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A – Applied Sciences and Engineering

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ESKİŞEHİR TECHNICAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY
A- Applied Sciences and Engineering

Eskişehir Teknik Üniversitesi Bilim ve Teknoloji Dergisi A – Uygulamalı Bilimler ve Mühendislik

Volume 24 - 19th Clay’2023 - Special Issue 2023

Eskişehir Technical University Journal of Science and Technology A - Applied Sciences and Engineering (ESTUJST-A) is a peer-reviewed and refereed international journal published by Eskişehir Technical University. Since 2000, it has been regularly published and distributed biannually and it has been published quarterly and only electronically since 2016.
The journal accepts only manuscripts written in English.

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Policy & Ethics

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Guyon I, Elisseeff A. An introduction to variable and feature selection. J Mach Learn Res 2003; 3: 1157-1182.

Izadpanahi S, Ozcınar C, Anbarjafari G, Demirel H. Resolution enhancement of video sequences by using discrete wavelet transform and illumination compensation. Turk J Elec Eng & Comp Sci 2012; 20: 1268-1276.

Books

Haupt RL, Haupt SE. Practical Genetic Algorithms. 2nd ed. New York, NY, USA: Wiley, 2004.

Kennedy J, Eberhart R. Swarm Intelligence. San Diego, CA, USA: Academic Press, 2001.

Chapters in books

Poore JH, Lin L, Eschbach R, Bauer T. Automated statistical testing for embedded systems. In: Zander J, Schieferdecker I, Mosterman PJ, editors. Model-Based Testing for Embedded Systems. Boca Raton, FL, USA: CRC Press, 2012. pp. 111-146.

Conference proceedings

Li RTH, Chung SH. Digital boundary controller for single-phase grid-connected CSI. In: IEEE 2008 Power Electronics Specialists Conference; 15–19 June 2008; Rhodes, Greece. New York, NY, USA: IEEE. pp. 4562-4568.

Theses

Boynukalın Z. Emotion analysis of Turkish texts by using machine learning methods. MSc, Middle East Technical University, Ankara, Turkey, 2012.

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Volume 24 - 19th Clay’2023 - Special Issue 2023

19th National Clay Symposium

The nineteenth of the National Clay Symposiums, traditionally organised by different universities every two years, was held between 6-9 September 2023, hosted by Eskişehir Technical University Faculty of Science, Physics and Chemistry Departments, with the support of institutions and organisations in our region, especially the Clay Sciences Association.

The fifth of the eighteen national clay symposiums held in the last 36 years was organised on 16-20 September 1991 by Anadolu University, Faculty of Arts and Sciences, Department of Physics in Eskişehir, with the contributions of the Turkish National Committee on Clay Sciences. After 32 years, Eskişehir Technical University hosted the participants of the National Clay Symposium for the second time on the 100th Anniversary of the Founding of our Republic.

This symposium was organised with the participation of many researchers and academicians from different universities, institutions and organisations in our country. 4 invited talks, 75 oral and 11 poster presentations were presented at the symposium. These papers include clay mineralogy, geology and geochemistry of clays; structures of clay minerals; physical and chemical properties; nano clay, nanocomposite; organoclays and their applications; geotechnical properties of clays; industrial and engineering applications; use in ceramics; the clay in hydrothermal and ore-forming systems; clay and archaeology; clay and health; clay and art; sepiolite/meerschaum; zeolite; clay and climate.

I would like to thank Eskişehir Technical University Rector Prof. Dr Adnan ÖZCAN, Vice Rectors Prof. Dr Yunus ÖZDEMİR and Prof. Dr. Onur KAYA, Members of the Organizing and Scientific Board, President of the Clay Sciences Association Prof. Dr. Asuman TÜRKMENOĞLU and the Board Members of the Association for providing all kinds of support in the realisation of the symposium. I want to thank the supporting organisations and hope the symposium will contribute to science.

The papers presented at the symposium and sent in full text were evaluated in the referee process to be published in the special issue of Eskişehir Technical University Journal of Science and Technology A-Applied Sciences and Engineering.

This special issue includes six articles recommended by the authors for publication and accepted for publication after being peer-reviewed.

Before concluding, we would like to take this opportunity to thank all the authors who submitted their work to ESTUJST-A. We are also thankful to the journal's Editor-in-Chief, Prof. Dr. Semra KURAMA, to reviewers for carefully revising published articles, to the scientific board for their devotion, and to everyone who contributed to this issue.

Prof. Dr. Sedef DİKMEN

ESKİŞEHİR TECHNICAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY
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A- APPLIED SCIENCES AND ENGINEERING

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EFFECT OF BENTONITE AND DOLOMITE ADDITIVES ON RIGID POLYURETHANE FOAM

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ABSTRACT

In this study, clay minerals such as bentonite and dolomite were included in the rigid polyurethane foam against the reference foam in order to increase the compressive tensile strength and reduce the thermal conductivity. The effect of different combinations and amounts of clay minerals on the test parameters of the foam was investigated. The surface morphology of the doped foams was investigated by scanning electron microscopy (SEM). Polyurethane foams were subjected to compressive-tensile strength and thermal conductivity tests. Improvement was observed in the thermal conductivity of polyurethane foams containing 1% bentonite and in the compressive and tensile strengths of polyurethane foams containing 2% dolomite. When clay minerals were added to polyurethane foam in combination, both thermal conductivity and compressive and tensile strengths were improved.

Keywords: Polyurethane, Bentonite, Dolomite, Strength, Thermal conductivity

1. INTRODUCTION

As the demand for energy increases with the increase in the world population, the issue of energy efficiency is becoming increasingly important. One of the most important issues in energy efficiency is thermal insulation. Polyurethane foam is a versatile material that can be rigid, flexible or semi-rigid, resulting from the chemical reaction between the functional group of isocyanate and the hydroxyl groups of polyol. Rigid polyurethane foams are closed-cell thermoset plastics that contain gas with low thermal conductivity inside the foam cells and provide high thermal insulation [1]. Due to their superior mechanical properties, excellent thermal insulation properties, low apparent density and high resistance to weathering, they are widely used in various industries, such as automobile, marine, construction, packaging, and furniture industries. The main application purposes are thermal insulation, acoustic, shock absorption, and sound absorption applications [2]. Rigid polyurethane foam materials are widely used as thermal insulation materials in different sectors, especially due to their low thermal conductivity coefficients. In general, the heat conduction coefficient of rigid polyurethane foams depends on the foam density, cell size, cell orientation, open/closed cell ratio, the type of gas contained in the cell, and the heat conduction coefficient of fillers, if any [3]. Since polyols and isocyanate used in polyurethane synthesis are petroleum-derived materials, constantly increasing oil prices, and the exhaustibility of petroleum resources, it is increasingly important to reduce the petroleum-derived input by researching inorganic additives and incorporating them into the composite material as fillers. In many studies, nanoclays have been successfully used in thermoplastic foams to reduce cell size and increase strength [4]. Clay is a naturally occurring, naturally occurring, fine-grained, crystalline material present in rocks and soils that exhibits plastic properties when water is added. Clay minerals find almost innumerable applications, and the diversity of uses is still increasing [5]. Clay minerals are hydrated aluminosilicates containing certain amounts of Mg, K, Ca, Na and Fe and contain two-dimensional repeating tetrahedral layers in their composition [6]. Bentonite is formed by the chemical weathering and decomposition of volcanic ash, tuff and lava, predominantly in colloidal silica structure, rich in aluminium and

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magnesium. It consists mainly of montmorillonite minerals and is defined as a light-coloured rock composed of very small crystals, soft, porous and easily shaped. The specific gravity of bentonite, which can be observed in various colours such as white, grey, brown and cream, varies between 2.7–2.8 g/cm^3. The theoretical formula of bentonite is $Si_8Al_4O_4(OH)_4.nH_2O$ and its chemical composition theoretically includes 65.4% SiO_2, 23.2% Al_2O_3 and 3.6% MgO [7]. Dolomite mineral, whose general composition is $CaMg(CO_3)_2$, is a mineral with different properties from calcite. Unlike calcite minerals, CaO is partially or completely replaced by MgO components. It has different usage areas such as ceramics, chemical industry, water filtration, and filler in the paint industry [8].

In these polymer composites, inorganic materials were used to reinforce polymers with the idea of taking advantage of the high heat durability the high mechanical strength of inorganic and the ease of processing polymers [9].

This study aimed to reduce the thermal conductivity coefficient while increasing the compressive tensile strength of polyurethane foams. Bentonite was added to rigid polyurethane foam material at 1, 5 and 10% by mass. Thermal conductivity and compressive tensile strength values of the reference foam and bentonite-added foam materials were measured. Then, dolomite was added to the rigid polyurethane foam material at 2, 10 and 15% by mass. The thermal conductivity and compressive tensile strength values of the reference foam and dolomite-added foam materials were measured.

2. MATERIALS AND METHODS

Polyol, polymeric MDI ([4,4′–Methylenebis (phenyl isocyanate)], additives and catalyst chemicals were obtained from Flokser Textile Company. CR1120 is provided as an additive to regulate the polyurethane cell size. N,N-Dimethylcyclohexylamine (DMCHA) was used as the catalyst and pentane was used as the blowing agent. Dolomite was obtained from Şişecam and bentonite was obtained from KarBen Bentonite Company. The chemical content of dolomite used in the study (wt.%) is as follows: 0.26%±0.05 SiO_2, 0.08%±0.03 Al_2O_3, 0.015%±0.05 Fe_2O_3, 31.90%±0.30 CaO and 20.25%±0.25 MgO. Its chemical composition data were obtained from the company where the dolomite was supplied.

The chemical content (wt.%) of bentonite is 61.28% SiO2, 17.79% Al2O3, 3.01% Fe_2O_3, 4.54% CaO, 2.70% Na2O, 2.10% MgO and 1.24% K_2O. The company from which the bentonite was supplied also provided this chemical composition data. A carbon-coated polished thin section of a polyurethane cell was examined using an FEI Quanta 650 field-emission gun scanning electron microscope, at 20 kV. Tensile strength (kPa) and compression strength (kPa) tests of the obtained polyurethane were performed using Devotrans DVT FU50 D NN. Additionally, thermal conductivity (W/mK) was measured using a Heat Flow Meter by Netzsch HFM 436 Lambda.

The bentonite and dolomite to be added to the rigid polyurethane foam material were kept in an oven at 100^{o}C for 24 hours before use, and the moisture in these materials was removed. Bentonite, whose moisture is removed, is added to 100 grams of polyether polyurethane foam at a ratio of 1, 5 and 10%. It is mixed with a high-speed mechanical mixer. After obtaining a homogeneous mixture, 3.9 grams of catalyst, 3.7 grams of cell organizer, and 8.5 grams of blowing agent are added and mixed. One hundred sixty grams of polymeric MDI are reacted and poured into a mold with dimensions of 35×35×7 cm and left to cure. The dehumidified dolomite is added to 100 grams of polyether polyolefin at a ratio of 2, 10 and 15%. It is mixed in a high-speed mechanical mixer. After obtaining a homogeneous mixture, 3.9 grams of catalyst, 3.7 grams of cell organizer, and 8.5 grams of blowing agent are added and mixed. 160 grams of polymeric MDI is reacted and poured into a mold measuring 35×35×7 cm and left to cure. When the thermal conductivity and compression-tensile values were analyzed, 1% bentonite and 2% dolomite combination foam were made in the same process as the clays with the best results.

3. RESULTS AND DISCUSSION

3.1. Foam Formulation

The amounts of polyol, additive, catalyst, blowing, MDI, bentonite and dolomite in polyurethane foams are given in Table 1.

Table 1. Polyurethane foam formulations

Sample Name	Polyol (g)	Additive (g)	Catalyzer (g)	Blowing Agent (g)	MDI (g)	% Bentonite	% Dolomite
Sample 1	99	3.7	3.9	8.5	160	1.0	–
Sample 2	95	3.7	3.9	8.5	160	5.0	–
Sample 3	90	3.7	3.9	8.5	160	10.0	–
Sample 4	98	3.7	3.9	8.5	160	–	2.0
Sample 5	90	3.7	3.9	8.5	160	–	10.0
Sample 6	85	3.7	3.9	8.5	160	–	15.0
Sample 7	97	3.7	3.9	8.5	160	1.0	2.0
Reference	100	3.7	3.9	8.5	160	–	–

3.2.SEM Analysis

SEM images of polyurethane foams synthesized by adding 1, 5, and 10 wt.% bentonite and 2, 10, and 15 wt.% dolomite to the polyol chemical were examined. The reference polyurethane foam synthesized without adding bentonite and dolomite is shown in Figure 1. The polyurethane cell sizes are similar and the pore structure is quite regular. In Figure 2, SEM images of the polyurethane foam with 1, 5, and 10% by mass of bentonite were given. It was seen that the pore structure of the foams with 1% added bentonite was similar to the reference foam. It was observed that the pore sizes of the polyurethane foams with 5% added bentonite started to become irregular. In comparison, the pore sizes of the polyurethane foams with 10% added bentonite became completely irregular and the cells were broken. In Figure 3, SEM images of polyurethane foams with 2, 10, and 15% dolomite added by mass were given and it was seen that the pore structure of 2% dolomite-doped foams was similar to the reference foam. It was observed that the pore sizes of 10% dolomite doped polyurethane foams started to become irregular, the pore sizes of 15% dolomite doped polyurethane foams became completely irregular and the cells were ruptured. When examined against the reference, it was observed that the polyurethane foam cell structure obtained with the combination of 1% bentonite and 2% dolomite was suitable.

