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Origin of Kaolin Deposits: Evidence From the Hisarcık (Emet-Kütahya) Deposits, Western Turkey

S. ALİ SAYIN

General Directorate of Mineral Research and Exploration (MTA), TR–06520 Ankara, Turkey
(E-mail: asayin@mta.gov.tr)

Abstract: Kaolin deposits, situated approximately 20 km south of Hisarcık, have been formed by the alteration of dacite and dacitic tuffs related to the Miocene volcanism associated with extensional tectonics. The Hisarcık kaolin deposits occur in the Kızılcukur, Ulaşlar and Kurtdere areas. Kaolinite is the only clay mineral associated with α-quartz, K-feldspar, plagioclase, alunite, natroalunite and hematite in some kaolins, whereas, other kaolinite accompanies smectite, which represents a moderate kaolinization. Low-cristobalite is the dominant silica mineral in these kaolins. In spite of strong kaolinization, the kaolins contain a high amount of finely-disseminated α-quartz in places, resulting in low Al_2O_3 values (13.80 wt% at the lowest). Variation in the thermal regime of the palaeohydrothermal system may affect the solubility of silica. In rainy seasons, due to a temperature drop, dissolved silica may be precipitated with the clays. The mineralogical zonations reveal that hydrothermal alteration is the main cause for the development of the kaolin deposits in the region. Hydrothermal silicification becomes more intense upwards. It results from dissolved silica moving in that direction, replacing and silicifying surrounding rocks, forming a silica zone (silica gossan) above the kaolin deposits. Basically, these silica gossans are the striking features on the exploration of the hydrothermal kaolin deposits. In places, the kaolin deposits also include thin silica veins and veinlets. Trace-element distribution data may not conclusively help to clarify the processes through which the kaolin formed. On the other hand, Pb and Sr enrichment within the deposits is supportive of the magmatic origin of hydrothermal solution. This is attributed to extensive Miocene volcanic activities in western Turkey. However, the data show that corrosive solutions, which may have arisen from the magma, have played a role in the kaolinization process together with hot meteoric waters. SEM studies show that there is a phase transition from montmorillonite to kaolinite.

Key Words: Alunite, Hisarcık, hydrothermal alteration, kaolinite, Kütahya, Natroalunite, Smectite, silica zone (silica gossan)

Kaolen Yataklarının Kökeni: Türkiye'nin Batısında Bulunan Hisarcık Kaolen Yataklarından Örnekler

Özet: Hisarcık'ın yaklaşık 20 km güneyinde bulunan kaolin yatakları, gerilme tektoniği ile ilişkili olan Miyosen volkanizması ürünü dasit ve dasitik tüflerin alterasyonu sonucu oluşmuşlardır. Hisarcık kaolenleri Kızılçukur, Ulaşlar ve Kurtdere bölgelerinde oluşmuştur. Bazı kaolin yataklarında tek kil minerali olarak bulunan kaolinit, alfa-kuvars, K-feldispat, plajiyoklaz, alünit, natro alunite ve hematit ile birlikte bulunur. Diğer taraftan, bazı kaolenlerde, kaolinite ek olarak simektit de bulunmakta olup, bu durum orta şiddette bir kaolenleşmeyi ifade etmektedir. Bu kaolenler, fazla miktarda alfa-kristobalit içerir. Yer yer, kaolenlerin kuvvetli kaolenleşmeye rağmen, yüksek miktarda ince taneli saçılmış alfa-kuvars bulundurması sonucu, oldukça düşük değerlerde Al_2O_3 (en düşük değer % 13.80) içerirler. Paleohidrotermal sistemdeki termal rejim degişikliği, silika çözünürlülüğünü etkiler. Yağmurlu mevsimlerde, sıcaklığın düşmesi sonucu, silika kil içerisinde çökelir. Çalışma sahasındaki mineralojik zonlanma, hidrotermal alterasyonun, bölgedeki kaolenlerin oluşumunda ana faktör olduğunu göstermektedir. Hidrotermal silisleşme yukarıya doğru oldukça etkilidir. Şöyleki, eriyik halindeki silisin yukarı doğru hareket ederek üstteki kayaçları silisifiye etmesi sonucunda kaolen yataklarının üst kesimlerinde silika zonları (silika gossan) oluşmuştur. Silika gossan'lar hidrotermal kaolen yataklarının aranmasında belirleyici unsurlardır. Kaolen yatakları, yer yer ince silis damar ve damarcıkları da içerirler. İz element dağılımı, kaolenleşmeyi oluşturan yöntemlerin tesbitinde tam bir bilgi vermemekle beraber, kaolen yataklarındaki Pb ve Sr zenginleşmesi, hidrotermal solüsyonların mağmatik kaynaklı olabileceği savını desteklemektedir. Bununla beraber, yukarıdaki veriler, mağmadan yükselen eritici solüsyonların sıcak meteorik sularla birlikte kaolenleşme işleminde rol oynadığını göstermektedir. SEM çalışmaları, montmorillonitten kaolinite doğru bir faz geçişi olduğunu göstermektedir.

Anahtar Sözcükler: Alünit, Hisarcık, hidrotermal alterasyon, kaolinit, Kütahya, Natroalünit, Simektit, silika zonu (silika gossan)

Introduction

The Kütahya region is known as an important ceramic centre in Anatolia since the XIII Century. For this reason numerous studies have been conducted on the geology, mineralogy and reserves of clay occurrences. Ataman & Baysal (1978), Yalçın (1984), Yalçın & Gündoğdu (1985) and Çolak *et al.* (2000) studied the clay mineralogy of the volcanoclastic sedimentary units in the Emet Basin. Due to boron occurences in the Bigadiç and Emet basins, some numerous studies were also conducted on the geology, mineralogy, genesis and reserves of the borate deposits (Helvacı 1977, 1983, 1984, 1986; Helvacı & Firman 1976; Erkül *et al.* 2005; Yücel-Öztürk *et al.* 2005). Studies of the kaolin occurences which were mainly related to geological settings and their reserves were done by Türk (1975), Okut *et al.* (1978), Işıklar & Demirhan (1982) and Demirhan (1986). According to these studies, kaolin deposits with 1.000.000 tonnes of both proven and probable reserves should economically be interesting for ceramic manufacturers in the region.

The Hisarcık kaolins were studied by Türk (1975), Işıklar & Demirhan (1982) and Demirhan (1986). These studies which were mainly based on the reserves of the kaolin deposits, did not take into account the mode of occurrences of kaolin. They also did not try to set up mineralogical and chemical relations between the kaolin and its parent rocks. In fact, kaolinization in the region is closely related to tectonic framework and alteration of the parent rocks. It is believed that this study will help to discover some new kaolin occurrences which are related to extensive Miocene volcanic activities within the tectonic framework in western Anatolia.

Materials and Methods

The samples taken from the parent rocks were mineralogically and petrographically studied. Two of them were also subjected to chemical analyses (major oxides and trace elements) and XRD analyses. The mineralogy of these samples was determined by optical microscopy. The mineralogy of clay samples was determined by X-ray diffraction (XRD – Rigaku Geigerflex). The XRD analyses were carried out using CuK– radiation with a scanning speed of 1°2Ø/min. Random powder samples were prepared for mineralogical identification. Some oriented <2 µm clay fraction samples prepared by gravity settling on glass slides were air-dried, solvated with ethylene glycol at 60 °C for two hours, and also heated at 350 °C and 550 °C for two hours. Semi-quantitative mineralogical determination of the clay samples was obtained by multiplying the intensities of the principal basal reflections of each mineral by suitable factors according to external methods developed by Gündoğdu (1982) after the method of Brindley (1980) and by combination of chemical analyses of the bulk samples.

Chemical analyses of major oxides were carried out on clays and two parent rock samples by x-ray fluorescence (XRF) spectrometry (Rigaku x-ray spectrometer RIX3000) using rock standards supplied by the MBH Reference Material and Breithlander companies and by Inductively Coupled Plasma Spectrometry (ICP, Perkin-Elmer 4300). Four selected clay and two parent rock samples were also subjected to trace elements analyses by ICP. Loss on ignition (LOI) for each clay sample was determined by first drying the samples overnight at 105 °C, followed by calculation of their water and other volatiles contents, such as CO_2 and SO_3, at 1000 °C.

The thermal behaviour of the clays was measured using a Rigaku Thermal Analyser (TAS100). 20 mg powder samples were used for the differential thermal analysis (DTA), thermal gravimetric analysis (TG), with heating to 1100 °C at the rate of 10 °C/min. Here, the <2 µm size fraction which was obtained by sedimentation followed by centrifugation of the suspention was used.

For microstructure investigation, some representative clay samples were prepared for SEM-EDX (Jeol 840A) analysis by breaking clay samples with a tool to obtain a fresh surface. The fresh surface of the sample was then coated with a thin film of evaporated gold.

All experimental studies were done at the Mineralogical and Chemical Analysis Laborotories of MTA.

