



The determination of alteration extent using minero-petrographical, geochemical, and geomechanical properties in granitic rocks from the Tavşanlı Zone (NW Turkey)

Ahmet Yıldız¹ · Metin Bağcı¹ · Sevgi Çetintaş² · Mehmet Demirbilek³ · Yaşar Kibici⁴ · Nurdane İlbeyli⁵

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Abstract

The effects of alteration on granites outcropping around Sivrihisar area within the Tavşanlı Zone (NW Turkey) were investigated considering minero-petrographical, geochemical, and geomechanical properties. For this aim, polarizing light microscope, scanning electron microscope, X-ray diffraction, chemical analyses, and geomechanical tests were conducted on the granitic samples. The new petrographic index, referred as feldspar alteration index, was developed from the quantitative ratios of total and altered constituents in feldspar minerals. Based on solution-precipitation processes, plagioclase and alkali feldspar were altered to smectite, sericite, and kaolinite along microfractures, cleavage, twinning, and zoning structure. Anorthite-rich core is more altered than the rim of zoned plagioclase due to higher solubility in water and selective alteration of calcic plagioclase. EDS studies indicate that Na, Si, and Ca decrease and Mg, Al, K, and Fe progressively increase. The normalized values of whole-rock chemical analyses of the granites show depletion of Si, Al, Na, and Ca reflecting the dissolution of plagioclase. Enrichment of Si, Al, Na, Ca, Mg, K, and Fe reveal precipitation of smectite, sericite, and kaolinite minerals during alteration. Minero-petrographical and geochemical changes led to an increase in water absorption and apparent porosity and a decrease in apparent density, P-wave velocity, Schmidt hammer rebound, and compressive strength. Significant relationships between FAI and geomechanical properties ($R^2 = 0.7116-0.8676$), FAI and P-wave velocity index (I_{vp}) ($R^2 = 0.8676$), and FAI and strength ratio (R_s) ($R^2 = 0.7614$) demonstrate that FAI can be used to determine the alteration degree of granites.

Keywords Granite · Alteration · Mineralogy · Petrography · Geochemistry · Geomechanical Properties · Turkey

Introduction

Alteration is a geological process that causes changes in the original features of rocks and classified into two groups: weathering and hydrothermal alteration. Classification

depends on the origin of altering fluids. Although these terms are frequently used in the same sense, formation conditions of these processes are different. Weathering takes place in superficial environments, whereas hydrothermal solutions channel throughout parent rocks in hydrothermal alteration process (Yildiz et al. 2010; Ceryan 2018). Granitic rocks are subjected to mineralogical, chemical, physical, and mechanical changes during alteration. Rock-forming minerals such as plagioclase, alkali feldspar, and biotite are altered to clays and to other secondary minerals. Elements are leached from altered minerals and redistributed in the crystal structure of neo-forming minerals. Granitic rocks become more porous and permeable, have more macro- and microfractures, and lose their strength and original appearance due to alteration (Gupta and Rao 1998, 2001; Arel and Tugrul 2001; Islam et al. 2002; Taboada et al. 2006; Ceryan et al. 2008; Lee et al. 2008; Momeni et al. 2015). These changes adversely affect the performance of granites in usage as natural stone and in other engineering activities.

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✉ Ahmet Yıldız
ayildiz@aku.edu.tr

- ¹ Afyon Kocatepe University, Engineering Faculty, Afyonkarahisar, Turkey
- ² Akdeniz University, Vocational School of Technical Sciences, 07058 Antalya, Turkey
- ³ Dumlupınar University, Engineering Faculty, Kütahya, Turkey
- ⁴ Bilecik Şeyh Edipali University, Vocational School, 11230 Bilecik, Turkey
- ⁵ Akdeniz University, Engineering Faculty, 07058 Antalya, Turkey

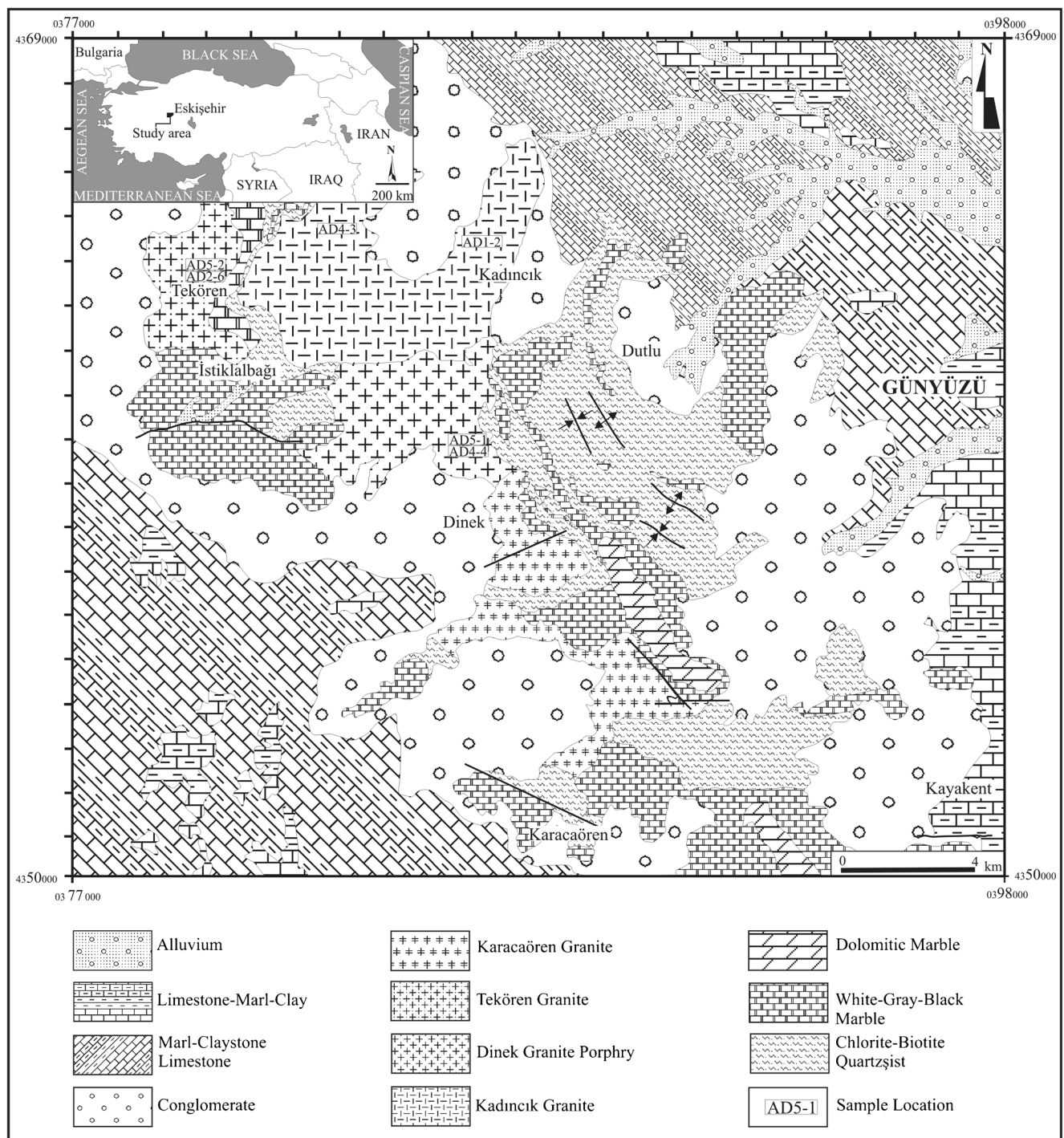


Fig. 1 The geological map of study area

Alteration indices are used to measure the extent of alteration in granitic rocks. These indices are divided into three groups: (1) petrographical indices—the micro-petrographical index (Irfan and Dearman 1978), secondary mineral content, microfractures and void ratio (Ceryan 1999; Pera Le et al. 2001), unsound constituent index (Gupta and Rao 2001), the micropetrographic strength index (Ips) and the replacement index (Rigopoulos et al.

2010), plagioclase solution degree index (Hu et al. 2014), and k-product index (Ceryan 2015); (2) chemical alteration indices—the product index (Reiche 1950), Parker index (Parker 1970), mobility index (Irfan 1996), chemical weathering degree (Esaki and Jiang 1999), and chemical alteration index (Nesbitt and Young 1982); and (3) engineering indices—the point load strength index (Irfan and Dearman 1978), tensile strength (Pasamehmetoğlu

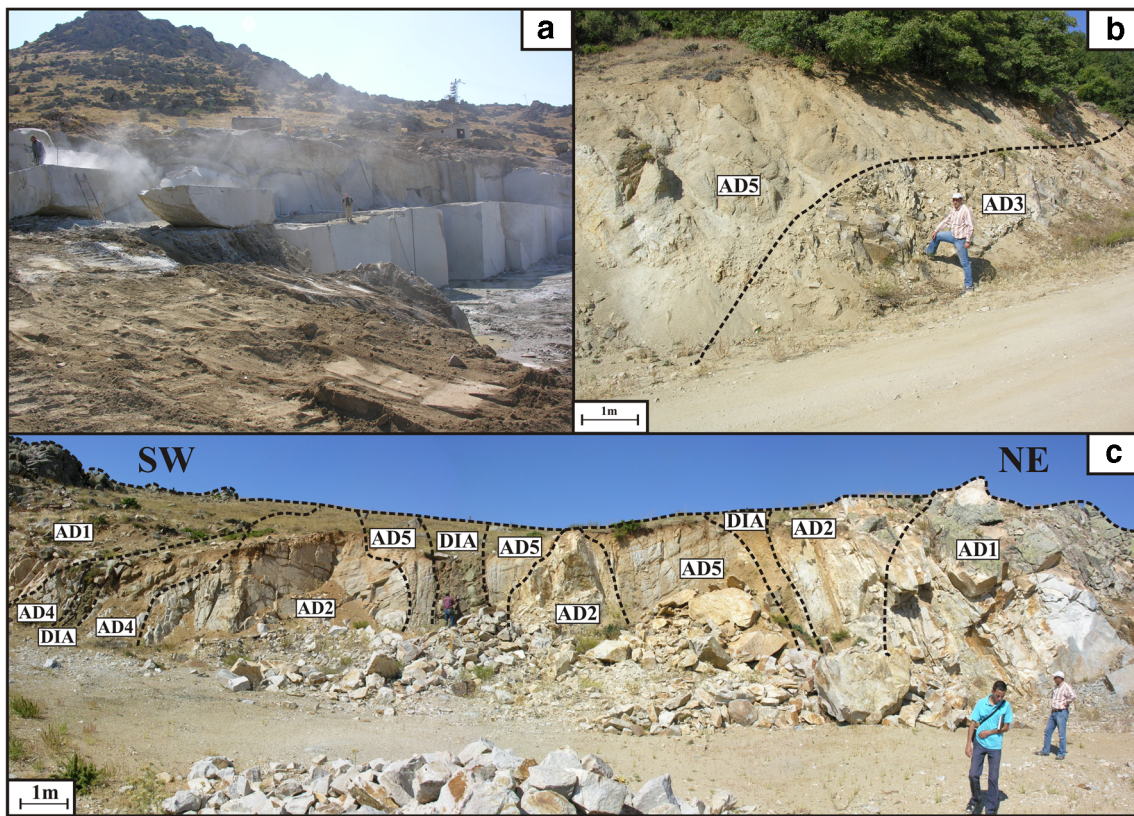


Fig. 2 Field view of granite outcrops from the Sivrihisar region; (a) active granite quarry in AD1 alteration zone, (b) the increasing of alteration degree from bottom to upper level, and (c) the different

alteration zones (AD1 to AD5) and diabasic dikes (DIAs) in inactive granite quarry at the Karacaören district

et al. 1981), P-wave velocity index (Ceryan et al. 2008), water resistance index (Franklin and Chandra 1972), and strength ratio (Gupta and Rao 2001).