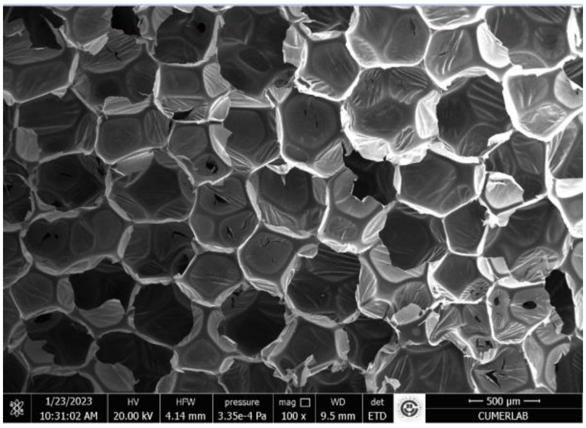
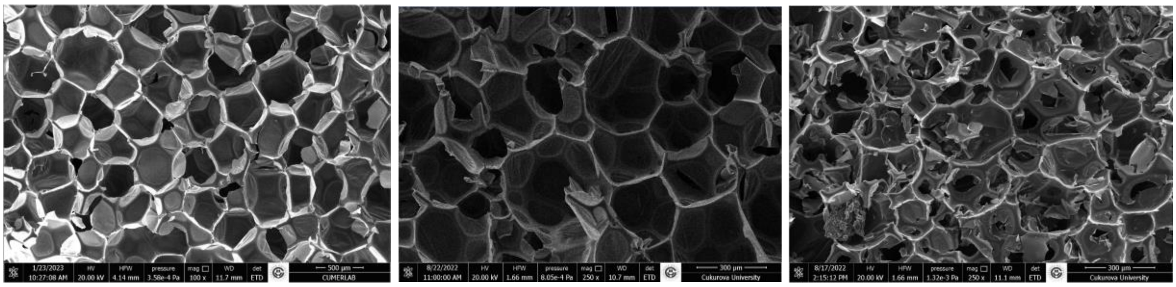
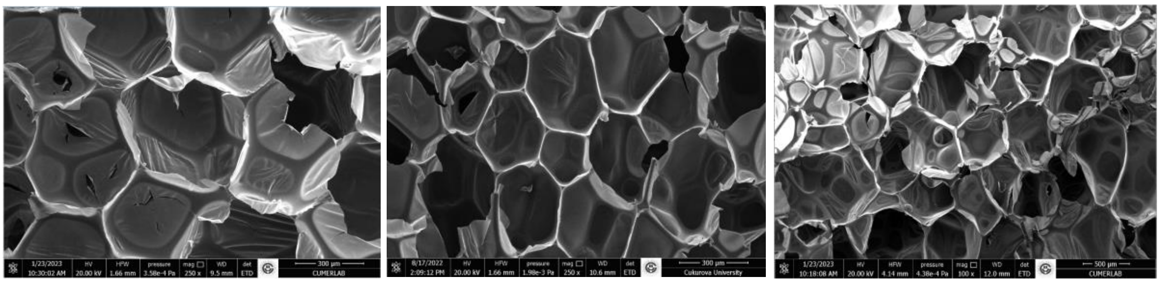


Figure 1. SEM image of reference foam without bentonite and dolomite additives



(a) **(b)** **(c)**

Figure 2. SEM image of polyurethane foam with 1% **(a)**, 5% **(b)** and 10% **(c)** bentonite additives



(d) **(e)** **(f)**

Figure 3. SEM image of polyurethane foam with 2% **(d)** 10% **(e)** and 15% **(f)** dolomite additives

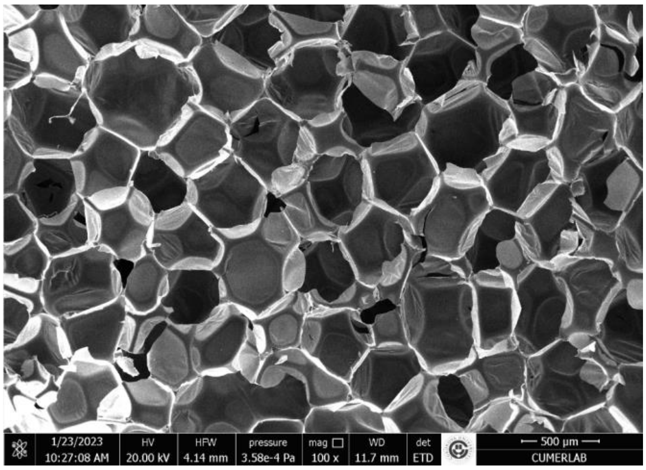


Figure 4. SEM image of polyurethane foam with 1% bentonite and 2% dolomite additives

3.3. Compression/Tensile and Thermal Conductivity Tests

Compression/Tensile strength and thermal conductivity values of the reference foam and synthesised polyurethane foams are given in Table 2.

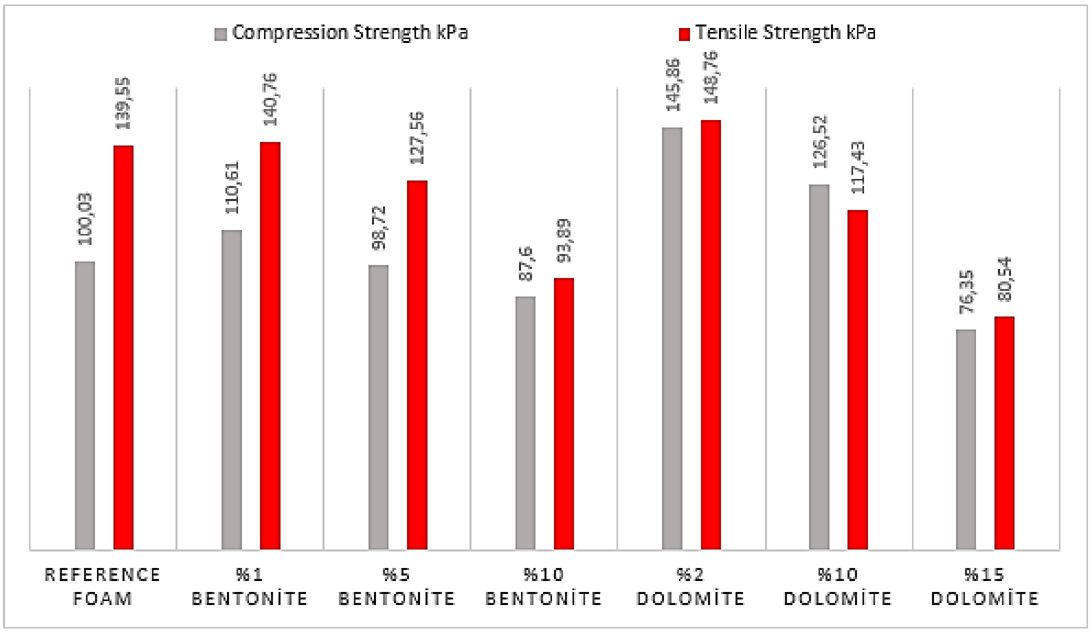


Figure 5. Compression/Tensile Strenght results of polyurethane foams with bentonite and dolomite

When the foam doped with 1% bentonite is analysed against the reference foam, it is seen that the compression tensile strength values increase. As the bentonite ratio increased, it was observed that the compression polyurethane foam cells ruptured, and the compression tensile strength values decreased. When the foam doped with 2% dolomite was analysed against the reference foam, it was observed that the compression tensile strength values increased. As the dolomite content increased, it was observed that the polyurethane foam cells ruptured and the compression tensile values decreased. While both bentonite and dolomite minerals show improvement in compressive and tensile strength values against the reference, it is clearly seen that 2% dolomite doped polyurethane foam shows a better result than 1% bentonite doped polyurethane foam.

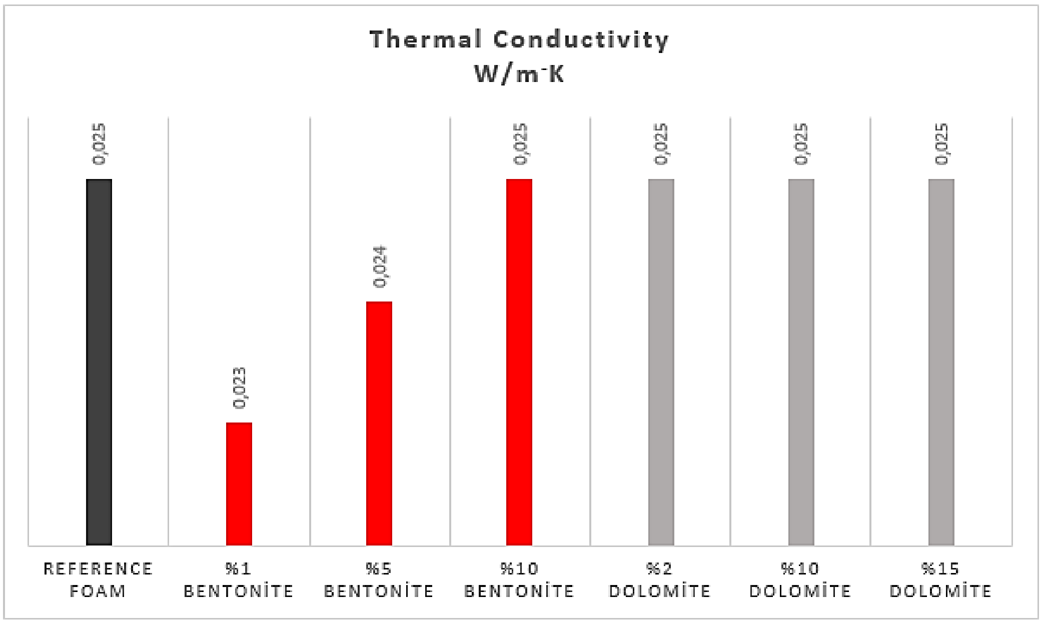


Figure 6. Thermal conductivity results of polyurethane foams with bentonite and dolomite

When the thermal conductivities of bentonite and dolomite doped polyurethane foams against the reference foam were analysed, it was seen that the thermal conductivity coefficient decreased from 0.025 to 0.023 with the addition of 1% bentonite to the polyurethane foam. The decrease in the thermal conductivity coefficient means the thermal insulation performance will improve. Although the thermal conductivity coefficient increased by increasing the amount of bentonite, it showed a better result than the reference. No improvement or decrease in thermal conductivity coefficients was observed in polyurethane foams to which dolomite was added.

Table 2. Combined recipe compressive tensile strength and thermal conductivity results

Sample Name	Compression Strengths (kPa)	Tensile Strenghts (kPa)	Thermal Conductivity (W/mK)
Sample 8	145.72	149.53	0.023
Reference	100.03	139.55	0.025

A combination recipe of polyurethane foams with 1% bentonite additive and 2% dolomite additive was made with the best results in thermal conductivity and compressive tensile strength and the highest compressive tensile and lowest thermal conductivity coefficient values were obtained as shown in Table 2.

4. CONCLUSIONS

In this study 1, 5 and 10% bentonite and 2, 10 and 15% dolomite were added to rigid polyurethane foams. When the SEM images were examined, the SEM images that resembled the reference foam were Sample 1 and Sample 4. Cell sizes and arrangements are very similar to the reference foam. It was observed that as the amount of dolomite and bentonite in the foam increased, the size of the polyurethane foam cells became irregular and broke. Irregular size of the foam cells and rupture of the foam cells cause the compressive and tensile strengths to decrease. When the bentonite added to Sample 2 and Sample 3 is examined against the reference, the decrease in compressive and tensile strength is due to the excessive amount of bentonite tearing the polyurethane foam cells and as a result, the number of carrier cells decreases. When the dolomite added to Sample 6 is examined against the reference, the decrease in compressive and tensile strength is due to the excessive amount of dolomite tearing the polyurethane foam cells. As a result, the number of carrier cells decreases. When the compressive and tensile strengths were examined, it was seen that the values of Sample 1, Sample 4 and Sample 5 were higher than the reference. When Sample 1, Sample 4 and Sample 5 were compared, it was seen that Sample 4 gave the best result. The reason is that the determined amounts of dolomite and bentonite increase the number of carrier cells. With the 1% bentonite additive amount in the foam cells, the average cell size decreased. Thus, the thermal conductivity also decreased. Thermal conductivity values are lower in Sample 1 and Sample 2 when examined against the reference. Sample 3 did not provide an improvement in the thermal conductivity value because the excess amount of bentonite ruptured the foam cells. It has been observed that depending on the amount of bentonite added to the polyurethane foam, it causes a decrease in the average cell size and a decrease in its thermal conductivity. It has been observed that dolomite used as a filling material increases the compressive and tensile strength of rigid polyurethane foam up to specific amounts. To simultaneously increase thermal conductivity and compressive tensile strength, the combination recipe Sample 8 containing 1% bentonite and 2% dolomite, which achieved the best results, was synthesized. When the combination recipe was compared with the reference foam, it was observed that there was an improvement in both compressive tensile strength and thermal conductivity values.

CONFLICT OF INTEREST

We state that there are no conflicts of interest of any type as regards the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Sinem Tümük: Literature survey, data collection and analysis, writting, supervising and reviewing.
Bilgehan Güzel: Literature survey, supervising and reviewing.
Erdem Delil: Literature survey, data collection.
All authors stated that there are no conflicts of interest regarding the publication of this article.

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USAGE OF BILECIK LEFKE STONE AND BENTONITE CLAY FOR PHOSPHORUS REMOVAL IN WATER

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ABSTRACT

The rapid increase in the world population, the development of the industry, the excessive usage of fertilizers in agriculture, and the increase in detergents and chemicals used for cleaning accelerate the pollution of water resources. Conservation and recovery of damaged water resources along with the deteriorated ecosystem is of great importance for living things. An important part of water pollution in lakes and rivers is the increase in the content of nutrients. Nutrient elements, especially phosphorus, cause the transparency of water to decrease gradually. Over time, this situation, called eutrophication, causes an algae bloom and the aquatic ecosystem is disrupted. Uncontrolled discharge of wastewater containing phosphorus in high concentrations accelerates this process. These nutrients must be removed in order to maintain water quality and reduce the risk of eutrophication. The main ways of removing phosphorus from water are physical, chemical and biological methods. Among these, as an alternative to settling with chemical substances, the usage of clay (based on fixation) has an important place. In this study, different dosages of bentonite, Lefke stone and ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) were used in water with three different pH values (4, 7, and 10) and three different phosphorus contents (20, 40, and 60 ppm). The per cent yields of the phosphorus removed with ferrous sulphate heptahydrate, Lefke stone and bentonite are 72%, 57% and 39%, respectively. In addition, it was determined that the dosage of additives used should be renewed depending on the phosphorus content of the environment and that the high pH value of the environment increased the efficiency, especially in the usage of ferrous sulphate heptahydrate. In conclusion, as an alternative to the usage of chemicals, it has been revealed that Lefke stone can be used for phosphorus removal in water, and its effectiveness can be further increased with further studies.

Keywords: Eutrophication, Bentonite, Phosphorus fixation

1. INTRODUCTION

The biggest reserves of Phosphorus (P), which is an important structural element for living creatures, in nature phosphatic rocks in the earth's crust, commercial fertilizers and water resources. Since non-volatile phosphorus does not pass into the atmosphere, the phosphorus cycle is different from other cycles (such as Oxygen, Nitrogen and Sulfur). Plants use and consume ortho-phosphates, which are the dissolved and ionized form of phosphorus. The only source of phosphorus for herbivorous animals is plants. Carnivorous animals meet their phosphorus needs by eating herbivorous animals [1].

