

Devitrification of Volcanic Glasses in Konya Volcanic Units, Turkey

ZEHRA KARAKAŞ¹ & SELAHATTİN KADİR²

¹ Ankara Üniversitesi Fen Fakültesi, Jeoloji Mühendisliği Bölümü, TR-06100 Ankara - TÜRKİYE
(e-mail: karakas@science.ankara.edu.tr)

² Maden Tetkik ve Arama Genel Müdürlüğü, Maden Analizleri ve Teknoloji Dairesi, TR-06520 Ankara.- TÜRKİYE

Abstract: The study area is composed of volcanic, sedimentary and volcano-sedimentary units, which are exposed south and southwest of the city of Konya. XRD analysis indicates that the volcanic units contain halloysite, kaolinite, smectite, illite and sepiolite type clay minerals and opal-CT, feldspar, quartz, minamiite and jarosite type non-clay minerals. SEM studies show that volcanic glasses, which are the main component of the volcanic units, appeared as curvilinear, vesicular-planar and in highly fractured shapes. Fractures and dissolution voids of the volcanic glasses are generally filled by hexagonal kaolinite, fibrous halloysite and smectite. Mineralogical and micromorphological observations indicate that clay minerals were neofomed by hydration of volcanic glasses. Neofomation of these minerals was probably controlled by the different chemical composition of the volcanic glasses in addition to the presence of feldspar.

Key Words: Clay Minerals, Feldspar, Devitrification, Volcanic Glass, Konya, Turkey

Konya Volkanik Birimlerinde Volkanik Camların Devitrifikasyonu Türkiye

Özet: İnceleme alanı Konya ilinin güney ve güneybatısında yüzeylenen volkanik, sedimanter ve volkano-sedimanter birimleri içerisine almaktadır. Volkanik birimlerde yapılan XRD incelemeleri sonucunda halloysit, kaolinit, simektit, illit ve sepiyolit tipi kil mineralleri ile opal-CT, feldspat, kuvars, minamit, jarosit gibi kil dışı mineraller belirlenmiştir. Volkanik birimlerin ana bileşenini oluşturan volkan camları SEM çalışmalarında kıvrılmış-levha (curvilinear), gözenekli-levha (vesicular-planar) ve yüksek kırıklı-levha (highly fracture-planar) şekillerinde izlenmiştir. Volkan camlarının kırık ve erime boşluklarında genellikle düzensiz hegzagonal kaolinit, lifsi halloysit ve simektit mineralleri belirlenmiştir. Mineralojik ve mikromorfolojik incelemeler kil minerallerinin volkan camlarının hidrolizi ile oluştuklarını göstermiştir. Bu kil minerallerinin oluşumu muhtemelen farklı kimyasal bileşime sahip volkan camları ve feldspat mineralinin varlığı ile kontrol edilmiştir.

Anahtar Sözcükler: Kil Mineralleri, Feldspat, Devitrifikasyon, Volkanik Cam, Konya, Türkiye

Methods

During the field work, samples of clay dominated volcanic rocks along stratigraphical sections and point samples from different parts of the study area were collected. The samples were examined by several techniques, including X-ray powder diffraction (XRD) (Rigaku-Geigerflex), differential thermal analysis-thermogravimetry (DTA-TG) (Rigaku TAS 100, E model) and scanning electron microscopy (SEM-EDX) (Jeol JSM 6400-Noran instruments Series II).

The mineralogical composition of the samples was determined by XRD, using CuK α radiation with a scanning speed of 1°2 θ /min. For the determination of bulk mineralogy, unoriented mounts of powdered whole rock samples were analyzed. Clay minerals were

determined on < 2 μ m clay fractions prepared by sedimentation followed by centrifugation of the suspension. The smear glass samples were prepared from the separated clay fraction. Air-dried, oriented, ethylene-glycol-solvated, and samples heated at 350°C and 550°C for one hour were used for identification. Semi-quantitative mineralogical analysis of both the clay fractions and the whole rock samples was done by the external standard method (Brindley 1980).