In this paper, we developed a new alteration index referred to as feldspar alteration index (FAI), to determine the extent of alteration in granites. Feldspars are both the most important rock-forming minerals and more unstable minerals in granites. So, alteration state of feldspars can be considered a measure of alteration degree of granites.

We studied alteration profiles on the Sivrihisar granites located at 141 km southeast of Eskişehir (NW Turkey). The first study on the alteration of granites from Sivrihisar was conducted by Yildiz et al. (2012). The preliminary results related to the applicability of feldspar alteration index (FAI) to the granites were obtained in this study. With the possible exception of the work of Hu et al. (2014), there is no detailed research on feldspar alteration degree in granites. In this work, the petrographical

Table 1 The alteration classification of the Sivrihisar granitic rocks (modified from Anonymous 1995; Arel and Tugrul 2001; Arıkan et al. 2007; Chiu and Ng 2014).

Alteration degree	Symbol	Descriptive term	General characteristics of granites	Schmidt hammer rebound value
I	AD1	Fresh rock	Unchanged from original rock texture. Not broken easily by geological hammer	50 < SHV ≤ 60
II	AD2	Slightly altered	Slight discoloration, slight weakening. Original rock textures generally retained but stained near joint surfaces. Not broken easily by geological hammer	40 < SHV ≤ 50
III	AD3	Moderately altered	Considerably weakened, penetrative discoloration. Large pieces cannot be broken by hand. Easily broken by geological hammer	30 < SHV ≤ 40
IV	AD4	Highly altered	Large pieces can be broken by hand. Does not readily disaggregate (slake) when dry sample immersed in water. Completely discolored compared with fresh rock.	20 < SHV ≤ 30
V	AD5	Completely altered	Considerably weakened slakes. Original texture apparent. Completely discolored compared with fresh rock. Easily indented by point of geological pick	10 < SHV ≤ 20
VI	AD6	Residual soil	Soil derived by in situ weathering or hydrothermal alteration. Original rock texture completely destroyed. Can be crumbled by hand and finger pressure into constituent grains	Not Applicable

Table 2 Main field and petrographic characteristics of the Sivrihisar granitic rocks (Modified from Kibici et al. 2008)

Properties	Field
Area	~ 50 km ²
Rock unit	Granite, granodiorite (Karacaören granite) (Kgr) Granite, granodiorite (Tekören granite) (Tgr) Granite porphyry (Dinek granite porphyry) (Gpr) Quartz diorite, granite (Kadıncık granite) (Kgd)
Grain size	Medium to coarse, porphyritic
Color	Gray, dark gray, dark green
Structure	Joint system
Orientation	Slight to moderate by feldspar
Enclave/dikes	Igneous enclave/aplitic-pegmatitic-diabasic
Properties	Petrography
Mineral composition	Plg (oligoclase-albite) + ksp (orthoclase-microcline) + qtz + bt + hbl
Texture	Hypidiomorphic
Mafic phase	Hbl, bt
Accessory phase	Zircon, titanite, apatite, allanite, opaques
Alteration	Clay minerals, sericite, calcite, epidote

Plg = plagioclase; ksp = alkali feldspar; qtz = quartz; bt = biotite; hbl = hornblende

characteristics were described and the quantitative ratios of total and altered constituents in feldspar minerals were counted using the image analysis system of the polarizing light microscope (PLM). The qualitative abundances of primary and alteration minerals were determined in x-ray diffraction (XRD) studies. The morphological and microchemical properties of feldspar alteration were observed by scanning electron microscope (SEM). Chemical, physical, and mechanical tests were conducted to characterize granites. Finally, the suitability of FAI for granite alteration was tested investigating the relationships among FAI, other weathering indices, and geomechanical properties. Our proposed method contributes to the discussion of granite alteration in Turkey and in the world.

Geological setting

Tavşanlı zone is located in the northernmost side of the Tauride-Anatolide platform in NW Turkey. Paleozoic metamorphic rocks such as gneiss, metagranite, schist, amphibolite, marble, and dolomitic marble constitute the basement rocks in the study area. Mesozoic granites intrude metamorphic basement rocks and are overlain unconformably by Pliocene and Quaternary sedimentary deposits (Kibici et al. 2008; Bağcı et al. 2010) (Fig. 1).

Sivrihisar pluton covers an area of ~ 50 km² and displays NW-SE trending outcrop. Kibici et al. (2008) and Bağcı et al.

(2010) investigated these rocks under four subgroups: Kadıncık granite, Dinek granite porphyry, Tekören granite, and Karacaören granite. Pegmatitic, aplitic, and diabasic dikes were formed along with deformation planes during their emplacements. In particular, N-S and NE-SW trending diabasic dikes (up to 2-m thickness) were important for their alteration (Demirbilek 2012). Fresh granites were mined as natural stone by national companies (Fig. 2a).

Macroscopic features such as change in color, differences in texture/structure, and Schmidt hammer rebound values (SHVs) were taken into account for alteration classification (Table 1). SHVs were obtained in situ. Alteration zones (AD1 to AD5) and diabase dikes (DIAs) were distinguished in an inactive granite quarry in the Karacaören area. With increasing degree of alteration, the color of the rocks changes from dark gray (AD1) to light yellow (AD2) and yellowish pink (AD4 and AD5). Lenticular alteration bodies and fragmentation were observed in the advanced stages of alteration (AD4 and AD5). The extents of the alteration zones are in parallel to NE-SW trending diabasic dikes and alteration degree decreases with distance from dikes, suggesting relation between diabasic dike emplacement and hydrothermal origin (Bağcı et al. 2010).

Materials and methods

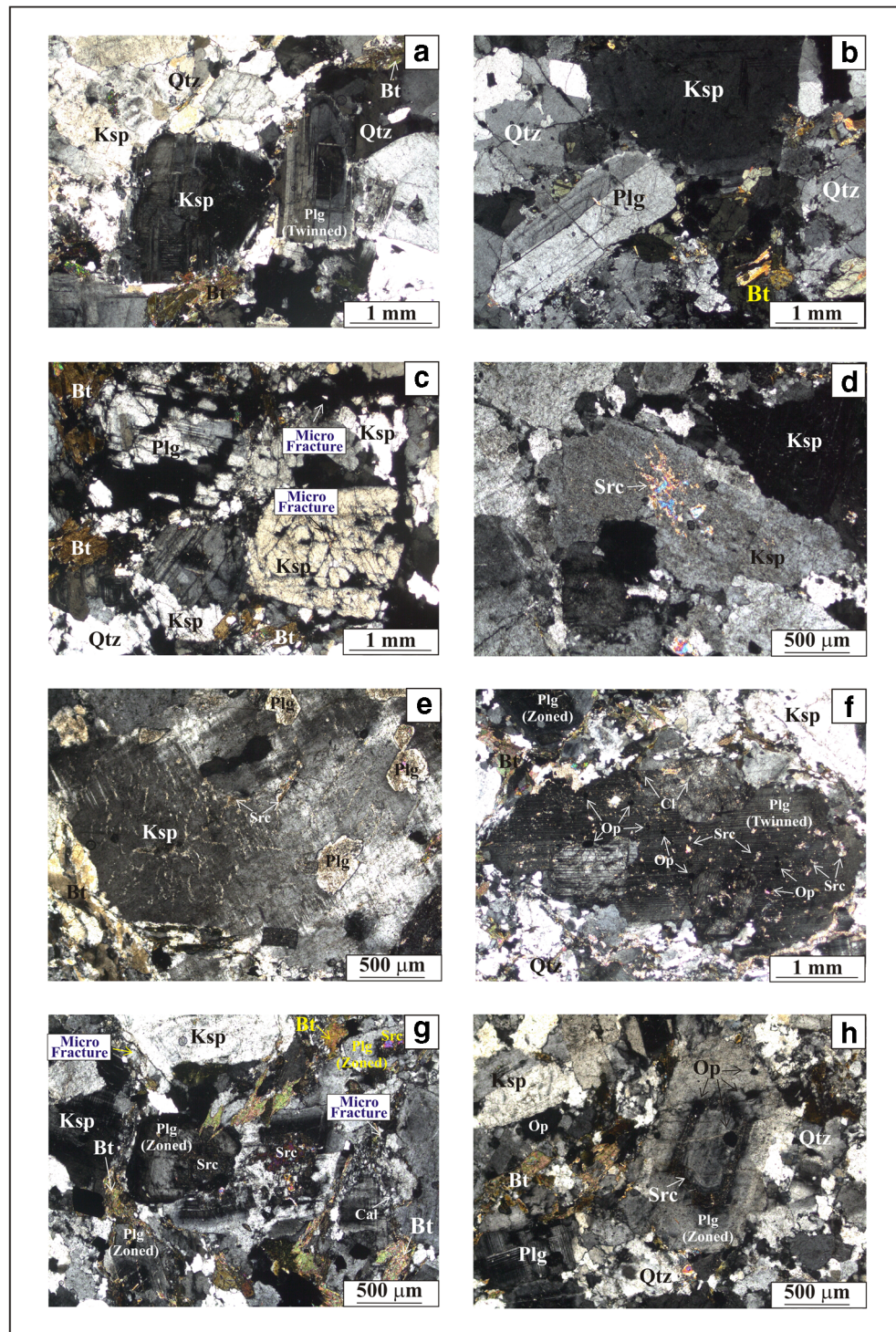
Granitic rocks were sampled from five different alteration zones around Kadıncık, Dinek, Tekören, and Karacaören areas. Fresh and altered samples were collected along road cuts and the quarry wall in the lateral direction (Fig. 2b, c).

Mineralogical-petrographical properties were determined with a polarizing light microscope, X-ray diffraction (XRD), and a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS). Mineral types and textural descriptions of granites were analyzed on thin sections with a polarizing light microscope. Plagioclase and K feldspar were used to reveal mineralogical-petrographical changes in granites during alteration. Therefore, the quantitative ratios of total and altered constituents in these minerals were counted using the image analysis system of the polarizing light microscope. The feldspar alteration index (FAI) was calculated using the following equation:

$$FAI = \frac{AFO}{TFO} \times 100$$

where FAI refers to the feldspar alteration index (%), AFO to the altered feldspar area (μm^2), and TFO to the total feldspar area (μm^2). In FAI calculations, 300–400 measurements were performed on thin sections of cube-shaped specimens prepared from 3 different surfaces.

