Evaluation of Selected Kaolin Clays as a Raw Material for the Turkish Cement and Concrete Industry

Aydin Aras[1], Mustafa Albayrak[1], Metin Arikan[2], Konstantin Sobolev[3] *

[1] General Directorate of Mineral Research and Exploration (MTA), Turkey
[2] Civil Engineering Department, Middle East Technical University (METU), Turkey
[3] Facultad de Ingenieria Civil, Universidad Autonoma de Nuevo Leon (UANL), Mexico

ABSTRACT

Turkey has a long tradition (starting from the prehistoric civilizations) and experience in exploring and processing clay raw materials into ceramic products. Many of these products, such as tiles and sanitary ware, are manufactured for domestic and export markets. Kaolin clay is one of the raw materials of major importance for the ceramic and paper industry, as well as for a number of auxiliary applications. There is an ongoing interest to apply kaolin clay in the construction industry as a raw material for the production of white cement clinker and as an artificial pozzolanic additive for concrete (in a form of metakaolin). This report presents the results related to search, assessment and evaluation of available resources for advanced cement and concrete additives.

Keywords: kaolin, metakaolin, construction, resources, ceramics, cement, x-ray diffraction, SEM

INTRODUCTION

Turkey has an abundance of natural resources and its mining industry is one of the sectors showing steady growth. Among the most commonly mined minerals are borax, magnesite, chromites, barite, feldspars, different clays, and limestone [1-21]. Local ceramic industry has more than 4000 years of experience in exploring and processing widely available raw materials into useful commodities. Currently, several ceramic products, such as tiles and sanitary ware are manufactured to meet international standards (ISO 9000) and significant amounts (about 45 %) of these products are exported [21]. The raw materials for these products, such as ball clays, fireclays, normal grade kaolin, and feldspar are widely available locally. Nevertheless, some raw materials (such as high quality kaolin, fireclays, ball clays) for fine ceramics, porcelain, and electrical insulators are imported [4, 21].

There were a number of fundamental investigations to evaluate the volumes and quality of ceramic raw materials in Turkey [1-20]. It was reported that kaolinite is of major importance for a number of applications [1-15]. However, only few reports on the availability and properties of Turkish kaolinites were actually published [1, 12, 19, 20].

Kaolinite is a common phyllosilicate mineral of the formula $Al_2Si_2O_5OH_4$. It was named after Kao-Ling (高嶺土), China, the location of its first major utilization. Kaolinite is composed of alternating layers of silicate (Si_2O_5) and gibbsite ($Al_2(OH)_4$) [22, 23]. Kaolinite crystals are usually arranged in pseudohexagonal plates forming flaky aggregates and it has the same chemistry as its polymorphs

* Corresponding author, e-mail: sobolev@fic.uanl.mx

halloysite, dickite and nacrite. Kaolin clay is formed as a result of the alteration of alumosilicates (feldspar, feldspathoid, spodumene, sillimanite) and volcanic glasses, sometimes altered by acidic hydrothermal solutions. Besides kaolinite, kaolin clay usually contains different minerals (such as quartz, feldspar, and calcite). It is mostly white, but it also can be grey, yellow or red.

Kaolinite is one of the most common minerals. Large volumes of kaolinite clays are used for the production of cement, ceramics, bricks and porcelain [24-28]; the greatest demand for kaolinite is in the paper industry to produce a high quality paper [29-31]. It is also used as filler for paint, rubber and plastics [24, 26, 27]. Kaolinite clay found its application in medicine, in toothpaste, in cosmetics and as a food additive. Recently, a specially formulated spray is used in fruit and vegetable production to repel the insects and prevent sun burn [32].

There is an ongoing interest to utilize selected clay minerals including kaolinites in construction industry [33-36]. Conventionally, special grade kaolin clay is used for the production of white cement clinker and subsequently, white cement. Since chemistry of white cement does not permit the existence of the ferrite phase (C_4AF), the purity of Si-, Ca-, Al- sources is essential for the quality of white cement. Kaolin clay for white cement must contain about 65-80% of SiO_2, not more than 1.0% of Fe_2O_3, less than 0.8% of TiO_2 and only traces of MnO [37]. Usually, suitable kaolin contains 70-73% of SiO_2, 18-20% of Al_2O_3, 0.4-1% of Fe_2O_3, and 0-0.8% of TiO_2 and no MnO [37].

A recent development comprises the application of metakaolin as an artificial pozzolanic additive for concrete. The strength and durability of conventional cement-based materials can be significantly improved when additives based on thermally activated kaolin are used [33-40]. Such additives are conventionally manufactured by firing high-grade purified kaolinite at 650-850 °C according to following reaction [36, 38]:

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \xrightarrow{650\text{-}850\,^{\circ}C} 2SiO_2 \cdot Al_2O_3 + 2H_2O\uparrow$$

The main beneficial effect of metakaolin in concrete and cement systems is related to its high pozzolanic activity (i.e. its ability to react with portlandite, $Ca(OH)_2$ released during the hydration of portland cement). Due to its ability to improve the packing of the cement matrix the application of super-fine particles of metakaolin results in a microfiller effect. The micro-bearing's effect is provided by the flaky particles of metakaolin resulting in better sliding of more coarse cement particles and, therefore, facilitating the flow of the system. Furthermore, metakaolin improves the morphology of the interface zone between the cement matrix and the aggregate's surface. Very light color shades, as well as an improved strength and durability of metakaolin based concrete make such additive one of the vital components of modern architectural concrete.

Shvarzman et al. demonstrated that useful properties of metakaolin are preserved even at a reduced content (about 30%) of kaolinite in the raw mix [36]. Based on this study, it was proposed that raw clays with 20-35% of kaolinite can be directly used for manufacturing of pozzolanic additives, eliminating the beneficiation stage [38]. Such an approach could significantly reduce the production expenditures related to intermediate wet beneficiation and subsequent drying of the raw materials. Furthermore, it would eliminate the waste streams generated during these stages. Consequently, thermally activated kaolin (TAK) can be made available at a significantly reduced cost, making feasible the application of such additive even in a regular-grade cement and concrete. Definitely, the properties of such product can be tailored to provide the improved strength and durability.

To verify this proposal, an extensive research program involving five R&D and educational institutions (METU, LAU, TCMA, MTA, TECHNION) was initiated and supported by TUBITAK (Scientific and Research Council of Turkey) [38]. This report presents the results related to search, assessment and evaluation of available resources for the advanced additives for Turkish cement and concrete industry.

AREA DESCRIPTION AND METHODS

Description of the Deposits

Five pits of three different deposits (namely, Düvertepe, Kütahya, and Şile) located in the Anatolian area of Turkey were investigated (Fig. 1). These deposits have different reserves (Table 1) and kaolin of different composition, crystallinity [41, 42], morphology and purity. Some of the pits under the investigation were found to be a not very effective kaolin sources for fine ceramics and paper industry applications. Therefore, the major mining activities at these pits were almost seized since 1970; other pits presented in this study are still supplying relatively small quantities of raw materials to local pottery industry. There is limited information on the potential applicability of these kaolin clays as a raw material for alternative applications, such as white cement and metakaolin based additives [38].