DTA-TG curves were recorded by using 10 mg of powdered sample in a Pt sample holder at an average heating rate of 10°C/min with an alumina reference.

On the basis of XRD results, clay-rich representative samples were selected for SEM-EDX analyses. These samples were prepared by adhering the fresh, broken

surface of the sample on an aluminum sample holder that had been covered with double-sided tape and coated with a thin film of gold, using a Giko IB.3 ion coater.

Introduction

The study area is composed of volcanic, sedimentary and volcano-sedimentary units which widespreadly occur south-southwest of the city of Konya (Figure 1). The basement rocks of the study area are represented by pre-Miocene ophiolitic complex, schist, quartzite and dolomitic limestone (Keller *et al.* 1977). These units are overlain uncomformably by volcanic rocks. The stratigraphic and radiometric age determination of volcanic rocks indicate that Sille volcanics are the first volcanic phase (Bering 1971; Keller *et al.* 1977). This unit is overlain by sedimentary and volcano-sedimentary rocks. Sedimentary rocks are composed of argillaceous dolomitic limestones. These units are overlain by Kızılören, Bulumya, Detse and Sadıklar ignimbrites, nuée

ardentes and andesitic-basaltic lava and dome (Figure 1). Ignimbrites are generally composed of altered to unaltered tuff. These units are covered by Upper Pliocene limestone and Quaternary fluvial and alluvium materials.

The geology of the study area was studied by Göğür & Kırıl (1973), Keller *et al.* (1977), Özcan *et al.* (1990), Ulu *et al.* (1994) and industrial raw materials by Suludere *et al.* (1986), Özgüner (1987) and Özgüner *et al.* (1987). The mineralogy and economic importance of the clay mineral deposits around Konya were studied by Temel *et al.* (1995) and Çelik *et al.* (1997). Halloysite, kaolinite and smectite are dominant in the volcanic units of the Konya area. Sudo & Matsuoka (1959), Zhou & Fyfe (1989), Tomita *et al.* (1993) and Kawano *et al.* (1997) also reported neoformation of clay minerals as hydration products of volcanic glasses. In this study, we examine the alteration of volcanic glasses to halloysite, kaolinite and smectite using various analytical methods.