Fig. 3 Microphotos of the Sivrihisar granites. Qtz, quartz; Ksp, alkali feldspar; Plg, plagioclase; Bt, biotite; Src, sericite; Cal, calcite; Cl, clays; Op, opaque minerals



Alteration minerals in granites were investigated using a Shimadzu XRD-6000 diffractometer (Ni filter, $\text{CuK}\alpha$ radiation, and a scanning speed of $2^\circ/\text{min}$). X-ray diffraction (XRD) analysis was conducted in two stages, including whole-rock and clay fraction analyses. Bulk mineralogy was analyzed using random powders. Clay mineralogy was determined on samples smaller than $2\ \mu\text{m}$. XRD analyses were

performed on air-dried (AD), ethylene glycol solvated (EG) and heated at $550\ ^\circ\text{C}$ (550) samples (Brown and Brindley 1980).

Morphological and microchemical analyses were performed using a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS). Before SEM analysis, freshly broken surface samples were coated

Table 3 The results of alteration indices of the Sivrihisar granites

Sample	FAI	CIA	I_{vp}	R_s
AD1-1	6.89	63.46	100.00	100.00
AD1-2	7.76	60.00	83.99	91.89
AD2-1	12.33	60.35	95.60	81.30
AD2-2	8.62	59.80	93.57	90.12
AD2-3	27.18	60.60	53.02	72.91
AD2-4	14.53	60.70	85.55	84.62
AD2-5	11.63	60.67	68.56	78.59
AD2-6	16.72	58.78	80.74	73.46
AD2-7	10.00	60.14	91.71	79.28
AD2-8	7.00	59.61	80.55	66.69
AD3-1	15.88	61.19	64.17	71.52
AD3-2	22.00	61.40	67.97	67.62
AD4-1	20.44	62.99	55.09	67.91
AD4-2	10.45	62.89	66.74	67.20
AD4-3	38.11	60.13	38.72	47.65
AD4-4	20.11	57.73	64.09	59.35
AD4-5	25.00	62.02	51.38	54.10
AD5-1	39.54	59.26	22.59	32.30
AD5-2	36.66	59.82	31.09	50.26
AD5-3	35.32		35.04	52.21
AD5-4	38.00	65.03	26.32	41.97

CIA chemical alteration index, R_s strength ratio, I_{vp} ultrasonic index, FAI feldspar alteration index

with carbon and examined using a Jeol-6400 Scanning Electron Microscope for morphological studies and microchemical analyses.

Major, trace, and rare earth element analyses were carried out with ICP-MS at the ACME Laboratory in Canada. Geochemical analyses have been carried out to reveal the chemical composition of the granites and chemical changes during alteration processes. Selected some major and trace element contents of the altered granites were normalized to the fresh granites to identify the element behaviors during alteration. The element mobility during alteration is determined using the method of MacLean and Kranidiotis (1987). Chemical changes were defined using the chemical alteration index (CIA) from Nesbitt and Young (1982).

The geomechanical properties, such as water absorption (TS EN 13755 2003), apparent density (TS EN 1936 2001), apparent porosity (TS EN 1936 2001), ultrasonic velocity (ISRM 2007), Schmidt hammer rebound (ISRM 2007), and uniaxial compressive strength (TS EN 1926 2000), were determined based on the standard test procedures suggested by TS EN and ISRM. Physical changes were determined using the P-wave velocity index (I_{vp}) (Ceryan et al. 2008), and the strength ratio was used to determine mechanical changes (Gupta and Rao 2001).

Table 4 The results of qualitative XRD analysis of granites from the Sivrihisar region

Sample	Primary minerals				Alteration minerals		
	Qtz	Ksp	Plg	Amp	Sm	Bt-Src	Kao
AD1-1	C	C	C	ND	T	M	T
AD1-2	C	C	A	T	M	C	ND
AD2-1	C	C	A	ND	T	T	M
AD2-2	C	C	C	ND	ND	C	ND
AD2-3	C	C	C	ND	ND	C	ND
AD2-4	C	C	C	ND	ND	T	ND
AD2-5	C	C	C	ND	ND	C	ND
AD2-6	C	M	A	T	M	C	M
AD2-7	C	C	C	ND	ND	T	M
AD2-8	C	C	A	ND	ND	T	T
AD3-1	M	A	C	T	ND	C	ND
AD3-2	C	C	C	ND	T	M	M
AD4-1	C	C	C	ND	ND	C	M
AD4-2	C	C	C	T	ND	C	ND
AD4-3	M	C	C	T	ND	C	ND
AD4-4	A	M	M	M	ND	C	ND
AD4-5	A	M	C	ND	M	M	T
AD5-1	C	M	M	M	ND	C	M
AD5-2	C	C	C	T	ND	C	ND
AD5-4	C	C	C	ND	M	T	M

Qtz quartz, Ksp alkali feldspar, Plg plagioclase, Amp amphibole, Sm smectite, Bt-Src biotite-sericite, Kao kaolinite, A abundant, C common, M minor, T trace, ND not detectable

Results

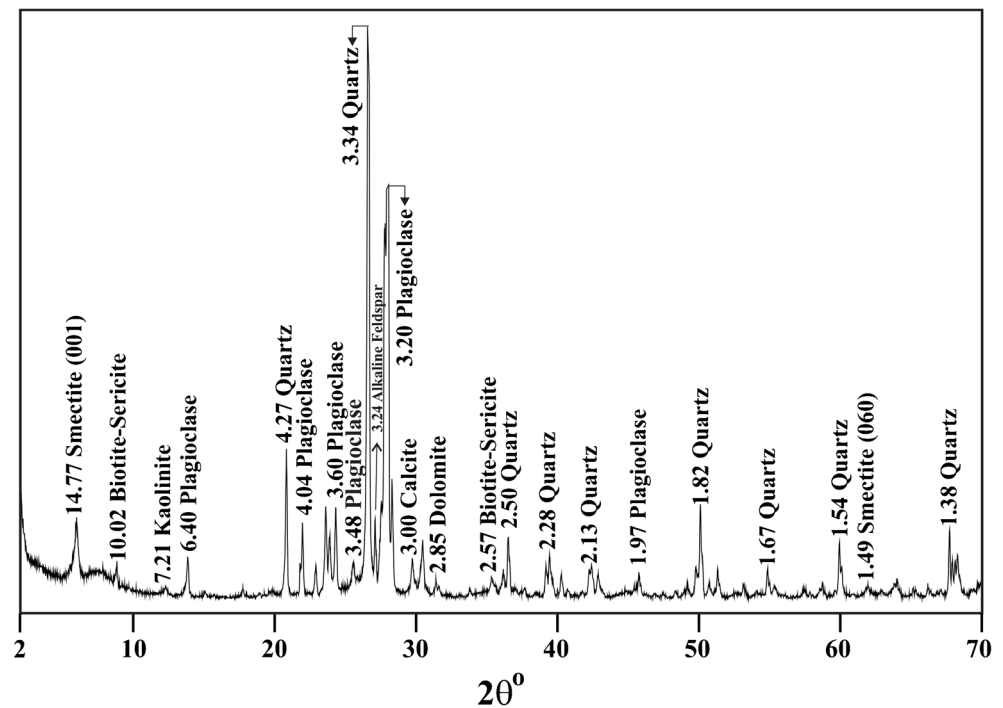
Mineralogy and petrography

Polarizing light microscope studies

Granites are mainly composed of plagioclase (oligoclase-andesine), alkali feldspar (orthoclase, microcline), quartz, biotite, and hornblende, as well as minor zircon, titanite, apatite, allanite, and opaque minerals (Table 2). Plagioclase minerals are characterized with their polysynthetic twinning and zoned structure. Microcline and orthoclase are the main alkali feldspars in the samples (Fig. 3a, b). Biotites are characterized by their greenish yellow pleochroism.

The most altered minerals were plagioclase and alkali feldspars. The minor effect of alteration was observed in biotites. The formation of microfractures was observed during the initial stage (AD2) of granite alteration. The microfractures are observed along the grain boundary and within plagioclase and alkali feldspar crystals (Fig. 3c, g). The dimensions of the altered areas were gradually enlarged with progressive alteration (Fig. 3d). Alkali feldspars were altered to sericite along cleavage and microfractures (Fig. 3e, f). Plagioclase twins

Fig. 4 Representative X-ray powder diffraction pattern of AD54 sample from the Sivrihisar granites



were easily recognized in the initial stage of alteration. However, the original twins were orientated and microfractured during alteration (Fig. 3g). The formation of sericite, calcite, clays, and opaque minerals was observed as secondary minerals of plagioclase and alkali feldspar (Fig. 3f–h). Alteration affected core of the zoned plagioclases, rather than the rim, indicating compositional differences in various zones (Fig. 3g, h). The pores occurred along cleavage, fractures, and twin planes with the progression of alteration in alkali feldspar and plagioclase. Secondary opaque mineral precipitations indicated a progressive alteration grade (AD5) in granites from Sivrihisar (Fig. 3f, g, h). Table 3 shows that the fresh/unaltered granite has a feldspar alteration index (FAI) value of 6.66%, and altered granite had a value of 35.44%.

X-ray diffractometer studies

Plagioclase, alkali feldspar, and quartz were common and abundant minerals, and mica (biotite-sericite) was also present in minor phases of fresh granites (Table 4; Fig. 4). The initial stage of alteration (AD2) was characterized by smectite, biotite-sericite, and kaolinite in trace and minor ratios. The amounts of these minerals increased in the progressive stages of alteration (AD4 and AD5). Kaolinite diffraction values of 7.19 Å $d(001)$ were unchanged by treatment with ethylene glycol, and disappeared as a result of heating at 550 °C. Smectites were characterized by a $d(001)$ value of 14.91 Å in an air-dried sample from AD54. An ethylene glycol treatment expanded $d(001)$ spaces to 17.19 Å due to extension in

the c -axis of the smectite. After heating at 550 °C, $d(001)$ spaces collapsed to 10.05 Å (Brown and Brindley 1980) (Fig. 5).

Scanning electron microscope determinations

Samples from different alteration zones were analyzed to produce morphological and microchemical results from the Sivrihisar granite using a scanning electron microscope. Plagioclase was more altered than alkali feldspar crystals. In the initial stage of alteration, alkali feldspar and plagioclase were altered to sericite minerals in voids along crystallographic discontinuities such as twinning planes, microfractures, and core of zoned plagioclase (Fig. 6a–c). The progressive stages of alteration were represented by the formation of smectite flakes, platy kaolinite crystals, and opaque minerals in pores of the dissolved plagioclase (Fig. 6d–f). The microfractures and pores indicate dissolution of plagioclase and alkali feldspar.