Phosphorus is the second most abundant element in the human body, after calcium. Phosphorus is needed by all living creatures, it is the main component of ATP, DNA, NADPH, phospholipids, and nucleic acids. P is also needed for cellular activities in the body, energy production, contraction of the heart, muscle-nerve movements, tooth-bone tissue, and kidney [2].

Phosphorus is also a necessary nutrient element for aquatic plants and algae. However, excessive transport of phosphorus into water causes pollution called eutrophication. Increased phosphorus in water accelerates phytoplankton growth. And then, fish, other aquatic creatures, microorganisms, and insects are affected by these negativities, respectively. In other words, phosphorus disrupts the natural balance

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in water and increases the growth of toxic algae in water [1, 2]. The main cause of water pollution in lakes and rivers is nutrient excess. Phosphorus and other nutrients in water cause the transparency of water to decrease gradually, which disrupts the ecological balance. This situation, called eutrophication, disrupts the aquatic ecosystem by causing algal blooms and the death of fish [3].

As a result of the uncontrolled discharge of wastewater containing high concentrations of phosphorus into the receiving environment, significant deterioration in water quality may occur. It may be necessary to purify phosphorus as well as nutrients such as carbon and nitrogen to provide the necessary nutrient rates to protect water quality and reduce the risk of eutrophication in receiving environments. In general, the primary source of phosphorus is cleaning materials such as soap, detergent, and shampoo. Although some of it is retained in the soil, the retention percentage of P is low in soils with high permeability. Eutrophication is gradually increasing with the usage of phosphorus agricultural fertilizers [4, 5].

High phosphorus concentration especially accelerates the growth of cyanobacteria. Wastewater causes problems such as increased oxygen consumption, eutrophication, and toxicity in the receiving environment due to its high nutrient content. Eutrophication causes an increase in phytoplankton and microorganisms, algal blooms that include toxin-secreting cyanobacteria, and algae collapse, depleting the dissolved oxygen in the bottom water. Thus, eutrophication damages the taste and colour of water and causes a decrease in fish and crustacean species, which are useful food products. As organic materials decompose in an oxygen-free environment, foul-smelling gases such as methane, ammonia and hydrogen sulfide are produced. These gases also have a toxic effect on marine creatures. Due to eutrophication, seaweed increases, and blocks the passage of sunlight. With the cessation of photosynthesis, the oxygen in the liquid decreases. And then, invertebrate aquatic creatures and fish may disappear [2, 5, 6, 7, 8].

In terms of environment and human health, wastewater must be treated and reused. However, the applicability of technologies developed for the treatment and reuse of wastewater is low due to the price of installation, maintenance, and repair. For this reason, alternative purification methods, which are cheap and easy compared to expensive technological purification methods, are used. Industrial facilities must ensure optimum removal efficiency for nitrogen-phosphorus removal. According to legal regulations, the most suitable treatment technology for nutrient removal is biological treatment [8].

Although efforts are made to reduce phosphorus inflow into wastewater, success is not obtained due to the diversity of P sources. For this reason, advanced treatment of wastewater comes to the fore. Even so, technologies that aim to remove and recover P in wastewater by chemical, physical, and advanced biological methods are not very developed. Among physical methods, phosphorus crystallization, flotation, electrodialysis, and reverse osmosis are frequently used. Advanced biological phosphorus removal can remove 97% of the total phosphorus, although it is expensive. Chemical removal aims to precipitate phosphorus in the form of phosphate with salts of calcium, aluminium, and iron ions [1].

Some of the chemicals commonly used in phosphorus settling are Ca compounds and Mg, Al, and Fe salts [7]. Acinetobacter, one of the bacterial species found in activated sludge systems, is another alternative that can be used to remove P from water [8]. However basically, in the removal of P from wastewater, reverse osmosis, electrodialysis, usage of adsorbents, slag, sewage sludge, fly ash, kaolinite, and activated carbons obtained from agricultural waste are used. Some of the agricultural raw materials used in activated carbon production are corn cob, olive seed, cotton stalk, fruit waste, sugar cane, wheat straw, paddy husk, and sunflower seed-hazelnut-almond shell [7, 5]. Compared to other methods, adsorption is more successful and economical in P removal. Therefore, in recent years, attempts have been made to purify wastewater with easily accessible and cheap materials [2]. It is frequently used due to the cheapness and simplicity of the adsorption process. In removing P from wastewater, in particular, biochar, coconut shell, calcium carbonate, calcium kaolinite, red mud, semi-burnt dolomite, fly ash, slag, zeolite, titanium dioxide, sand, and pumice are quite successful [7].

In particular, some clay types are frequently used in P removal. It is one of these examples, called bentonite in America, is also frequently encountered in the Montmorillon region of France. So, bentonite is also called montmorillonite. The general chemical formula of bentonite is (Na, Ca) (Al, Mg) 6(Si_4O_{10}) 3(OH) 6×n H_2O [1]. Bentonites are the most abundant clay-containing materials used in wastewater treatment. It is used successfully in both heavy metal removal (copper, lead, cadmium, and zinc) and phosphorus removal [9]. One of the most important factors affecting phosphorus adsorption is pH. Besides, decreasing temperature also increases the adsorption capacity [1]. In choosing the most suitable adsorbent to be used in phosphorus removal; Attention is paid to the physical and chemical properties of the adsorbent, its ability to adsorb phosphorus, cost, and simplicity of obtaining [2].

Many studies have been conducted on this subject. Ayar [1] tried to remove P in water with bentonite clay. He determined that the best removal was at neutral pH. After all, He observed that physical and chemical interactions were effective together in P removal. Li, W. et al. [10] tried P removal with a mixture of kaolin clay and ferric chloride with different moles. They found that phosphates were completely removed by iron at neutral pH. Dirim [6] in the Lower Kelkit Watershed, aimed to remove P from water with plants in his laboratory study. As a result, he determined that the highest phosphorus removal was in *Lemnaminor* species with 84%, *Ceratophyllum demersum* species with 75% and that other plant species could only remove around 50% phosphorus. *Typhaangustifolia* showed lower performance than other species with a rate of 18%.

In this study, for the purpose of P removal in water, bentonite clay, which is a natural adsorbent and abundant in Bilecik, and Lefke stone, which is specific to the Bilecik Osmaneli region, were used.

2. MATERIAL AND METHOD

2.1. Material

For the research experiments, Lefke stone located in Osmaneli county of Bilecik province, bentonite extracted by ESAN Clay and Bentonite factory from Bozüyük county of Bilecik province and Tekkim brand ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) were used.

2.1.1. Bentonite

Bentonites are the chemical decomposition of volcanic ash, tufa and lava containing glassy material. Montmorillonite, which creates bentonite and consists of layers, is an octahedral structure located between two tetrahedral layers. There are water molecules and exchangeable cations in this structure. Water and organic matter enter between these unit layers and extend the structure. The main components of Ca-bentonite and their approximate ratios are as follows: (66%) SiO_2 and (13%) Al_2O_3 [14].

Pure Ca-bentonite was used in the study. Bentonite mineral contains 50% montmorillonite. After the crushing and drying stages, it was ground below 75 microns. Two different concentrations (5% and 10%) were tried in the experiments (Figure 1).

Figure 1. A sample of the dust of bentonite clay

2.1.2. Lefke stone

Lefke stone, a type of sandstone, was used in the construction of mosques, madrasahs and inns during the Seljuk and Ottoman Empires periods. Besides, this stone was used in Eskişehir government mansion, Istanbul Haydarpaşa train station, Bebek and Bostancı mosques. Lefke stone is a type of sandstone found naturally in the Osmaneli county of Bilecik province, and the ratio of clay and silt materials is less than approximately 15%. The grains in the stone consist of quartz, feldspar, lithic fragments, hematite, and other opaque minerals [15, 16]. After the Lefke stone was crushed and sieved at 250 microns, it was dried in the oven at 105°C for 24 hours and its moisture was removed. Two different concentrations (5% and 10%) were tried in the experiments.

Lefke stone is especially used in the restoration of historical buildings and the design of special structures (such as fountains and bridges) (Figure 2).

Figure 2. A sample of the dust of Lefke stone

2.1.3. Ferrous sulphate heptahidrat ($FeSO_4.7H_2O$)

10 mg/ml (10.000 ppm) ferrous sulphate heptahydrate was prepared as stock. Three different initial concentrations (100 mg/l, 150 mg/l, 200 mg/l) were tried in the experiments.

2.2. Method

In the research, for three materials in different concentrations (Ferrous Sulphate Heptahydrate, Bentonite, and Lefke Stone), phosphorus removal efficiencies were examined at three different dosages of phosphorus concentration (20, 40, and 60 mg/l) and at three different pH values (4, 7, 10) at the end of 30 minutes. Vanadomolybdophosphoric acid colourimetric method was applied for phosphorus analyses [18]. For the colourimetric method used for the determination of total orthophosphate in samples, solution A+B was prepared by combining solution A and solution B reagents and HCl. Standard solutions were obtained using stock phosphorus solution (1000 ppm P). It was prepared as 0, 5, 10, 20 ppm for 20 ppm P concentration, 0, 10, 25, 50 ppm for 40 ppm P concentration, and 0, 20, 40, 60 ppm for 60 ppm P concentration [17].

For the analysis, 7ml sample + 1ml pure water + 2ml A+B solution were combined and after ten minutes waiting period, the absorbance was read on the spectrophotometer at 470 nm.

Equation 1 was used in the calculation of phosphorus removal efficiency [17].

$$\text{Phosphorus removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

C_i: Initial phosphorus concentration (mg/l)
C_f: Final phosphorus concentration (mg/l)

2.2.1. Statistical analysis

One-way ANOVA was used to analyze the means of the final P concentrations for the different applications. Differences were evaluated at the 0.05 significance level and the Duncan post hoc test was used with the software program SPSS17.0.

3. RESULTS AND DISCUSSION

The results obtained in the study were tabulated for each pH value along with each absorbent type and dosage (Table 1-3). Final P concentrations and one-way ANOVA results were also added to the table.

The lowest value was obtained in the application of ferrous sulphate (200mg/l), the second lowest value was obtained in the application of Lefke stone (10%), and the pH value was effective in the application of ferrous sulphate (Table 1)

Table 1. Final concentration and removal per cent obtained for initial phosphorus content of 20 ppm

Additive Material	**Dosage**	**pH**					
		4		**7**		**10**	
		ppm	***Removal %***	***ppm***	***Removal %***	***ppm***	***Removal %***
Bentonite	5%	12.80 c	36	13.71 d	31	12.29 e	39
	10%	13.54 d	32	9.78 c	51	11.21 c	44
Lefke stone	5%	11.38 b	43	9.43 b	53	11.55 d	42
	10%	8.88 a	56	8.53 a	57	9.55 b	52
Ferrous sulphate	100 mg/l	15.29 f	24	13.55 d	32	13.81 f	31
	150 mg/l	14.52 e	27	12.13 d	39	9.55 b	52
	200 mg/l	14.13 d	29	12.19 d	39	5.51 a	72

Remark: Columns with different letters significantly differed from each other as indicated by the Duncan test ($p \leq 0.05$).

Likewise, the lowest value was obtained in the application of ferrous sulphate (200mg/l), and the second lowest value was obtained in the Lefke stone (10%) application (Table 2).

Table 2. Final concentration and removal per cent obtained for initial phosphorus content of 40 ppm

Additive Material	**Dosage**	**pH**					
		4		**7**		**10**	
		ppm	***Removal %***	***ppm***	***Removal %***	***ppm***	***Removal %***
Bentonite	5%	33.90 d	15	28.27 b	29	33.17 f	17
	10%	32.95 c	18	28.42 b	29	30.40 c	24
Lefke stone	5%	29.00 b	28	30.24 d	24	31.64 d	21
	10%	25.93 a	35	26.66 a	33	29.60 b	26
Ferrous sulphate	100 mg/l	38.14 g	5	33.73 f	16	32.49 e	19
	150 mg/l	37.05 f	7	32.56 e	19	30.55 c	24
	200 mg/l	36.12 e	10	28.85 c	28	25.91 a	35

Remark: Columns with different letters significantly differed from each other as indicated by the Duncan test ($p \leq 0.05$).

A decrease was observed in the effect levels of the dosages used in response to the increasing phosphorus content. This effect was especially observed in the effectiveness of ferrous sulphate (Table 3).

Table 3. Final concentration and removal per cent obtained for initial phosphorus content of 60 ppm

Additive Material	**Dosage**	**pH**					
		4		**7**		**10**	
		ppm	***Removal %***	***ppm***	***Removal %***	***ppm***	***Removal %***
Bentonite	5%	56.12 d	6	57.63 f	4	59.06 f	2
	10%	48.53 c	19	50.98 e	15	57.26 e	5
Lefke stone	5%	44.86 b	25	50.24 d	16	54.08 d	10
	10%	40.94 a	32	46.90 b	22	49.10 b	18
Ferrous sulphate	100 mg/l	58.26 e	3	52.89	12	51.59 c	14
	150 mg/l	56.23 d	6	47.60 c	21	48.74 b	19
	200 mg/l	55.74 d	7	44.59 a	26	44.83 a	25

Remark: Columns with different letters significantly differed from each other as indicated by the Duncan test ($p \leq 0.05$).

As a result of the applications made for an initial phosphorus concentration of 20 ppm, the lowest content was obtained in the application of ferrous sulphate (200mg/l) with 5.51 ppm, and the second was in the application of Lefke stone (10%) with 8.53 ppm. The dosage differences used in each application were also found to be significant statistically. Considering the percentage of the removal values, it varied between 24% and 72%. Bentonite application reached 51% value at pH:7 condition and gave proportionally lower values in other conditions. Lefke stone application showed dosage-dependent changes, regardless of pH value. The most striking thing is that the application of ferrous sulphate gave the highest value only for the pH:10 condition. Elgarhy et al. [11] achieved the highest efficiency of 85% for pH 6 value in their sodium-bentonite clay studies. Among the 20.5-10% adsorbent dosages, 10% gave the best results. El Refaey [12] found that the P sorption value varied depending on the thermal process applied to bentonite in their study with Ca-modified Bentonite. Besides, the sorption ability of phosphorus decreased with the increasing temperature of the thermal treatment. Markou et al. [13] stated that Ca-bentonite applied at 5% reduced the phosphorus content in wastewater by over 80%. In our study, Ca-bentonite, which was supplied as a commercial product, was produced for different purposes and it is thought that its effect was limited depending on the details of the production processes.

Although the content values obtained as a result of the applications made for the initial phosphorus concentration of 40 and 60 ppm (Tables 2 and Table 3), showed statistical differences, the percentage removal values were limited between 3% and 35%. This situation shows the need to re-determine the adsorbent dosages to be used for high P concentrations.