Experimental Methods

Surface samples of kaolin clay, about 1500 kg in total, were collected from the investigated pits. The labels and the location of the sampling points (including the GPS coordinates) are presented in Table 2. Representative 1-kg samples of kaolin clay were taken from the initial materials using the quartering method. These samples were dried to less than 0.5% moisture content, crushed and milled (to the size of less than 95 μm) prior to their analysis. Totally, 15 samples were collected and investigated (Table 2).

The following sample characterization techniques were used:

- XRF method for chemical composition;
- XRD for mineralogical composition;
- DTA-TG for thermal behavior;
- SEM for kaolin texture and morphology;
- EDS for the spatial distribution of different elements.

RESULTS AND DISCUSSION

Characterization of Kaolin

The investigated samples were composed mainly of quartz and kaolinite with low to medium crystallinity as defined by the Hinckley Index [41, 42]. The chemical analysis of the investigated samples is given in Table 3. The chemical analysis (Table 3) agrees with the mineralogical composition of samples determined by the x-ray diffraction (Figs. 2, 3) and DTA-TG (Fig. 4) analysis, as well as confirmed by the SEM-EDS investigation (Figs. 5-7). Based on the characteristic weight loss at 500-650 °C corresponding to dehydroxylation of kaolinite (Fig. 4) the kaolinite content was calculated. The samples from the most valuable deposits such as Düvertepe and Kütahya had more than 70% kaolinite, whereas small group of samples (predominately, from Şile) had the kaolinite content of less than 40%. However, the majority of investigated samples (Düvertepe and Şile) had an average kaolinite content of 40 - 55% (Table 3).

Düvertepe Kaolin Deposit

The Düvertepe area is one of the most important sources for quality kaolin in Turkey. It is located about 80 km South-East of Balikesir, on the Northern side of the Simav stream (Fig. 1).

Düvertepe deposit is underlined by ophiolitic rocks which contain limestone blocks. The kaolins are formed via hydrothermal alteration of Neogene acidic tuffs. Most of these tuffs have rhyolitic composition (Okut et al., 1984 [7]) or were actually tuffaceous sandstones as proposed by Fujii et al.

[4]. The Neogene acidic tuffs are bordered by a NW-SE striking fault. There are few kaolin pits located in this area which are confined by the faults. There are some differences in mineralogy and occurrence of kaolins in these pits. A relatively high content of sublimated sulfur is observed in the regions next to the faults. On the other hand, massive amounts of breccias of altered rocks cover the kaolinized rock. This indicates the presence of intense tectonic activities after the formation of kaolin rock. In some regions, the alteration of dacitic layers is observed; these are accompanied with chalcedony, while other areas demonstrated a high quartz content revealing that the primary rock was composed of sandstone.

Düvertepe Kaolin Deposit: Kale, Söğüt, Camiş and Matel Mining Pits

X-ray diffraction analyses of investigated samples revealed that they consist of kaolinite and quartz. Threfore, two samples, No. 1 and No. 2 (DK-1 and DS-1), had a relatively high content of SiO_2 (79.5% and 80%, respectively).

The amount of SiO_2 in sample No. 3 (DC-1) was lower (70%) and it had a higher content of Al_2O_3 (20%) suggesting a higher kaolinite amount (44.8%). Sample No. 4 (DM-1) demonstrated a similar chemical composition as sample No. 3 (DC-1). The DTA-TG curves of these two samples are almost identical (Fig. 4). The endotherm observed at 559 and 561 °C with characteristic weight loss of 5.6 and 5.7 % for samples No. 3, DC-1 and No. 4, DM-1, respectively is due to dehydroxylation and conversion of kaolin to metakaolin. The sharp exotherm at 979 and 980 °C, respectively is attributed to crystallization of mullite.

Düvertepe Kaolin Deposit: Şapçı Mining Pit

The Şapçı pit is located on the South side of the Simav stream located opposite the Kale and Söğüt mining area (Fig. 1). Primarily, the kaolinized rock is underlined by the acidic tuffs and breccias. These were formed as a result of hydrothermal alteration of a fault in a direction of N60W. It is proposed that the kaolinite deposits were formed by the alteration of the acidic tuffs and breccias. The quartz and kaolinite are the main minerals in these deposits, with some inclusions of alunite and illite. The available kaolinite is mostly well-crystallized. The Şapçı deposit possesses similar mineralogical and genesis features as neighboring Kale, Söğüt and Camiş pits.

Sample No. 5 (DŞ-1, collected from the Şapçı pit) had a significantly reduced SiO_2 content (55%) compared to previous samples and a relatively high content of Al_2O_3 (32.2%). Still, quartz grains were abundant as it is observed at the SEM microphotographs and confirmed with EDS (Fig. 5). Plate-like, book-shaped kaolinite crystals are clearly visible near the quartz particles (Fig. 5). Based on Al_2O_3 to SiO_2 ratio it can be expected that these kaolin clays are of very high quality. The dehydroxylation endotherm (Fig. 4) at 575 °C is associated with a relatively high weight loss (8.8 %) due to release of OH^- groups and subsequent kaolin-metakaolin conversion. The recrystallization exotherm was observed at 993 °C (Fig. 4). This sample had the kaolinite content of 70.4% (Table 3).

Kütahya Kaolin Deposit

The samples were taken from two separate kaolin pits of Kızılçukur and Ulaşlar located in the Kütahya - Emet region which is well-known for the kaolin clay of high quality.

Kütahya Kaolin Deposit: Ulaşlar Mining Pit

Three alteration zones have been distinguished in the Ulaşlar kaolin pit (Fujii et al., 1995) [4]:
- Low Kaolinization Zone
- White Clay Zone
- Siliceous Clay Zone

Steeply dipping granule-rich intercalations are found within the white massive zone. The intercalations are primarily composed of kaolinite, smectite and cristobalite. However, these contain significant amounts of hematite, and are of black color. Similarly, the siliceous clay zone also contains kaolinite and cristobalite.

Sample No. 6 (KU-1) taken from the Ulaşlar kaolin pit has relatively high SiO_2 content (67.0 %) and low Al_2O_3 content (21.5 %). The high content of SiO_2 originates from the presence of quartz and tridymite minerals detected by XRD (Fig. 2). The kaolin - metakaolin conversion endotherm was observed at 564 °C with a weight loss of 6.7 % (which correspond to the kaolinite content of 53.6%) and the recrystallization exotherm occurred at 994 °C (Fig. 4).

Kütahya Kaolin Deposit: Kızılçukur Mining Pit

It was proposed that the Kızılçukur mining area was formed by the alteration of Neogene dasitic crystal tuff that was slightly welded (Fujii, 1995) [4]. Three alteration zones have been distinguished in the pit:

- Low- Grade Altered Zone
- Kaolin Zone
- Siliceous Kaolin Zone

The Low- Grade Altered Zone forms the outmost bottom level of the deposit and comprises quartz, feldspar and kaolinite. It is overlaid by the white kaolin zone, which consists of kaolinite and quartz in addition to K-feldspar, calcite and natroalunite. The siliceous zone exists as blocks within the kaolin zone. There is also a jarosite level located in the north part of the deposit which was formed by the sublimation of sulfur. The absence of cristobalite (i.e. all cristobalite had transformed to quartz) proves that this formation is older than Ulaşlar pit.

