

MINERALOGICAL TRANSFORMATION
AND MICROSTRUCTURE OF THE KILLIK REGION CLAYS

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Abstract

Killik region (Mihalıççık, Eskişehir, Turkey) is one of the most important loughlinite clay mineral deposits in Turkey and in the world. Along with loughlinite, analcime and dolomite minerals are also found in this deposit, which is not operable. Anorthoclase (94.61%) and quartz (4.94%) minerals (K2 sample) were obtained as the final product by applying Na ion exchange and thermal exchange processes to the minerals (K1 sample) taken from this deposit. In this study, XRD, Raman and infrared spectroscopies, and SEM techniques were used to characterize the phase structure of the K1 and K2 samples. As a result of this research, obtaining high purity anorthoclase mineral will encourage new research on new usage areas of anorthoclase mineral.

Key words: loughlinite, anorthoclase, x-ray diffraction, FTIR, Raman, SEM

Introduction. Loughlinite, which is known as natural Na-sepiolite, belongs to the palygorskite-sepiolite group of phyllosilicates class of clay minerals [1]. Its chemical formula is $\text{Na}_2\text{Mg}_3\text{Si}_6\text{O}_{16}\cdot 8\text{H}_2\text{O}$ [2]. It is a fibrous clay mineral and differs from laminar clays by having channels in its structure. Its structure consists of talc-like chains parallel to the fibre axis [1]. It is formed by an alternation of blocks and channels, which grow up in the fibre direction. These channels can hold zeolitic water and other molecules. It contains three kinds of water molecules: zeolitic water (within channels), crystal water (water coordinated at the edges of the octahedral layer), and structural water (OH groups). The zeolitic water lies in the channels and its loss is reversible. If loughlinite is heated above approximately

400 °C, crystal water is lost, and a phase transformation takes place. After calcination at 800 °C, loughlinite changes into a loughlinite “anhydride” through the loss of the zeolitic water [1,2].

Anorthoclase which is known as K-analbite is an alkali feldspar with the combination $((\text{Na}, \text{K})\text{AlSi}_3\text{O}_8)$ and with a monoclinic structure belonging to the space group C2/m. The feldspar crystal structure is composed of a three-dimensional framework of corner shared SiO_4 tetrahedra with each oxygen ion shared between two Si^{4+} . Si^{4+} is frequently substituted by the addition of an interstitial alkali metal or alkaline-earth ions [3–5]. The mixture including anorthoclase and quartz can be suitable for producing ceramics such as electrotechnical porcelain, glass-ceramics, stoneware materials, ceramic wares, porcelains, porcelain stoneware, and bricks [4,6,7].

There is no study on Killik region minerals which investigates their thermal behaviours during the sintering. This research is the first study of the mineralogical and microstructural transformation during the firing of samples obtained from the Killik region clays.

Materials and methods. The natural sample K1 used in this study was obtained from the Killik area (Mihalıççık District, Eskişehir Province, Turkey) and no further purification was carried out. The Killik area is in the Sarıyar-Beyazı Neogene basin 4–5 km to the north of the Mihalıççık range consisting of Paleozoic rocks [8]. All chemicals used in the study were obtained from Fluka and were analytical grade. An ion-exchange form was prepared by treating 10 g of the K1 sample with 100 ml of 1 M KCl solution in a shaker at 80 °C for 2 h. After treatment, the sample was filtered and washed with distilled water, dried at 110 °C overnight, and then milled and sieved by a ninety-mesh sieve. The particles under the ninety-mesh were used in further experiments. The pellets of the K-ion-exchanged sample were sintered at 900 °C for 2 h and the K2 sample was obtained as the result of the heat activation.

X-ray powder diffraction was employed for mineralogical analyses using a Rigaku Rint 2200 instrument under the following measurement conditions: CuK radiation, detector scintillation, voltage 40 kV, and current 40 mA.

Quantitative estimations of mineral matter of the K1 and K2 samples were made with the help of SIROQUANT software by processing the individual diffractograms. This system allows the proportion of up to twenty-five different minerals in a mixture to be quantified from a conventional powder XRD pattern using Rietveld techniques.