Geological Setting

Figure 1 shows the geological map of the south of the Hisarcik (Emet) region. In the region, the basement rock is Palaeozoic crystalline schist consisting of marble, biotite schist, calcareous schist and chlorite schist of the Menderes Massif (Okut *et al.* 1978). This metamorphic basement rock unit was cut by the Palaeocene Egrigöz granite which is to the west of the study area (Çolak *et al.* 2000). This unit is overlain by an Upper Cretaceous

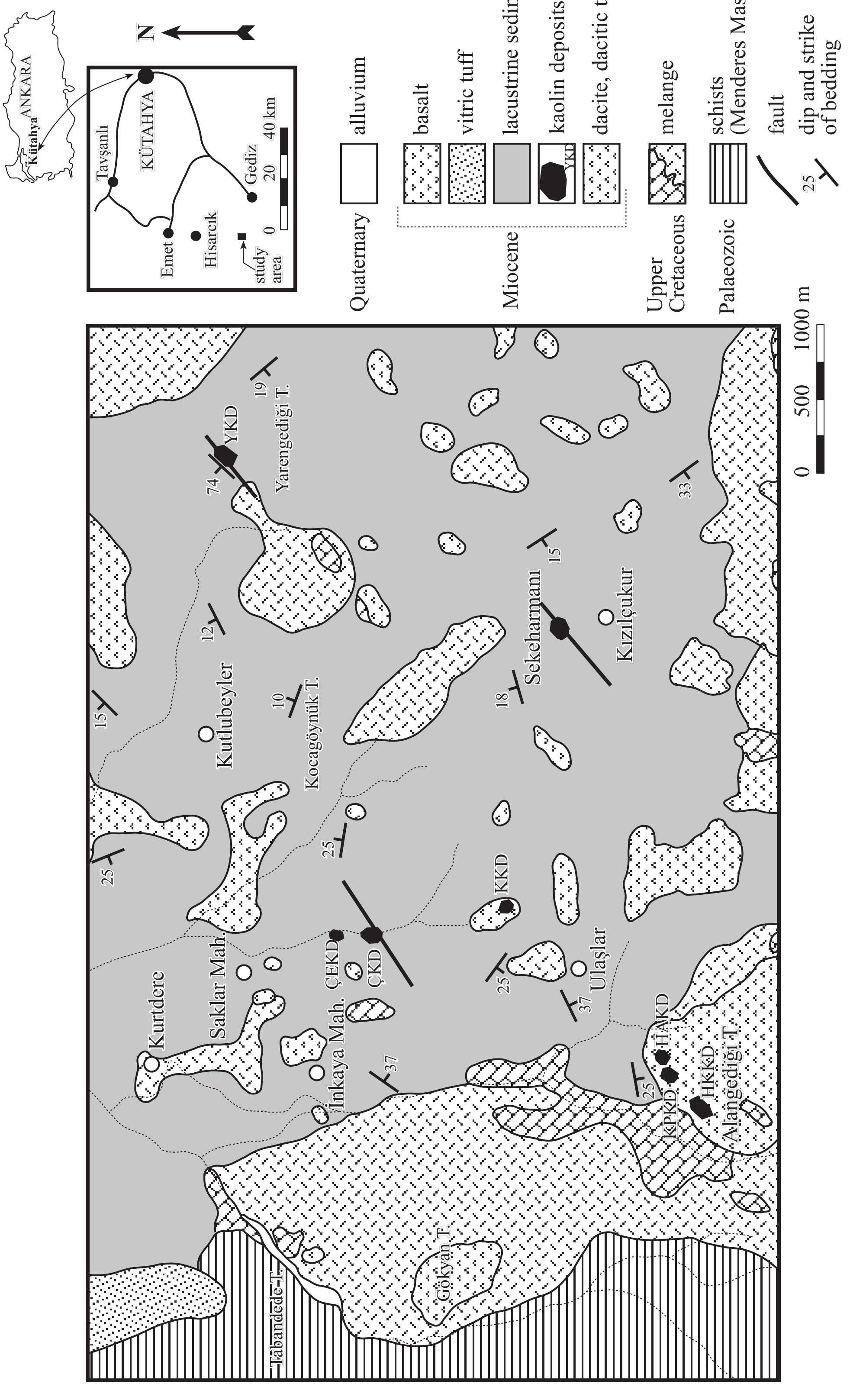

Figure 1. Geological map of Hisarcık area (compiled after Okut *et al.* 1978).

ophiolitic mélange. It consists of carbonated serpentinised ultrabasic rocks, recrystallized limestones, silicifed marbles, spilites and metamorphic schists. The products of calc-alkaline and alkaline Miocene volcanism overlie the ophiolitic mélange in the study area. The kaolinized rocks mineralogically appear to be dacite and dacitic tuffs. The Neogene lacustrine sediments which overlie the Lower Miocene volcanics, consist of basal conglomerate, claystone, clayey limestone, sandstone, pebblestone and thin layers of tuff and tuffites. In the Middle Miocene section bedded rhyodacitic lavas and their tuffs unconformably overlie the Neogene lacustrine sediments, which are to the south of the study area. In the study area, partly altered vitric tuffs overlie the Neogene lacustrine sediments. Middle Miocene thin-layered basaltic lavas are the youngest volcanic products in the study area. The existence of a huge amount of plateau basalts, called the Quaternary Kula volcanics, which are to the south west of the study area, indicates rapid uplift of mantle magma (Tokçaer *et al.* 2005).

The volcanic activity in the region was closely related to the tectonic history of western Turkey. It has been proposed that north–south-directed shortening and compression related to the collision of the Pontides (Rhodope-Tauride Platform, Sakarya Continent) and the Anatolide-Tauride platform, contunied until the Late Miocene and was subsequently followed by north–south-oriented extension (Şengör & Yılmaz 1981; Şengör 1982; Şengör *et al.* 1985). Within this tectonic regime, it has been suggested that the compressional and extensional regimes were associated with calc-alkaline and alkaline volcanism, respectively (e.g., Yılmaz 1989, 1990; Savaşçın & Güleç 1990; Güleç 1991; Savaşçın 1991; Aldanmaz 2006). However, it appears that north–south-oriented extensional tectonics may have begun as early as the latest Oligocene–Early Miocene and the diminishing of the earlier compressional regime had occurred by the Late Oligocene in western Turkey (e.g., Seyitoğlu & Scott 1991, 1992 a, b; Seyitoğlu *et al.* 1992, 1997; Hetzel et. al 1995). According to these workers, it is understood that calc-alkaline volcanism was associated with extension as opposed to compression. The north–south extension is generally ascribed to the combined effect of the westward extrusion of Anatolia and back-arc spreading behind the Aegean trench (Okay & Satır 2000; Bozkurt 2003; Bozkurt & Mittwede 2005; Bozkurt & Rojay 2005).

The age of the volcanic activity in the region was based only on palaeontological and stratigraphical observations by Okut *et al.* (1978). According to these workers, the volcanic activity continued until the end of the Pliocene. On the other hand, the K-Ar dating studies on the volcanics clearly show that the volcanic activity related with kaolin development in the region began in the Early Miocene and continued to the end of the Middle Miocene (e.g., Ercan *et al.* 1985; Seyitoğlu *et al.* 1997; Yılmaz *et al.* 2001). These rocks consist of a series of lavas; the earliest lava flows are rhyolites, dacites and trachytes. The next lava flows are trachyandesites and andesites and finally more recent flows are olivine-bearing andesitic basalts and abundant pyroclastic layers (Helvacı 1984). Seyitoğlu *et al.* (1997) did K-Ar dating studies on the volcanics around the Hisarcık kaolin deposits and concluded that there was a change in the nature of volcanism in the Miocene; from dominantly calc-alkaline and silicic in the Early Miocene to mainly alkaline and more mafic volcanism in the Middle Miocene.

General Features of Kaolin Occurences

The Hisarcık kaolinite region is divided into three areas, the Kızılçukur area, the Ulaşlar area and the Kurtdere area.

The Kızılçukur Kaolin Deposits

Kızılçukur Kaolin Deposits are present in two districts (i) the Sekeharmanı kaolin deposit and (ii) the Yarengediği Tepe kaolin deposit

Sekeharmanı Kaolin Deposit (SKD): The Sekeharmanı kaolin deposit is situated about 160 m north of Kızılçukur village, trending approximately in an east–west direction. The deposit is lense shaped and white in colour. According to drill hole data, the deposit is 170 m in length and 80 m in width. The maximum thickness of the deposit is 15.5 m. A normal fault with a northeast–southwest direction passes through the centre of the deposit. Kaolinite is the only clay mineral in the deposit. Borehole K6 shows that the kaolinite deposit passes into a smectite-rich zone (Figure 3). In addition to disseminated quartz, silica is concentrated as silica veins and veinlets within the kaolin deposit. Silica zones (silica gossan) are also present above the kaolin deposit (Figure 3). Alunite,