The sample No. 7 (KK-1) was taken from the Kızılçukur kaolin pit. According to the XRF analysis, the amount of SiO_2 was as low as 55% and the amount of Al_2O_3 was high - 31.5%, which is clear sign of high kaolinite content. This observation is also supported by the results of DTA-TG, where the dehydroxylation endotherm at 580 °C was characterised by weight loss of 9.2 % (corresponding to 73.6% of kaolinite) and the mullite recrystallization exotherm occurred at 993 °C (Fig. 4). In spite of very high kaolinite content, the quartz crystals could be seen clearly on the SEM image, with Si detected by the EDS (Fig. 7).

Şile Deposit

The basement rocks of Şile Kaolin Deposit are presented by Silurian quartzites, Devonian limestones, claystones and graywackes. On the top of these, the Triassic red sandstones and claystones, Cretaceous andesitic flysches, as well as conglomerates and fluvial sediments of the above are found. In some areas the andezitic flysch became clayey via hydrothermal alteration. The clays were settled on the eroded basement and have the Upper Neogene age.

The Neogene formations are divided into three parts:
- Low clay and lignites
- Sandstones and lignites
- Sandstone and siltstone

The origin of clays is generally related to the formation of lignites and the humic acid of lignites increase the quality of clays. Şile region provides about 65% of clays currently used for the production of ceramics in Turkey, primarily for the production of floor and wall tiles, sanitary- and tableware, as well as electro-porcelain. For this reason, the region of Şile is of vital importance for the Turkish ceramic sector.

Şile Deposit: Avcıkoru-Karatepe and Domalı Mining Pits

Samples No. 8 - 10 were obtained from the Şile Avcıkoru-Karatepe Daştan mining pit. These samples have very similar chemical composition: the content of Al_2O_3 ranges between 22.5 and 25.5% and the amount of SiO_2 varies between 60.5 and 61.5%. Samples No. 11 – 12 were taken from Şile - Domalı (shore village) at Matel mining pit. These samples also show similar properties that are typical for the region. The morphology of kaolinite crystals in sample No. 12, ŞD-2 was studied by SEM (Fig. 6). The kaolinite crystals are complex and some of them have a platy, propeller-like appearance. Si, Al and O peaks of kaolinite can be seen in the output of EDS (Fig. 6). The DTA-TG data (Fig. 4) show the dehydroxylation endotherm at 553 °C (accompanied by the weight loss of 5.2 %, corresponding to 41.6% of kaolinite) and recrystallization exotherm at 951 °C (Fig. 4).

Şile Deposit: Etiler and Filyos Mining Pits

Samples No. 13 - 14 were obtained from the Üvezli Village, Etiler mining pit. Sample No. 15 was taken from Filyos-3 quarry (Toprak Holding Company). The samples No. 13 - 15 share similar chemical characteristics having relatively high content of SiO_2 and a small amount of Al_2O_3 (Table 3).

CONCLUDING REMARKS

The properties of kaolin clays originating from three districts in the Anatolian area of Turkey (represented by three deposits) were studied for their prospective application as a raw material for cement and concrete additives. The investigated kaolin deposits were formed by hydrothermal alteration of Neogene acidic tuffs and were underlined mainly by the ophiolitic rocks. According to the results of research, the investigated kaolin samples were primarily composed of quartz and kaolinite with low to medium crystallinity. The chemical analysis data are in good agreement with the mineralogical composition of samples provided by x-ray diffraction and the results of DTA-TG and SEM-EDS investigations.

The kaolin clays under investigation are commonly utilized as a ceramic raw material, but currently are not used in cement and concrete industry. It is proposed to subdivide these products broadly into two groups with high and low content of Al_2O_3, with 20% being a subdivision limit. Here, low Al_2O_3 kaolin could be utilized for manufacturing of white cement clinker (subject to other composition restrictions); and kaolin with high Al_2O_3 content can be used for production of pozzolanic additives. The characteristic step on the TG curve at 500-650 °C corresponding to the dehydroxylation of kaolinite and formation of metakaolin may be considered as an important criterion of raw kaolin quality. For such particular application as pozzolanic additives, a weight loss of higher than 8% would correspond to kaolin of higher quality with more than 65% of kaolinite, whereas kaolin clay with weight loss of 5-8% (kaolinite content of 40-65%) may be classified as medium quality raw materials still suitable for manufacturing the pozzolanic additives.

ACKNOWLEDGEMENTS

This study was performed under TUBITAK research grant İÇTAG – 680, in cooperation with TCMA research team: Asim Yeğinobali, Tomris Ertün, Pelin Turker and Bahadir Erdogan. Authors express their gratitude to Pelin Turker for SEM investigations and, especially, to Ipek Şener and Bahadir Erdogan for preparation of the samples. The constructive and helpful comments on the research program of Prof. Konstantin Kovler are highly appreciated. The financial support of TUBITAK, TCMB, LAU, MTA, and CONACYT is gratefully acknowledged.