EDS results from the zoned plagioclase crystals showed that the core was more altered than the margin of the plagioclase (Fig. 7a, b). The margin of plagioclase represents typically the oligoclase and andesine compositions and has Si, Al, Na, and Ca contents (spectrum 1 in Fig. 7a, b). The core of plagioclase exhibits depletion of Na, Si, and Ca; and gradational enrichment of Mg, Al, K, and Fe (spectra 2 and 3 in Fig. 7a, b). The mobility of these elements explains alteration of plagioclase to sericite and smectite minerals (Fig. 7a–d). Besides, Si and K were decreased and Mg, Al, Ca, and Fe increased during alteration of alkali feldspar to smectite (spectra 1 and 2 in Fig. 7e). The magnesium, calcium, and

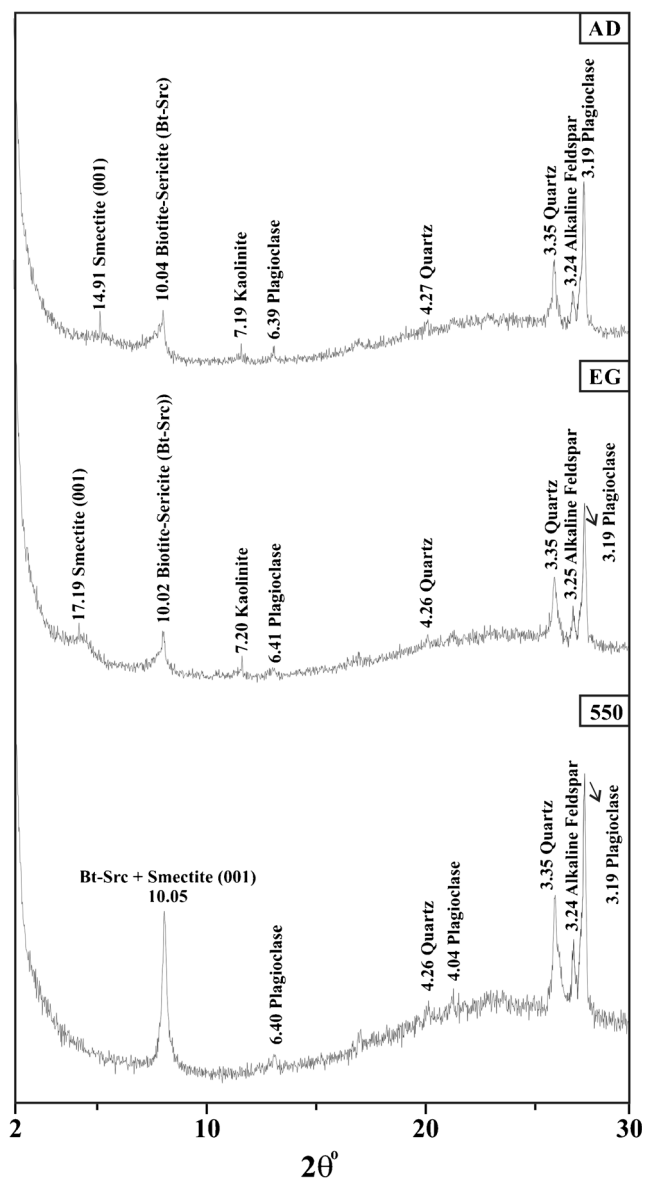


Fig. 5 Representative XRD patterns of clay fraction of AD54 sample from the Sivrihisar granites. D, air-dried; EG, ethylene glycolated; (550), heated at 550 °C

iron enrichments in the altered alkali feldspar represent altering solutions composition (spectra 2 and 3 in Fig. 7e). The presence of ZrO_2 , P_2O_5 , SO_3 , BaO, and PbO on quartz surfaces points to the enrichment of these metallic elements during progressive stages of alteration (spectra 2 and 3 in Fig. 7f).

Geochemistry

The results of major, trace, and rare earth element analyses were used to identify the geochemical characteristics of the granites, and to determine the changes in the contents of various elements during alteration (Table 5). On the total alkali versus silica diagram (Le Maitre 2002), fresh (AD1) and

slightly altered (AD2) rocks plot within the granite field, while moderately altered (AD3), highly altered (AD4), and completely altered (AD5) rocks plot within the granodiorite and quartz monzonite fields (Fig. 8). The CIA developed by Nesbitt and Young (1982) is presented in Table 3. The change in CIA values is directly proportional to the degree of alteration of the granites from Sivrihisar. The fresh rocks (AD1) have lower CIA values (than completely altered samples (AD5)). The results of major, trace, and rare earth element analyses of the altered granites were compared to those of fresh samples (AD1-1) to elucidate the elemental behaviors during granite alteration (Fig. 9). The positive values show enrichment and negative data indicate the depletion of elements with respect to the fresh rocks. While Si was enriched in zones AD2 and AD4, Si depletion was observed in zones AD3 and AD5. Al and Na exhibit similar tendencies during granite alteration. The contents of these elements decreased in the early zones (AD2 and AD3) of alteration, whereas significant enrichment occurred for Al and Na with increasing alteration. Fe, Mg (except for AD2), Ca, and K concentrations show a continuous increase from zone AD2 to AD5. Ti, Mn, P, Hf, Ta, and Zr show immobile behavior during granite alteration. Behavioral patterns of large ion lithophile elements (LILEs), such as Ba, Rb, and Sr, were all similar (except for the enrichment of Sr in AD5). They display enrichments in alteration zones AD2 and AD4, and depletions in zones AD3 and AD5. Y was enriched with increasing alteration, and the total rare earth elements (ΣREE) exhibited similar tendencies (Fig. 9).

Geomechanical properties

Results of the geomechanical tests carried out on granites from Sivrihisar are given in Table 6. Geomechanical properties changed due to an increasing degree of alteration (Fig. 10). Water absorption was 0.11% in the first stage of alteration (AD1-1). However, this value reached 2.39% in the advanced stage (AD5) of alteration. The apparent density changed from 2.68 g/cm³ (AD1) to 2.50 g/cm³ (AD5) in an inverse proportion to the degree of alteration. P-wave velocity values decreased in relation to the degree of alteration. The average value of P-wave velocity in stage AD1 was 4597 m/s, while the value for stage AD5 was 1039 m/s. Similarly, SHVs decreased with an increasing degree of alteration. Uniaxial compressive strength (UCS) varied similarly to P-wave velocity, and increasing degrees of alteration led to reductions in the uniaxial compressive strength of the granites. The highest UCS of the granite from Sivrihisar in the first stage of alteration (AD1) was 1072 kgf/cm², which decreased to 346.2 kgf/cm² in the advanced stage of alteration (AD5). Ultrasonic index (I_{vp}) and strength ratio (R_s) were calculated using P-wave velocity and UCS values (Table 3). The highest I_{vp}

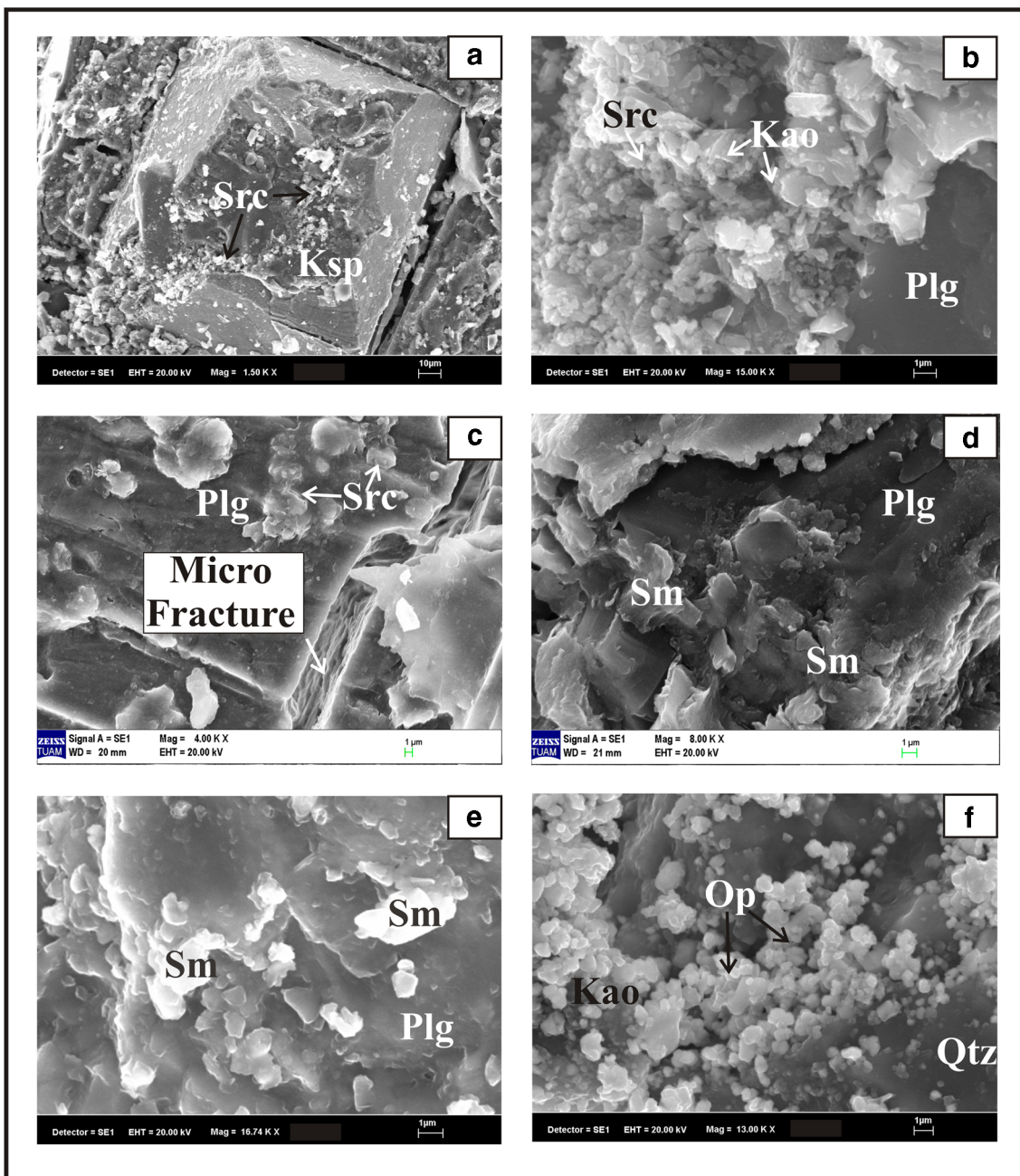


Fig. 6 Scanning electron micrographs of the Sivrihisar granites. Qtz, quartz; Ksp, alkali feldspar; Plg, plagioclase; Src, sericite; Sm, smectite; Op, opaque minerals

and R_s values, which varied inversely with the degree of alteration, were obtained in the first stage of alteration (AD1).

Discussions

Mineralogy and geochemistry of alteration

Granitic rocks are the most common plutonic rocks in the earth's crust. The original features of rocks are weakened and deteriorated during weathering and hydrothermal

alteration (Arel and Tugrul 2001; Lee et al. 2008; Ceryan et al. 2008; Momeni et al. 2015). Rock-forming minerals in granites, such as plagioclase, alkali feldspar, and biotite, are converted to clays and other secondary minerals. Leaching of elements from altered minerals combining with elements in the liquid phase and in situ enrichment are the most important mineralogical and geochemical processes that occur during the alteration of granitic rocks (Islam et al. 2002; Lee et al. 2008).