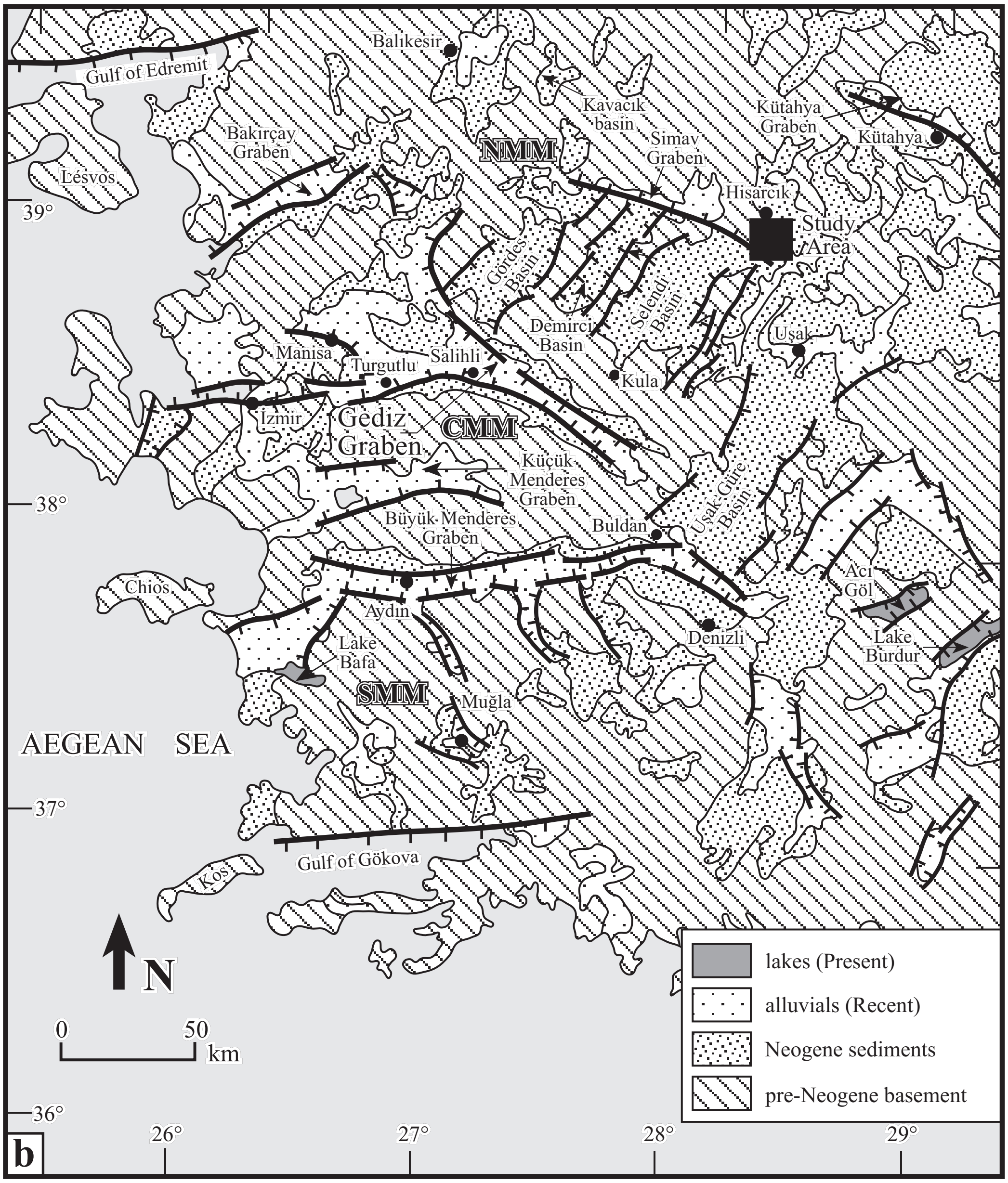

Figure 2. Outline geological map of Turkey showing Neogene and Quaternary basins and subdivision of the Menderes Massif. Note that (?) Miocene and Neogene sediments are not differentiated due to the lack of data (from Bozkurt 2000). CMM– central Menderes Massif, NMM– northern Menderes Massif, SMM– southern Menderes Massif.

natroalunite, K-feldspar and hematite are found as accessory minerals in the deposit.

Yarengediği Tepe Kaolin Deposit (YKD): The Yarengediği Tepe lense-shaped kaolin deposit, which is situated at 2750 m northeast of Kızılçukur village, trends in a northeast–southwest direction and crops out for about 50 m. The maximum width of the outcrop is 30 m. From the open pit, the thickness of the deposit is estimated to be about 15 m. The kaolin is white in colour. A normal fault in the deposit, trends N55°E and dips 74°NW.

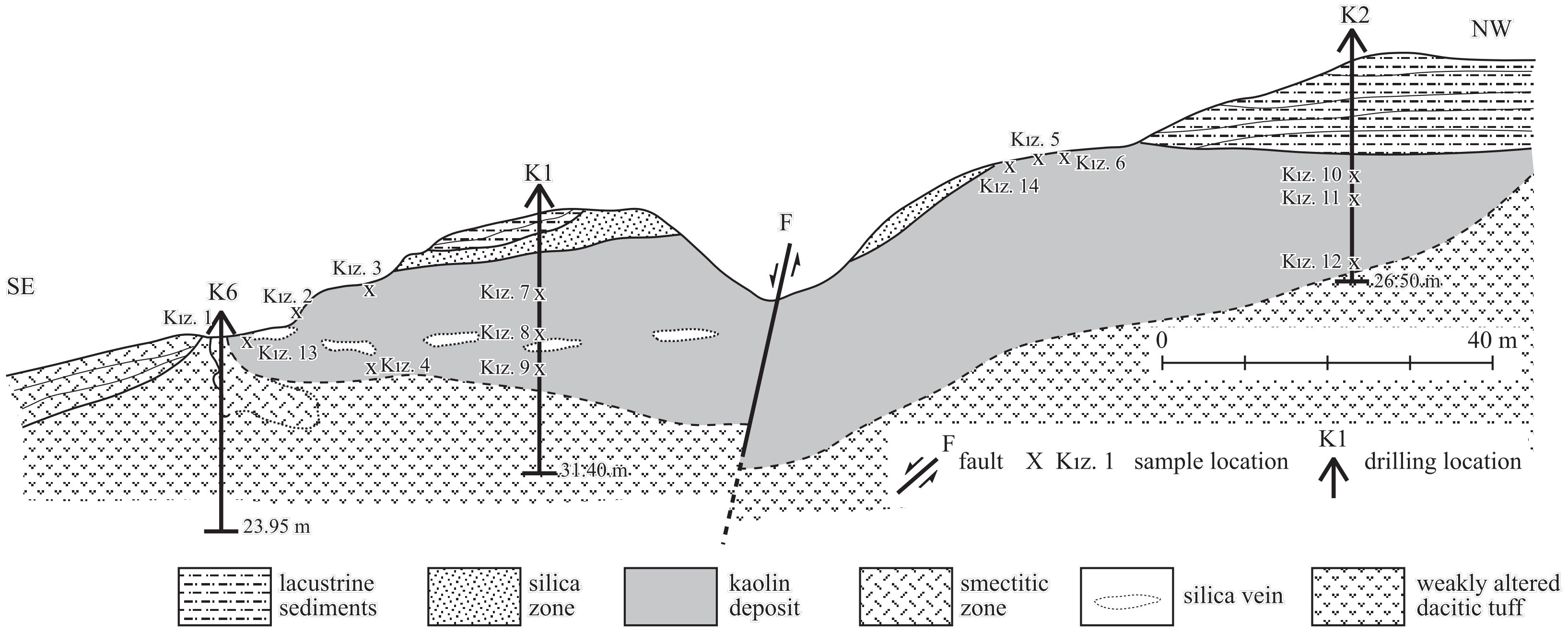

Figure 3. Schematic geological profile of Kızılçukur kaolin deposit (Sekeharmanı kaolin deposit, SKD).

Kaolinite is the dominant clay mineral, and montmorillonite appears in minor amounts. The deposit contains about 30% quartz and 10% plagioclase, and natroalunite is present as an accessory mineral.

Ulaşlar Kaolin Deposits

The Ulaşlar kaolins appear as three occurrences trending in a northeast–southwest direction on the northern slope of Alangediği Tepe, 1 km SW of Ulaşlar village. These are the Hisarcık Kooperatifi kaolin deposit, the Kütahya Porselen kaolin deposit and the Halil Acar kaolin deposit.

Hisarcık Kooperatifi Kaolin Deposit (HKKD): This lense-shaped kaolin deposit appears white in colour, becoming slightly reddish towards the north. Drill-hole data indicated that the kaolin body is 160-m long and 90-m wide and 10-m thick. A normal fault present at the south of the kaolin body trends in east–west direction. A drill hole on the northern part of the deposit, cuts a kaolin vein, 7-m thick, below the main kaolin body. Tuffs and lacustrine sediments are present between the main kaolin body and the kaolin vein. This suggests that during Miocene, lacustrine sediments were interfingered with volcanic products. Kaolinite is dominant at the centre of the deposit but montmorillonite increases at the southern part of the deposit towards the host rock. Quartz and low-cristobalite are quite high, up to 50% in the deposit.

Kütahya Porselen Kaolin Deposit (KPKD): This lense-shaped kaolin body is white in colour. Drill-hole data show that the dimensions of the deposit is 80-m long and 60-m wide. A kaolin vein 12.35-m thick was observed beneath the kaolin deposit, as seen in the Hisarcık Kooperatifi kaolin deposit. Kaolinite is the dominant clay mineral up to 90%, but montmorillonite is present up to 10% in the deposit. Quartz and low-critobalite are up to about 40% and 20%, respectively. Alunite is present in most kaolin deposits in the region. K-feldspar, plagioclase and hematite are present as accessory minerals.