REFERENCES

1. Gözler, M.Z., Karayazici, F., Kasapoğlu, İ., Işiker, A.K., Çetinel,G., Yiğit, E., Özpeker, I., İrkeç,A.T., Seyhan, İ., İşcan A., Özel,A., Göver, Y., Özker, E., Bozdoğan, İ., Dündar, A., Subaşi, C., Korkmaz, T., Önemli, Ö.F., Erdoğan,F., Fenemen,A., Uman, Ö., Sipahi, H., Arkun, O., Elarslan, H., Demirhan, H., Büyükçayir, I., Demirata, A.N., Aksoy, O., Renda, D., Uyanik, M., İça, M., Gökkaya, H., Bulutoğlu, F., Çelik, H., Sayin, Ş.A., Erkök, M., Kahraman, E., Özer, R. (Ceramics-Refractory-Glass Raw Materials Investigation Team), 1995. State Five Year Plan – Mining Task Supreme Commission – Industrial Raw Materials Group I: Kaolin – Ceramic Clays – Feldspar – Pyrophyllite – Wollastonite – Talk, Vol. 1, DPT, Ankara, 197. DPT: 2418 – ÖIK: 477 (in Turkish). http://ekutup.dpt.gov.tr/madencil/sanayiha/oik477c1.pdf
2. Ozdemir, H. and Sezer, I., 1988. Clay Potential of Turkey. Industrial Minerals. MTA, Turkey, 35-39 (in Turkish).
3. Fujii, N., Kucuksille, N., Yalhı, T., and Ozcelik, N., 1980. Some Kaolin Deposits in the West Anatolia Province. MTA, Report No.6818 (in Turkish).
4. Fujii, N., Kayabalı, İ., Saka, A.H., 1995. Data book of ceramic raw material of selected areas in Turkey. MTA, Monograph Series No. 1, 144.
5. Okut, M. and Gok, S., 1975. Preliminary report on the kaolin deposits at Duvertepe, Sindirgi district, MTA-EHM Open-File Report No. 1233 (in Turkish).
6. Okut, M., Demirhan, M., and Köse, Z., 1978. Kaolin deposits in the Emet-Simav district, Kütahya region" MTA-EHM Open-File Rep. No. 1233 (In Turkish).
7. Okut, M., Köse, Z., Çakar, A. B., and Elmaci, M., 1984. Progress report of the study on the kaolin deposits at Düvertepe and its surroundings, Balikesir-Sindirgi district, MTA-Open-File Rep., No. 7573 (in Turkish).
8. Sincan, M., 1979. Final report on the kaolin deposits in Mihaliççik area, Eskişehir region, MTA Open-File Rep. No. 6509 (in Turkish).
9. Turk, Y., 1976. Study on the tile raw materials in the Uşak region, MTA Open-File Rep. No. 5570 (in Turkish).
10. Saraloğlu, A. and Konak, O., 1987. Mining geology on the kaolin deposits of Giresun-Espiye-Çimakli region, MTA Open-File Rep. No. 8248 (in Turkish).
11. Demirhan, M., 1986. Study on the kaolin concessions in the Kütahya-Simav and Altintaş areas, and the Balikesir-Sindirgi area, MTA Open-File Rep. No, 1849 (in Turkish).
12. Gençoğlu, H., Bayhan, H., and Yalçin, H., 1989. Mineralogy and genesis of the kaolin deposits around Bilecik-Söğüt area, Proc. Nation. Clay Conf., Turkey, 97-112 (in Turkish with English abstract).
13. Irkeç, A., Yersel, H., Kirikoğlu, M. and Demir, N., 1985. Refractory clay and kaolin deposits in the Bayramiç-Çan area, Çanakkale region, MTA Open-File Rep. No. 7654 (in Turkish).
14. Kalyoncuoğlu, A., Özkan, O., and Aktaran, I., 1977. Exploration on the refractory clay and kaolin deposits in Inhisar-Yakacik-Çatli-Küre-Yeniköy (Bilecik Söğüt) area, MTA-EHM Open-File Rep. No.1380 (in Turkish).
15. Karaağaç, Ç., 1975. Detailed geological investigation on the Karaçayir kaolin deposit, Uşak region, MTA Open-File Rep. No. 5389 (in Turkish).
16. Küçüksille, N., 1979. Report on the alunite-bearing kaolin deposits at Güzelyurt, Niğde-Aksaray, MTA Open-File Rep. 6500 (in Turkish).
17. Arkun, O., 1977. Exploration of kaolin in the Bor area, Aksaray-Güzelyurt, MTA Open-File Rep. No. 5716 (in Turkish).
18. Yersel, H., İrkeç, A., Kirikoğlu, M., Elmaci, M., Demir, N. and Demirhan, M., 1987. Mining geology on the refractory clay and kaolin deposits in the Bayramiç-Çan area, Çanakkale region, MTA Open-File Rep. No. 8245 (in Turkish).
19. Ece, O.I., Nakagawa, Z.-E., and Schroeder, P.A., 2003. Alteration of volcanic rocks and genesis of kaolin deposits in the Şile region, Northern Istanbul, Turkey. I: Clay Mineralogy. Clays and Clay Minerals, Vol. 51, No. 6, 675-688.
20. Arslan, İ.H., Yiğit, E. , Özel, P., Seyhan, İ., Cengiz, E., Yücel, O., Şahiner, M., İnel, İ., Tezcan, İ., Çiçek, S., Demirhan, H., Ulu, E., Erçetin, Y., Aras, A., Kirikoğlu, M., Güngör, N., Sever, M., Karakaya, E., Bozdoğan, İ. (Industrial Raw Materials Investigation Team), 2001. VIII - State Five Year Plan – Mining Task Supreme Commission – Industrial Raw Materials Group I: Ceramic Clays – Kaolin – Feldspar – Pyrophyllite – Wollastonite – Talk, DPT, Ankara, 204. DPT: 2611 - ÖİK. 622 (in Turkish). http://ekutup.dpt.gov.tr/madencil/sanayiha/oik622.pdf
21. Website of Turkish Ceramic Federation, 2005. http://www.serfed.com/dernek/serkap.asp
22. Newman, A., 1987. Chemistry of Clay and Clay Minerals, Min. Soc. Mon., London, 6, 480.
23. Konta, J., 1980. Properties of ceramic raw materials. Ceramic monographs. Handbook of ceramics, Schmid - Freiburg, 1-32.
24. Murray, H., 2000. Traditional and new applications for kaolin, smectite, and palygorskite: a general overview, Applied Clay Science, Vol. 17, No. 5-6, 207-221.

25. Cravero, F., Gonzalez, I., Galan, E., and Dominguez, E., 1997. Geology, mineralogy, origin and possible applications of some Argentinian kaolins in the Neuquen basin. Applied Clay Science, Vol. 12, No. 1-2, 27-42.
26. Prasad, M., Reid K. and Murray H., 1991. Kaolin: processing, properties and applications. Applied Clay Science, Vol. 6, No. 2, 87-119.
27. Murray, H., 1991. Overview — clay mineral applications. Applied Clay Science, Vol. 5, No. 5-6, 379-395.
28. Burst, J., 1991. The application of clay minerals in ceramics. Applied Clay Science, Vol. 5, No. 5-6, 421-443.
29. Murray, H., and Kogel, J., 2005. Engineered clay products for the paper industry, Applied Clay Science, Vol. 29, No. 3-4, 199-206.
30. Velho J. and Gomes, C., 1991. Characterization of Portuguese kaolins for the paper industry: beneficiation through new delamination techniques. Applied Clay Science, Vol. 6, No. 2, 155-170.
31. Bundy, W., and Ishley J., 1991. Kaolin in paper filling and coating. Applied Clay Science, Vol. 5, No. 5-6, 397-420.
32. Schupp, J.R., Fallahi, E., and Chun, I.-J., 2004. Effect of Particle Film on Fruit Sunburn, Maturity and Quality of "Fuji" and "Honeycrisp" Apples. Acta Hort. (ISHS) Vol. 636, 551-556. http://www.actahort.org/books/636/636_70.htm
33. Wild, S., Khatib, J., and Jones, A., 1996. Relative strength, pozzolanic activity and cement hydration in superplasticized metakaolin concrete, Cement and Concrete Research, 26, No. 10, 1537-1544.
34. Sabir, B., Wild, S., and Khatib, J., 1996. On the workability and strength development of metakaolin concrete. In International Congress on Concrete in the service of Mankind, Concrete for Environment Enhancement and Protection, Theme 6, Waste Materials and Alternative Products, University of Dundee (eds R.K Dhir and D.T. Dyer) Spon, London.
26, 651-662.
35. Caldarone, M., Gruber, K., and Burg, R., 1994. High-Reactivity Metakaolin: A New Generation Mineral Admixture, Concrete International, Vol. 16, No. 11, 35-40.
36. Shvarzman, A., Kovler, K., Grader, G., Shter, G., 2003. The effect of dehydroxylation / amorphization degree on pozzolanic activity of kaolinite. Cement and Concrete Research, Vol. 33, No. 3, 405-416.
37. Sobolev, K., 2001. White Cement: Problems of Production and Quality. Cement and Concrete World, No. 4, 34-42.
38. Arikan, M., Sobolev, K., Yeğinobali, A., Ertün, T., Albayrak, M., Aras A., Kovler, K., and Shvarzman, A., 2003. Development of Cement and Concrete Additives Based on Thermally Activated Kaolin. TÜBİTAK Project Proposal İÇTAG – 680 (in Turkish).
39. Kakali, G., Perraki, T., Tsivilis, S., and Badogiannis, E., 2001. Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. Applied Clay Science, Vol. 20, No. 1-2, 73-80.
40. He, C., Makovicky, E., and Osbæck, B., 1994. Thermal stability and pozzolanic activity of calcined kaolin. Applied Clay Science, Vol. 9, No. 3, 165-187.
41. Plancon, A., Giese, R. F., and Snyder R., 1988. The Hinckley index for kaolinites. Clay Minerals, Vol. 23, No. 3, 249-260.
42. Guggenheim, S., Bain, D.C., Bergaya, F., Brigatti, M.F., Drits, V.A., Eberl, D.D,. Formoso, M.L.L., Galán, E., Merriman, R.J., Peacor, D.R., Stanjek, H., and Watanabe, T., 2002. Report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature Committee for 2001: Order, disorder and crystallinity in phyllosilicates and the use of the 'Crystallinity Index'. Clay Minerals, Vol. 37, No. 2, 389-393.