Infrared spectra of the K1 and K2 samples were recorded ($4000\text{--}400\text{ cm}^{-1}$) with a Bruker Optics IFS66v/s FT-IR spectrometer at a resolution of 2 cm^{-1} at room temperature. The Raman spectra were obtained using a Bruker Senterra Dispersive Raman microscope spectrometer with 532 nm excitation in the spectral region of $1200\text{--}90\text{ cm}^{-1}$. Chemical analyses (XRF) were carried out using Rigaku ZSX Primus equipment.

Results and discussion. Mineralogy. In this study, the chemical composition of the K1 sample by XRF was determined as 41.70% SiO₂, 13.34% Al₂O₃, 1.84% Fe₂O₃, 5.34% CaO, 13.34% MgO, 6.33% Na₂O, 0.95% K₂O, 0.21% TiO₂, and 19.92% LOI. The Na⁺ content reflects the presence of loughlinite and analcime which is a mineral belonging to the zeolite group. High SiO₂ values are observed in loughlinite as well as analcime [9]. The Al₂O₃ value in the loughlinite in the Killik area is higher than that of other samples of loughlinite. Moreover, the MgO content is higher and the Na₂O content is lower in the loughlinite of Killik than in that of the loughlinite of Wyoming, USA. The presence of some of the Al³⁺, Fe²⁺, Ca²⁺, Na⁺, and K⁺ is probably due to analcime and dolomite [10]. In Figure 1, the XRD pattern of the K1 sample used in this study shows characteristic features of loughlinite, analcime, and dolomite. When the K-ion-exchanged K1 sample is heated at 900 °C for 2 h, the crystal lattice in the K1 sample is destroyed and the K1 sample transforms into anorthoclase and quartz phases, as shown in the K2 sample. Anorthoclase in the K2 sample is a major phase. A minor quantity of quartz is present.

In this study, the different phases of the samples K1 and K2 have been characterized by analyzing the whole X-ray diffraction patterns by way of materials analysis using diffraction (MAUD) which is a Rietveld-based mineral quantification software. It is used as a learning tool for the quantification of mineral matter. Quantitative mineral compositions of K1 and K2 samples were determined using MAUD method. Accordingly, the K1 sample consists of 53.41% loughlinite, 21.09% analcime, and 25.28% dolomite. Similarly, the K2 sample is composed of 94.61% anorthoclase and 4.94% quartz. In the K1 and K2 samples, the predominant phases are loughlinite and anorthoclase minerals, respectively.

Fourier Transforms Infrared Spectrophotometry (FTIR). Figure 2 illustrates the FTIR spectrum of the K1 and K2 samples at room temperature. In the FTIR spectrum of the K2 sample, the high-frequency deformation mode at 1683.35 cm⁻¹ is assigned to water strongly bonded to the magnesium cation. The water deformation mode at 1635.04 cm⁻¹ is assigned to the zeolitic water in the channels of loughlinite [11]. The deformation bands appeared at 1630–1660 cm⁻¹ associated with zeolitic and coordination water. Suggesting that bound water molecules are still preserved and trapped within the structure of the K1 sample, even at 900 °C. Such behaviour could be explained by internally tilted and collapsed channels with encounter diffusion retarding the escape of coordinated water from the crystal structure. Hydroxyl stretching frequencies were observed at 3446.23, 3546.23, 3566, 3612.95, 3676.95, 3687.98, and 3718.81 cm⁻¹ [12,13]. The bands at 3687.98, 3676.98, 686.98, and 650.69 cm⁻¹ are attributed to hydroxyl groups attached to octahedral Mg ions, and such a frequency was found in sepiolite. The others are assigned to the hydroxyl stretching vibration of the Si-OH structural group [13,14]. The libration mode of H₂O of the K1 sample is also seen at 494.02–424.04 cm⁻¹ [13]. The carbonates in the samples were demonstrated by

