bozkaya, G. 2007. Metamorphic-hosted pyrophyllite and dickite occurrences from the hydrous Al-silicate deposits of the Malatya-Pütürge region, Central Eastern Anatolia, Turkey. Clays and Clay Minerals, 55, 4, p. 423-442.

Boztuğ, D., Jonckheere, R. C. 2007. Apatite fission track data from central Anatolian granitoids (Turkey): Constraints on Neo-Tethyan closure. Tectonics, 26(3).

Boztuğ, D., Tichomirowa, M., Bombach, K. 2007. $^{207}Pb/^{206}Pb$ single-zircon evaporation ages of some granitoid rocks reveal continent-oceanic island arc collision during the Cretaceous geodynamic evolution of the central Anatolian crust, Turkey. Journal of Asian Earth Sciences, 31(1), 71-86.

Brindley, G.W. 1980. Quantitative X-ray mineral analysis of clays: In: Crystal Structures of Clay Minerals and Their X-ray Identification, G.W.Brindley and G.Brown (eds.), Mineralogical Society, London, 411-438.

Brindley, G.W., Wardle R. 1970. Monoclinic and triclinic forms of pyrophyllite and pyrophyllite anhydride. Am. Miner., 48, 42-61.

Brown, G., Brindley, G.W. 1980. X-ray diffraction procedures for clay mineral identification. In Crystal Structuresof Clay Minerals ang their X-ray Identification, Mineralogical Society, London, 305-360.

Chagnon, A., Desjardins, M. 1991. Détermination de la composition de la chlorite par diffraction et microanalyse aux rayons X. Canadian Mineralogist, 29, 245-254.

Collins, D.R., Catlow, C.R.A. 1991. Energy-minimized hydrogen-atom positions of kaolinite. Acta Cryst., Vol.47, pp.678-682.

Cravero, F., Marfil, S., Maiza, P. 2010. Statistical analysis of geochemical data: A tool: to discriminate between kaolinite deposits of hypogene and supergen origin. Patagonia, Argentina. Clay Minerals, 183-196.

Davies, J. H., Von Blanckenburg, F. 1995. Slab breakoff: a model of lithosphere detachment and its test in the magmatism and deformation of collisional orogens. Earth and Planetary Science Letters, 129(1), 85-102.

Domínguez, E., Murray, H.H. 1995. Genesis of the Chubut river valley kaolinite deposits, and their industrial applications. Pp. 129-134 in: Proceedings of the 10th International Clay Conference, 1993 (G.J. Churchman, R.W. Fitzpatrick & R.A. Eggleton, editors) CSIRO Publishing, Melbourne, Australia.

Domínguez, E., Murray, H.H. 1997. The Lote 8 Kaolin Deposit, Santa Cruz, Argentina. Genesis and paper industrial application. Pp. 57-64 in: Proceedings of the 11th International Clay Conference (H. Kodama, A.M. Mermut & J.K. Torrance, editors) Ottawa, Canada.

Duda, R., Rejl, L. 1990. Minerals of The World. Arch Cape Press, New York, 520 p.

Ece, O.I., Nakagawa, Z.E. 2003. Alteration of volcanic rocks and genesis of kaolinite deposits in the Şile region, northern İstanbul, Turkey. Part II: differantial mobility of elements. Clay Minerals, 38, p.529-550.

Ece, Ö.I., Schroeder, P.A. 2007. Clay mineralogy and chemistry of halloysite and alunite deposits in the Turplu area, Balıkesir, Turkey. Clays and Clay Minerals, 55, 18-35.

Ece, O.I., Nakagawa, Z.E., Schroeder, P.A. 2003. Alteration of volcanic rocks and genesis of kaolinite deposits in the Şile region, northern İstanbul, Turkey. I: Clay Mineralogy. Clays and Clay Minerals, Vol.51, No.6, p.675-688.

Ece, Ö.I., Schroeder, P.A., Smilley, M.,Wampler, M. 2008, Acid-sulfate alteration volcanic rocks and genesis of halloysite and alunite deposits in the Biga Peninsula, NW Turkey. Clay Minerals, 43, 281-315.

Ece, Ö.İ., Ekinci, B., Schroeder, P.A., Crowe, D., Esenli, F. 2013. Origin of the Düvertepe kaolinite-alunite deposits in Simav Graben, Turkey: Timing and Styles of hydrothermal mineralization. Journal of Volcanology and Geothermal Research, 255, 57-18.

Efe, A., Gökçe, A. 1999. Maden köyü (İmranlı-Sivas) çevresindeki Pb-Zn yataklarının jeolojisi ve sıvı kapanım incelemeleri. C.Ü. Mühendislik Fakültesi Dergisi Seri A-Yerbilimleri, 16, 29-38.

Esqueviv, J. 1956. Synthèse des phyllites zincifères. Bull. Gr. Fr. Argilés, 8, 3, pp. 23-27.