Halil Acar Kaolin Deposit (HAKD): This lense-shaped kaolin occurrence appears white in colour and is 50-m long, 40-m wide and 10-m thick. The deposit contains about 40% kaolinite, 20% montmorillonite and 40% low-cristobalite. Plagioclase and natroalunite are also present as accessory minerals. Two drill holes were made 20 m to the south and northwest of deposit and showed that thickness of the deposit varies from 4.40 m to 5.90 m in the two locations.

Kurtdere Kaolin Deposits

The Kurtdere kaolin occurrences are present in two districts: (i) the Saklar district kaolins and (i) the İnkaya district kaolins.

Saklar District Kaolins: Three kaolin deposits occur within the Saklar district. They trend in north–south direction along a stream called Çitkaya Dere. These are namely, the Kulalan kaolin deposit (KKD), the Çitkaya kaolin deposit (ÇKD) and the Çitkaya Eczacıbaşı kaolin deposit (ÇEKD) and are located at 1.7 km, 800 m and 500 m south of Saklar district, respectively.

These lense-shaped and white coloured kaolin deposits trend in approximately a north–south direction. The lengths and widths of the deposits vary from 30 m to 70 m and 20 m to 50 m, respectively. The maximum thicknesses of the kaolin deposit are estimated to be about 10 m. A fault with a northeast–southwest direction passes through the centre of the Çitkaya kaolin deposit. The kaolin bodies are composed of about 40% kaolinite and 60% quartz. In places, it appears that the kaolin bodies are overlain by silica zones with varying thickness between 30 cm and 5 m.

According to drill hole data, veins of Ca- and Na-montmorillonite were observed beneath the Çitkaya and Çitkaya Eczacıbaşı kaolin deposits and have thicknesses of 5.40 m and 2.25 m, respectively.

İnkaya District Kaolin (İKD): This vein-like kaolin deposit, overlain by clayey limestone (lacustrine sediments), is situated 750 m south of İnkaya district. The kaolin is soft and white in colour. The dimensions of the outcrop which trends in north–south direction are 35-m long and 10-m wide. The thickness of the kaolin body is 7 m. An east–west-trending thrust fault present in the south end of the kaolin body is seen to have displaced the kaolin body to the west under the lacustrine sediments. The kaolin body is almost completely composed of kaolinite, indicating that it is the purist kaolin occurrence in the region. Quartz, K-feldspar and plagioclase are accessories and are less than 5%.

Mineralogical and Chemical Results

Thin section studies of parent rock (dacite and dacitic tuff) samples show that the mineral content is plagioclase feldspars (mainly oligoclase and andesine) with lesser amounts K-feldspar (mainly sanidine), biotite and muscovite. The majority of phenocrcysts are partly altered to clay minerals, chlorite and calcite. Hypidimorfic quartz crystals are also common. Rock fragments up to 0.5 cm in size, which mainly consist of altered feldspar and minor amount of mafic minerals are present in most of the samples. All phenocrysts and rock fragments are set in an altered glassy matrix which is composed mainly of clay minerals, chlorite, calcite and cryptocrystallin quartz. In some rocks, the glassy matrix is stained a red and yellowish colour by iron oxide minerals. Sample Kız.1, taken from the weakly altered dacitic tuff, consists of K-feldspar, quartz and biotite with minor amounts of hematite. The glassy matrix was converted into kaolinite and montmorillonite (Table 1). Samples Ulş.4 and Ulş.5, taken from partly altered dacitic tuff, contain quartz, K-feldspar, plagioclase, biotite and a few rock fragments, which consist of mica schist, quartz schist and cherts within the altered glassy matrix. The alteration products are mainly of montmorillonite and kaolinite and mixed-layer clay (probably smectite/illite) in minor amounts (Table 1). Samples Ulş.4, Ulş.5 and Kız.1 represent parent rocks of the Ulaşlar and Kızılçukur kaolin deposits, respectively.

The XRD results of the bulk samples taken from kaolin deposits are presented in Table 1. Kaolinite and montmorillonite are the only clay minerals present within the deposits, associated with quartz, low-cristobalite, plagioclase, K-feldspar, biotite, alunite, natroalunite and hematite.

The Kızılçukur kaolins contain mostly kaolinite as the principal clay mineral, while montmorillonite is only observed as an accessory mineral in sample Kız.17 from Yarengediği Tepe kaolin deposit. Quartz is the only silica mineral varying approximately from 20% to 60% within these deposits. In the southwest of the study area, kaolinite and smectite are present together (Ulaşlar kaolin deposits). Here, in the Ulaşlar kaolins, quartz and low-cristobalite are present together. In the central part of the study area, kaolinite is the only clay mineral present (Saklar district kaolin deposits) similar to the Kızılçukur kaolin deposits. The amount of kaolinite here is less than that of the Kızılçukur kaolins. Quartz is disseminated within these deposits. Drill holes opened in the vicinity of the Saklar district kaolin deposit showed that kaolinite passes into smectite within the alteration zone away from the kaolin deposits. A small kaolin occurence (İnkaya kaolin deposit) situated at the western part of the study area is almost completely composed of kaolinite

The XRD patterns of the clays show that the d(060) values of the smectites are 1.49 Å, indicating a dioctahedral character (Figure 4). Samples which, were subjected to further investigation procedures improved by the Greene-Kelly test (Greene-Kelly 1952, 1953) for subgroup diagnosis of the group, showed that all smectites in the clays are Ca and Na montmorillonites.

TG-DTA studies were carried out on the <2 µm clay fractions of representative clay samples from the Kızılçukur and Ulaşlar kaolin deposits (Figure 5). It was noticed that the weight loss of the dehydroxilation of kaolinite begins at 450 °C and continues up to around 700 °C. The maximum temperature (peak temperature) of the complete expulsion of the structure water is at 531.8 °C in sample Kız.3 and at 526.3 °C in sample Kız.4. The endothermic peaks of the two samples are moderately sharp and more asymmetric. The exothermic peaks of samples Kız.3 and Kız.4 were observed at 992.3 °C and 989.4 °C, representing mullite formation. The endothermic peak at 114.4 °C corresponds to the removal of adsorbed water which most probably represents interlayer water of smectite crystals in sample Ulş.7. The main endothermic peak of kaolinite is shifted to the right (576 °C), due to the second endothermic peak overlapping. The exothermic peak at 974.9 °C represents formation of mullite. The second small exothermic peak at 1000 °C formation of cristobalite, which occurred due to crystallisation of excess silica. The endothermic peaks at 72.5 °C and 44.7 °C of sample Ulş.1 represent the removal of adsorbed water. The main endothermic peak which developed at 518.9 °C is asymmetric and less sharp, due to the effects of the degree of crystallinity and the presence of smectite. Here, the exothermic peak at 985.4 °C also represents the formation of mullite as seen in samples Kız.3, Kız.4 and Ulş.7.

The Hinckley crystallinity index, obtained from the XRD pattern of the clay samples, revealed that the Hisarcık (Emet) kaolinites are composed mainly of moderately ordered kaolinite crystals.

Table 1. Mineralogical distrubition and semi quantitative analyses of Hisarcık (Emet) kaolin deposits.

Sample	kaolinite	montmorillonite	quartz	cristobalite	K-feldspar	plagioclase	alunite	natroalunite	mica	mixed-layer	hematite
Kız.1	–	ac	+ –		+				+ +		ac
Kız.2	+ + + +		+				ac				
Kız.3	+ + + –		+ –				ac				
Kız.4	+ + + +		+		ac			ac			
Kız.5	+ + + –		+ –					ac			
Kız.6	+ + + –		+ –		ac			ac			
Kız.7	+ +		+ + +		ac			ac			
Kız.8	+ +		+ + +		ac			ac			
Kız.9	+ + +		+ +				ac				
Kız.10	+ + +		+ +				ac				
Kız.11	+ + + –		+ –								
Kız.12	+ + + –		+ –				ac				
Kız.13	+ + –		+ + –					ac			
Kız.14	+ + –		+ +						–		
Kız.15	+ + +		+ +				ac				
Kız.16	+ +		+ +		+	ac	ac				
Kız.17	+ + +	ac	+ –			–	ac				
Ulş.1	+ +	–	–	+ +			ac				
Ulş.2	+ +	+	ac	+ +							
Ulş.3	+ + –		+	+ –							
Ulş.4		+ + +	–		–	–			ac	–	
Ulş.5	–	+ –	–	–		–			+	–	
Ulş.6	+	+ +	ac	+ +							
Ulş.7	+ + –	–	–	+–							
Ulş.8	+ + –	ac	+ +		ac	ac	–				
Ulş.9	+ + –	–	+	+		ac		ac			
Ulş.10	+ + + –	–	+		ac		ac				ac
Ulş.11	+ +	+		+ +		ac		ac			
Sak.1	+ +		+ + +				ac				
Sak.2	+ +		+ + +				ac				
Sak.3	+ +		+ + +			ac					
Sak.4	+ +		+ + +								
Ink.1	+ + + + +		ac		ac	ac					

Calcite is present only in Sample 17 as accessory mineral. +: approx. 20 wt.%, – : approx. 10 wt.%, ac: accessory Samples Kız.1, Ulş.4 and Ulş 5 represent parent rocks; Samples taken from (Kız.1 to Kız.16, Sekeharmanı), (Kız.17, Yarengediği T.), (Ulş.1 to Ulş.7, Hisarcık Kooperatifi), (Ulş.8 to Ulş.10, Kütahya Porselen), (Ulş.11, Halil Acar), (Sak.1 and Sak.2, Kulalan), (Sak.3, Çitkaya), (Sak.4, Çitkaya Eczacıbaşı) and (İnk.1, İnkaya) kaolin deposits. Samples Kız.7, 8, 9, 10, 11, 12, 15, and 16 taken from bore holes.