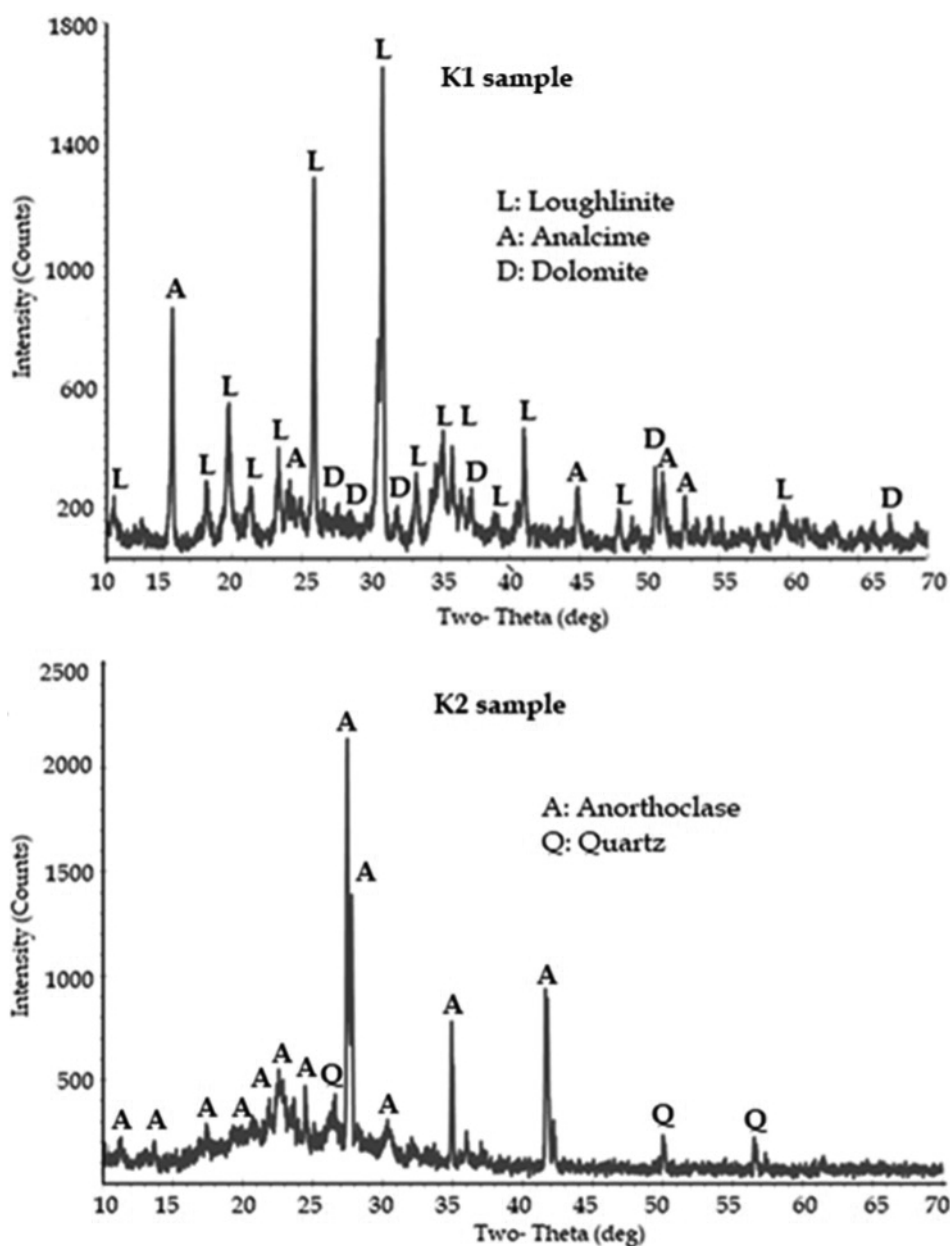


Fig. 1. X-ray diffractograms of the K1 and K2 samples

the strong absorption bands between 3050 and 2850 cm^{-1} , 2650 and 2500 cm^{-1} ; 1500 and 1400 cm^{-1} , and 881 cm^{-1} , and 729 cm^{-1} [9]. The band at 728.94 cm^{-1} is assigned to the in-plane bending mode of CO_3^{2-} in the dolomite structure. The appearance of both the 2855.34 cm^{-1} , 2523.71 cm^{-1} , 1456.63 cm^{-1} , and 728.94 cm^{-1} absorption bands in a sample is especially useful for indicating the presence of