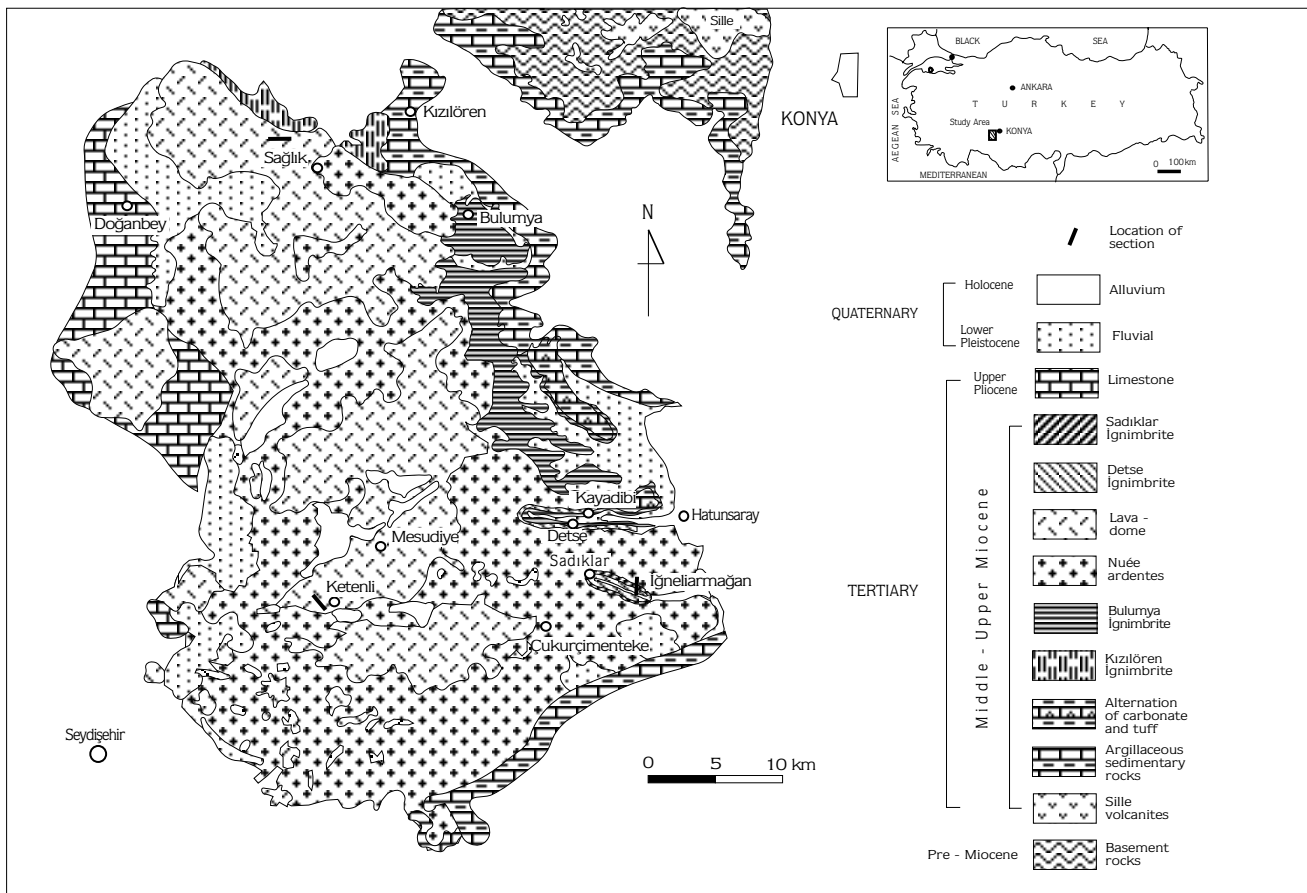


Figure 1. The location and the geologic map of the study area (Modified from Keller *et al.* 1977).

XRD Determinations

XRD analyses were carried out on completely and partly altered volcanic rocks, which were collected along different measured stratigraphic sections, and as point samples (Figure 1). Kaolinite, halloysite and smectite as clay minerals and opal-CT, feldspar and quartz as non-clay minerals were identified in the samples (Figure 2). In addition, small amounts of jarosite, minamiite, illite and sepiolite were also determined.

Halloysite is found in the İğneliarmağan section at the southwest of the volcanic units (Figure 1). Halloysite is associated with opal-CT, feldspar, quartz and minamiite (Figure 2). Jarosite is found beside these minerals in the upper part and halloysite is generally concentrated in the middle part of the sequence. There is an inverse ratio between halloysite and opal-CT so that an increase in halloysite causes a decrease in opal-CT.

Kaolinite is mainly dominant in the northern part of the Konya volcanic units around the Sağlık section (Figure 1). This clay mineral is associated with opal-CT, in addition to feldspar (albite), quartz and smectite (Figure 2). In this section, there is an inverse relationship between kaolinite and opal-CT similar to that of halloysite.

Smectite is found at all levels of the Ketenli section, but it is predominantly concentrated in the middle and upper parts of the section (Figures 1 & 2). In this region, smectite is mainly accompanied by opal-CT, and in a few samples feldspar, illite and kaolinite are determined.