Table 1. Characteristics and Kaolin Reserves in Turkey (after [1])

Locations of Kaolin Quarries	Al_2O_3 %	Application Areas	Reserves, tons	
			Estimated	Explored
Balikesir-Sindirgi	13-33	Fine ceramics, tiles, refractory, paper	70,000,000	25,000,000
Balikesir-Ayvalik	15-32	Ceramics and tiles faience	1,000,000	500,000
Balikesir-Ivrindi	20-31	Fine ceramics and faience tiles	970,000	500,000
Balikesir-Gönen	23-28	Ceramics	150,000	50,000
Çanakkale-Çan	17-35	Ceramics and refractory	5,000,000	2,000,000
Bursa-Kemalpasa	20-24	Paper	1,000,000	1,000,000
Istanbul-Arnavutköy	15-35	Refractory	800,000	-
Subtotal			78,920,000	29,050,000
Eskisehir-Mihaliççik	20-33	Ceramics and faience tiles	3,330,380	1,000,000
Bilecik-Sögüt	15-23	Ceramics	1,000,000	500,000
Kütahya-Gevrekseydi	20-24	Paper	724,924	200,000
Kütahya-Altintas	20-31	Ceramics, faience, tiles and paper	1,206,000	500,000
Kütahya-Emet	20-30	Ceramics, tiles, faience	1,070,286	100,000
Kütahya-Simav	20-24	Ceramics, tiles, faience	370,000	50,000
Usak-Karaçayir	11-21	Ceramics, tiles, faience	800,000	500,000
Subtotal			8,501,590	2,850,000
Kayseri-Felahiye	23-34	Ceramics and refractory	450,000	20,000
Konya-Saglik	15-30	Faience tiles and ceramics	607,000	100,000
Nevsehir-Avanos	18-33	Ceramics, electro porcelain, tiles	1,277,000	100,000
Nigde-Aksaray	15-32	Tiles, faience and paper	1,500,000	1,000,000
Subtotal			3,834,000	1,220,000
Trabzon-Arakli-Arsin	14-23	Tiles, faience	200,000	50,000
Rize-Ardesen-Findikli	14-23	Tiles, faience	275,000	50,000
Giresun-Bulancak	12-24	Tiles, faience	7,785,000	2,000,000
Ordu-Ulubey	17-23	Paper	730,000	100,000
Other	-	-	-	700,000
Subtotal			8,990,000	2,900,000
Total			100,245,590	36,020,000

Table 2. Locations of Kaolin Quarries under Investigation

No.	Code	GPS Coordinates (x, y, z)	Kaolin Quarries
Düvertepe (Balıkesir) Deposit			
1	DK-1	643, 23453, 43441	Kalemaden Mining Pit, Ahmet Şengönül's Area
2	DS-1	630, 23498, 43406	Söğüt Mining Pit
3	DC-1	644, 23290, 43355	Camiş Mining Pit, Şişe Cam's Area
4	DM-1	599, 23596, 43314	Matel Mining Pit, Matel and Eczacıbaşı Quarry
5	DŞ-1	768, 24383, 37431	Şapcı Mining Pit, Gürbüz Kaolin Quarry
Kütahya (Emet) Deposit			
6	KU-1	1241, 88346, 36777	Ulaşlar Mining Pit, M. Bozkurt's Area (Kütahya Porselen)
7	KK-1	1227, 91459, 37521	Kızılçukur Mining Pit
Şile Deposit			
8	ŞA-1	139, 00241, 58394	Avcıkoru-Karatepe Mining Pit, Daştan Mining Area (Ruhsat-Ergören Mining)
9	ŞA-2	139, 00241, 58394	
10	ŞA-3	139, 00241, 58394	
11	ŞD-1	142, 99734, 57568	Domalı Mining Pit, (Sahilköy), Matel Area
12	ŞD-2	136, 98752, 57429	
13	ŞE-1	118, 00233, 58945	Etiler Mining Pit, Ergören Area
14	ŞE-2	122, 05401, 53496	
15	ŞF-1	123, 04344, 57599	Filyos-3 Quarry, Toprak Holding Area

Table 3. Chemical Analysis of Investigated Kaolin Samples

No.	Code	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	TiO_2 %	CaO %	MgO %	Na_2O %	K_2O %	MnO_2 %	P_2O_5 %	L.O.I. %	Weight Loss, TG %	Estimated Kaolinite %
1	DK-1	79.5	13.5	0.1	0.5	0.2	< 1.0	< 1.0	0.1	< 1.0	0.1	5.10	4.9	39.2
2	DS-1	80.0	13.3	0.1	0.4	0.4	< 1.0	< 1.0	< 1.0	< 1.0	0.1	5.05	4.4	34.9
3	DC-1	70.0	20.0	0.3	0.6	0.3	< 1.0	< 1.0	< 1.0	< 1.0	0.3	7.35	5.6	44.8
4	DM-1	71.5	20.3	0.2	0.4	0.1	< 1.0	< 1.0	0.1	< 1.0	0.1	6.90	5.7	45.6
5	DŞ-1	55.5	32.2	1.0	0.3	0.5	< 1.0	< 1.0	0.1	< 1.0	0.2	10.1	8.8	70.4
6	KU-1	67.0	21.5	0.3	0.5	0.2	< 1.0	< 1.0	0.4	< 1.0	0.2	9.40	6.7	53.6
7	KK-1	55.0	31.5	0.3	0.1	0.1	< 1.0	< 1.0	< 1.0	< 1.0	0.2	10.8	9.2	73.6
8	ŞA-1	60.5	25.5	1.8	1.1	0.2	0.7	0.1	2.8	< 1.0	< 1.0	7.10	7.1	56.8
9	ŞA-2	61.0	24.5	2.2	1.1	0.2	0.5	0.1	2.0	< 1.0	< 1.0	7.30	6.2	49.6
10	ŞA-3	61.5	22.5	3.0	1.0	0.2	0.6	0.1	2.4	< 1.0	< 1.0	6.75	5.9	47.2
11	ŞD-1	58.0	26.0	2.5	1.1	0.3	0.7	0.1	2.1	< 1.0	< 1.0	8.45	6.7	53.6
12	ŞD-2	57.3	26.7	2.7	1.2	0.1	0.7	0.1	2.5	< 1.0	< 1.0	7.90	5.2	41.6
13	ŞE-1	67.8	20.2	2.0	1.2	0.1	0.5	0.1	1.9	< 1.0	< 1.0	5.40	4.7	37.6
14	ŞE-2	75.8	14.0	1.7	1.2	0.2	0.5	0.1	1.5	< 1.0	< 1.0	4.05	3.0	24.0
15	ŞF-1	69.8	18.5	1.9	1.2	0.1	0.3	0.1	1.8	< 1.0	< 1.0	5.40	4.9	39.2