Evans, B.W., Guggenheim, S. 1988. Talc, pyrophyllite, and related minerals, *in* Hydrous Phyllosilicates (exclusive of micas): Bailey, S.W. ed., Washington DC, Reviews in Mineralogy, Mineralogical Society of America, v.19, p. 225-294.

Fawcett, T. G., Crowder, C. E., Brownwell, S. J., Zhang, Y., Hubbard, C., Schreıner, W., Hamıll, G. P., Huang, T. C., Sabıno, E., Langford, J. L., Hamılton, R., Lou~R, D. 1989. In Methods and Practices in X-ray Powder Diffraction, edited by R. Jenkins, Section 13.3. International Centre for Diffraction Data, Swathmore, USA.

Foster, M.D. 1962. Interpretation of the composition and a classification of the chlorites. U.S. Geological Survey Professional Paper, 414-A, 1-33 p.

Gençoğlu, H., Bayhan, H., Yalçın, H. 1989. Bilecik-Söğüt yöresi kaolinite yataklarının mineralojisi ve kökeni. IV. Ulusal Kil Sempozyumu, C.Ü. Sivas, 20-23 Eylül, Bildiriler Kitabı (Eds. D.Boztuğ and H.Yalçın), 97-112.

Göncüoğlu, M.C., Dirik, K., Kozlu, H. 1997. Pre-Alpine and Alpine Terranes in Turkey: Explanatory notes to the Terrane Map of Turkey. Ed.D. Papanikolaou, F.P. Sassi, IGCP Project No:276 Final Volume: Terrane Maps and Terrane Descriptions. Annales. Géol.Pays Helléniques, 37, 515-536.

Görür, N., Tüysüz, O., Şengör, A.M.C. 1998. Tectonic evolution of the Central Anatolian Basins. International Geology Review, 40, 831-850.

Gündoğdu, M.N., Yalçın, H., Temel, A., Clauer, N. 1996. Geological, mineralogical and geochemical characteristics of zeolite deposits associated with borates in the Bigadiç, Emet and Kırka Neogene lacustrine basins, Western Turkey. Mineralium Deposita, 31, 492-513.

Hemley, J.J., Montoya, J.W., Marinenko, J.W., Luce, R.W. 1980. Equilibria in the system Al_2O_3-SiO_2-H_2O and some general implications for alteration/mineralization processes: Economic Geology, v. 75, p. 210-228.

Hinckley, D.N. 1963. Variability in “crysallinity” values among the kaolinite deposits of the coastal plain of Georgia and South Carolina. Clays and Clay Minerals, 11, 22-235.

Kalkancı, Ş. 1974. Etüde geologique et petrochimique du sud de la region de Suşehri. Geochronologie du massif syenitique de Kösedağ (Sivas Turquie). These de doctoral de 3^{e} cycle, L’universite de Grenoble, 135 p.

Kalkancı, Ş. 1978. Suşehri güneyinin jeolojik ve petrokimyasal etüdü. Kösedağ siyenitik masifinin jeokronolojisi (NE Sivas-Türkiye). TJK 32. Bilimsel ve Teknik Kurultayı, Bildiri Özetleri, 33-34.

Kadir, S., Akbulut, A. 2009. Mineralogy, geochemistry and genesis of the Taşoluk kaolinite deposits in pre-Early Cambrian metamorphites and Neogene volcanites of Afyonkarahisar, Turkey. Clay Minerals, 44, 89-112.

Kadir, S., Erman, H., Erkoyun, H. 2011. Mineralogical and geochemical characteristics and genesis of hydrothermal kaolinite deposits within Neogene volcanites, Kütahya (western Anatolia), Turkey. Clays and Clay Minerals, 59(3), 250-276.

Kadir, S., Erkoyun, H. 2013. Genesis of the hydrothermal Karaçayır kaolinite deposit in Miocene volcanics and Palaeozoic metamorphic rocks of the Uşak-Güre Basin, western Turkey. Turkish Journal of Earth Sciences, 22(3), 444-468.

Kadir, S., Külah, T., Eren, M., Önalgil, N., Gürel, A. 2014. Mineralogical and geochemical characteristics and genesis of the Güzelyurt alunite-bearing kaolinite deposit within the Late Miocene Gördeles ignimbrite, central Anatolia, Turkey. Clays and Clay Minerals, 62, 486-508.

Karakaya, M.Ç., Karakaya, N., Temel, A. 2001. Kaolin occurrences in Erenler Dağı volcanics, southwest Konya Province, Turkey. Int. Geol. Rev. 43/8, 711-722.

Karakaya N., Karakaya-Çelik, M. 2001. Şaplıca (Şebinkarahisar, Giresun) volkanitlerinin hidrotermal alterasyon türlerinin mineralojik ve jeokimyasal özellikleri. Türkiye Jeoloji Bülteni, 44, 75-89.

Keller, W.D. 1976. Scan electron micrographs of kaolins collected from diverse environments of origin-I: Clays and Clay Minerals, v. 24, p. 107-113.