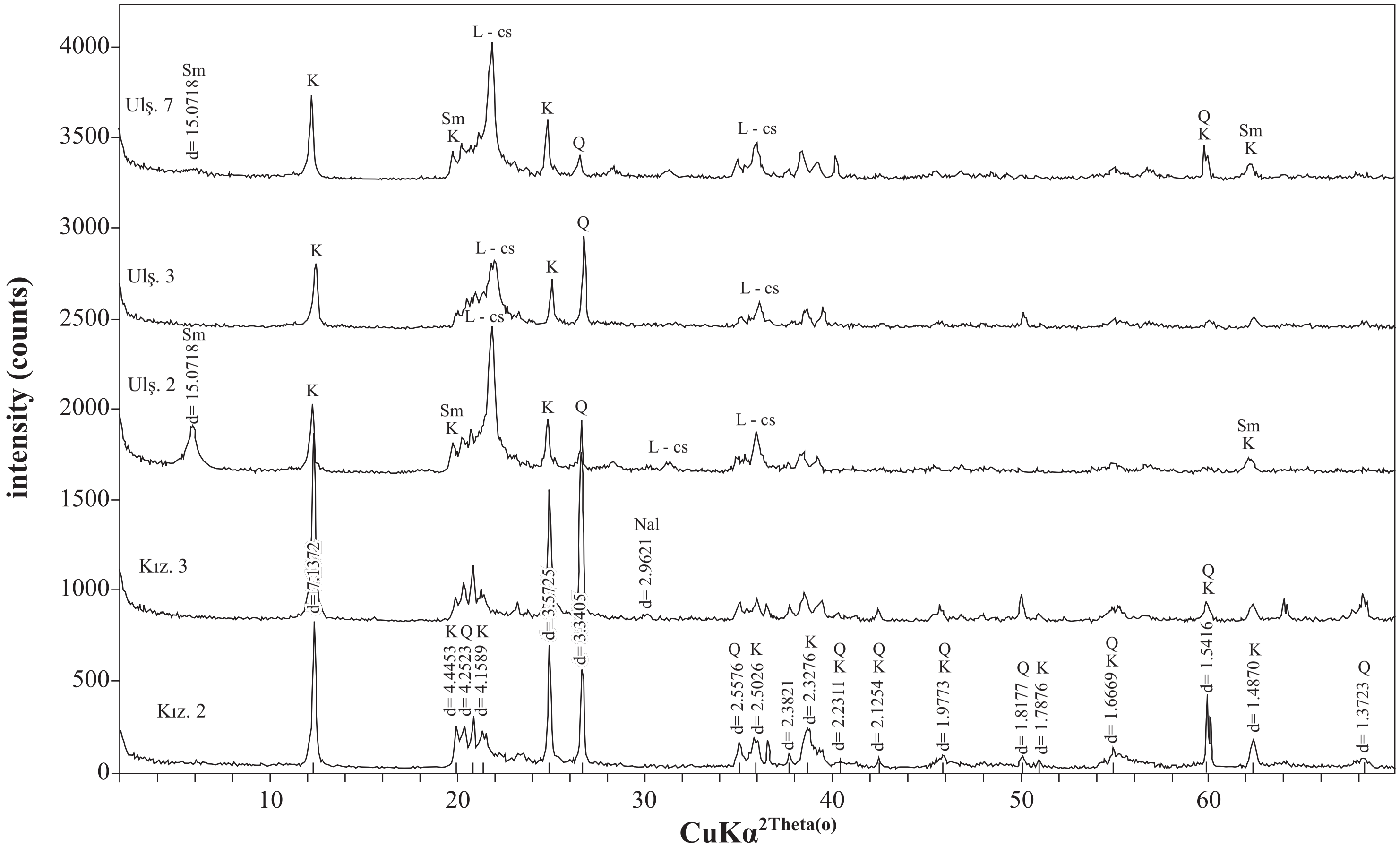

Figure 4. XRD patterns of selected clay samples from the Hisarcık kaolin deposits. K– kaolinite, Sm– smectite, Q– quartz, L-cs– low-cristobalite, Nal– natroalunite.

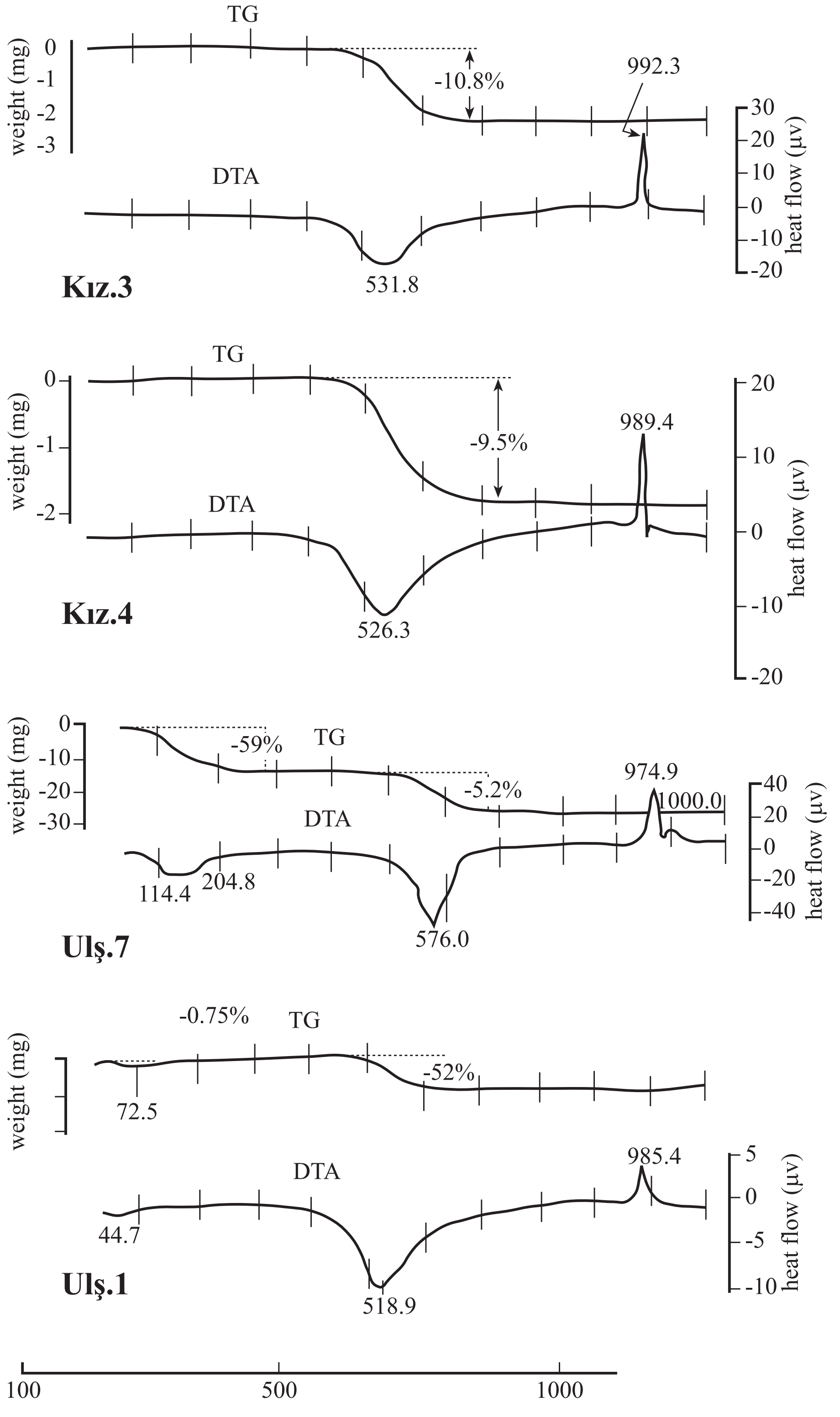

Figure 5. Typical DTA-TG curves from Kızılçukur kaolin deposits (samples: Kız.3, Kız.4) and Ulaşlar kaolin deposit (samples Ulş.7 and Ulş.1).