Smectite, sericite, and kaolinite are the main alteration minerals in the granitic rocks from Sivrihisar. SEM studies

Fig. 7 The semi-quantitative EDS results of the Sivrihisar granites. Qtz, quartz; Ksp, alkali feldspar; Plg, plagioclase; Src, sericite; Sm, smectite; Cal, calcite; Op, opaque minerals

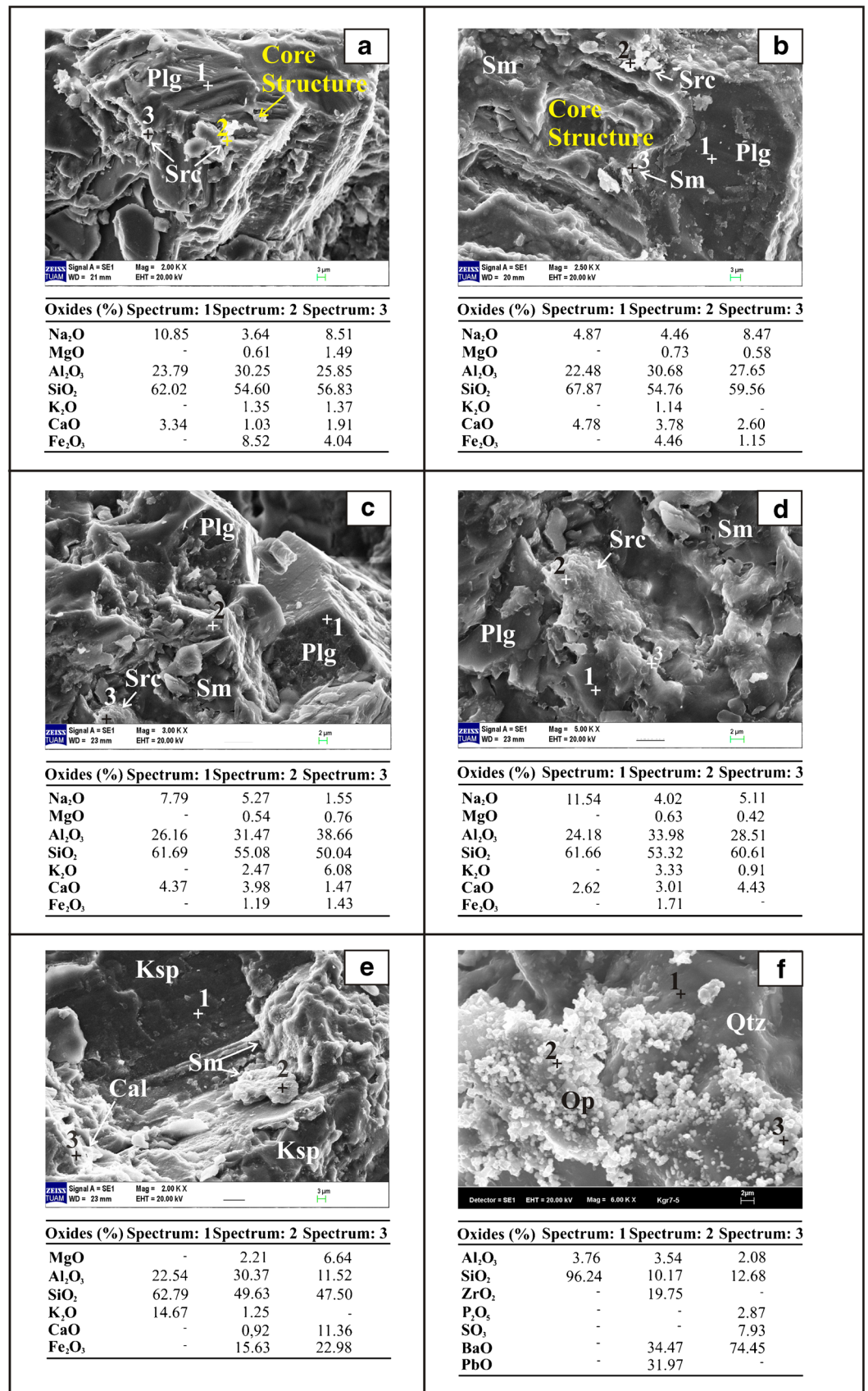
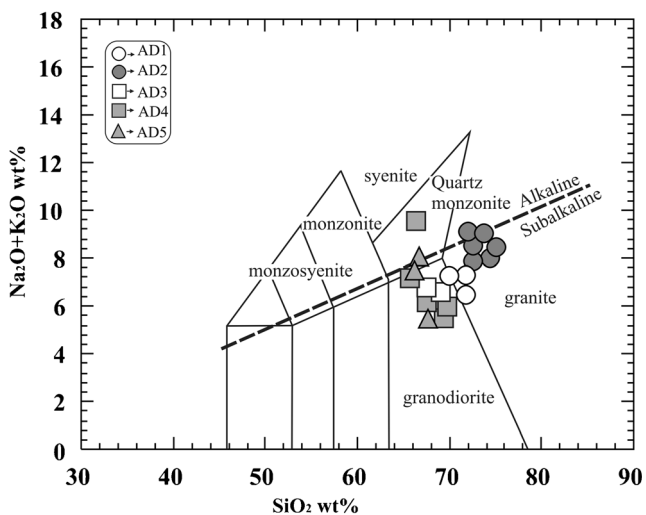


Table 5 The results of the major oxides (wt%) and trace and rare earth element analysis (ppm) of granites from the Sivrihisar region

Sample	AD1-1	AD1-2	AD2-1	AD2-2	AD2-3	AD2-4	AD2-5	AD2-6	AD2-7	AD2-8
SiO ₂	69.56	69.23	74.43	74.40	72.56	73.68	75.16	63.19	73.10	72.64
TiO ₂	0.27	0.25	0.03	0.03	0.03	0.04	0.03	0.40	0.03	0.03
Al ₂ O ₃	16.01	15.45	14.14	14.09	14.75	14.66	13.99	16.73	14.80	15.13
Fe ₂ O ₃	3.02	2.78	1.10	1.10	1.50	0.91	0.88	4.16	1.07	0.90
MnO	0.10	0.07	0.02	0.02	0.02	0.02	0.02	0.08	0.01	0.02
MgO	0.62	0.80	0.09	0.08	0.08	0.09	0.08	1.93	0.05	0.08
CaO	3.01	3.16	1.30	1.29	1.70	0.45	0.60	4.77	1.26	1.74
Na ₂ O	4.34	4.61	4.13	3.76	4.32	3.91	4.05	4.74	3.66	4.18
K ₂ O	1.87	2.53	3.86	4.42	3.57	5.13	4.42	2.22	4.89	4.33
P ₂ O ₅	0.11	0.11	0.04	0.03	0.04	0.04	0.04	0.23	0.05	0.03
L.O.I.	0.90	0.70	0.70	0.60	1.20	0.90	0.60	1.20	0.90	0.70
Sum	99.80	99.70	99.82	99.79	99.78	99.82	99.83	99.66	99.83	99.76
Rb	85.50	75.60	109.90	124.00	105.00	163.50	141.60	60.30	126.90	134.00
Sr	405.50	881.90	135.60	150.90	169.00	97.30	87.80	1018.20	135.70	185.60
Ba	548.00	986.00	1107.00	1447.00	1578.00	1156.00	966.00	896.00	1128.00	1723.00
Zr	160.90	152.80	26.90	22.90	37.70	30.40	43.60	161.50	26.90	28.10
Hf	4.30	4.80	1.50	1.00	1.50	1.40	1.60	4.20	1.30	1.20
Ta	0.50	0.50	0.60	0.60	0.70	1.20	1.20	0.50	0.60	0.40
Y	16.10	14.30	11.40	8.00	8.40	16.00	20.60	17.80	16.30	8.30
Cu	1.90	3.60	4.40	2.50	4.10	1.20	1.30	8.10	12.70	1.90
Zn	45.00	51.00	9.00	6.00	6.00	2.00	2.00	44.00	6.00	4.00
Pb	3.40	5.70	7.30	4.80	8.00	8.40	9.60	3.70	7.30	5.60
Ni	3.20	5.70	3.90	1.30	9.30	2.60	2.30	12.10	3.20	1.80
Co	2.50	3.60	0.60	0.50	0.70	0.40	0.50	8.80	0.80	0.40
La	34.50	33.80	6.20	4.80	4.80	8.90	8.30	50.10	10.00	14.30
Ce	66.20	68.10	12.90	8.80	9.50	19.70	16.90	100.70	17.70	28.50
Pr	6.68	7.04	1.41	0.97	1.00	2.44	1.98	10.61	2.28	3.13
Nd	22.50	25.50	5.20	3.70	3.90	9.10	7.50	38.90	8.30	11.60
Sm	3.61	3.95	1.31	1.02	1.00	2.82	2.13	6.12	2.02	2.28
Eu	0.88	0.96	0.42	0.49	0.52	0.44	0.38	1.52	0.50	0.59
Gd	2.61	2.92	1.31	0.96	1.04	2.83	2.54	4.24	1.95	1.78
Tb	0.45	0.43	0.27	0.21	0.20	0.52	0.52	0.59	0.38	0.27
Dy	2.73	2.45	1.71	1.26	1.33	2.99	3.38	2.92	2.41	1.42
Ho	0.55	0.46	0.37	0.25	0.26	0.50	0.64	0.55	0.51	0.28
Er	1.80	1.36	1.11	0.79	0.82	1.56	1.93	1.60	1.79	0.78
Tm	0.27	0.22	0.18	0.12	0.15	0.23	0.31	0.23	0.28	0.13
Yb	1.93	1.48	1.20	0.87	0.96	1.55	1.97	1.64	1.80	0.84
Lu	0.33	0.23	0.19	0.14	0.16	0.24	0.32	0.24	0.29	0.14
Sample	AD3-1	AD3-2	AD4-1	AD4-2	AD4-3	AD4-4	AD4-5	AD5-1	AD5-2	AD5-4
SiO ₂	68.27	69.12	69.42	69.92	65.62	66.35	69.37	66.71	66.26	68.65
TiO ₂	0.25	0.27	0.22	0.19	0.34	0.23	0.23	0.26	0.28	0.28
Al ₂ O ₃	16.00	15.57	16.27	15.93	17.13	16.87	15.61	16.71	16.39	16.25
Fe ₂ O ₃	3.53	3.02	2.29	2.77	3.07	2.22	3.05	2.60	3.22	3.26
MnO	0.10	0.10	0.10	0.11	0.08	0.05	0.09	0.06	0.07	0.07
MgO	0.69	0.71	0.64	0.56	1.09	0.93	0.54	0.97	1.27	0.55
CaO	3.48	3.23	4.08	3.74	4.19	2.79	3.16	3.41	3.54	3.18
Na ₂ O	4.20	4.11	4.10	4.12	5.05	4.45	4.19	5.22	4.33	4.34
K ₂ O	2.47	2.45	1.38	1.54	2.12	5.11	2.21	2.86	3.14	1.22
P ₂ O ₅	0.10	0.09	0.07	0.08	0.17	0.11	0.10	0.11	0.19	0.11