DTA-TG Determinations

DTA curves of both halloysite and kaolinite of the area are similar (Figure 3). But the first endothermic peak of halloysite at 60.7°C could not be seen at kaolinite. Kaolinite is defined by endothermic peak at 509.5°C and exothermic peak at 989.9°C. However, halloysite shows two endothermic peaks at 60.7°C, 499.1°C and exothermic peak at 939°C. Ideal-well crystallized kaolinite is characterized by endothermic peak at 500-600°C and exothermic peak at 900-1000°C. DTA curve of Konya kaolinite represents ideal-well crystallized kaolinite with typical thermal reactions. The endothermic peak of kaolinite is larger and exothermic peak is sharper than that of halloysite. This may indicate that the crystallinity of Konya kaolinite is better than that of halloysite.

The DTA curve of smectite shows small endothermic peaks at 106.1, 633.7 and 892.9°C (Figure 3). The last endothermic peak is followed by an exothermic peak at 905.9°C. The first endothermic peak represents absorbed water, the second and third endothermic peaks show dehydroxylation (Mackenzie 1957; Paterson & Swaffield 1987).

SEM-EDX Determinations

SEM-EDX studies were carried out on volcanic glass-dominated volcanic rock samples. Volcanic glasses are found in curvilinear, surface-planar and highly fractured forms. Most of these glasses were fractured and rich in dissolution voids (Figure 4a, b and c). Halloysite fibers are developed perpendicular to the void surface of the curvilinear and vesicular-planar type volcanic glasses (Figure 5a). In addition, halloysite fibers are also developed on the surface of volcanic glass inside fractures and around the volcanic glass particles (Figure 5b). Irregular hexagonal sheets of kaolinite and smectite are also formed in dissolution voids (Figure 5c, d and e).

There is a white-gray zone between the volcanic glasses and neoformed halloysite or kaolinite (Figure 5a and c). The chemical compositions of the volcanic glasses and adjacent neoformed clay minerals were determined by EDX (Figure 6). Kaolinite, halloysite and the adjacent volcanic glasses have similar elemental compositions (Table 1). But the volcanic glass in the kaolinite-dominated samples contains less Al and more Si than those of kaolinite. Smectite also has a composition similar to that of the adjacent volcanic glass, rich in Al, Si and Fe (Table 1).

Discussion and Conclusions

Middle-Upper Miocene tuffaceous volcanic units are widely exposed south-southwest of Konya. Halloysite, kaolinite and smectite type clay minerals were identified in volcanic units which are dominated by volcanic glasses. SEM analyses of these glasses show curvilinear, vesicular-planar and highly fractured structures. Moreover, halloysite, kaolinite and smectite minerals are concentrated on the surface of volcanic glass and inside the fractures and dissolution voids. Melson & Thompson (1973), and Morganstein & Riley (1974) found that neoformed minerals developed on the surface and along

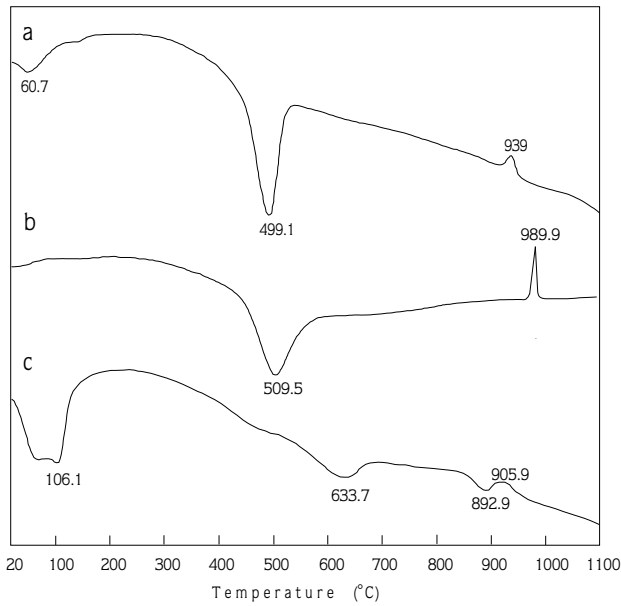


Figure 3. DTA-TG curves of (a) halloysite (KD-2); (b) kaolinite (Sağ-3); and (c) smectite (Ket-13).