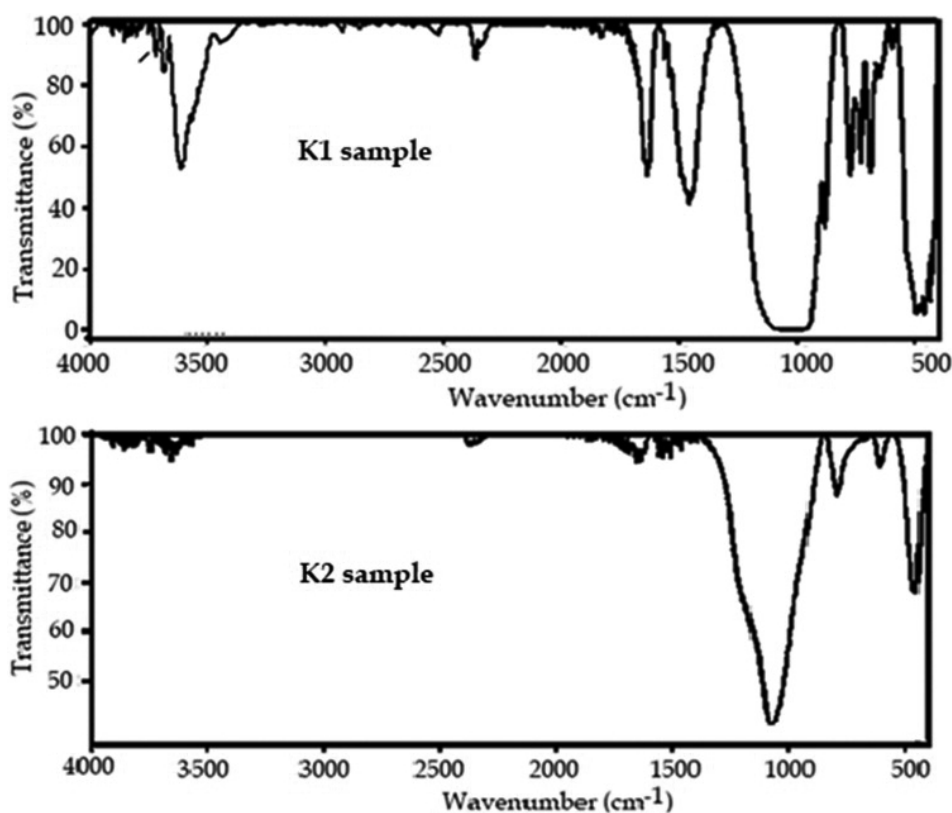


Fig. 2. FTIR spectra of the K1 and K2 samples

dolomite [14]. In the FTIR spectrum of the K2 sample, the heat-induced changes of peaks in the region $4000\text{--}3000\text{ cm}^{-1}$ and $1700\text{--}1600\text{ cm}^{-1}$ are not observed mainly due to the dehydration of zeolitic and bound water in the channels of the sample [13]. The band related to CO_3^{2-} in the K1 sample was not observed in the K2 sample. This data reaches an agreement with the XRD pattern of the K2 sample. The bands in the frequency range 773.91 and 458.72 cm^{-1} are assigned to the symmetric stretching vibration of Si–O–Si combination bands [5,15]. In the K2 sample, these peaks shift from 773.91 to 795.70 cm^{-1} and from 458.72 to 458.78 cm^{-1} [5,12,15]. The absorption at 1050.41 cm^{-1} in the K1 sample is attributed to the Si–O in-plane vibration. This peak shifts to 1075.09 cm^{-1} on heating. The FTIR bands at 2365.05 and 2345.23 cm^{-1} can be assigned to Si–H bands as observed in the K2 sample [15].