Table 5 (continued)

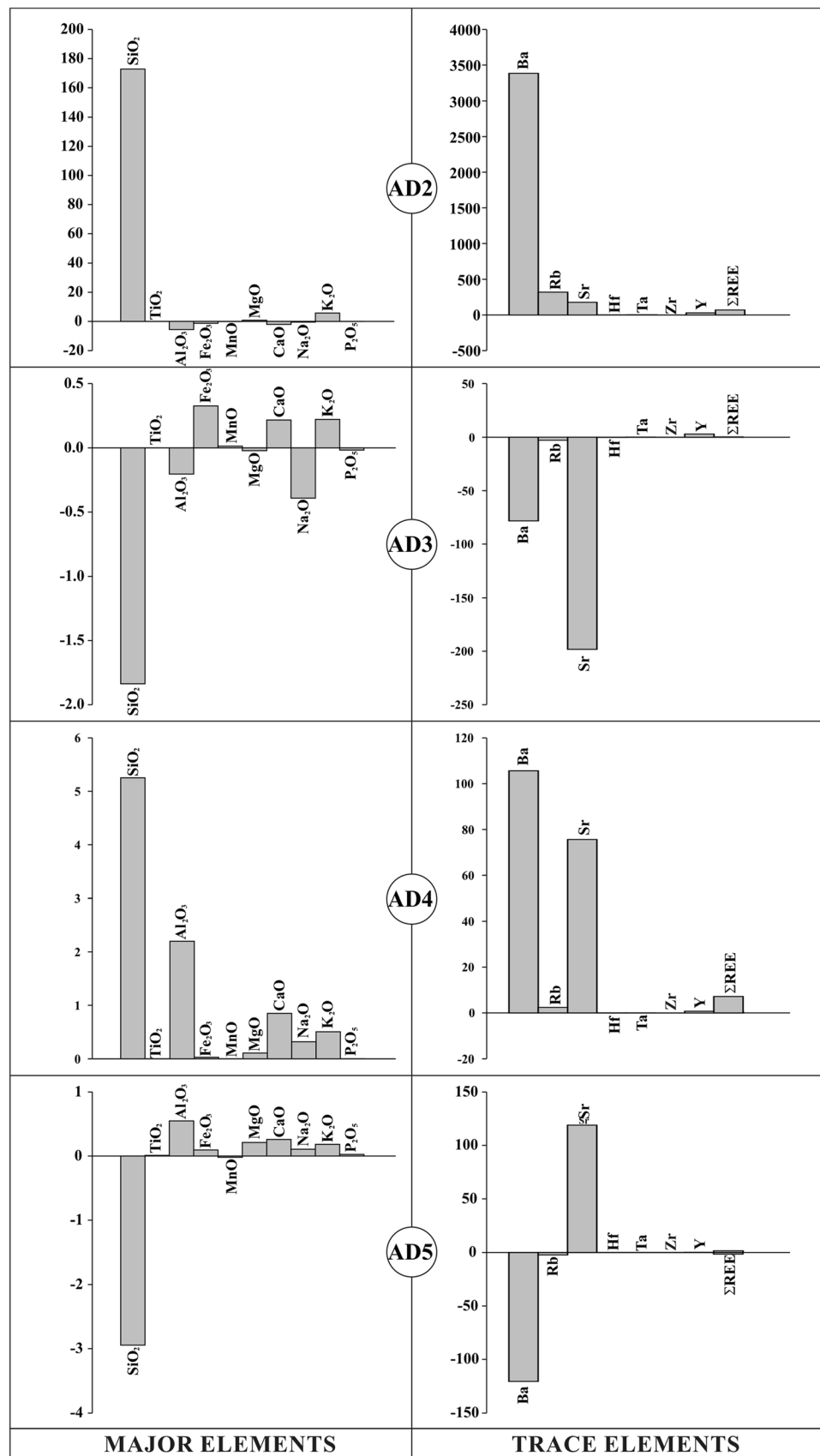
Sample	AD1-1	AD1-2	AD2-1	AD2-2	AD2-3	AD2-4	AD2-5	AD2-6	AD2-7	AD2-8
L.O.I.	0.70	1.10	1.30	0.90	0.80	0.50	1.30	0.80	1.00	1.90
Sum	99.79	99.78	99.84	99.86	99.67	99.60	99.81	99.72	99.69	99.83
Rb	80.90	77.10	43.00	47.80	61.30	160.80	66.50	102.10	76.50	59.90
Sr	476.60	429.70	416.30	392.40	1067.20	1000.70	413.40	981.80	941.20	400.10
Ba	666.00	735.00	387.00	354.00	906.00	1783.00	561.00	705.00	988.00	276.00
Zr	162.70	156.40	118.40	124.50	190.30	141.70	142.50	164.50	125.30	188.00
Hf	4.60	4.30	3.40	3.70	5.60	3.90	3.90	5.00	3.60	5.30
Ta	0.60	0.60	0.30	0.40	0.60	0.40	0.50	0.40	0.50	0.70
Y	17.70	19.30	15.60	13.70	17.60	10.00	16.10	11.60	12.90	22.20
Cu	5.30	4.40	1.90	2.90	7.20	6.80	2.80	8.90	7.00	2.60
Zn	45.00	44.00	44.00	41.00	50.00	31.00	42.00	40.00	38.00	39.00
Pb	3.30	2.00	1.10	2.10	3.50	9.80	2.60	9.80	4.60	2.90
Ni	6.90	1.80	1.90	4.10	3.80	5.40	5.10	8.40	10.00	4.70
Co	3.20	3.00	2.20	2.20	4.90	4.30	2.70	5.40	6.40	2.30
La	36.80	33.10	29.00	14.70	43.90	30.90	42.70	35.90	32.40	32.20
Ce	71.20	64.90	59.00	29.70	87.00	61.10	84.10	72.40	66.30	59.50
Pr	7.17	6.69	6.20	3.23	9.15	6.56	7.72	7.51	7.02	6.58
Nd	24.10	22.70	21.50	11.80	33.60	24.80	26.90	27.70	26.00	22.90
Sm	3.84	3.91	3.59	2.16	5.32	3.63	3.81	4.11	4.26	4.35
Eu	0.91	0.92	0.92	0.72	1.35	0.97	0.92	1.05	1.10	1.05
Gd	2.84	3.11	2.70	1.82	3.90	2.59	2.80	2.82	3.12	3.42
Tb	0.49	0.54	0.44	0.32	0.58	0.35	0.49	0.38	0.45	0.60
Dy	2.98	2.97	2.64	1.87	2.88	1.76	2.63	1.90	2.25	3.49
Ho	0.60	0.63	0.49	0.41	0.55	0.31	0.58	0.36	0.43	0.72
Er	1.87	1.94	1.57	1.36	1.56	0.92	1.80	0.96	1.22	2.28
Tm	0.30	0.32	0.27	0.25	0.24	0.14	0.30	0.15	0.19	0.35
Yb	1.97	2.12	1.72	1.78	1.72	0.92	2.09	1.09	1.27	2.53
Lu	0.35	0.36	0.29	0.32	0.26	0.15	0.35	0.17	0.19	0.42

**Fig. 8** TAS (total alkali vs. silica) chemical nomenclature diagram (after Le Maitre 2002) of the Sivrihisar granites

showed that the alteration of plagioclase and alkali feldspar led to the formation of these minerals. Plagioclase and alkali feldspar were hydrated and converted into clay minerals during the alteration of granite (Velde 1995). Physicochemical and environmental conditions controlled the formation of kaolinite and smectite minerals in the alteration zones. If solutions reached a pH of 4–5, kaolinite is found in the alteration zones (Karakaya et al. 2001). However, smectite forms under alkaline conditions with high ratios of cation/H⁺ (Christidis and Markopoulos 1995). Sericite is an intermediate product of the alteration of plagioclase and alkali feldspar to smectite and kaolinite. In XRD studies, kaolinite and smectite increased; however, sericite decreased with progressive alteration.

PLM and SEM studies show that the core structure of the zoned plagioclase crystals was more altered than the margin of the crystals. The calcium content in the core of plagioclase excessively decreases suggesting dissolution of plagioclase (spectra 2 and 3 in Fig. 7a, b). The sericite, smectite, and illite

Fig. 9 Mass changes of major elements (g) and trace elements (ppm) during alteration of the Sivrihisar granites



minerals in pores along twinning planes, microfractures, and core of dissolved plagioclase reveal that these minerals are direct precipitated by the infiltrating fluids (spectra 2 and 3 in Fig. 7a–e). The microtextural characteristics of feldspars and clay minerals closely resemble those from southern Iberian massif (Spain). The textural relations between clay minerals and feldspars with finely and randomly oriented crystalline clay minerals infilling secondary porosity of the feldspar are considered evidence of solution-precipitation mechanism in alteration of plagioclase and alkali feldspar in granitic stocks from southern Iberian massif (Spain) by Jimenez-Espinoza et al. (2007). Although plagioclase minerals display compositional zoning and Ca-rich core of the crystals alters more easily (Inskeep et al. 1991; Williams et al. 1993; Oliva et al. 2004; Vazquez et al. 2016), the reason of easy alteration of the crystal core is still debatable. Banfield and Eggleton (1990) and Lee et al. (2008) interpreted that the alteration of the inner side of plagioclase is defined as selective alteration of calcic plagioclase. According to these authors, intrusive diffusion of water begins at defect or dislocation sites on crystal surfaces or crystal boundaries, and H⁺ ions in water replace the soluble compounds (preferentially Ca cation). Therefore, compositionally different sides of plagioclase minerals are selectively dissolved due to intrusive

diffusion of hydrogen ions. Blum and Stillings (1995) interpreted that anorthite-rich plagioclase have higher experimental dissolution rates which can contribute to the more rapid development of internal permeability in igneous rocks. Jimenez-Espinoza et al. (2007) considered that high fracturation and high Ca-rich plagioclase contents with an interconnected textural arrangement are key factors to produce the pervasive weathering in the Santa Elena granodiorite, which is rich in plagioclase. The differential weathering between alkali feldspar and plagioclase occurs in weathering profiles in granitoid rocks from Sila Massif (Calabria, Italy). Plagioclase crystals display diffuse dissolution features and have secondary clay and sericite formations limited to their core as a result of chemical weathering. Besides, hydrothermal alteration rarely affects alkali feldspar in Sila plutonic rocks. Scarciglia et al. (2016) reported that these weathering differences are due to in situ hydrolysis of plagioclase, incomplete sericitization, and low fluid/rock ratios. The breakdown in the inner part of plagioclase grains and alteration minerals such as smectite, chlorite, and illite in pores inside the grains and microcracks was also observed in Late Cretaceous-Paleogene granitoids from central Japan (Nishimoto et al. 2008; Nishimoto and Yoshida 2010). They argued that Ca-rich core dissolved due to the higher solubility of Ca-rich plagioclase in water and selective dissolution and that direct precipitation process controlled the formation of alteration minerals. According to White et al. (2001), faster plagioclase reaction in bedrock weathering profiles from Panola granite is derived from a higher anorthite component of plagioclase and wetter and warmer climate. They indicated that mineral weathering depends on the movement of reactants and products in the fluids, which is controlled by the hydraulic conductivity of the rocks.