fractures of the volcanic glasses. The presence of dissolution voids on different forms of volcanic glass may indicate hydration of volcanic glasses (Figure 4). Because, volcanic glasses dissolve faster than other volcanic components due to the dominant non-bridging silicate sites in the amorphous structure (Casey & Bunker, 1990). Volcanic glasses there play an important role in the formation and transformation processes of clay minerals as a cation supplier within alteration environments. Thus, clay minerals are neoformed on or adjacent to volcanic, glasses because of the reaction of water with the volcanic glasses; so that halloysite, kaolinite and smectite are neoformed (Figure 7). The similar elemental compositions of volcanic glasses and adjacent clay minerals support this idea (Table 1). However, the Al content of the volcanic glass adjacent to kaolinite is lower than that of kaolinite. Therefore, the necessary Al for formation of kaolinite is obtained from volcanic glass as well as feldspar, which are the main components of the altered tuff in the Sağlık section

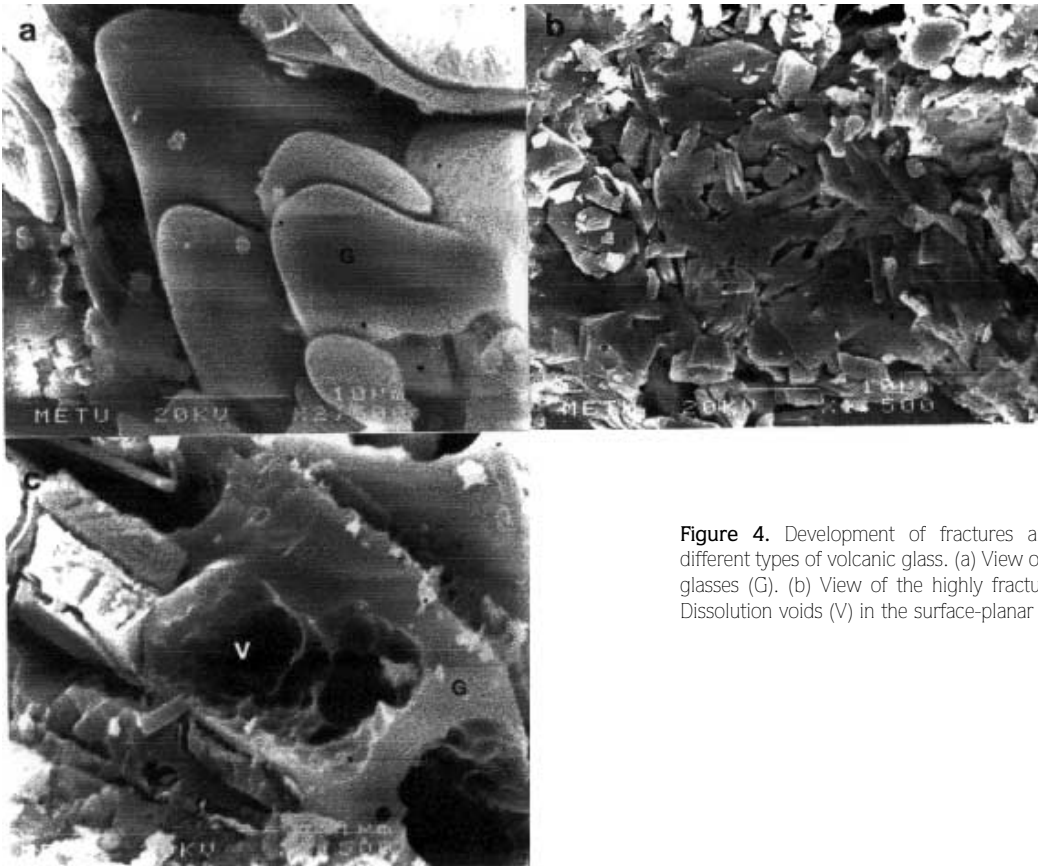


Figure 4. Development of fractures and dissolution voids in different types of volcanic glass. (a) View of the curvilinear volcanic glasses (G). (b) View of the highly fractured volcanic glasses. (c) Dissolution voids (V) in the surface-planar volcanic glasses (G).