SEM studies of some selective samples from the Kızılçukur and Ulaşlar kaolin deposits can be summarized as follows: The well-formed hexagonal-shaped kaolinite crystals up to 1 μm in diameter occur as single kaolinite plates at the upper section of the deposit. The orientation of plates is rather random. The porosity of the clay is reasonable high (sample Kız.3, Figure 6a). Well- or ill-formed tiny kaolinite crystals are tightly packed showing a very low porosity at the lower section of the deposit (sample Kız.4, Figure 6b). Kaolinite plates and flakes are associated with K-feldspar and cubic alunite crystals (Figure 6c, d). Fine platy particles and wavy flakes of kaolinite gather to form mega flocks (sample Ulş.1, Figure 6e). The pseudo-rosette texture of montmorillonite crystals appear to break into small kaolinite crystals (sample Ulş.2, Figure 5f). This micrograph represents in-situ alteration of montmorillonite crystals.

The chemical analyses of the clays show that the Al_2O_3 content varies from 13.80% to 33.50%. Only in the İnkaya district, Al_2O_3 values reache to 37.5%. The Al_2O_3 content within the clays depends upon the intensity of kaolinization; more kaolinization indicates more kaolin minerals, thus higher Al_2O_3 content. As seen in the Kızılçukur kaolin deposit in the south, Al_2O_3 content is generally over 24%, except for samples Kız.7 and Kız.8. These low Al_2O_3 values, 15.70 and 15.22%, respectively, are due to silicification of the clay body. At the Saklar kaolin district, Al_2O_3 values of the clays are very low, although there is strong kaolinization. This is also due to intense silicification of the deposit as seen in samples Kız.7 and Kız.8. The Al_2O_3 contents of the Ulaşlar kaolin deposit, which represents moderate kaolinization, varies from 17.30% to 27.86%. The clay samples of the Sekeharmanı section of the Kızılçukur kaolin deposit have negligible MgO, CaO and K_2O values, except samples Kız.6 and Kız.16 which have 0.43% and 2.70% K_2O, respectively. On the other hand, due to the presence of smectite, K-feldspar and alunite, the Ulaşlar and Saklar kaolins have a considerable amount of MgO, K_2O and CaO up to 3.90%, 3.60% and 2.60%, respectively. In all studied clays, the Na_2O content varies from 0.01% to 0.72% and may be attributed to the presence of plagioclase, natroalunite and Na-montmorillonite. Total iron values, which range from 0.15% to 3.70% are mainly related to iron minerals (dominantly hematite). A small amount of iron ore could be in the structure of clay minerals and feldspar. SO_3 contents of the clays vary from 0.20% to 2.42% and are attributed to alunite and natroalunite. Due to the considerable amount of associated minerals, mainly quartz and low-cristobalite, the SiO_2 values of the clays reach up to 78.56%.

Some trace-element distribution in both weakly altered (Kız.1) and partly altered (Ulş.4) dacitic parent rocks and kaolin deposits show distinct variations which depends mainly on the chemical composition of the parent and associated rocks, the altering solution and the intensity of the kaolinization process.

Discussion: Origin of Kaolin Deposits

In this study, kaolinization is found to occur by the reaction of the parent rocks with thermal water. Meteoric water may be heated by contact with hot rocks adjacent to a magma chamber or heated by vapours coming from magma. The theory of magmatic steam heating of magmatic water to produce thermal waters (often not more than 300 °C) has been accepted by White (1957), Ellis & Wilson (1960) and Schoen *et al.* (1974). On the other hand, Einarsson (1942) proposed that the heating of meteoric water by contact with magma heated country rocks is the predominant mechanism. An increased geothermal gradient due to the graben tectonism could be the heat source for the Emet geothermal field (Gemici *et al.* 2004). Geological and hydrogeochemical investigations showed that the temperature of the hot spring waters of the Hisarcık area (approximately 6 km north of the study area) do not exceed 100 ºC (Gemici *et al.* 2004). In addition, Pb and Sr enrichment within the kaolin deposits implies that during Miocene volcanic activity, hot solutions which may have risen from magma, have also played a role in the kaolinization process.

The origin of the kaolin is discussed in five headings, namely; fractures, mineral paragenesis and silica zones, trace elements, temperature and textures of kaolins.

Fractures

In Miocene, in western Turkey, related to the extensional tectonics, calc-alkaline and alkaline volcanism has been dominant in the region (e.g., Seyitoğlu & Scott 1991, 1992a, b; Seyitoğlu *et al.* 1992, 1997; Hetzel *et al.* 1995; Aldanmaz 2006). As a result of the extensional tectonic regime, a series of graben and normal faults with mainly trending northeast–southwest and east–west

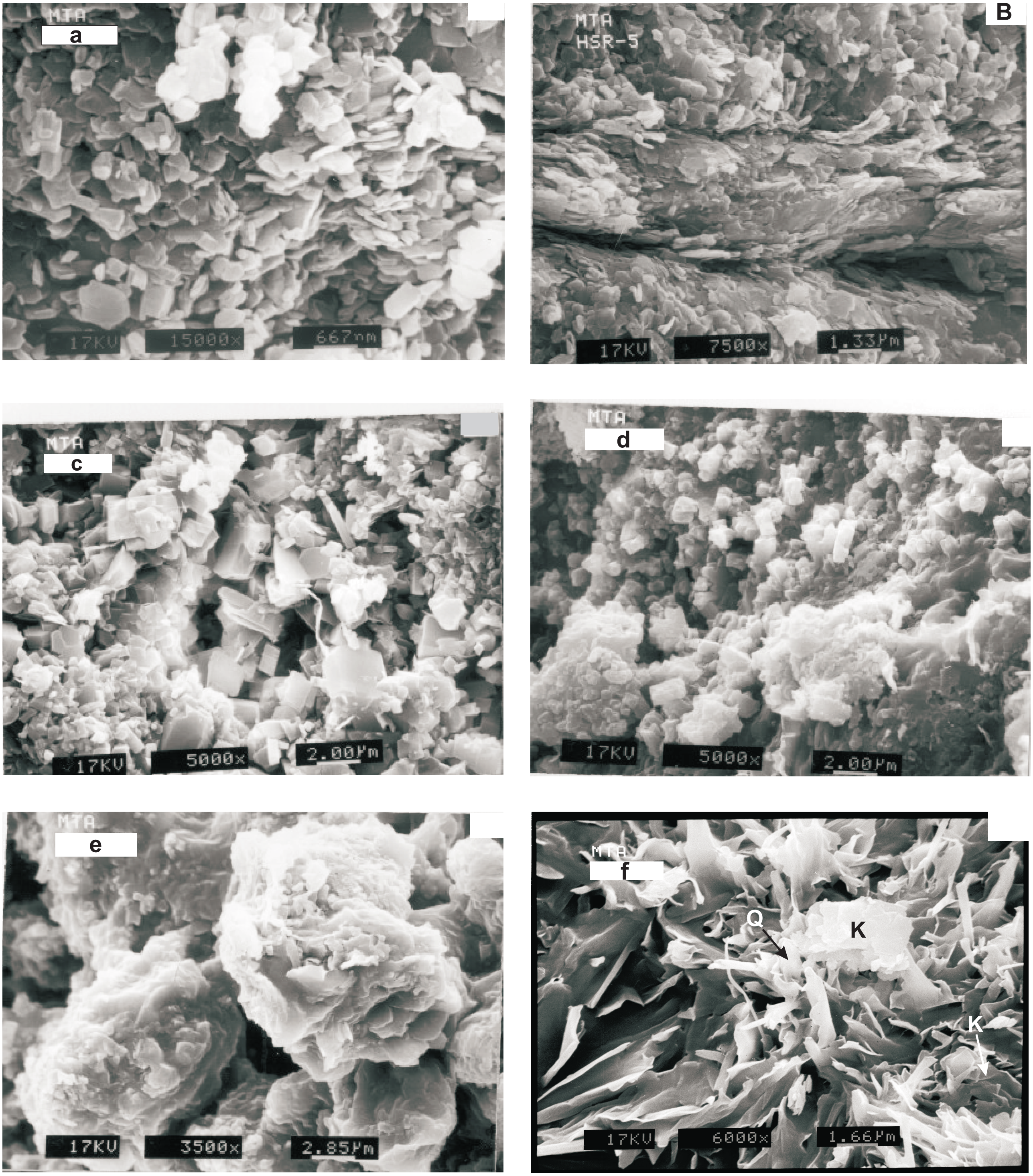

Figure 6. SEM images of clays: **(a)** small well-formed hexagonal-shaped kaolinites are loosely packed in sample Kız.3; **(b)** tightly-packed well- or ill-formed tiny kaolinites in sample Kız.4; **(c)** angular K-feldspar (probably sanidine) crystals are mixed with flocks of kaolinites crystals in sample Kız.16 (these samples are from Kızılçukur kaolin deposit); **(d)** tightly-packed kaolinite plates and flakes associated with cubic alunite crystals in sample Ulş.1; **(e)** fine platy particles and wavy flakes or kaolinites forming mega floks in sample Ulş.1; **(f)** small kaolinite crystals appear growing on the surface of the pseudo-rosette texture of montmorillonite crystals in sample Ulş.2 (the samples in e–f are from Ulaşlar kaolinite deposit). K– kaolinite, Q– quartz.

directions have been observed in the region (e.g., Koçyiğit *et al.* 1999; Bozkurt 2000, 2001, Figure 2; Bozkurt & Sözbilir 2004, 2005). Similar faults system are also present in the study area (Figure 1). It is assumed that the activity of volcanism may have been more intense due to extensional tectonics. Consequently, thermal solutions related to this volcanism may have been associated with the fault systems mainly in northeast–southwest and east–west directions with the series of grabens in western Turkey. Thermal waters most probably ascended along these fault zones within the dacites and dacitic tuffs.