Raman microprobe spectroscopy. Figure 3 shows Raman spectra of the K1 and K2 samples. In the Raman spectrum of the K1 sample in the $60\text{--}1500\text{ cm}^{-1}$ region, $1200\text{--}400\text{ cm}^{-1}$ characteristic bands for silicate minerals occur, mostly related to the stretching vibrations of Si–O or Al–O. The peak at 1412.10 cm^{-1} corresponds to the CO_3 stretching vibration of dolomite [16]. The

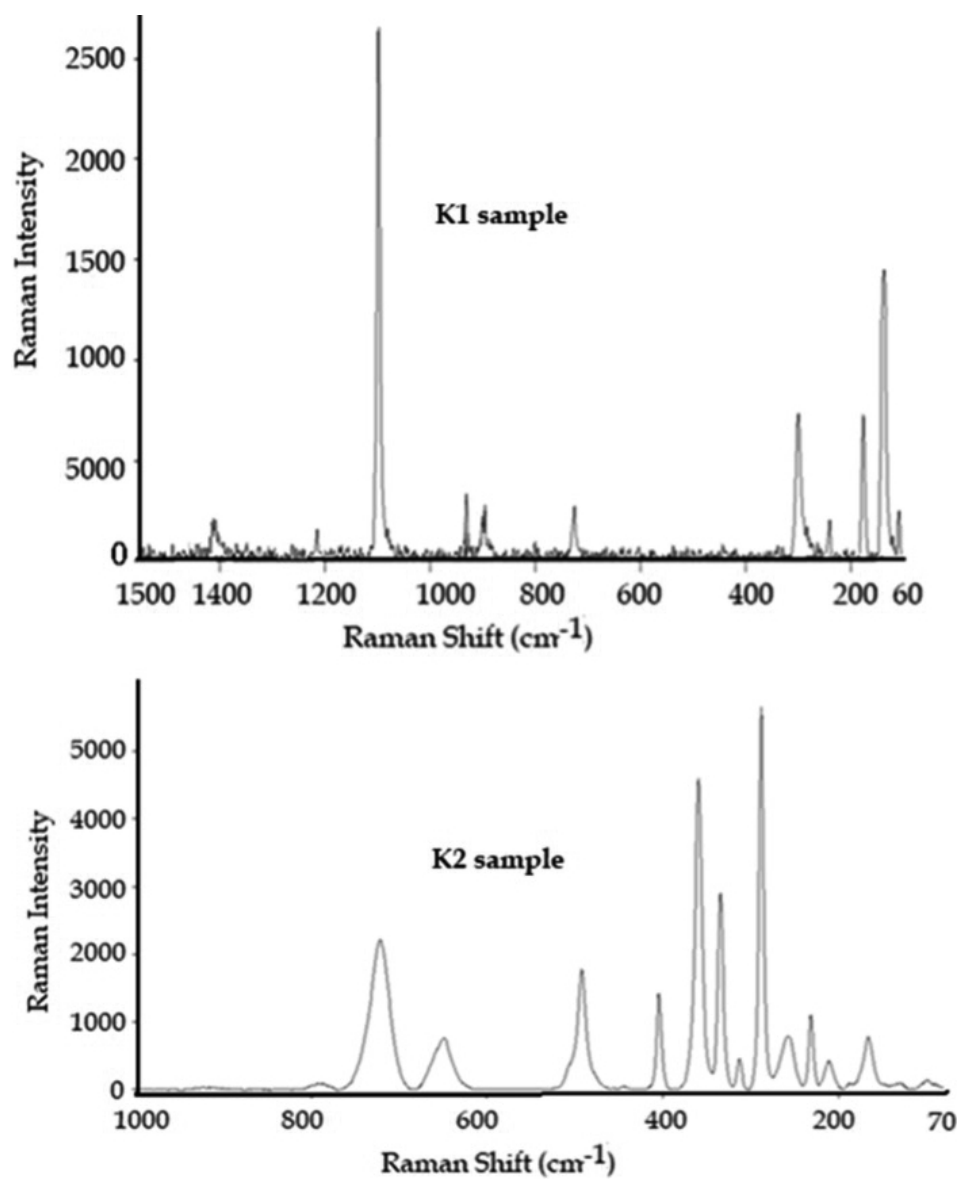


Fig. 3. The Raman spectra of the K1 sample in the 60 to 1500 cm^{-1} region and the K2 sample in the 70 to 1000 cm^{-1} region