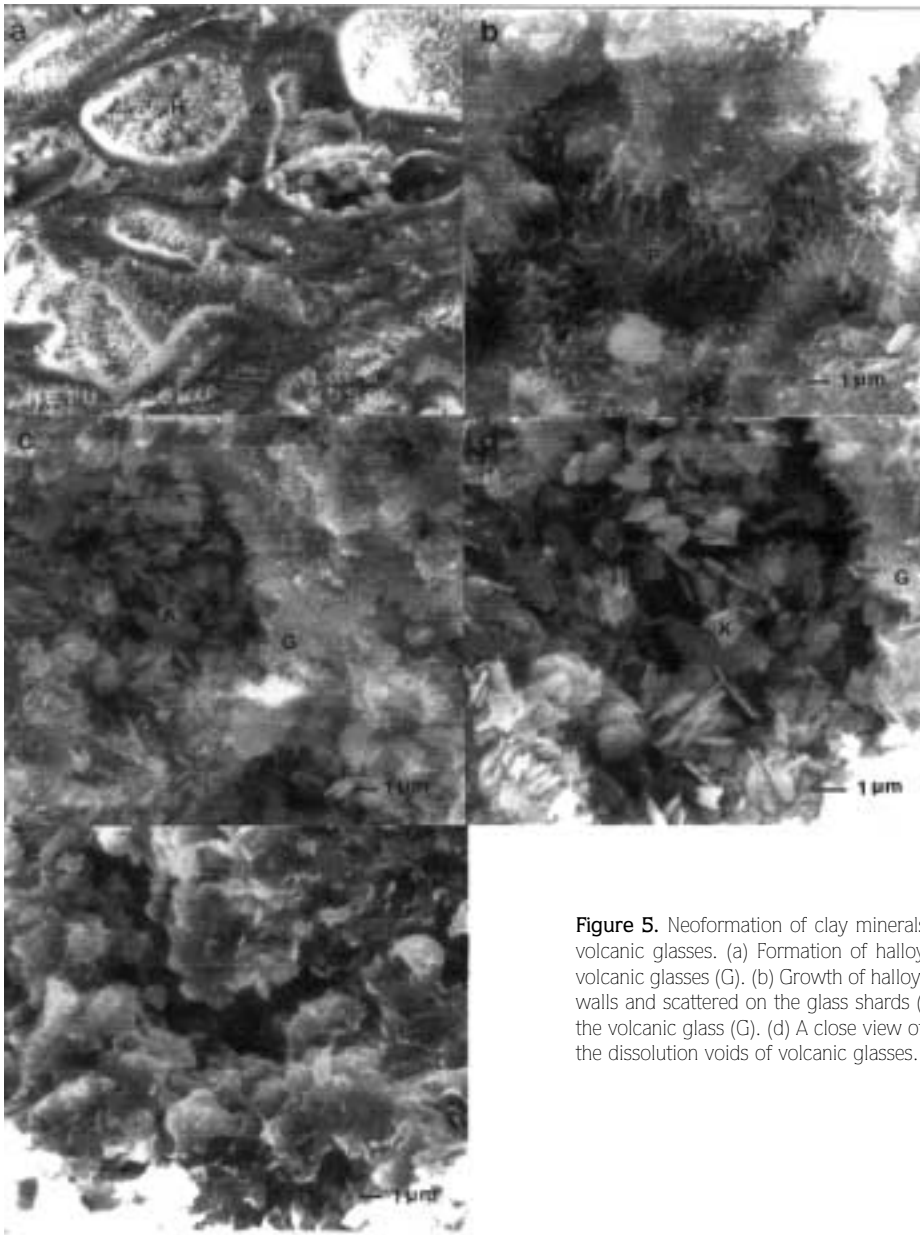


Figure 5. Neoformation of clay minerals in fractures and dissolution voids of the volcanic glasses. (a) Formation of halloysite (H) fibers in dissolution voids of the volcanic glasses (G). (b) Growth of halloysite fibers (H) perpendicular to the fracture walls and scattered on the glass shards (P). (c) Kaolinite (K) in dissolution voids of the volcanic glass (G). (d) A close view of kaolinite (K). (e) Smectites (S) growing in the dissolution voids of volcanic glasses.