Mineral Paragenesis and Silica Zones

In all clay deposits, the mineralogical zones were revealed by field observation and drillings. A typical example of alteration zones is seen at the Sekeharmanı kaolin deposit (Figure 2). Here, (i) the kaolinite dominant zone at the centre; (ii) the smectite dominant zone is further from the centre, (from drillhole K6); (iii) next are weakly altered zones, (here montmorillonite and kaolinite are in minor amounts, sample Kız.1); and (iv) a silica zone at the top of the kaolin deposit. Reyes (1991), Sayın (1984, 2001, 2004) and Hedenquist *et al.* (1996) have observed typical mineralogical zonation with a kaolinite ± alunite zone in the centre and an outer smectite ± illite-rich zone in hydrothermal kaolin deposits. The hydrothermal Kohdachi (Japan) kaolin deposit contains three alteration zones: a halloysite zone with weak silicification, a halloysite + kaolinite zone and a kaolinite zone (Kitagawa & Köster 1991). Such zonation is generally not present in supergene kaolin deposits. In particular, the presence of a silica zone overlying the kaolin occurrences clearly suggests the presence of hypogene altering solutions. The occurrence of silica zones was also observed within the hydrothermal kaolin deposits of Mexico (Keller & Hanson 1968, 1969), Japan (Iwao 1968) and Turkey (Sayın 1984, 2004). As suggested by Keller & Hanson (1968) silica derived mainly from the parent rocks (here, dacite and dacitic tuff) was concentrated within the rising hot solution. Because of a temperature drop, dissolved silica in the solution precipitated on the kaolin deposits forming the silica zones. These silica zones consist of tiny quartz crystals. Silica may also replace and silicify the dacites and dacitic tuffs. Dill *et al.* (1997) pointed out similar upwards hydrothermal silicification in the western Peru kaolin deposit. They suggested that this silicification resulted from hot brines coming into contact with cold water in an aquifer. As seen in Figure 3, some silica veins and veinlets are also widespread within the kaolin deposits. These silica zones are the striking features of hypogene kaolin deposits. These silica zones were identified as opal zones by Türk (1975), Okut *et al.* (1978), Işıklar & Demirhan (1982) and Demirhan (1986). In fact alpha-quartz may be crystallized from the hydrothermal solutions at elevated temperature rather than opal. In the Otake geothermal area, quartz has crystallized above 100 °C, whereas opal has occurred below 80 °C from the hydrothermal solutions (Hayashi 1973).

In western Turkey, volcanic activity related kaolin deposits contain considerable amounts of alpha-quartz, so it is proposed that magma related hot corrosive solutions may elevate the temperature of the medium in which amorphous silica may have been crystallized, or alpha quartz has been formed from the solution directly (Keller & Hanson 1968, 1969; Sayın 1984).

Sulphides (mainly pyrite) are not present within the parent rocks or the kaolin deposits. Therefore, superficial alteration probably did not occur. The SO_3 content of the parent rocks (sample Kız.1 and Ulş.4) is smaller than that of the samples taken from the kaolin deposits (Table 2). The presence of alunite and natroalunite within the kaolin deposits indicates a sulphate-rich solution system under the conditions of strong hydrogen-metasomatism. The high-sulphate contents of the Hisarcık thermal waters is related to rocks and minerals (mainly gypsum) in the red unit below the Emet borate deposits and also to the relatively high S concentration within the Emet borate deposits (Gemici *et al.* 2004). This implies that sulphate enrichment within the thermal waters and the kaolin bodies is related to the hypogene process rather than to a supergene process. Despite the high sulphate concentrations (up to 1309 mg/kg), gypsum and anhydrite are undersaturated for all of the thermal waters, indicating that the solution of SO_4 is still taking place in the reservoir (Gemici *et al.* 2004). The frequent association of alunite and kaolinite is to be expected on the basis of phase equilibrium data for both hot spring and higher temperature environments (Hemley *et al.* 1969). They also emphasize that rather high acidity definitely is implied in an equilibrium silicate-alunite system at the elevated temperatures involved in their experimentation.

Table 2. Major oxide (in wt%) and trace-element (in ppm) analyses of the samples from the Hisarcık (Emet) kaolin deposits.

Sample	Kız.1	Kız.2	Kız.3	Kız.4	Kız.5	Kız.6	Kız.7	Kız.8	Kız.9	Kız.10	Kız.11	Kız.12	Kız.15	Kız.16
SiO_2	63.50	53.50	63.70	58.20	58.00	60.60	78.10	78.56	66.66	66.54	62.28	61.95	65.42	68.91
TiO_2	0.60	0.60	0.40	0.35	0.20	0.66	0.20	0.20	0.15	0.10	0.15	0.15	0.20	0.30
Al_2O_3	20.20	33.50	27.10	30.20	28.50	26.83	15.70	15.22	24.05	24.80	26.95	27.80	25.18	20.35
Fe_2O_3	3.40	0.60	0.20	0.20	0.75	0.30	0.15	0.40	0.20	0.15	0.70	0.30	0.30	1.59
MgO	0.70	0.10	0.10	0.10	0.01	0.01	0.01	0.01	0.01	0.10	0.01	0.01	0.10	0.01
CaO	0.30	0.10	0.10	0.03	0.01	0.01	0.15	0.10	0.01	0.01	0.01	0.01	0.01	0.10
Na_2O	0.70	0.10	0.10	0.10	0.70	0.21	0.40	0.10	0.10	0.10	0.10	0.01	0.01	0.37
K_2O	6.40	0.10	0.10	0.10	0.10	0.43	0.10	0.10	0.10	0.10	0.10	0.10	0.10	2.70
MnO	0.10	0.10	0.20	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
P_2O_5	0.10	0.30	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
LOI	3.67	10.75	8.05	10.06	11.16	9.72	5.18	5.33	8.74	8.17	9.51	9.62	8.57	5.55
Total	99.65	99.75	100.15	99.55	99.63	99.06	100.19	100.22	100.22	100.27	100.01	100.15	100.09	100.00
SO_3	0.10	1.90	0.25	0.29	1.76	0.40	0.20	0.22	0.30	0.32	0.22	0.32	0.29	0.48
Ba	865	875	252											
Ce	30	20	4											
Co	94	50	50											
Cr	692	141	92											
Cu	240	10	10											
La	45	40	40											
Li	10	40	50											
Nb	20	20	20											
Ni	890	390	100											
Pb	185	2200	284											
Rb	227	10	10											
Sc	20	20	20											
Sr	111	2897	1384											
V	88	79	68											
Y	160	56	15											
Zn	55	14	10											
Zr	219	481	223											

Sample	Kız.17	Ulş.1	Ulş.2	Ulş.3	Ulş.4	Ulş.8	Ulş.9	Ulş.10	Ulş.11	Sak.1	Sak.2	Sak.3	Sak.4	Ink.1
SiO_2	63.35	72.20	64.50	73.00	60.00	65.44	62.70	57.70	65.10	76.70	77.10	78.05	78.20	45.20
TiO_2	0.10	0.45	0.40	0.40	0.40	0.70	0.45	0.30	0.40	0.80	0.70	0.55	0.60	0.16
Al_2O_3	25.70	19.50	25.30	18.80	17.30	20.90	24.00	27.86	22.00	15.72	15.22	13.80	14.10	37.50
Fe_2O_3	0.45	0.50	0.40	0.50	3.70	0.46	0.35	3.22	0.71	0.40	0.38	0.73	0.72	0.67
MgO	0.18	0.20	0.50	0.10	3.90	0.14	0.28	0.30	0.55	0.15	0.15	0.15	0.15	0.20
CaO	0.45	0.15	0.30	0.10	2.60	0.22	0.16	0.16	0.32	0.16	0.15	0.25	0.18	0.26
Na_2O	0.43	0.01	0.10	0.10	0.10	0.38	0.72	0.06	0.60	0.16	0.15	0.20	0.16	0.20
K_2O	0.10	0.10	0.10	0.20	3.60	0.66	0.16	0.17	0.10	0.16	0.15	0.20	0.16	0.20
MnO	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
P_2O_5	0.10	0.10	0.10	0.10	0.20	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
LOI	9.37	7.00	8.10	5.80	7.60	10.38	10.57	10.07	8.98	5.34	5.27	5.10	5.18	13.80
Total	100.33	100.31	99.50	99.20	99.50	99.48	99.59	100.02	99.86	99.79	99.47	99.23	99.65	100.39
SO_3	0.30	0.20	0.58	0.25	0.25	3.10	2.47	1.42	1.36	0.50	0.48	0.42	0.40	--
Ba			136	198	389									
Ce			10	20	40									
Co			50	50	50									
Cr			287	258	477									
Cu			<10	<10	10									
La			40	55	<40									
Li			40	20	50									
Nb			20	20	20									
Ni			330	660	1100									
Pb			82	135	20									
Rb			<10	<10	268									
Sc			20	20	20									
Sr			1382	696	35									
V			64	50	65									
Y			<10	15	27									
Zn			<10	<10	48									
Zr			263	230	200									

Trace Elements

In this study, the content of trace elements within the Kızılçukur and Ulaşlar kaolin deposits are compared with that of their parent rocks Kız.1 and Ulş.4, respectively; Ba is associated with K in minerals and is probably related to K-feldspar, mica and alunite. Sr is closely associated with Ca- or K-bearing minerals; feldspar, mica, Ca-smectite and alunite. Due to lack of alunite, the weakly altered tuff (Kız.1) and partly altered tuff (Ulş.4) contain very low Sr, 111 and 35 ppm, respectively. It explains that enrichment of Sr is mainly related to alunite.