strong symmetrical band at 1098.04 cm^{-1} is characteristic of dolomite. It is ascribed to the Mg-CO_3 and/or Ca-CO_3 stretching vibration [16,17]. The peak at 1060.36 cm^{-1} corresponds to Si-O asymmetric stretching vibration. Additionally, the Al/Si-O symmetric stretching vibrations in analcime/loughlinite are observed as three bands at 916.82, 881.21, and 443.28 cm^{-1} in the Raman spectrum. The band at 725.41 cm^{-1} is also assigned to the bending vibration of CO_3^{2-} in the

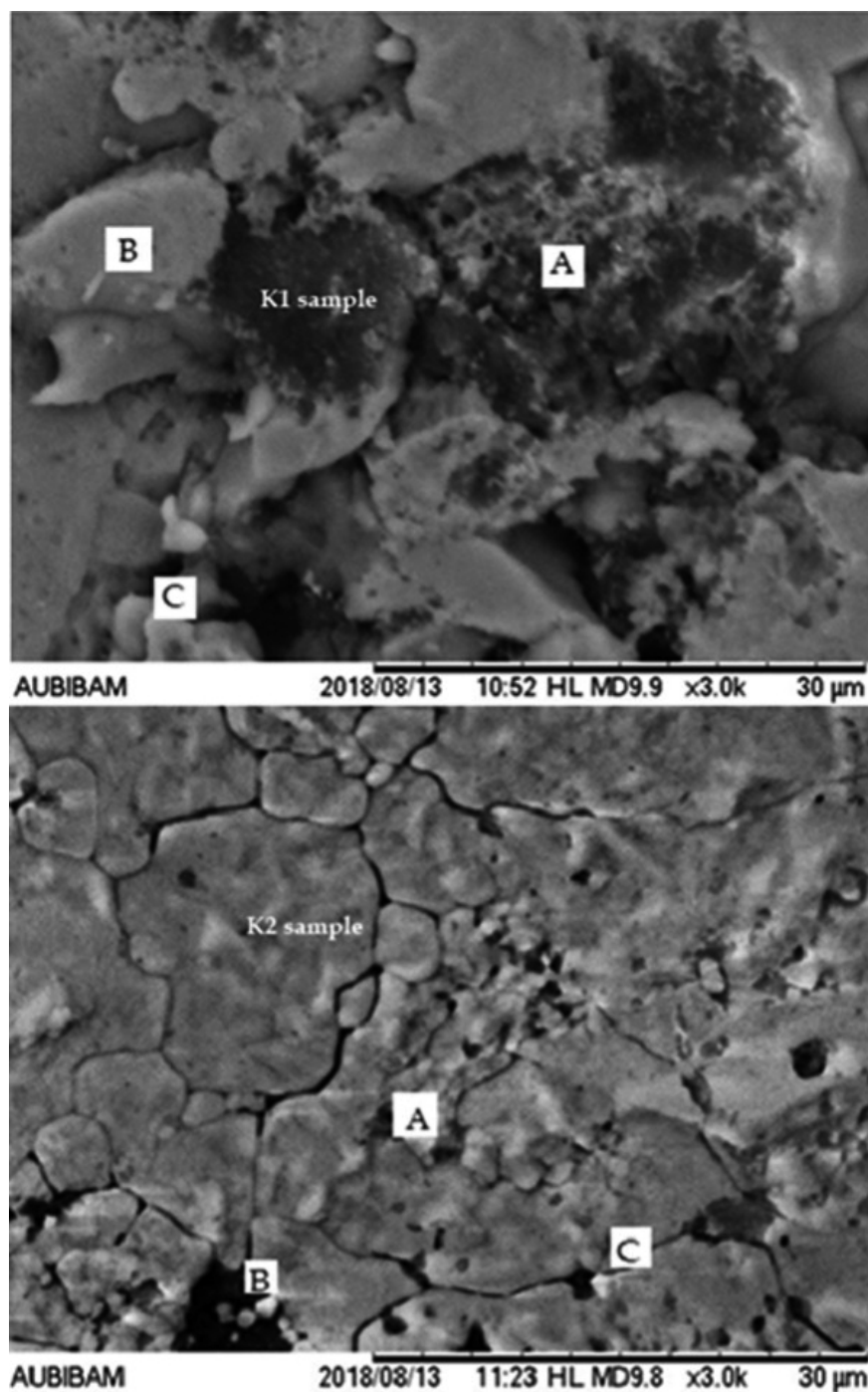


Fig. 4. SEM photographs of the K1 and K2 samples at room temperature (secondary electrons, 3K magnification)

dolomite phase of the K1 sample [16–18]. The bands observed at 110.67 cm^{-1} and 235.52 cm^{-1} are attributed to the asymmetric stretching vibration of K–O and the deformation vibration of Na–O, respectively. Additionally, the strong absorption bands at 176.60 and 299.98 cm^{-1} are ascribed to the CaO_3 stretching vibration of the K1 sample [16,17]. They are lattice modes of the dolomite phase of the K1 sample. The lower energy peak at 65 cm^{-1} is prescribed for the lattice modes [17,18]. In the Raman spectrum of the K2 sample in the 70–1000 cm^{-1} region, the presence of anorthoclase in the K2 sample is identified by the bands at 166.86, 282.21, 481.17, 512.63, and 773.15 cm^{-1} [12,17].

In the present spectra, bands observed at 481.17, 512.63, and 773.15 cm^{-1} could be attributed to the Si–O–Si and O–Si–O bending vibrations in the tetrahedral layer of the anorthoclase. Furthermore, the sample K2 shows a strong intensity band at 282.21 cm^{-1} . This band is assigned to the Si–O–Si stretching vibration. In addition to these, the bands at 74.03 and 98.21 cm^{-1} are assigned to the Na/K–O lattice vibrations [18]. The bands at 787.03, 633.13, 254.78, 211.17, and 128.70 cm^{-1} are assigned to quartz [12].