4. CONCLUSION

This study investigated the possibilities of using Lefke stone extracted from Bilecik province and Ca-bentonite clay produced for phosphorus removal in wastewater. First of all, it was understood that Lefke stone with its natural form could be an alternative against to chemical usage. The advantage of not being affected much by the ambient pH value, as well as being easily available and economical, has brought the method to the fore. Although bentonite clay contributed to P removal at some levels, further studies are needed to increase its effectiveness. It is necessary to investigate more effective usage possibilities by examining the production processes of Ca-bentonite, particle size selection and carrying out some modification studies. Similar pre-treatments can increase the effectiveness of Lefke stone. Besides, better results in water with high P content can be obtained by using different combinations of these adsorbents when they are used in appropriate dosages.

AUTHORS' CONTRIBUTIONS

Ramazan MERAL: Literature survey, data collection and analysis, writing, supervising and reviewing.
Betül ÇANGA: Literature survey, data collection and analysis and writing.
Çayan ALKAN: Literature survey, writing and editing.
All authors read and approved the final manuscript.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

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WHOLE ROCK AND CLAY MINERALOGY OF EARLY MIOCENE SEDIMENTARY ROCKS OUTCROPPING IN THE NORTHEAST OF KORKUT (MUŞ-TÜRKİYE)

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ABSTRACT

This study was carried out to reveal the origins and formations of the minerals by determining the mineralogical compositions of Early Miocene aged sedimentary rocks outcropping in the northeast of Korkut district, 20 km from Muş. 75 rock samples were taken by measuring two stratigraphic sections from Mollababa Formation (Aquitanian) and Aktaş Formation (Burdigalian) cropping out in the study area. XRD (X-ray diffraction) WR (whole-rock) analyzes were performed on these rock samples, and calcite, quartz, feldspar, clinoptilolite and clay minerals were determined in their compositions. CF (clay fraction) mineralogical compositions were determined by performing XRD detailed clay analyzes on 20 selected rock samples. In clay fractions; chlorite, illite, serpentine, mixed-layered chlorite-vermiculite (C-V) and non-clay minerals such as calcite, quartz and feldspar were determined. SEM-EDS (scanning electron microscope - energy dispersive X-ray spectroscopy) studies were carried out on five selected samples, and in addition to clay minerals such as feldspar, calcite, chlorite and C-V, fossils were also observed. When all the data were evaluated, it was interpreted that the chemical and biogenic origin of the calcite mineral, the detrital origin of the quartz, feldspar, chlorite and serpentine minerals, the neoformation product of clinoptilolite, C-V mineral formed from dark-colored minerals with negative transformation.

Keywords: Aktaş formation, Mollababa formation, Muş, X-ray diffraction, Origin

1. INTRODUCTION

This study was carried out in order to determine the mineralogical compositions of Early Miocene aged sedimentary rocks outcropping in the northeast of Korkut district, 20 km away from Muş province (Figure 1), and to reveal the origin and formation of minerals, to fill the gap in the literature since no mineralogical examination has been carried out in the study area before.

Muş Basin is located in the southern part of the Eastern Anatolia Region (Figure 2). The basin is 35 km wide and 75 km long [1]. The Muş Basin, extending in a NW-SE direction, was interpreted as an intermountain basin by Kurtman and Akkuş [2] and Şaroğlu and Yılmaz [3] and as a post-collision cratonic basin by Akay [4]. It is characterized by E-W trending folds and NW-SE trending dextral strike-slip faults. These geological structures show that a N-S directional compressional tectonic regime prevailed during the formation of the basin [1]. In the Muş Basin, the carbonate rocks of the Bitlis massif and the ophiolite mélange form the basement of the basin. The sedimentation that continued from the Late Cretaceous to the Quaternary enabled the formation of a basin fill approximately ten kilometers thick on this basement [5].

Oligocene and Early Miocene aged rocks around Mollababa village, where the study was conducted, were introduced by Sakınç [6] as Kazanan Formation (Shattian), Mollababa Formation (Aquitanian) and Aktaş Formation (Burdigalian) (Figure 3). The Kazanan formation consists of an alternation of carbonate sandstone, biosparite, sandy limestone, carbonate lithic tuff and pebbly carbonate sandstone [6]. Mollababa Formation presents alternating sequences of carbonate sandstone and marl in its lower part. The upper part of the unit; it consists of bioclastic limestone and biocalcarenites with abundant large benthic foraminifera. Aktaş Formation forms of carbonate sandstones and clayey limestones with

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abundant microfossils from bottom to top, and sandy limestones towards the top. The boundary between Mollababa and Aktaş Formations is conformable (Figure 4).

Figure 1. Location map of the study area (blue square) (After [7])

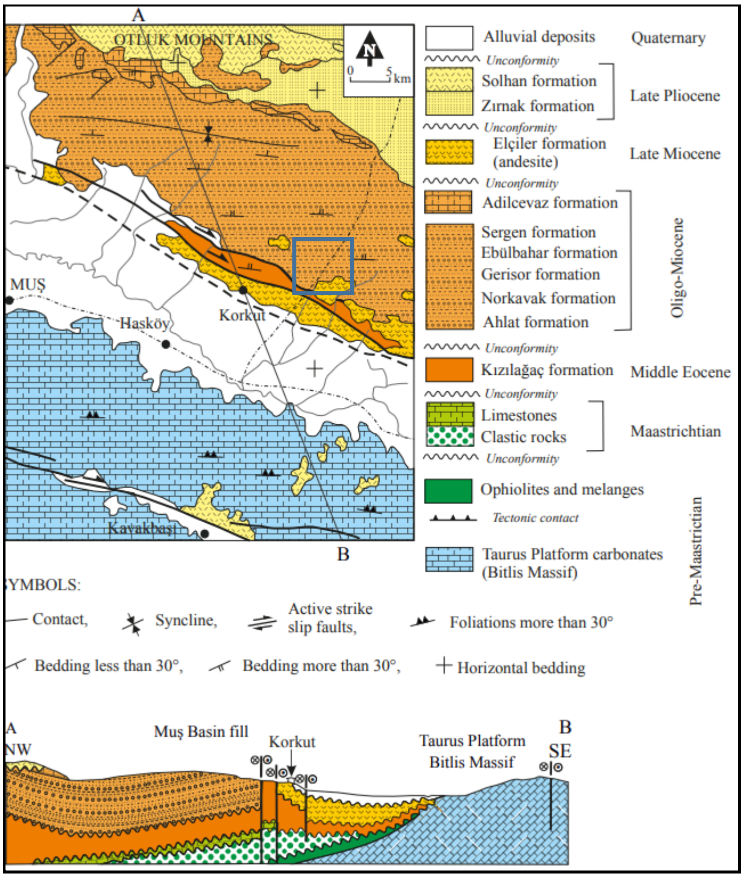


Figure 2. General geological map and cross-section of the Muş basin [1] (The blue square indicates the study area)

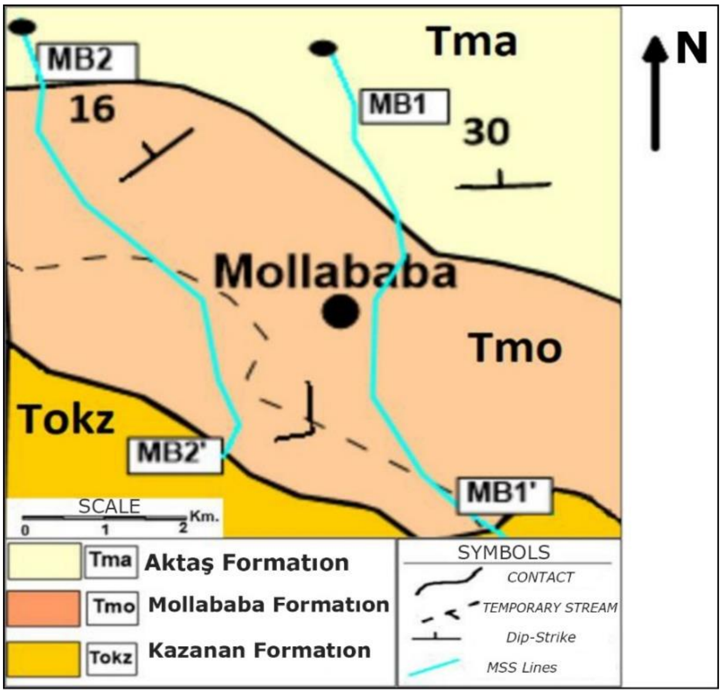


Figure 3. Geological map of the study area and measured stratigraphy section (MSS) routes (Tokz: Chattian, Tmo: Aquitanian, Tma: Burdigalian, MB1: Mollababa 1 MSS, MB2: Mollababa 2 MSS) (edited from [8])

Figure 4. Boundary of Mollababa and Aktaş Formations near Mollababa village (Looking east)

2. MATERIALS AND METHODS

75 rock samples compiled along two measured stratigraphic sections from the Mollababa Formation (Aquitanian) and Aktaş Formation (Burdigalian) constituted the material of the study (Figure 5 and 6).

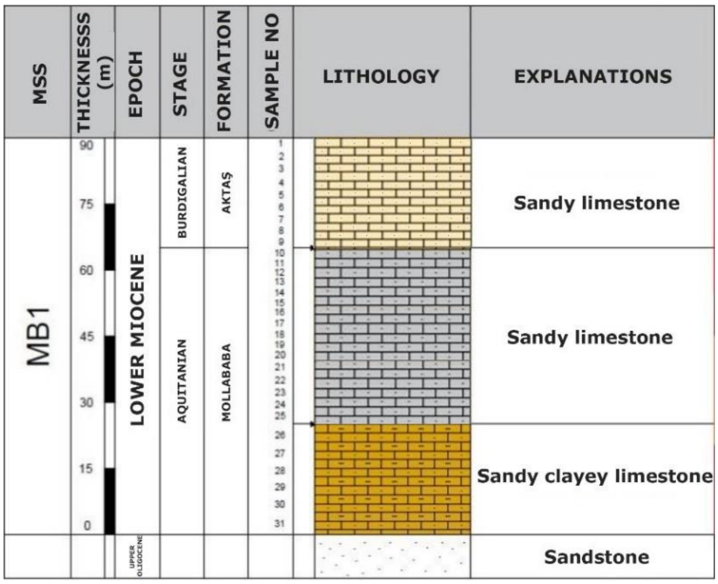


Figure 5. Mollababa 1 (MB1) measured stratigraphic section

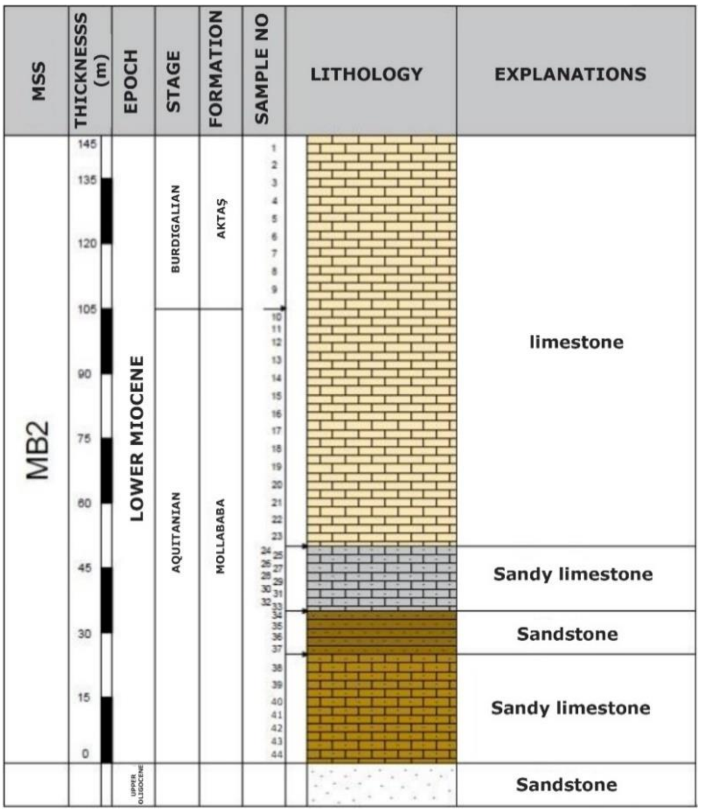


Figure 6. Mollababa 2 (MB2) measured stratigraphic section

All 75 rock samples were firstly reduced with a jaw crusher in Van Yüzüncü Yıl University Engineering Faculty Laboratories, and then they were pulverized using an agate mortar. XRD images of the powder samples were taken at 4°-70° MTA General Directorate Mineral Analysis and Technology Department XRD laboratory. Normal, ethylene glycol, 300°C and 550°C heat treatment diffractograms (between 4°-30°) of 20 selected samples determined to contain clay minerals were taken in the same laboratory. The raw data of these diffractograms were combined using X'Pert HighScore software. Diffractograms were evaluated with the help of relevant literature and by applying the Hanawalt method, and the minerals forming the whole rock and clay fraction of the samples were determined.

SEM-EDS studies were carried out on five selected samples in the SEM laboratory of Van Yüzüncü Yıl University Science Application and Research Center. In this study, ZEISS SIGMA 300 model FE-SEM was used. During FE-SEM analysis, a Secondary Electron (SE) detector was used, which provides more detailed information about morphological features. Microchemical analyzes were performed with an AMETEK EDAX brand EDX detector connected to the FE-SEM device. While interpreting SEM and EDS studies, Welton [9] was used as the main source.

3. RESULTS

3.1. X-Ray Diffraction Analyses

X-ray diffractograms have been evaluated by using Brown [10], Grim [11], Thorez [12], Brindley [13], Brown [14], Velde [15], Wilson [16], Moore and Reynolds [17], and mineral determinations were made by applying the Hanawalt method [18]. In the whole rock analysis of the samples, calcite, quartz, feldspar, clay minerals and clinoptilolite were determined (Tables 1 and 2). Examples of X-ray whole-rock diffractograms are presented in figures 7 and 8.

Table 1. Whole rock mineralogy of samples of Aktaş formation.