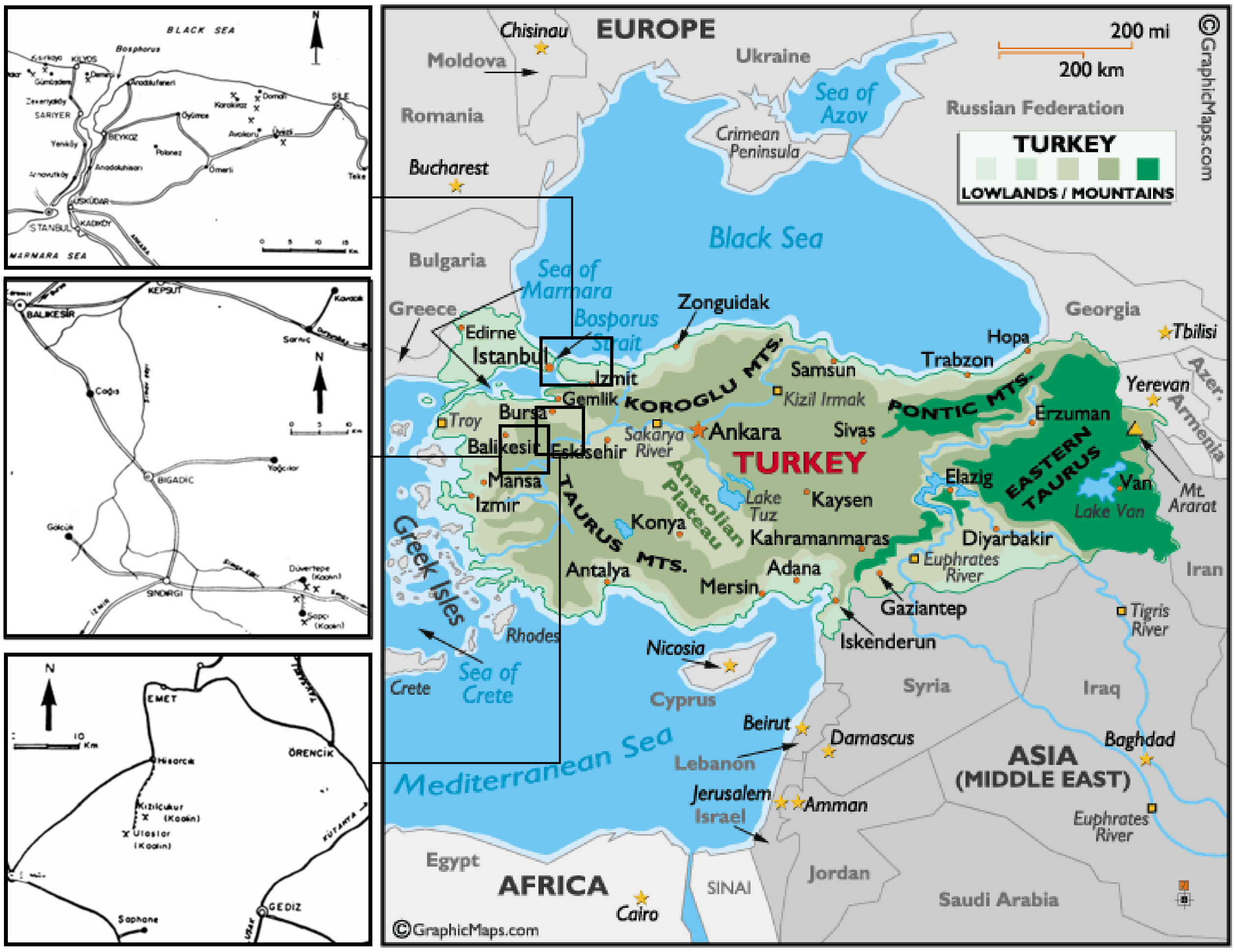


Fig. 1. Location of Kaolin Deposits under Investigation

a) Şile; b) Düvertepe (Balıkesir); c) Kütahya (Emet): Kızılçukur and Ulaşlar

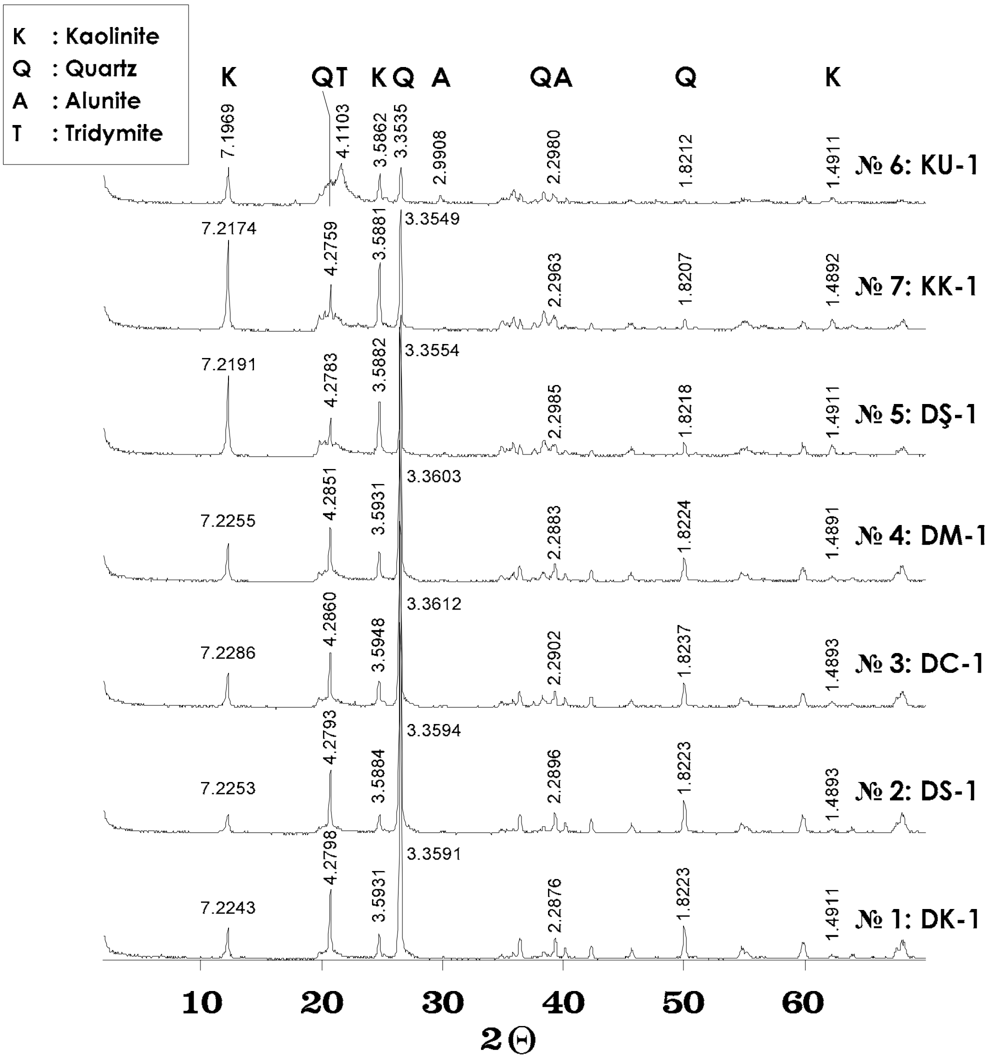