Moreover, in the region (8 km north of the study area), Helvacı & Orti (1998) pointed out that enrichment of Sr and B in the basins implies a volcanic origin. In addition, Kistler & Helvacı (1994) postulated that ions in solution were supplied by the leaching of Tertiary volcanic rocks (enriched with B and Sr) and basement metamorphic rocks and transported to the basins by thermal springs and hydrothermal solutions associated with volcanism. Since enrichment of these elements would take place within the same Miocene tectonic regime, similarly, enrichment of Sr within the kaolins suggested hydrothermal process associated with volcanism. Rb is directly related to K-feldspar. Therefore, it is concentrated only in samples Kız.1 and Ulş.4, which indicates that most Rb was removed during the strong kaolinization process.

The Kızılçukur kaolin deposit shows a lower Cr, Co, Ni, Cu, Zn, La, V and Y content than those observed in weakly altered parent rock. The kaolin deposit and the weakly-altered parent rock both contain Sc and Nb in the same amount. The kaolin deposit contains higher Zr and Pb contents than those seen in the weakly altered parent rock. It is most probable that zircon is an accessory mineral in the coarse and/or finest size particles in the kaolin deposits. Wiewiora (1978) suggested that the concentration of Zr in the kaolin deposit may be due to the adsorption phenomena of finest clay particles and that this is independent of the origin of kaolin.

The Ulaşlar kaolin deposit shows a higher Zr, La and Pb content and lower Ni, Zn, V, Cu, Cr and Y content than those seen in the partly altered parent rock (Ulş.4), but both the kaolin deposit and the parent rock have the same Co, Sc and Nb content. On the basis of ionic radii, the occupation of octahedral sites in the clay lattice (mainly smectite group) by V, Cr, Ni, Co, Sc and Li is quite possible. These trace elements (V, Cr, Ni, Co and Sc) may also be adsorbed on the accessory iron oxides or may substitute for iron in these minerals. Ni, and Co for Fe^{+2} and Cr, V and Sc for Fe^{+3}. The concentration of Cr, Co, Ni and V within the weakly and partly altered rocks, due to high total Fe_2O_3 values of 3.4% and 3.7%, respectively, is consistent with this concept. High Li contents in samples Kız.2 and Kız.3 of Kızılçukur kaolin deposit show that adsorption phenomena of the clays should be more important for Li concentration. Mosser (1982) suggested that the very high Li values (up to 800 ppm) are probably due to the kaolinite in the Massif Central. Kitagawa & Köster (1991) also showed that only the Li and Cu content of hydrothermal kaolin samples is markedly higher than those in weathering kaolin deposit. In contrast, Cu is not concentrated within the studied kaolins. Enrichment of Pb within the kaolins emphasizes the persistence of the hypogene process. Similarly, Dill *et al.* (1997) observed Pb enrichment within the hydrothermal kaolin deposits hosted by alkaline-calc alkaline volcanic rock series in Peru. They observed Pb in lesser amount within the weathering kaolins in the region. Beeson (1980) also pointed out Pb and Sr enrichments within the hydrothermal kaolin zone relative to the country rock at Sarkhanlu (northwest of Iran), although nine other trace elements (As, Bi, Co, Cu, Fe, Mn, Mo, Ni and V) were depleted in the zone. He suggested that the removal of nine elements resulted from mineralogical changes during the alteration process and from the leaching potential of the hydrothermal solutions. The Kızılçukur and Ulaşlar kaolins have a Ce content lower than that of their parent rocks. Enrichment of Ce in kaolins could be due to concentration of apatite in the clay zone. Moreover, Ce might have been adsorved by the kaolin particles which display a large surface.

Pb and Sr enrichments strikingly appear in both the Kızılçukur and Ulaşlar kaolin deposits. On the other hand, the rest of the trace elements do not behave like these elements. As a result of extentional tectonics in this part of Turkey, the occurrence of some crustal contamination with time would be inevitable. Therefore, changes in the nature of volcanism would affect trace elements distribution within the alkaline and calc-alkaline parent rocks and the kaolin deposits. On the other hand, the degree of kaolinization may also affect the distribution of the trace elements. The low trace element concentration may be due to strong kaolinization. The mineral paragenesis within the kaolin bodies may also affect trace elements concentrations. The adsorption phenomena of the kaolinite crystals could be an influence in the distribution of some trace elements in kaolin deposits. During kaolinization, the chemistry of the hot solutions passing through the country rocks could has also affected the distribution of the trace elements within the clays.

Temperature

The kaolinization process appears to be very strong in the Kızılçukur and İnkaya kaolin deposits. Strong kaolinization also persisted on the Saklar kaolins. Here, despite intense kaolinization, the kaolin deposits contain a high amount of finely crystalline quartz. The strong kaolinization of dacitic tuff and dacite represents desilication. It is assumed that seasonal variation in rainfall may have achieved this phenomena in these districts. Thus, during the drier seasons of the year, the hydrothermal water and surrounding rocks become hot. Under this condition hydrolysis would be accelerated by the high temperature and simultaneously the concentration of dissolved silica would increase. During heavy rain periods, descending of much more cool meteoric water in the relatively porous dacitic tuff may have cooled the system enough to exceed the saturation point for silica, and therefore finely crystalline quartz might have been precipitated. Here, it is assumed that in the central part of the study area, high permeability of the surrounding rocks may play an important role, fluxion of the cool meteoric water into the hot system associated with dacite and dacitic tuffs.

The solubility of silica of the Hisarcık thermal water is 18 mg/l at 20 ºC and 36 mg/l at 50 ºC (Gemici *et al.* 2004). Here, the water table may have some influence in the solubility of silica. In the hot springs of Steamboat Springs, Nevada, the solubility of silica is about 315 ppm at 90 °C and 110 ppm at 25 °C (White *et al.* 1956). They concluded that solubility of silica is almost same both in acid and alkaline springs, but equilibrium is attained in acid solutions, at exceedingly slow rates. The solubility of quartz increases with increasing temperature at hydrothermal conditions (Dove & Rimstidt 1994). Based on some experimental studies they indicated that the presence of alkali cations markedly increase the dissolution rates of quartz and amorphous silica.

The presence of smectite within the Ulaşlar kaolin deposits clearly indicates a moderate or weak kaolinization process, suggesting an environment in which alkali and the calc-alkali ions/H^+ ratio is very high. This implies that complete removal of alkali and calc-alkali ions from the solution could not be possible because of low temperature.

Textures of Kaolins

SEM images of the authigenic kaolinite crystals are dicussed as follows: The upper section of the Kızılçukur kaolinites represents a porous texture (Figure 6a, sample Kız.3), whereas kaolinite crystals are tightly packed, showing a very low porosity at the lower section of the deposit (Figure 6b, sample Kız.4). Keller & Hanson (1975) and Sayın (1984) suggested that due to relatively low pressure weight of overburden, the clays show the former texture, on the contrary, higher rock pressure of overburden creates the latter texture in the hydrothermal kaolin zones. The small kaolinite crystals appear to have been formed from the breaking down of the pseudo-rosette structure of montmorillonite, which also suggests a phase transition between montmorillonites and newly-formed kaolinites (Figure 6f). Keller (1976) and Sayın (1984) studied hydrothermal kaolin deposits in detail and observed similar phase transition between montmorillonite and kaolinite. Exley (1976) suggested that montmorillonite represents an intermediate mineral phase, sometimes accompanied by mica in the St. Austell kaolinite deposits, Cornwall. He concluded that “the formation of these minerals is closely linked, while that of kaolinite is a separate process and perhaps dependent on their destruction”. Similarly, montmorillonite and mica were converted into kaolinite by H^+ ions from the altering solution (Kukovsky 1969).

Conclusions

The Hisarcık kaolin deposits, which were formed by hydrothermal alteration of dacite and dacitic tuffs, related to Miocene volcanism, display a mineralogical zonation. Field observation reveals that kaolinizaiton process has been active mainly along the northeast–southwest- and east–west-trending faults in the study area. This can be projected to whole western Turkey with future studies. In places despite intensive kaolinization, the presence of a high amount of finely-crystalline quartz is attributed to temperature gradients. Pb and Sr enrichment within the kaolin deposits implies that corrosive solutions which may have risen from magma, have played an important role in the kaolinization process. NE–SW- and E–W-trending fault zones with their related silica occurrences (silica zones) which consist of alpha quartz in the region, can be also used as a guide for exploration of the hydrothermal kaolin deposits related to volcanic rocks. Therefore, these silica zones and tectonic framework should be carefully studied together in the region.

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