Sample No	Quartz	Feldspar	Calcite	Clay Minerals	Clinoptilolite
MB1-1	+	+	+	+	-
MB1-2	+	+	+	+	-
MB1-3	+	+	+	+	-
MB1-4	+	+	+	+	-
MB1-5	+	+	+	+	-
MB1-6	+	+	+	+	-
MB1-7	+	+	+	+	-
MB1-8	+	+	+	+	-
MB1-9	+	+	+	+	-
MB2-1	+	+	+	+	+
MB2-2	+	+	+	+	-
MB2-3	+	+	+	+	+
MB2-4	+	+	+	+	+
MB2-5	+	+	+	+	+
MB2-6	+	+	+	+	-
MB2-7	+	+	+	+	-
MB2-8	+	+	+	+	-
MB2-9	+	+	+	+	-

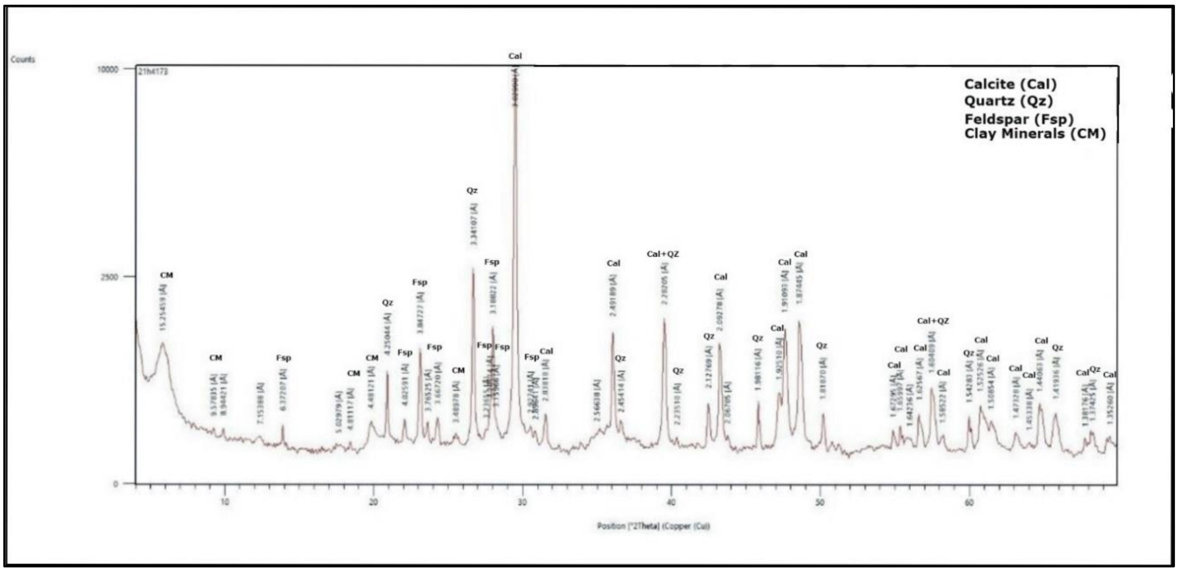


Figure 7. X-ray (WR) diffractogram of MB1-4 (Aktaş Formation) sample

Table 2. Whole rock mineralogy of samples of the Mollababa formation.

Sample No	Quartz	Feldspar	Calcite	Clay Minerals	Clinoptilolite
MB1-10	+	+	+	+	-
MB1-11	+	+	+	+	+
MB1-12	+	+	+	+	+
MB1-13	+	+	+	+	-
MB1-14	+	+	+	+	-
MB1-15	+	+	+	+	-
MB1-16	+	+	+	+	-
MB1-17	+	+	+	+	-
MB1-18	+	+	+	+	-
MB1-19	+	+	+	+	-
MB1-20	+	+	+	+	-
MB1-21	+	+	+	+	+
MB1-22	+	+	+	+	+
MB1-23	+	+	+	+	-
MB1-24	+	+	+	+	+
MB1-25	+	+	+	+	-
MB1-26	+	+	+	+	+
MB1-27	+	+	+	+	+
MB1-28	+	+	+	+	+
MB1-29	+	+	+	+	+
MB1-30	+	+	+	+	+
MB1-31	+	+	+	+	+
MB2-10	+	+	+	+	-
MB2-11	+	+	+	+	-
MB2-12	+	+	+	-	-
MB2-13	+	+	+	-	-
MB2-14	+	+	+	+	-
MB2-15	+	+	+	-	-
MB2-16	+	+	+	+	-
MB2-17	+	+	+	+	-

Table 2. Whole rock mineralogy of Mollababa formation samples (continue)

Sample No	Quartz	Feldspar	Calcite	Clay Minerals	Clinoptilolite
MB2-18	+	+	+	+	-
MB2-19	+	+	+	+	-
MB2-20	+	+	+	+	-
MB2-21	+	+	+	+	-
MB2-22	+	+	+	+	-
MB2-23	+	+	+	+	-
MB2-24	+	+	+	+	-
MB2-25	+	+	+	+	-
MB2-26	+	+	+	+	-
MB2-27	+	+	+	+	-
MB2-28	+	+	+	+	-
MB2-29	+	+	+	+	-
MB2-30	+	+	+	+	-
MB2-31	+	+	+	+	-
MB2-32	+	+	+	+	+
MB2-33	+	+	+	+	-
MB2-34	+	+	+	+	-
MB2-35	+	+	+	+	+
MB2-36	+	+	+	+	+
MB2-37	+	+	+	+	+
MB2-38	+	+	+	+	+
MB2-39	+	+	+	+	+
MB2-40	+	+	+	+	-
MB2-41	+	+	+	+	+
MB2-42	+	+	+	+	-
MB2-43	+	+	+	+	-
MB2-44	+	+	+	+	-

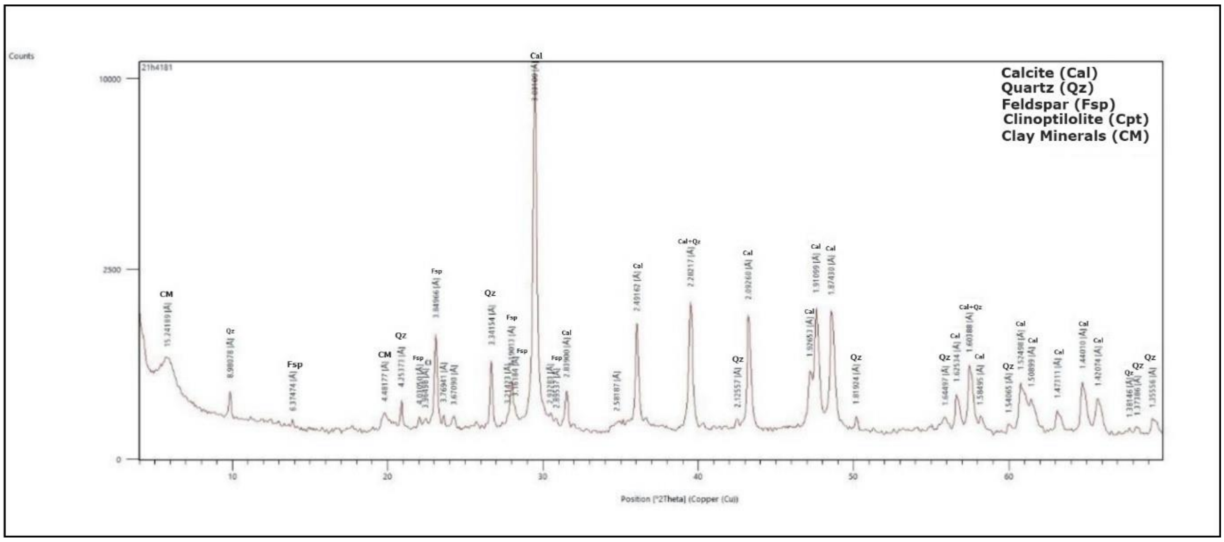


Figure 8. X-ray (WR) diffractogram of MB1-12 (Mollababa Formation) sample

XRD detailed clay analyses were performed on 20 selected rock samples and their clay mineralogical compositions were determined. Clay size components: chlorite, illite, serpentine, mixed layer chlorite-vermiculite (C-V) and calcite, quartz and feldspar as non-clay minerals were detected (Tables 3 and 4).

Table 3. Clay fraction mineralogy of samples of Aktaş formation

Sample No	Chlorite-Vermiculite	Calcite	Quartz	Feldspar
MB1-4	+	+	+	+
MB1-8	+	+	+	+
MB2-2	+	+	-	+
MB2-6	+	+	+	-
MB2-9	+	+	-	+

Table 4. Clay fraction mineralogy of samples of Mollaba formation

Sample No	Chlorite	Chlorite-Vermiculite	Illite	Serpentine	Clinoptilolite	Calcite	Quartz	Feldspar
MB1-12	-	+	-	-	+	+	-	-
MB1-16	-	+	-	-	-	+	+	+
MB1-18	-	+	+	-	-	+	+	+
MB1-23	-	+	-	-	-	+	+	+
MB1-26	-	+	-	-	+	+	+	+
MB1-28	-	+	-	-	+	+	+	+
MB1-30	-	+	-	-	+	+	+	+
MB2-12	-	+	-	-	-	+	+	+
MB2-16	-	+	-	-	-	+	+	+
MB2-24	-	+	-	-	-	+	+	+
MB2-27	-	+	-	-	-	+	+	+
MB2-32	-	+	-	+	+	+	+	+
MB2-36	-	+	-	+	+	+	+	+
MB2-41	+	+	+	+	-	+	+	+
MB2-44	+	+	+	+	-	+	+	+

Examples of X-Ray whole-rock diffractograms are presented in Figures 9 and 10.

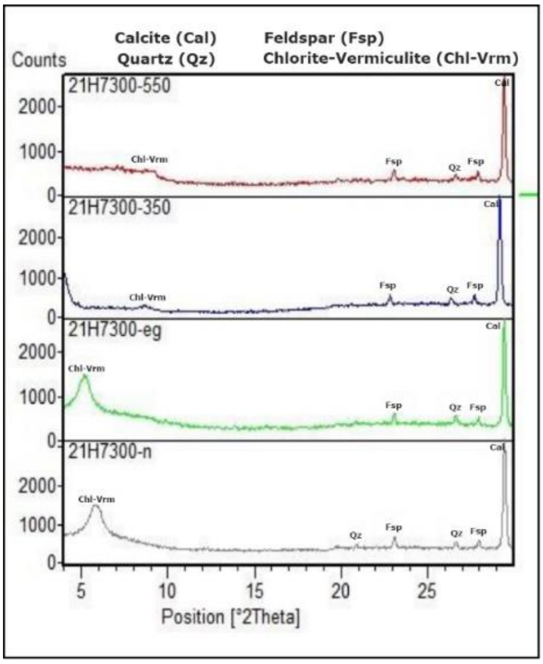


Figure 9. X-ray (CF) diffractograms of MB1-4 (Aktaş Formation) sample

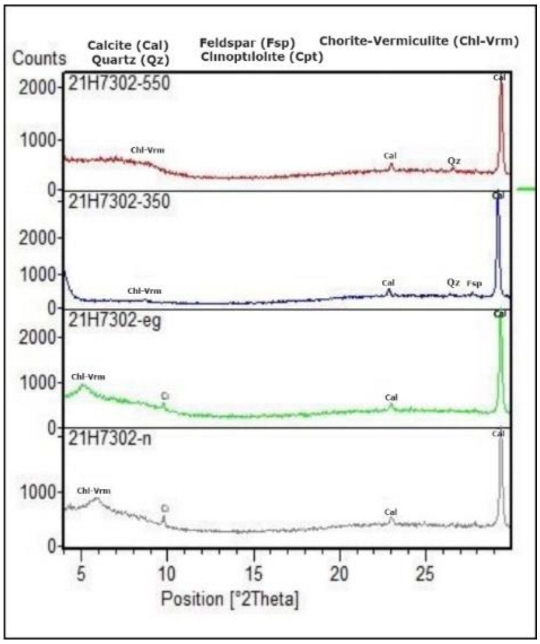


Figure 10. X-ray (CF) diffractograms of MB1-12 (Mollababa Formation) sample

3.2. SEM and EDS Studies

SEM and EDS studies were carried out on 5 selected samples. Whole rock mineralogy of the samples is shown in table 5; clay fraction mineralogy is presented in table 6.

Table 5. Whole rock mineralogy of samples analyzed by SEM and EDS

Formation	Sample No	Quartz	Feldspar	Calcite	Clay Minerals	Clinoptilolite
Mollababa	MB1-24	+	+	+	+	+
Mollababa	MB2-16	+	+	+	+	-
Mollababa	MB2-32	+	+	+	+	+
Mollababa	MB2-41	+	+	+	+	+
Mollababa	MB2-44	+	+	+	+	-

Table 6. Clay fraction mineralogy of samples analyzed by SEM and EDS

Formation	Sample No	Chlorite	Chlorite - Vermiculite	Illite	Serpantine	Clinoptilolite	Calcite	Quartz	Feldspar
Mollababa	MB2-32	-	+	-	+	+	+	+	+
Mollababa	MB2-41	+	+	+	+	-	+	+	+
Mollababa	MB2-44	+	+	+	+	-	+	+	+

In SEM and EDS studies, fossil fragments (Figure 11), calcite (Figure 12), chlorite (Figure 13), and mixed layer chlorite-vermiculite (Figure 14) were observed.