Fig. 2. The Results of X-ray Analysis of Samples from Düvertepe and Kütahya

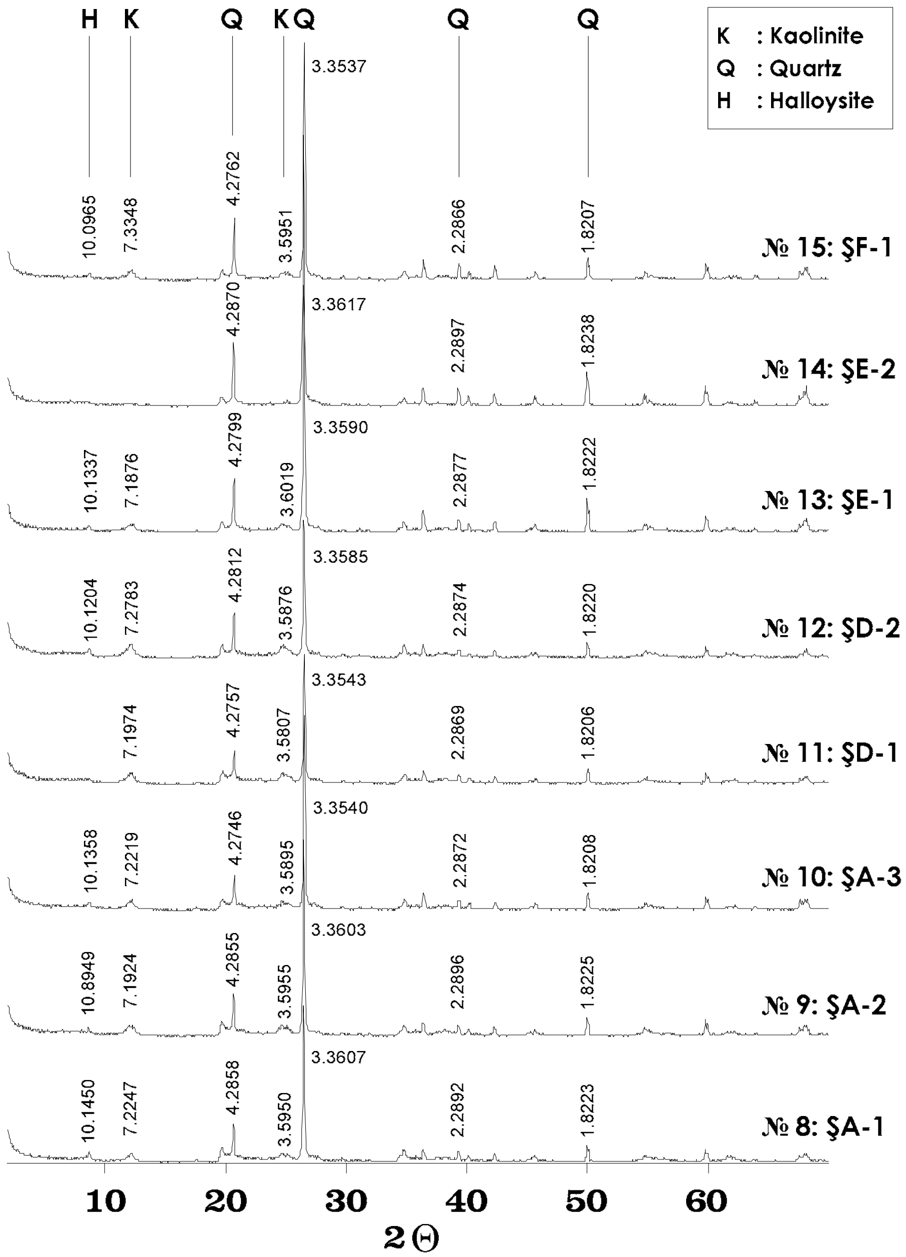


Fig. 3. The Results of X-ray Analysis of Samples from Şile

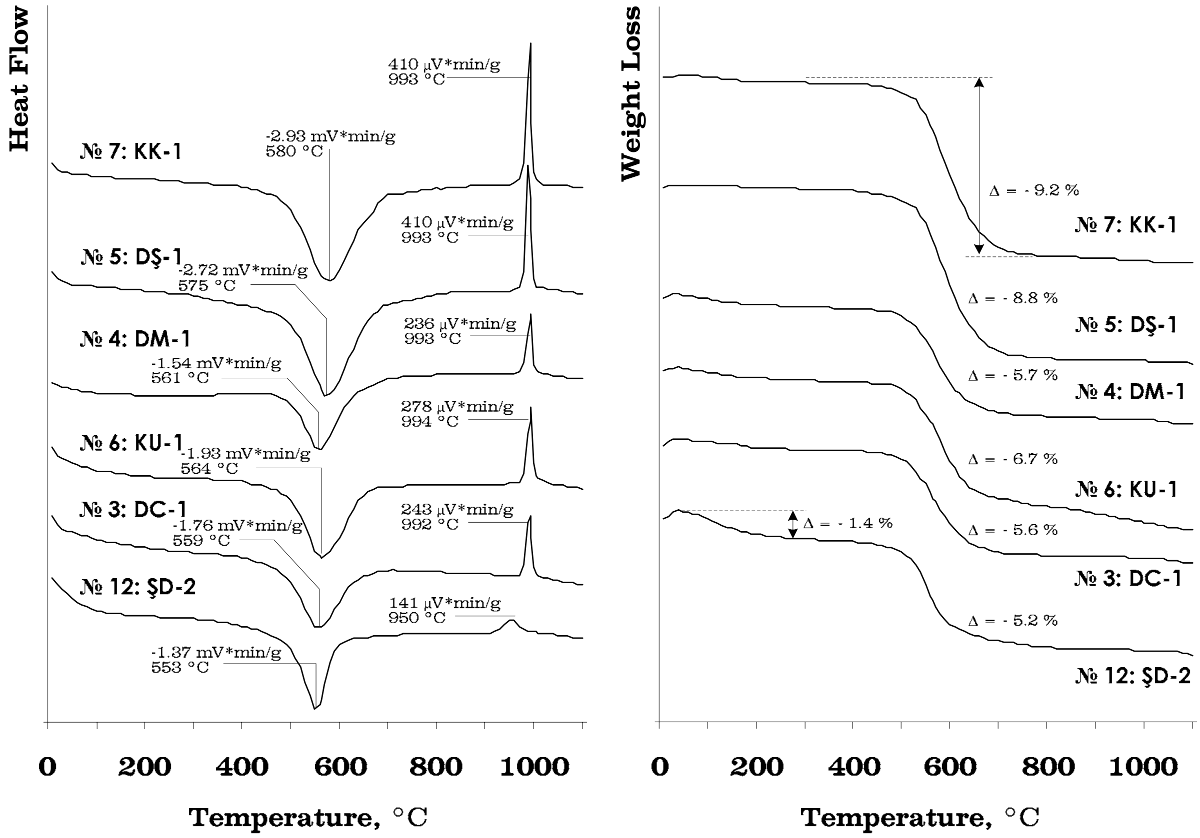
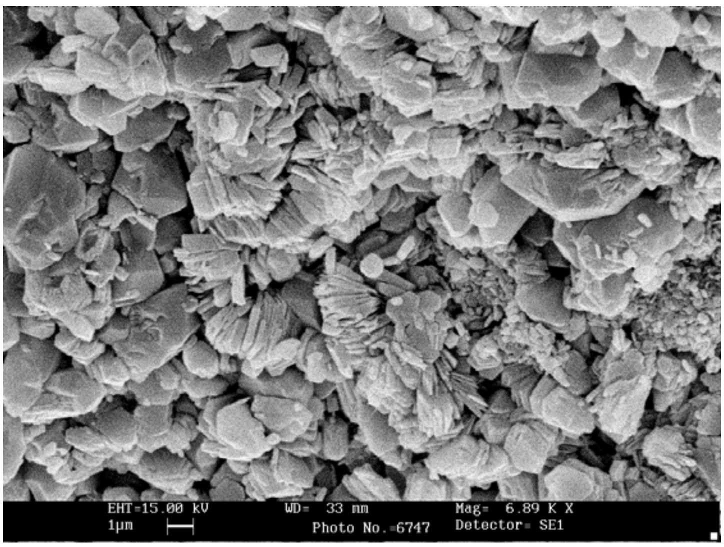