Scanning electron microscope (SEM) and energy-dispersive X-ray (EDX). Every particle in Fig. 4 was analyzed by EDX spectroscopy to determine its composition.

The composition was then used to determine a mineral designation for each particle. Mineral particles of various shapes can be observed in the SEM image of the K1 and the K2 samples shown in Fig. 4. According to the XRD of the K1 sample, there are analcime, loughlinite, and dolomite phases in the structure. The particle at point C in the K1 sample was identified as dolomite because its main chemical components are CaO and MgO. The particle at point B shows a greater percentage ratio of Na_2O than particle A in the EDX spectrum. This mineral could be analcime. The particle at point A is primarily attributed to loughlinite that was formed in needle crystals. The major phase of the K1 sample was loughlinite, as expected from the XRD result. As can be seen the major phase in the K2 sample is the anorthoclase phase (point A) and the minor phase is the quartz phase (the particles at point B). In addition, shrinkage cracks (point C) are also seen in the K2 sample.

Conclusions. This research is a study carried out to bring the minerals of the Killik region to the industry. As far as I know, there is no other scientific study for the industrial applications of clays from this region. One of the most important results of this study is that anorthoclase mineral, which is found at low rates among other minerals, is obtained at high purity. This result will encourage research on new usage areas of anorthoclase. Some research on industrial usage areas of anorthoclase mineral has started in recent years. The production of dental porcelain is one of these industrial areas. With the increase in new studies on new industrial uses of anorthoclase, it will be possible to bring the clays of the Killik region to the economy.

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