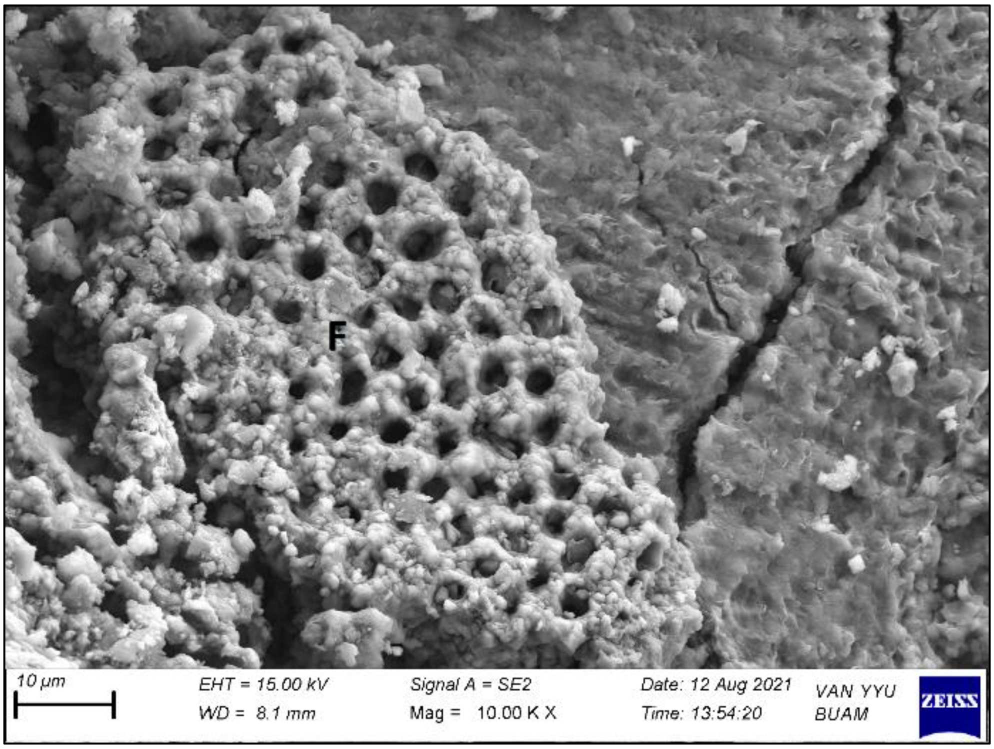
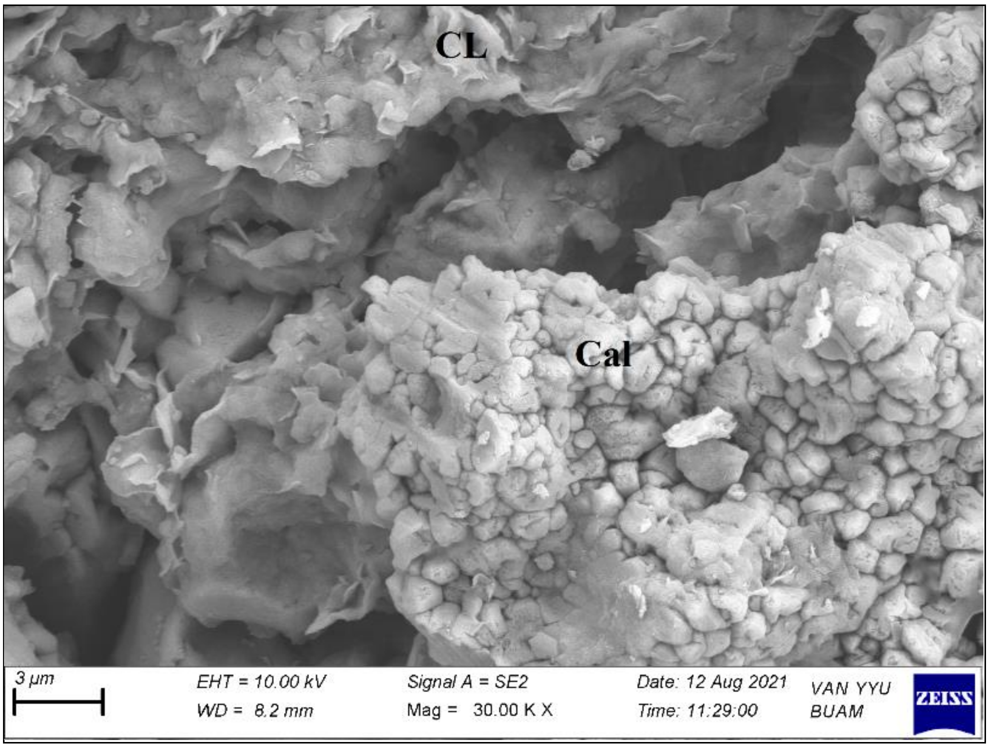


Figure 11. Fossil fragment (F) observed in the SEM study of sample MB2-16



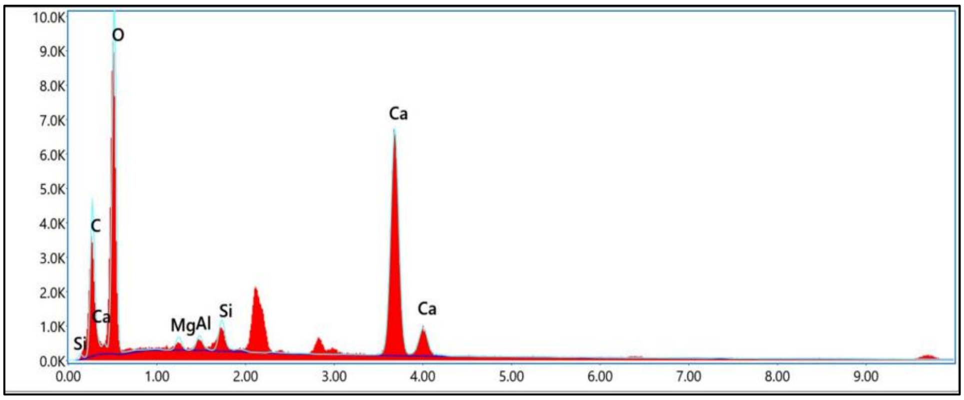
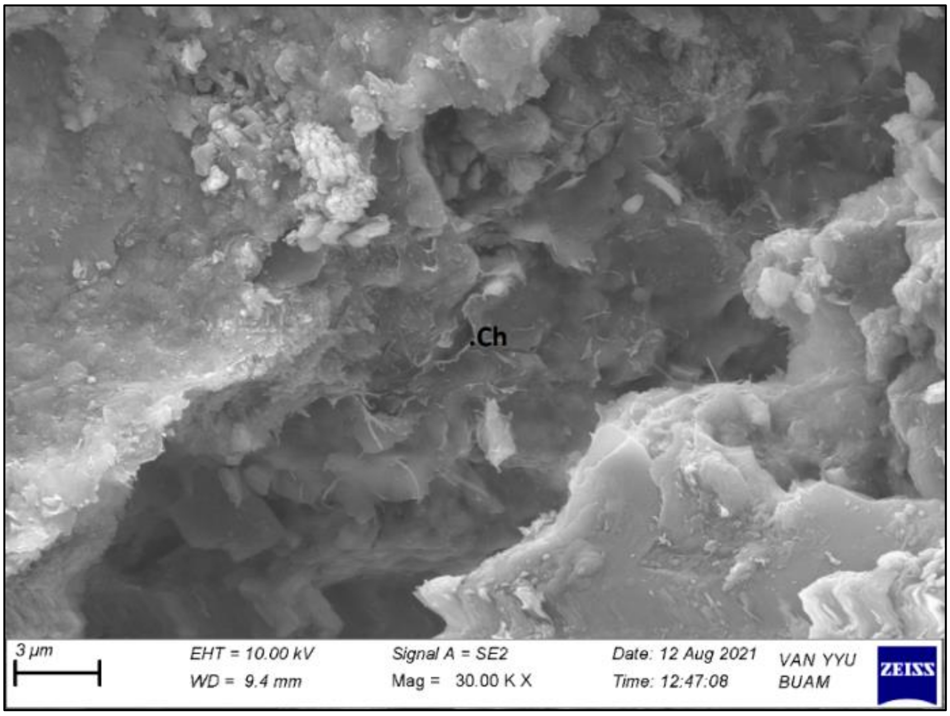


Figure 12. Microphotograph showing the microcrystalline calcite (Cal) and clay leaflets (CL) observed in the MB1-24 sample (above) and microchemical analysis diagram of calcite (below)



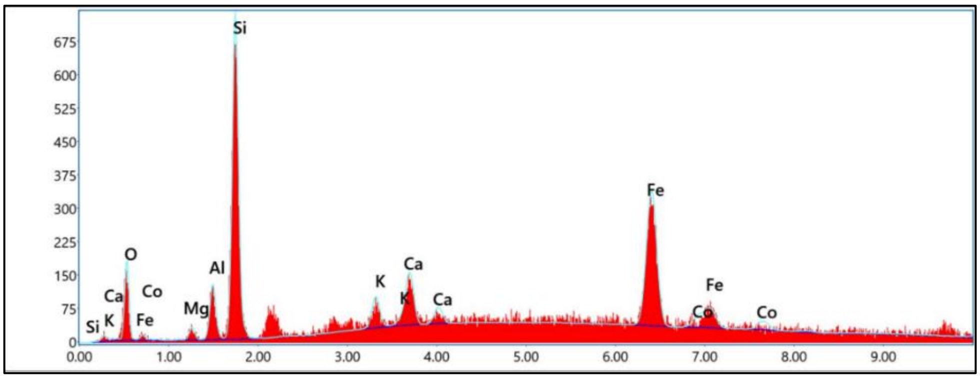


Figure 13. Microphotograph (above) and microchemical analysis diagram (below) of the chlorite (Ch) mineral observed in sample MB1-41

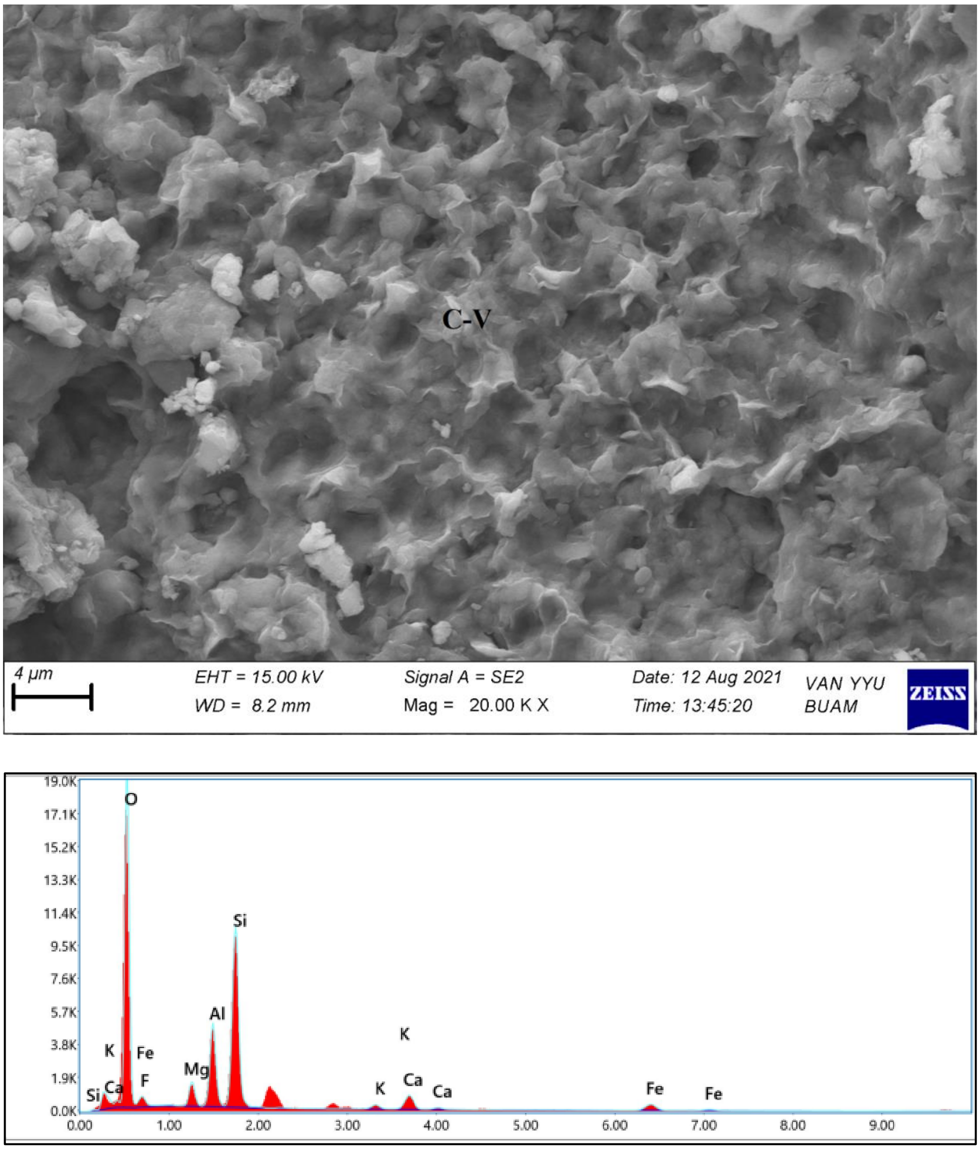


Figure 14. Microphotograph (above) and microchemical analysis diagram (below) of the chlorite-vermiculite (C-V) mixed layer clay mineral observed in the MB2-16 sample.

4. DISCUSSION AND CONCLUSIONS

In the Muş Basin, where this study was carried out, the carbonate rocks of the Bitlis massif and the ophiolitic mélange form the basement of the basin. The sedimentation that continued from the Late Cretaceous to the Quaternary enabled the formation of a basin filled approximately ten kilometers thick on this basement [5]. Oligo-Miocene aged rocks constitute a significant part of this basin fill, four kilometers thick [1].

Serdar [19] studied the Oligocene aged clayey rocks cropping out around Karakale, Taşlıca and Gültepe villages (Muş), and found that the samples taken from these rocks along measured sections showed quartz, feldspar, mica, calcite, amphibole and clay minerals in whole-rock compositions, and smectite illite, chlorite, serpentine and mixed-layer chlorite-smectite and illite-smectite in clay fractions. The Oligocene-aged units studied by Serdar [19] are conformably overlain by the Early Miocene-aged rocks studied in this study. In addition to non-clay minerals such as quartz, feldspar, mica and calcite, minerals such as chlorite, serpentine and illite were determined in both studies. In this study, different minerals such as clinoptilolite and mixed-layer chlorite-vermiculite were detected. In Serdar's study [19], smectite, mixed-layer chlorite-smectite and illite-smectite stand out as different minerals.

The rocks in which both studies were carried out were formed in a continental shelf environment [20,8]. For this reason, it is normal that the calcite mineral determined in the whole rock mineralogy was formed by chemical means. $CaCO_3$ can precipitate from seawater as a result of the following process [21].

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$$
$$CO_3^{2-} + Ca^{2+} \leftrightarrow CaCO_3$$

In SEM and EDS studies, micrite formed in this way was determined (Figure 12). Calcite can also be found in fossil shells such as foraminifera, red algae, bryozoa, ostracod, echinodermata, pelecypod, gastropod, and brachiopod [22]. It can be interpreted that the fossil shells described by Eser [8] and observed in the SEM study (Figure 11) also contain the mineral calcite. Therefore, it can be interpreted that the calcite mineral is of chemical and biogenic origin.

Quartz, feldspar and mica minerals were determined especially in rocks containing clastic material. For this reason, it has been interpreted that they were transported from pre-Miocene rocks.

The clinoptilolite mineral, determined in whole rock and clay fractions of the rocks, is not found in Oligocene aged rock samples [19]. Oligocene aged Kazanan Formation contains carbonate lithic tuff (Sakınç [6]). It can be said that clinoptilolite, a zeolite group mineral, was formed by the devitrification of volcanic glass contained in tuff clasts carried into Early Miocene rocks as clastics.