Sample No	Sample type	Al	Si	Fe	Mg	K	Ti
KD-2	Volcanic glass	32.49	60.87	6.65			
KD-2	Halloysite	35.43	48.64	15.93			
Sağ-3	Volcanic glass	4.31	95.69				
Sağ-3	Kaolinite	31.48	68.52				
Ket-13	Volcanic glass	22.18	66.73	5.88	2.88	1.30	1.03
Ket-13	Smectite	21.85	69.31	4.35	2.57	1.47	0.46

Table 1. Elemental compositions (EDX) of volcanic glasses and adjacent neoformed halloysite, kaolinite and smectite.

KD-2: Kayadibi, Sağ-3: Sağlık, Ket-13: Ketenli.

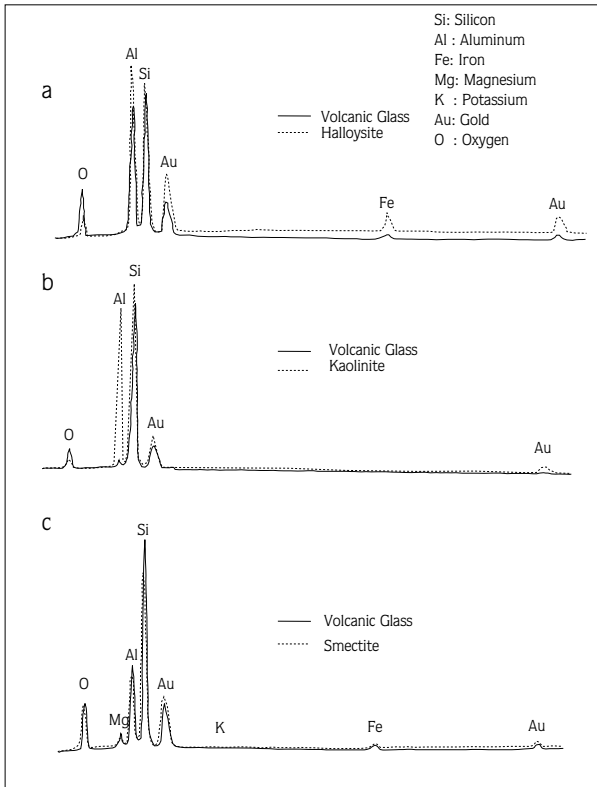


Figure 6. The result of EDX analysis showing the relationship of neoformed clay minerals with adhering volcanic glasses. (a) Halloysite (KD-2); (b) Kaolinite (Sağ-3) and (c) Smectite (Ket-13).

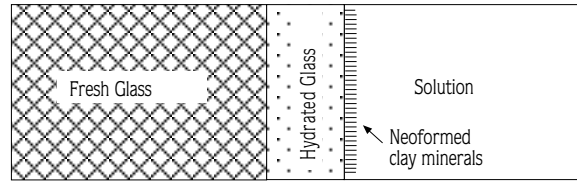


Figure 7. Schematic development of neoformed clay minerals by interaction of volcanic glass with solution (not to scale).

(Figure 2). Formation of kaolinite by decomposition of feldspars was also demonstrated by Hemley & Jones (1964).

Mineralogical and micromorphological observations indicate that clay minerals were predominant on the hydrated surfaces of volcanic glasses in volcanic units. Volcanic glasses in different compositions and the presence of feldspar probably causes neoformation of different types of clay minerals.

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