Alteration, hydrolysis, and hydration of rock-forming minerals and formation of secondary minerals play an important role in the behavior of elements during the alteration of granitic rocks (Islam et al. 2002; Ceryan et al. 2008; Lara et al. 2018). Depletion of elements during alteration is caused by the migration of soluble and complex ions in parent rocks. However, enrichment of elements indicates structural integration, adsorption, or precipitation of solution (Zielinski 1982). In our study, the leaching of Si, Al, Na, and Ca results from alteration of plagioclase. However, enrichment of Si, Al, Na, Ca, Mg, K, and Fe reveal that these elements precipitated in smectite, sericite, and kaolinite minerals during alteration. K, Na, Ca, Mg, and Fe were abundantly leached, and Al was enriched during kaolinization of granites (Coggan et al. 2013; Chiu and Ng 2014; Kajdas et al. 2017).

Formation of smectite entails the loss of alkalis and enrichment of magnesium when pore fluids have low salinity and alkalinity (Christidis 1998; Yildiz and Kuşçu 2004). Rock-forming minerals in magmatic rocks affect the behavior of LILE elements (e.g., Ba, Rb, and Sr) during alteration (Yalçın and Gümüşer 2000). Sr enrichment was observed

Table 6 The results of geomechanical tests of the Sivrihisar granites

Sample	WA	AP	PWV	SH	UCS	
AD1-1	0.11	2.66	0.36	4597	60	1072.1
AD1-2	0.25	2.68	0.65	3861	58	985.1
AD2-1	0.51	2.58	1.30	4395	47	871.6
AD2-2	0.26	2.60	0.65	4302	44	966.2
AD2-3	1.73	2.56	2.38	2438	46	781.6
AD2-4	0.68	2.63	1.75	3933	49	907.2
AD2-5	1.11	2.56	2.80	3152	45	842.5
AD2-6	0.34	2.61	0.93	3712	43	787.6
AD2-7	0.24	2.56	0.70	4216	48	850.0
AD2-8	0.30	2.60	0.80	3703	42	715.0
AD3-1	0.24	2.56	0.63	2950	39	766.8
AD3-2	0.40	2.60	1.20	3125	36	725.0
AD4-1	1.04	2.53	2.69	2533	28	728.0
AD4-2	0.55	2.58	1.44	3068	29	720.4
AD4-3	1.45	2.55	3.69	1780	25	510.8
AD4-4	0.80	2.56	2.09	2947	28	636.3
AD4-5	0.60	2.55	1.45	2362	28	580.0
AD5-1	2.39	2.57	5.96	1039	10	346.2
AD5-2	0.42	2.55	4.08	1429	16	538.9
AD5-3	2.35	2.51	5.89	1611	15	559.8
AD5-4	1.80	2.50	4.80	1210	15	450.0

WA water absorption (wt%), γ apparent density (g/cm^3), AP) apparent porosity (wt%), UCS uniaxial compressive strength (kgf/cm^2), PWV P-wave velocity (m/s), SHV Schmidt hammer rebound

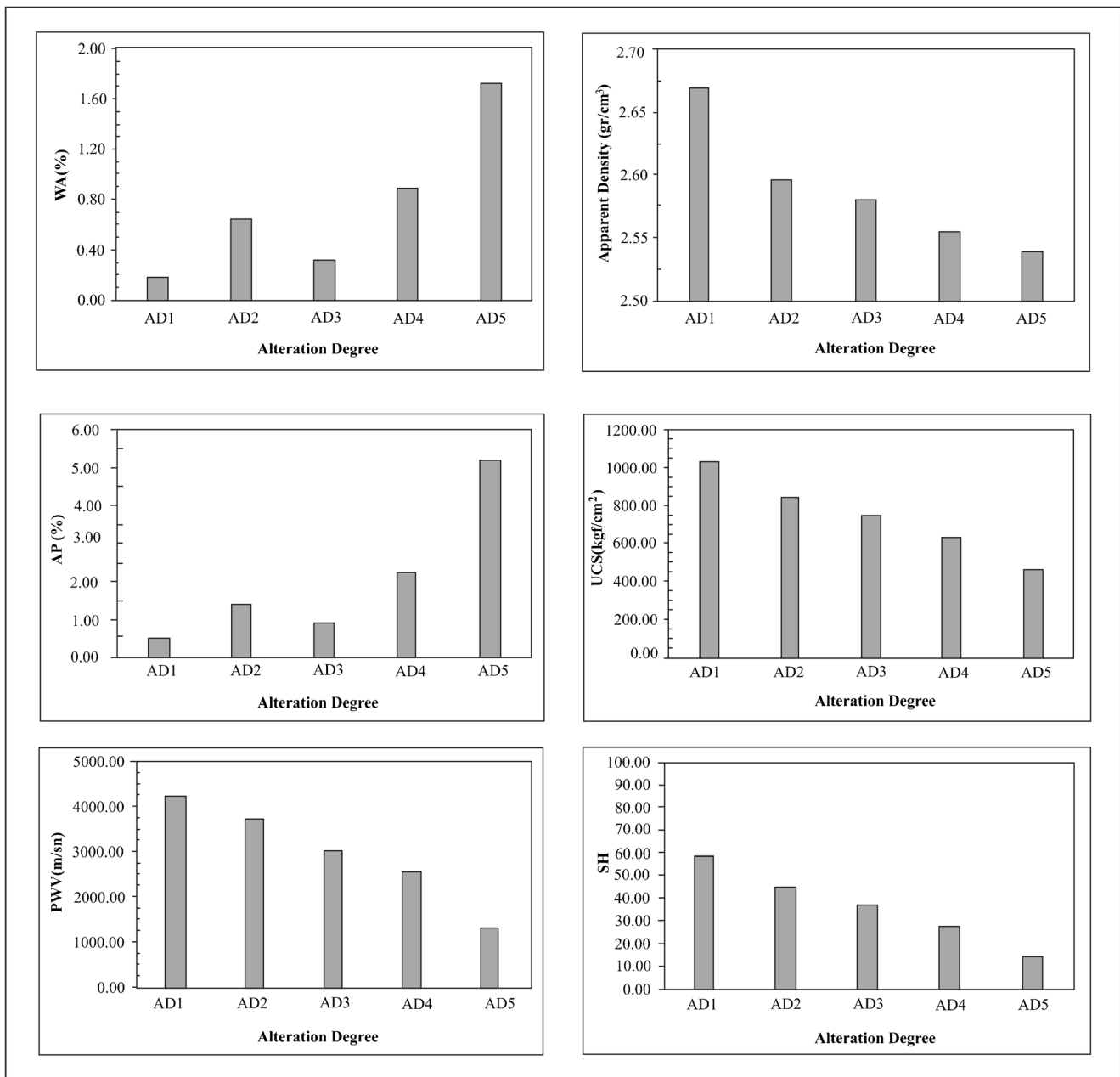


Fig. 10 The geomechanical properties versus alteration stages for the Sivrihisar granites

during the alteration of K- and Ca-bearing minerals. Alteration of alkali feldspar and hornblende caused leaching of Ba, Rb, and K_2O .

Geomechanical properties

Minero-petrographical and geochemical changes in igneous rocks during alteration cause variations in physical and mechanical properties of rocks. Deterioration of original appearance, increase in porosity, decrease in density, and reduction in strength are important physical and

mechanical changes during alteration (Yildiz et al. 2010; Heidari et al. 2013; Momeni et al. 2015). Alteration and opacification processes of the main constituent minerals affect the cracking process of each mineral individually (Ündül 2016). Water absorption and apparent porosity of studied samples increased; however, apparent density, P-wave velocity, SHV, and UCS decreased with progressive alteration (Fig. 10). The variations in water absorption, apparent porosity, P-wave velocity, SHV, and UCS are consistent with the results of Gupta and Rao (1998), Coggan et al. (2013), Heidari et al. (2013), and Momeni et al. (2015).

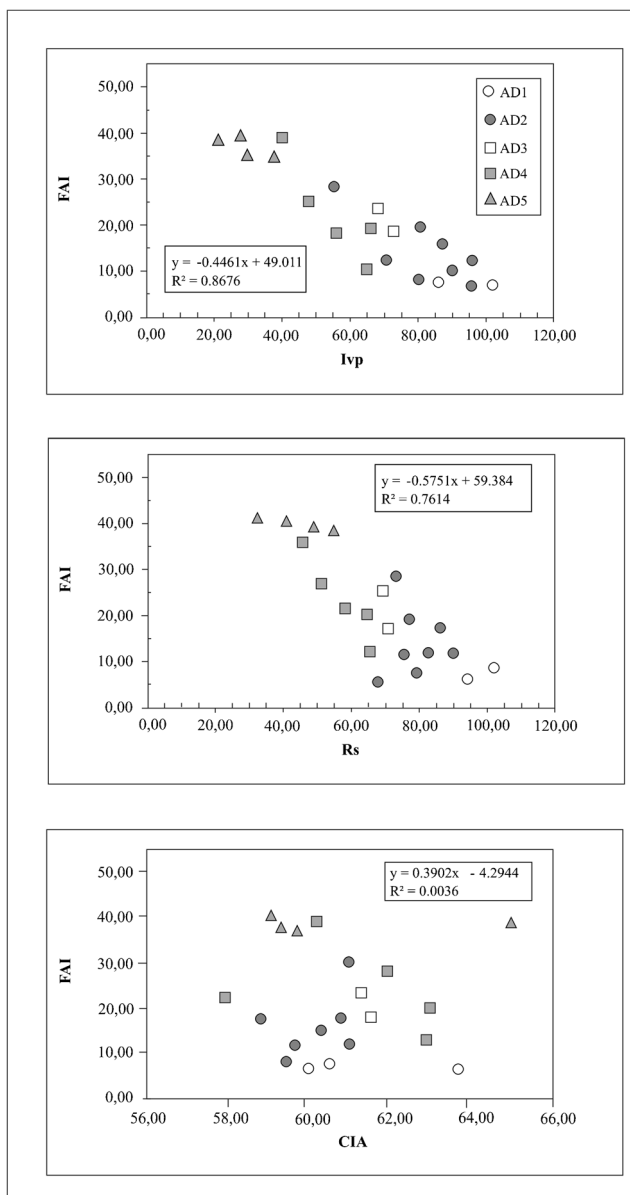


Fig. 11 The relationship among feldspar alteration index (FAI), chemical alteration index (CIA), ultrasonic index (I_{vp}), and strength ratio (R_s)

The development of microfractures (Fig. 3c, g and Fig. 6c) and dissolution structures (Figs. 6 and 7) in studied samples enhance porosity with progressive alteration. Increasing porosity promotes the apparent density, P-wave velocity, and UCS to decrease. The higher porosity and formation of smectite (Fig. 6d, e; Fig. 7b–e) lead to an increase water absorption (AD5 and AD6). The dissolution of feldspar effect on physical properties such as porosity, permeability, and water adsorption was also concluded by Heidari et al. (2013) and Tan et al. (2017). Alteration degree influences P-wave velocity through rock matrix. The higher values of the ultrasonic velocity were obtained in fresh granites. However, the remarkable reduction in the P-wave velocity values was recorded altered granites from Northern Portugal. Vasconcelos et al. (2008) interpreted

that these differences in P-wave velocity values were related to the increase in voids, pores, and microfractures based on alteration. The propagation of microfractures and transformation of plagioclase and alkaline feldspar into smectite and sericite generate weakness zone along boundary between feldspar crystals with different alteration degree, break intergranular bonds, and framework of granites. These alteration processes result in reduction of UCS values (from 1072.16 kgf/cm² in AD1 to 985 kgf/cm² in AD5) of the granites from Sivrihisar.