Illite, serpentine, chlorite, and mixed-layer chlorite-vermiculite type clay minerals were determined in the clay fractions of the samples. Illite is the clay size equivalent of mica minerals transported from the Bitlis Metamorphics. It can be interpreted that the serpentine mineral, which is commonly found in ophiolitic rocks as a decomposition product of the olivine mineral, is derived from the ophiolite basement rocks (serpentinite) (it is of detrital origin). It was determined in the SEM-EDS study that chlorite minerals are rich in iron elements (Figure 13). It is highly probable that the iron-rich chlorites were transported from ophiolite rocks, which are the basement rocks of the Muş basin.

The rocks of the study area were formed in the marine environment. Mixed-layer chlorite-vermiculite minerals can form in marine environments through the degradation (negative transformation) of chlorite [23]. This transformation takes place as follows.

Chlorite —> Chlorite -Vermiculite —> Vermiculite —> Vermiculite-Montmorillonite

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Türker YAKUPOĞLU and Kerem ERDOĞANLI contributed to the study conception and design equally. All authors read and approved the final manuscript.

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MINERALOGICAL AND GEOCHEMICAL PROPERTIES OF THE MIOCENE ROCKS OUTCROPPING AROUND TUZLUCA (IĞDIR-TÜRKİYE)

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ABSTRACT

In this study, the Miocene lithostratigraphic units (Turabi, Çincavat and Tuzluca formations) outcropping in the Neogene Kağızman-Tuzluca Basin in the west of Iğdır province were studied. The units are represented by evaporitic, carbonate and clayey rocks. This study aims to determine the mineralogical and geochemical properties of these rocks and to interpret the data to evaluate paleodepositional conditions. For this purpose X-ray diffraction (XRD) whole rock and clay fraction, Optical Microscope (OM) studies, X-ray fluorescence (XRF) element identifications and, Field Emission Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (FESEM-EDS) analyses of rock samples taken along the sections measured in the field were carried out. Quartz, feldspar, mica, calcite, gypsum and halite minerals were determined in whole rock compositions of the samples. Smectite, illite, chlorite and paligorskite minerals were found in the clay fractions. OM, FESEM-EDS and XRF studies indicate that the origins of gypsum, halite, calcite and palygorskite minerals are authigenic while chlorite, illite, quartz, feldspar and mica were detrital. The predominance of smectite, as well as the presence of chlorite, illite and palygorskite indicate that the basin developed under alkaline conditions, mostly hot and humid, and occasionally arid and cold climates. The positive correlation of SiO_2 with MgO signifies the input of clay and other clastic materials to the basin. While high positive correlation (R^2=0.80) between Zn and Fe_2O_3 indicates the Zn element is of biological origin; high concentrations of Zn, Cu, Ni and Co suggest the high activity of the microorganisms.

Keywords: Tuzluca, XRD, XRF, FESEM-EDS, Origin

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1. INTRODUCTION

This study aims to interpret the mineralogical and geochemical properties of the Miocene units (evaporite, claystone, mudstone, sandstone, marl) cropping out near the Tuzluca district of Iğdır province (Türkiye) (Figure 1) in terms of paleodepositional conditions. It is the first comprehensive study on the determination of the whole rock and clay fraction mineralogy of the sedimentary rocks in the Tuzluca section of the Neogene Kağızman-Tuzluca Basin.

Most of the lacustrine basins in Türkiye were formed during the Paleogene and the Neogene periods [1-5]. The Neogene Kağızman-Tuzluca Basin (KTB) is one of the main Cenozoic basins located on the Eastern Anatolian Plateau (Figure 2). Mineralogical [6, 7, 8], geochemical [9], sedimentological [10-13], structural geological [14], and paleontological [15, 16] studies have been carried out in the basin until today. In previous studies regarding basin fill sediments, two different basin models have been proposed: the pull-apart basin [10, 13, 14] and the intermountain basin [11, 12].

In the eastern part of the Kağızman-Tuzluca Basin (Tuzluca section), the basement rocks consist of the Upper Cretaceous ophiolitic rocks (serpentinites), volcanics and marbles.

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Formations which constitute the main subject of this study, were firstly divided into three and named by Eşder [6]. Şen et al. [15] established the stratigraphy used today. These are Turabi (Lower Miocene), Çincavat (Middle Miocene) and Tuzluca (Upper Miocene) Formations (Figure 1). The boundaries of these formations are comformable with each other. Turabi Formation, consisting of evaporite, sandstone, claystone and marl, was deposited in environments ranging from fluvial to lake, but mainly in swamp environments. Flood plain sediments, caliche and temporary fluvial sediments form Çincavat Formation which the red color dominates. Evaporites, mudstones and siltstones are the main lithologies of this unit. Tuzluca Formation, which presents thick sequences near Tuzluca, consists mainly of bedded halite and gypsum, which are the product of a shallow saline lake environment. Claystone and marl are interlayered with evaporites.

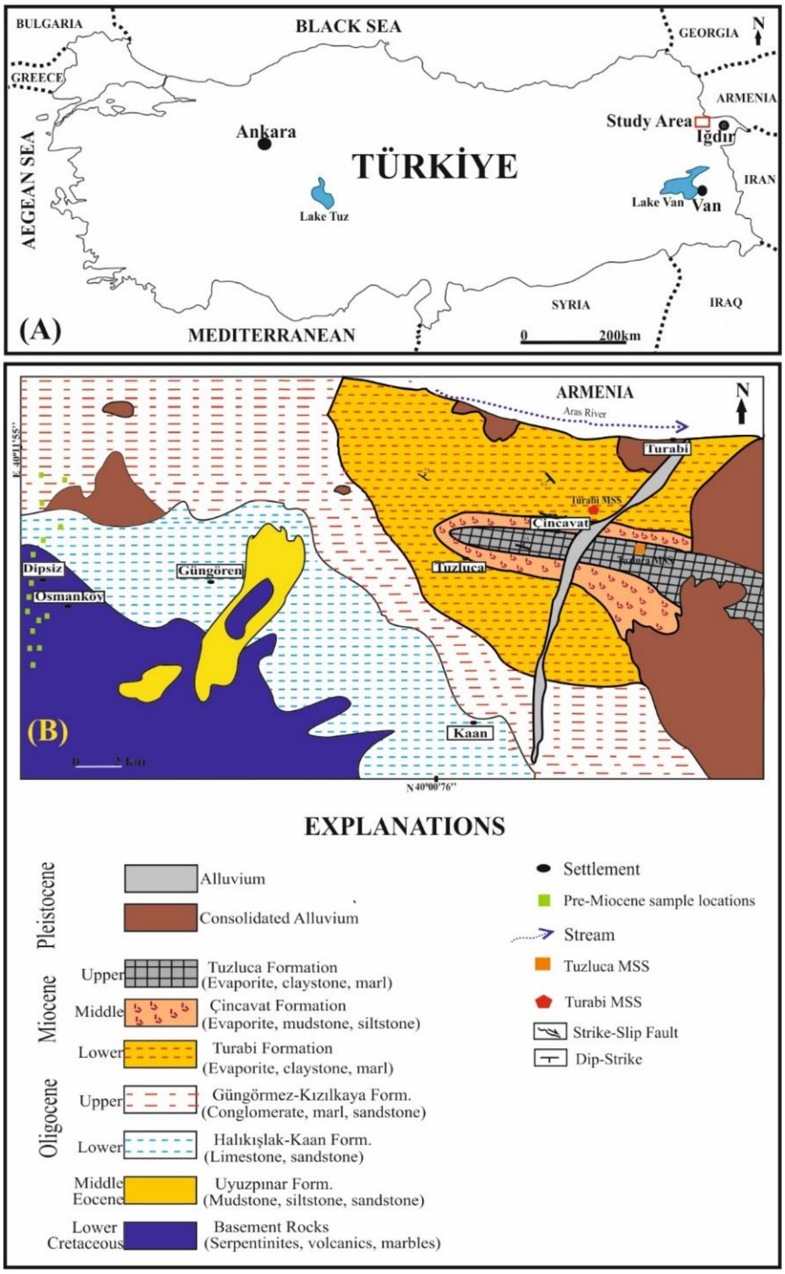


Figure 1. Location map (A) and geological map (B) of the study area (modified from [5])

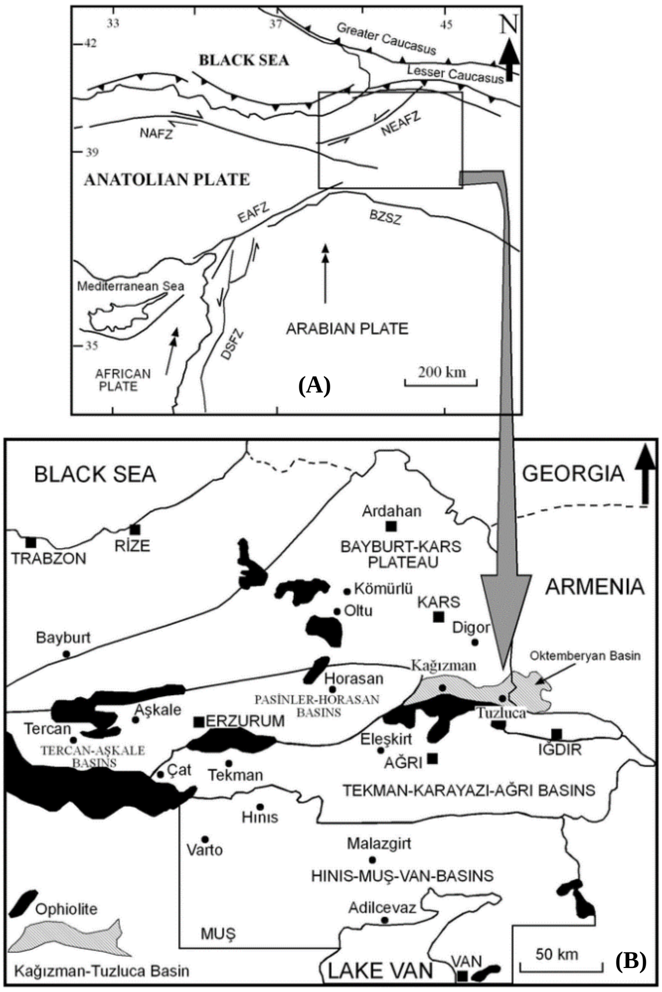
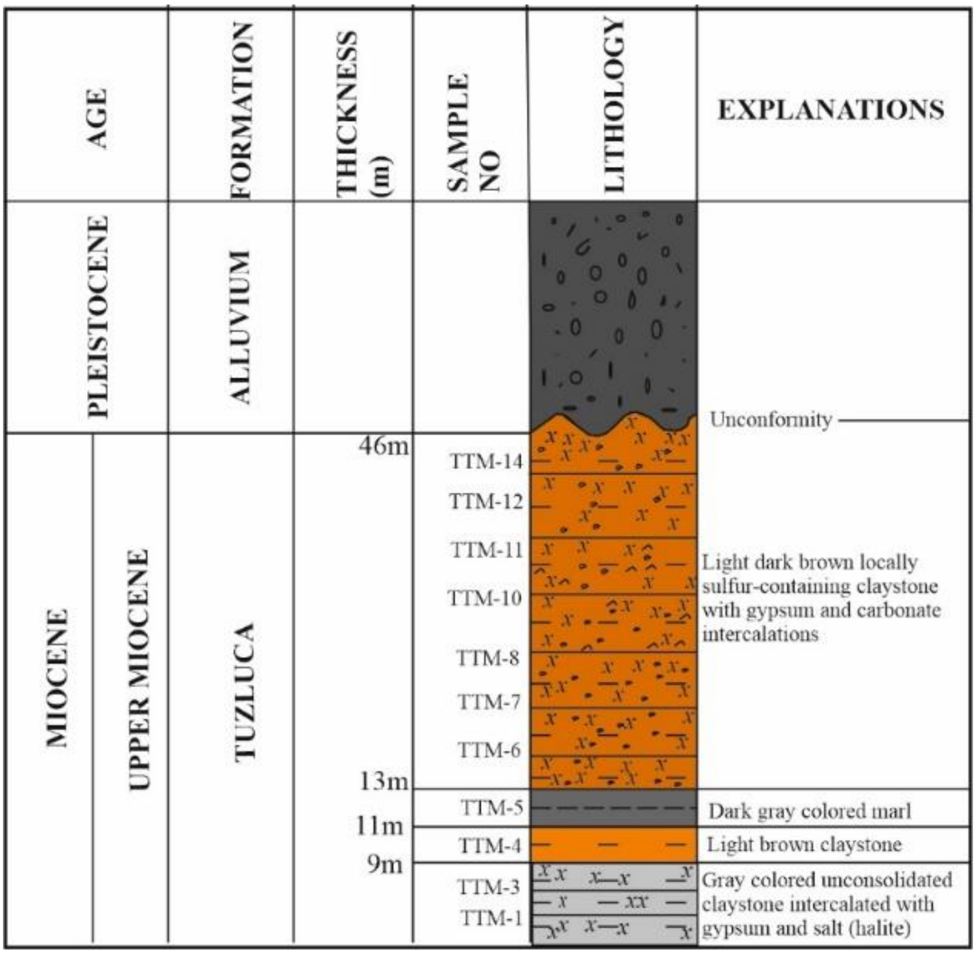


Figure 2. Structural geological elements of Eastern Anatolia (A) (DSFZ Dead Sea Fault Zone, KAFZ North Anatolian Fault Zone, KAFZ Northeast Anatolian Fault Zone, DAFZ Eastern Anatolian Fault Zone, BZSZ Bitlis-Zagros Suture Zone) and location map of Eastern Anatolian basins (B) (Modified from [5])

2. MATERIALS AND METHODS

This study utilized a total of 11 rock samples gathered from the stratigraphic section measured at the Tuzluca salt pit (Figure 3), along with 21 rock samples obtained from the stratigraphic section measured near Turabi village (Figure 4). Additionally, 15 rock samples sourced from pre-Miocene rocks were included in the study material.