Fig. 4. The Results of DTA-TG Investigation



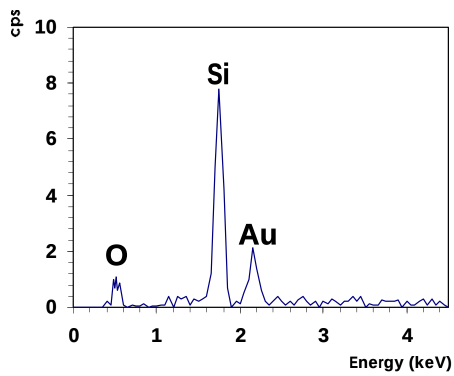


Fig. 5. The Results of SEM - EDS Investigation of Sample No. 5 (DŞ-1)

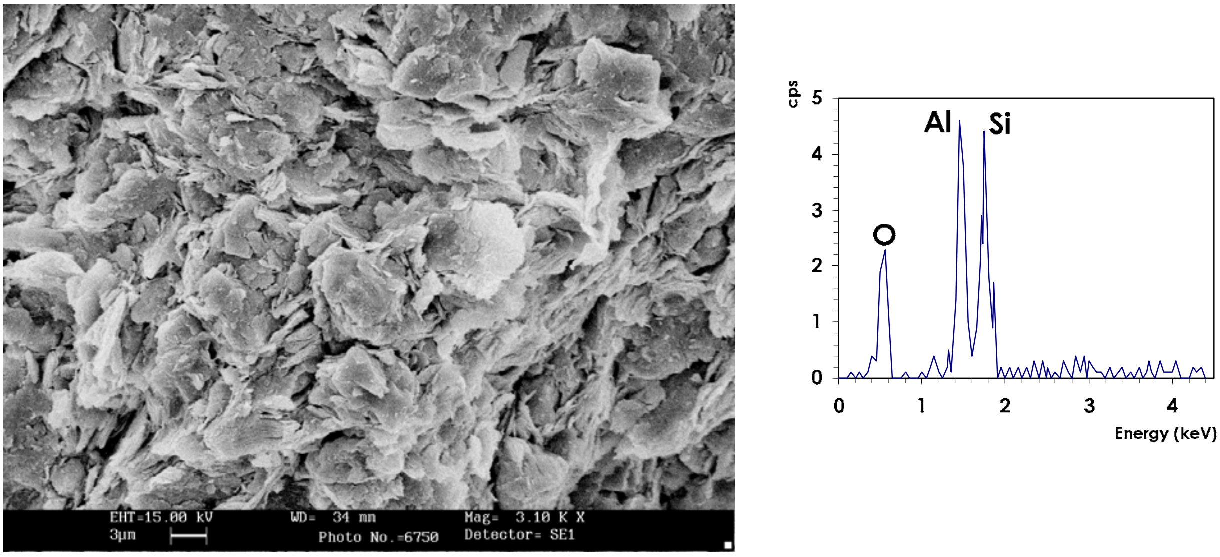


Fig. 6. The Results of SEM - EDS Investigation of Sample No. 12 (ŞD-2)

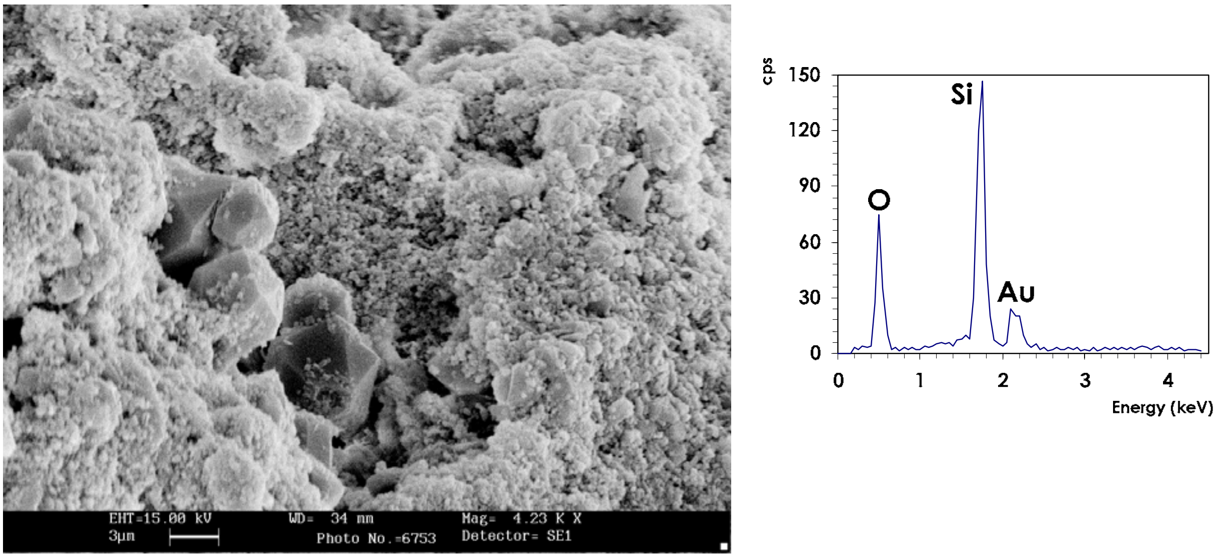


Fig. 7. The Results of SEM - EDS Investigation of Sample No. 7 (KK-1)