Kusznir, N. J., Park, R.G. 1987. The extensional strength of the continental lithosphere: its dependence on geothermal gradient, and crustal composition and thickness. In: Coward, M.P., Dewey, J.F., Hancock P.L., (eds.) Continental Extensional Tectonics, Blackwell, Oxford, pp. 35-52.

Millot, G. 1970. Geology of Clays. (trans. W.R.Farrand and H.Paquet). Springer Verlag, New York, Berlin, 429pp.

Moore, D.M., Reynolds, R.C.JR. 1997. X-ray diffraction and the identification and analysis of clay minerals. Oxford University, 378 p.

Murray, H. H. 1988. Kaolin minerals: their genesis and occurrences. In: Bailey SW (ed) Reviews in mineralogy, hydrous phyllosilicates. Mineralogical Society of America Publication no. 19

Murray, H. H., Smith J. M. 1973. The geology and mineralogy of the Grahamstown, South Africa kaolinite deposit. In: Programs and abstracts, 22nd annual clays minerals conference, Clay Minerals Society

Murray, H.H., Keller, D. W. 1993. Kaolins, kaolins and kaolins; In Kaolin genesis and utilization. Special publication no. 1. The Clay Minerals Society, pp 1-24

Sayın, Ş.A. 1987. Türkiye'nin farklı bölgelerine ait kaolinitlerde kristalleşme derecesi. III. Ulusal Kil Sempozyumu Bildiriler Kitabı, 21-27 Eylül 1987, s. 57-72.

Sudo, T., Shimoda, S., Yotsumoto, H., Aita, S. 1981. Electron Micrographs of Clay Minerals: Elsevier, Tokyo, Developments in Sedimentology, v. 31, 203 p.

Şener, M., Gevrek, A. I. 2000. Distribution and significance of hydrothermal alteration minerals in the Tuzla hydrothermal system, Çanakkale, Turkey. Journal of Volcanology and Geothermal Research, 96(3), 215-228

Şengör, A.M.C., Yılmaz, Y. 1981. Tethyan evolution of Turkey: A plate tectonic approach. Tectonophysics, 75, 181-241.

Tüysüz, O. 1993. Karadeniz'den Orta Anadolu'ya Bir Jeotravers: Kuzey Neo-Tetisin Tektonik Evrimi. Türkiye Petrol Jeolojları Derneği Bülteni, 5, 1-33.

Toraya, H., Iwai, S., Marumo, F. 1980. The structural investigation of a kaolinite mineral by X-ray powder pattern-fitting. Mineralogical Journal (Japan). 10, 4, 168-180

Uysal, Ş., Bedi, Y., Kurt, İ., Kılınç, F. 1995. Koyulhisar (Sivas) dolayının jeolojisi. Maden Tetkik ve Arama Genel Müdürlüğü Rapor No: 9838, 120 s Ankara (unpublished).

Ünal, Ercan, H., Işik, Ece, Ö., Schroeder, P. A., Karacık, Z. 2016. Differentiating Styles of Alteration Within Kaolin-Alunite Hydrothermal Deposits of Çanakkale, NW Turkey. Clays and Clay Minerals, 64(3), 245-274.

Yalçın, H. 1991. Hidrotermal kaolinitlerin morfolojisi ve kimyası : Eskişehir ve Malatya yörelerinden örnekler. V. Ulusal Kil Sempozyumu, Anadolu Üniversitesi, Eskişehir, 16-20 Eylül, Bildiriler Kitabı (Ed. M.Zor), 74-86.

Yalçın, H., Gümüşer, G. 2000. Mineralogic and geochemical characteristics of of Late Cretaceous bentonite deposits at the north of Kelkit valley, Northern Turkey. Clay Minerals, 35, 807-825.

Yalçın, H., Bozkaya, Ö. 2003. Sivas Batısındaki (Yıldızeli-Akdağmadeni) hidrotermal kaolinite ve I-S oluşumlarının mineralojisi ve jeokimyası. Türkiye Jeoloji Bülteni, 46, 1-23.

Yalçın, H., Bozkaya, Ö., Tetiker, S. 2005. Kangal kömür yatağının kil mineralojisi ve jeokimyası. 12. Ulusal Kil Sempozyumu, Yüzüncüyıl Üniversitesi, Van, 5-9 Eylül, Bildiriler Kitabı, s. 16-31.

Yılmaz, A., Okay A., Bilgiç T. 1985. Yukarı Kelkit Çayı yöresi ve güneyinin temel jeoloji özellikleri ve sonuçları. Maden Tetkik ve Arama Genel Müdürlüğü Rapor No: 7777, 124 s. Ankara (unpublished).

Yıldız, A., Başaran, C. 2015. Sediment-Hosted Kaolin Deposit from Çakmaktepe (Uşak, Turkey): its Mineralogy, Geochemistry, and Genesis. Clays and Clay Minerals, 63(4), 235-261.