Index properties of granites

Mineralogical and petrographical characteristics such as abundances, distribution, geometry, and alteration degree of primary minerals and microfractures of granites control their petrophysical (e.g., unit weights and ultrasonic P-wave velocity), mechanical (unconfined compressive strength (UCS)), and elastic properties (e.g., Young's modulus, Poisson's ratio) (Ündül 2016). Changes in these characteristics during alteration were used for determination of alteration degree of granites. The determination of rock alteration is very important for industrial applications and engineering projects. Several researches proposed various alteration indices based on those characteristics for this purpose. The quantitative index (Lump 1962), micropetrographic index (Irfan and Dearman 1978), secondary mineral content, microfracture and void ratio (Ceryan 1999; Pera Le et al. 2001), unsound constituent index (Gupta and Rao 2001), the micropetrographic strength index (Ips), and the replacement index (Rigopoulos et al. 2010), mineralogical alteration index (Yildiz et al. 2010), and k-product index (Ceryan 2015) are the most commonly used mineralogical and petrographical indices in various magmatic rock types.

Given the above indices, the ratio of sound and unsound constituents, important rock-forming minerals such as quartz and feldspar, and width and length of microcracks and voids are important parameters considering in determination of alteration degree of magmatic rocks. However, few researchers studied in detail alteration state of feldspar minerals as an indicator of alteration degree. The changes in plagioclase crystals during chemical weathering were revealed using scanning electron microscope images by Hu et al. (2014). The solution state of plagioclase was considered a measure of weathering degree of granites in Hong Kong. The plagioclase solution degree index was proposed as a new index in this study. In contrast to the former indices, the alteration states of plagioclase and alkaline feldspar were used in the present study, because plagioclase and alkaline feldspar are both primary minerals in granites and more unstable than other minerals of granites during alteration. In our study, a feldspar alteration index (FAI) has been developed as a new method to examine

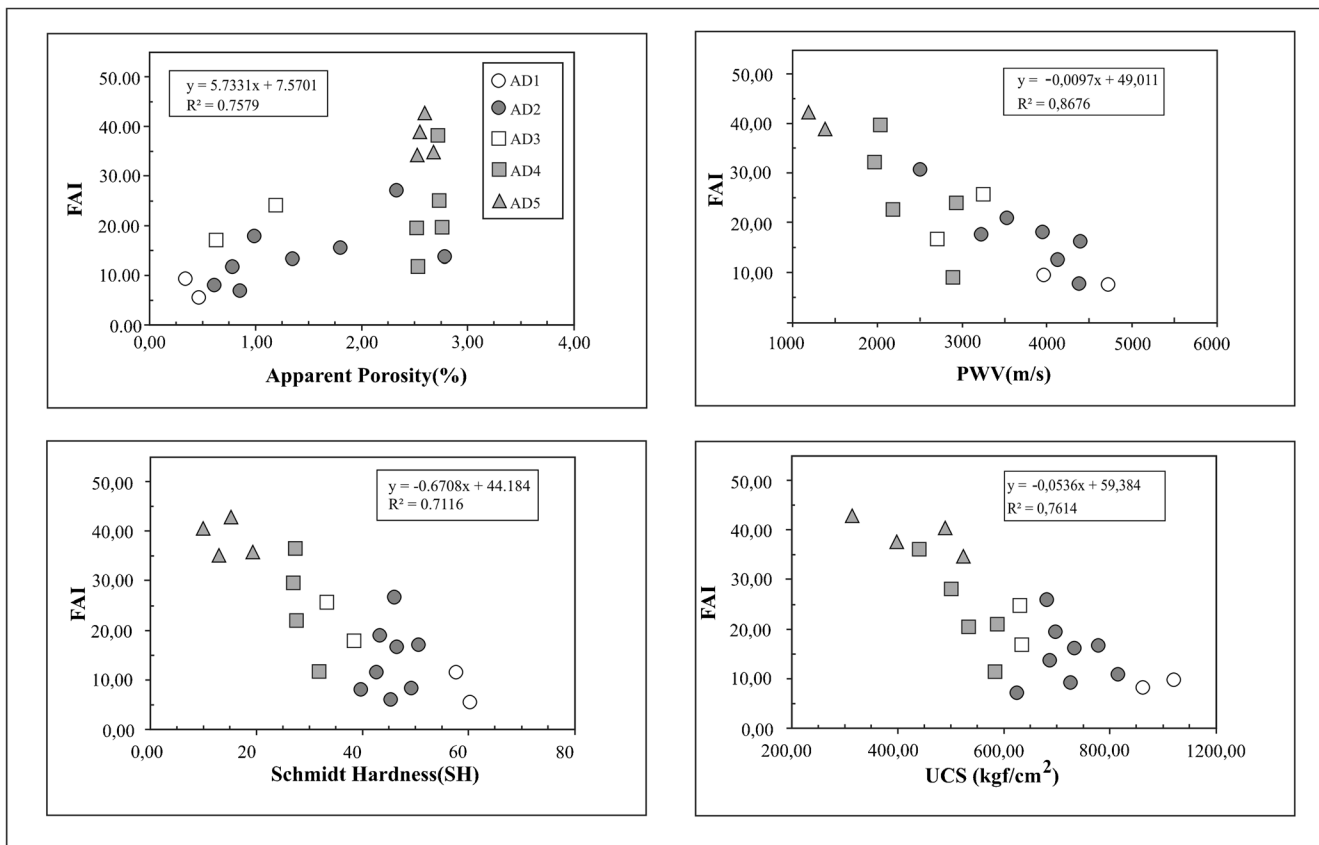


Fig. 12 Relationship between FAI and geomechanical properties of the Sivrihisar granites

minero-petrographical changes during alterations in granites from Sivrihisar.

FAI was correlated to the P-wave velocity index (I_{vp}), strength ratio (R_s), and geomechanical properties in order to prove the effectiveness of FAI in measurement alteration of granites. The FAI forms significant negative correlation ($R^2 = 0.8676$) with I_{vp} . Figure 11 shows that P-wave velocity index (I_{vp}) decreased with progressive alteration. An inverse relationship was found between FAI and strength ratio (R_s). The correlation coefficient (R^2) of the relationship between FAI and R_s was 0.7614 (Fig. 11). However, as shown in Fig. 11, no correlation was obtained between FAI and CIA values.

The feldspar alteration index (FAI) shows good to excellent correlation ($R^2 = 0.7116$ – 0.8676) with geomechanical properties (Fig. 12). The apparent porosity (AP) varied proportionally to FAI. The correlation coefficient (R^2) of the relationship between FAI and apparent porosity was 0.7579. The inverse relationships were observed with FAI and P-wave velocity (PWV) ($R^2 = 0.8676$), SHV ($R^2 = 0.7116$) and UCS ($R^2 = 0.7614$) (Fig. 12), indicating that the hardness and mechanical strength of granites decrease with progressive alteration. The good to excellent correlations among feldspar alteration index (FAI), existing alteration indices, and geomechanical properties substantiate that FAI quantifies physical and mechanical changes in granites during alteration and that FAI can be

applied for the assessment of the alteration extent of granitic rocks.

Conclusions

This study examines minero-petrographical, geochemical, and geomechanical changes during alteration of granites from Sivrihisar. Samples were collected based on macroscopic features, such as changes in color, textural/structural changes, and Schmidt hammer rebound values (SHVs), and classified into five groups according to their alteration degree. A feldspar alteration index (FAI) was proposed as a new method to determine the alteration extent of granites.

PLM, XRD, SEM-EDS, and chemical analyses provide detailed information on minero-petrographical and geochemical changes associated with alteration of Sivrihisar granites. Granites consist mainly of plagioclase, alkali feldspar, quartz, biotite, and hornblende, including small amounts of zircon, titanite, apatite, allanite, and opaque minerals. Plagioclase and alkali feldspar are the most easily altered primary minerals. According to SEM results, solution-precipitation was a major mechanism of the alteration of feldspar minerals. Plagioclase and alkali feldspar are altered along microfractures, cleavage, twinning, and zoning structure.

Smectite, sericite, and kaolinite minerals precipitated in microfractures and pores of these minerals. Anorthite-rich core is more altered than the rim of zoned plagioclase, exhibiting depletion of Na, Si, and Ca, and gradational enrichment of Mg, Al, K, and Fe. The results of the chemical analyses of the altered granites (from AD2 to AD5) were compared with those of fresh samples (AD1) to examine geochemical changes during alteration. The depletion trends for Si, Al, Na, and Ca reflect dissolution of plagioclase. However, enrichment of Si, Al, Na, Ca, Mg, K, and Fe reveals precipitation of smectite, sericite, and kaolinite minerals during alteration.

The intense alteration affected the physical and mechanical properties of the granites from Sivrihisar. Hence, water absorption (from 0.11 to 2.39%) and apparent porosity (from 0.36 to 5.96%) increased. Conversely, apparent density (from 2.68 to 2.50 g/cm³), the Schmidt hammer rebound value (from 60 to 10), P-wave velocity (from 4597 to 1039 m/s), and uniaxial compressive strength (from 1072 to 346.2 kgf/cm²) decreased during alteration. We proposed a new method referred to as feldspar alteration index (FAI) for determination of the minero-petrographical changes during alteration in Sivrihisar granites. The correlation of FAI was applied with P-wave velocity (I_{vp}) and strength ratio (R_s) indices and geomechanical properties, proving suitability of FAI. The good to excellent correlations were observed for FAI vs. I_{vp} ($R^2 = 0.8676$) and FAI vs. R_s ($R^2 = 0.7614$), FAI vs. apparent porosity ($R^2 = 0.7579$), FAI vs. P-wave velocity ($R^2 = 0.8676$), FAI vs. Schmidt hammer rebound value ($R^2 = 0.7116$), and FAI vs. uniaxial compressive strength ($R^2 = 0.7614$). Hence, we conclude that FAI can be used to determine the degree of alteration of granites.

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