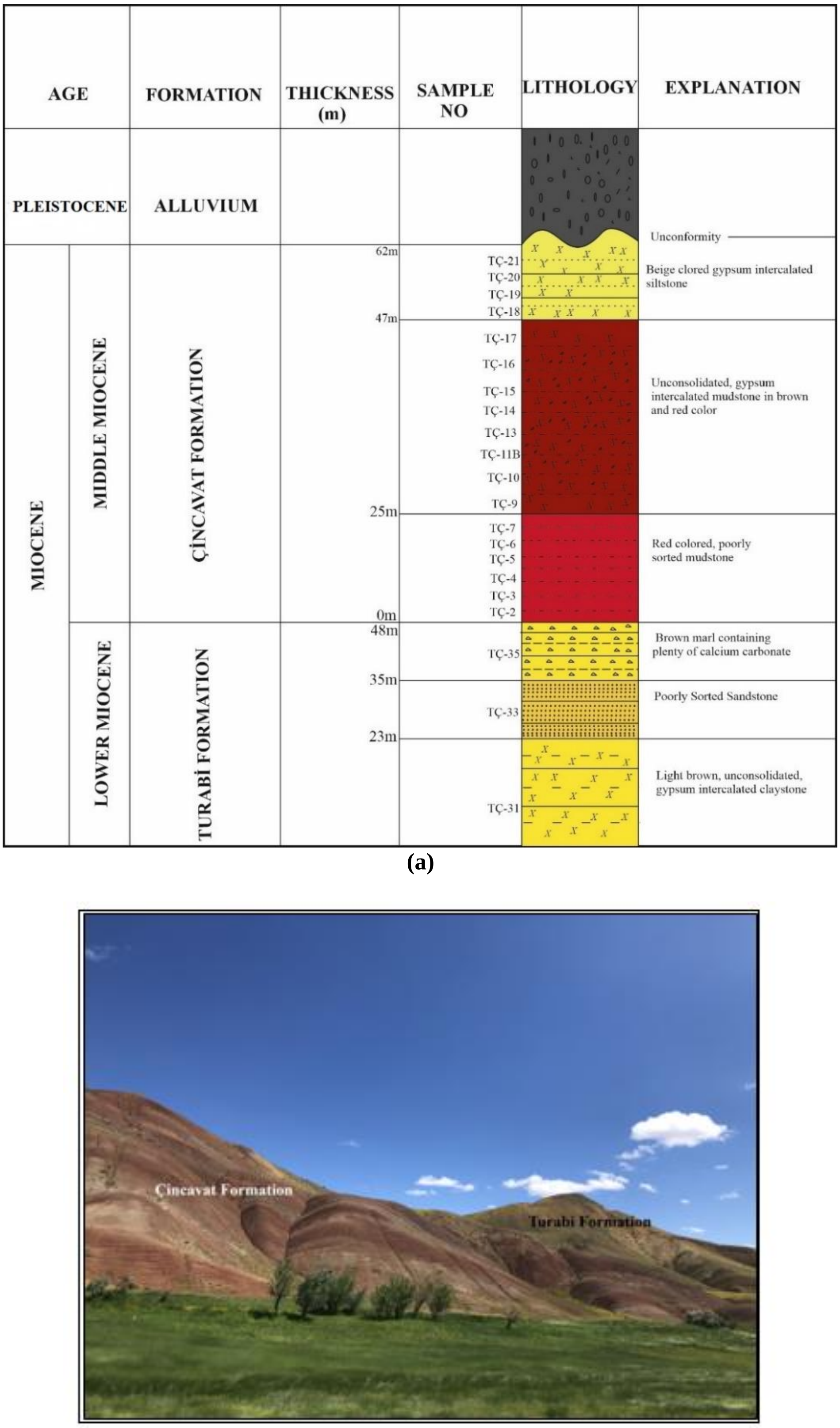
Detailed XRD clay analyses of all 32 rock samples taken along measured stratigraphic sections were carried out in the XRD Laboratory of the General Directorate of Mineral Research and Exploration (MTA), Department of Mineral Analysis and Technology. Diffractograms were evaluated with the help of relevant literature and by applying the Hanawalt method [17], and the minerals forming the whole rock and clay fraction of the samples were determined. Semi-quantitative abundances of minerals forming the bulk composition of the rocks were determined using Brindley and Brown [18]. Wilson [19]



(a)

(b)

Figure 3. Measured stratigraphic section of Tuzluca (salt pit) (a) and a view from the location of section (b)



(a)

(b)

Figure 4. Measured stratigraphic section of Turabi village **(a)** and a view from the formations **(b)**

and Moore and Reynolds [20] were used for the abundances, typical reflectances and mineral density factors of clay mineral fractions.

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) studies were carried out on 5 selected samples in the SEM laboratory of Van Yüzüncü Yıl University-Science Application and Research Center. In this study, the ZEISS SIGMA 300 model FESEM was used. During FESEM analysis, a Secondary Electron (SE) detector was used, which provides more detailed information about morphological features.

Microchemical analyses were performed with an AMETEK EDAX brand EDX detector connected to the FESEM device. While interpreting SEM and EDS studies, Welton [21] was used as the main reference.

An optical Microscope (OM) study was carried out in order to determine the minerals that make up the rocks and the texture of the rock and the rocks are named. For this purpose, a total of 15 sample thin sections were made at Dokuz Eylül University Torbalı Vocational School Rock Mechanics Laboratory, and they were examined and photographed using a polarizing microscope at Van Yüzüncü Yıl University Geological Engineering Department Microscope Laboratory.

Geochemical analysis of 10 selected samples was carried out at Ankara University Earth Sciences Application and Research Center by X-ray fluorescence (XRF).

3. RESULTS

3.1. Optical Microscope Study

The samples collected from pre-Miocene rocks in the Tuzluca section of the Kağızman-Tuzluca Basin were examined by optical microscope (the sample numbers, rock names, and nicol types are presented in Figure 5). Alterations were observed in almost all of the samples.

In serpentinites, serpentinization developed along pyroxene cracks and fractures, causing the pyroxenes to partially weather. A reticular texture has formed within the rock. Secondary quartz mineral with serpentinization has been formed. Iron oxidation has occurred in rock fractures (Figure 5a). Chloritization (0.1 mm size) is intensely observed in serpentinites (Figure 5b).

In basalts, olivine crystals have a highly fractured and fissured structure. Plagioclases are completely carbonated, and chloritization is observed in pyroxenes (Figure 5c). Plagioclase, pyroxene and olivine phenocrysts are in the matrix consisting of dense volcanic glass (Figure 5d). Calcite mineral is seen as the secondary mineral that fill gas space in the dacite sample (5e). Plagioclase minerals and volcanic glass have completely argilisied, and chloritization has been observed in Mg-Fe silicates (Figure 5e, f).

In the troctolite sample, olivine and plagioclase phenocrysts are evident. A Fe-rich zone was formed in olivine and iddingsitization has taken place. Polysynthetic twinning is observed in plagioclase (Figure 5g).

In the sandstone samples, the cement material is sparite (5h) or micrite (5j) and iron oxidation alteration has happened (Figure 5h, j).

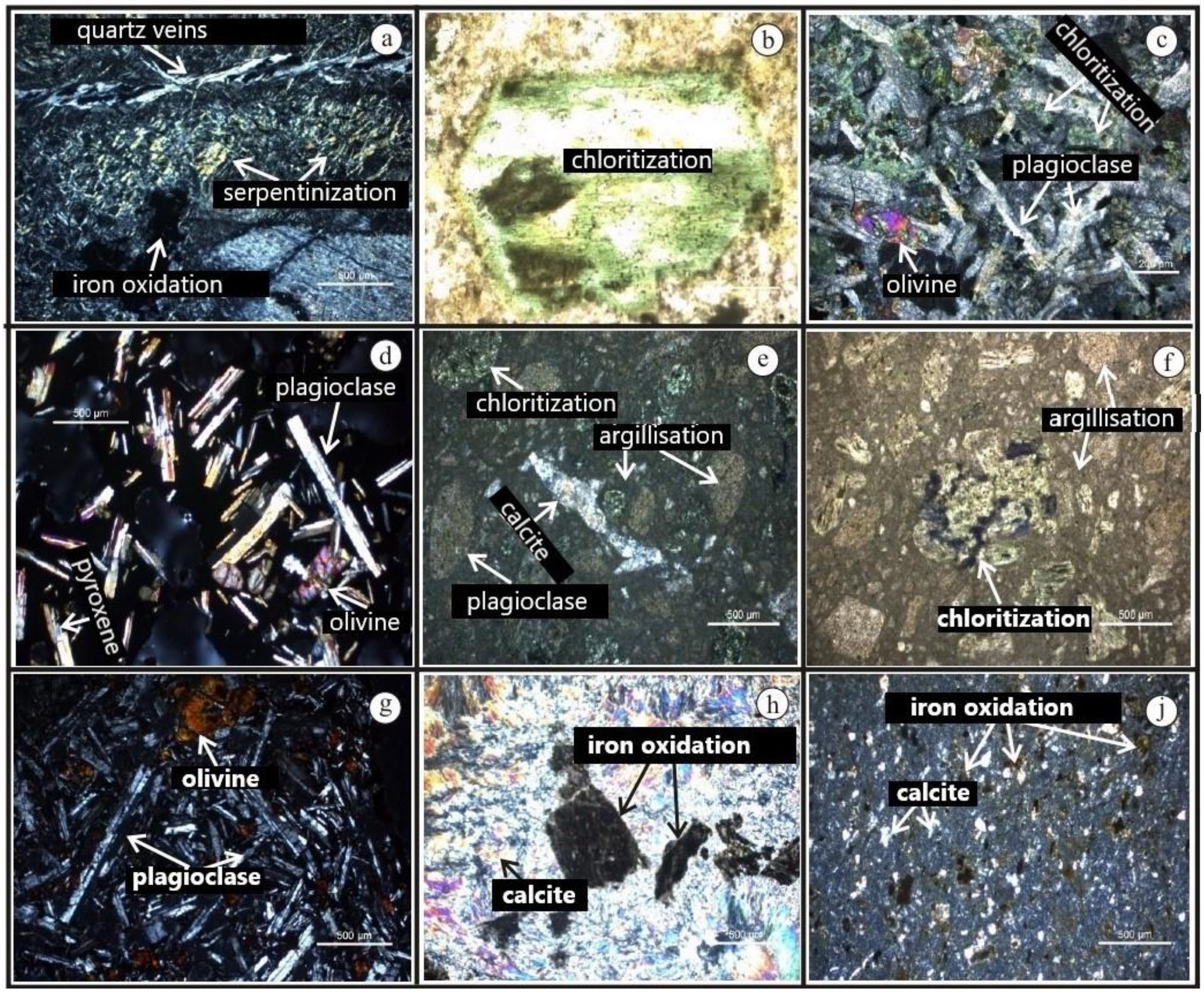


Figure 5. Photographs of thin sections of rock samples examined under optical microscope **(a)** KY9, Serpentinite, XPL **(b)** KY10, Serpentinite, PPL **(c)** KY6, Basalt, XPL **(d)** KY7, Basalt, XPL **(e)** KY13, Dacite, XPL **(f)** KY12, Dacite, PPL **(g)** KY8, Troctolite, XPL **(h)** KY3, Sandstone, XPL **(j)** KY4, Sandstone, XPL.

3.2. XRD Analyses

Quartz, feldspar, calcite, gypsum and halite are found in whole rocks of eleven samples taken from the Tuzluca Formation; Chlorite, smectite and palygorskite minerals were detected in the clay fractions (Table 1). In the samples, gypsum is 40-50%, halite 5-10%, quartz and calcite 20-30%, smectite and palygorskite 10-20%. 10% are other minerals. X-ray diffractograms of representative samples were put in Figure 6.

XRD analyses were performed on 3 rock samples of Turabi Formation and 18 rock samples of Çincavat Formation taken along the measured stratigraphic section of Turabi village. Quartz, feldspar, calcite, gypsum in whole rock; chlorite, smectite and illite/mica minerals in clay fractions were detected. Unlike the Tuzluca (salt pit) samples, palygorskite is not found in these formations. The mineral contents of the Çincavat Formation rocks are 40-50% quartz, 20-30% gypsum, 30-40% smectite and 10% other minerals. In the Turabi Formation, roughly 40-50% quartz, 10-20% feldspar, 10-20% calcite, 10-20% smectite and 10% other minerals (Table 1).

Table 1. Mineralogical composition of samples. Qz: Quartz, Fsp: Feldspar, Cal: Calcite, Gp: Gypsum, HI: Halite, Plg: Palygorskite, Chl: Chlorite, Sme: Smectite, Ilt/Mca: Illite and mica, acc: Accessory, +: Mineral abundance ratio, +: 10-30%; acc: ±10% (Mineral name abbreviations were taken from [22]).

Formation	**Sample No**	**Lithology**	**Qz**	**Fsp**	**Cal**	**Gp**	**HI**	**Plg**	**Chl**	**Sme**	**Ilt/Mca**
Tuzluca	TTM-1	Gypsum	acc	acc	acc	++++	++	acc	acc		
Tuzluca	TTM-3	Gypsum	acc	acc	acc	+++++					
Tuzluca	TTM-4	Claystone	+++	acc	acc			+	acc	+	
Tuzluca	TTM-5	Marl	++	acc	++			+	acc	+	
Tuzluca	TTM-6	Claystone	++	acc	++			+	acc	+	
Tuzluca	TTM-7	Gypsum	acc	acc	acc	+++++					
Tuzluca	TTM-8	Gypsum	acc	acc	acc	+++++					
Tuzluca	TTM-10	Claystone	acc	acc	acc	+++	++	acc	acc		
Tuzluca	TTM-11	Claystone	++	acc	++			+	acc	+	
Tuzluca	TTM-12	Claystone	++	acc	++			+	acc	+	
Tuzluca	TTM-14	Gypsum	acc	acc	acc	+++++					
Çincavat	TÇ-2	Mudstone	++	acc	++				acc	+	
Çincavat	TÇ-3	Mudstone	+++	acc	acc				acc	+ +	
Çincavat	TÇ-4	Mudstone	++	acc	++				acc	+	
Çincavat	TÇ-5	Mudstone	+++	acc	+				acc	+	
Çincavat	TÇ-6	Mudstone	+	++	acc				acc	++	
Çincavat	TÇ-7	Mudstone	++	+	acc				acc	++	
Çincavat	TÇ-9	Mudstone	++	+	acc				acc	++	
Çincavat	TÇ-10	Gypsum	+	acc	acc	+++			acc	+	
Çincavat	TÇ-11B	Gypsum	acc	acc	acc	+++++					
Çincavat	TÇ-13	Mudstone	+++	acc	acc				acc	++	
Çincavat	TÇ-14	Mudstone	+++	acc	acc				acc	+	
Çincavat	TÇ-15	Mudstone	+	acc	acc	+			acc	+++	
Çincavat	TÇ-16	Mudstone	++	acc	acc	+			acc	++	
Çincavat	TÇ-17	Mudstone	+	acc	acc	++			acc	++	
Çincavat	TÇ-18	Siltstone	+++	acc	acc	++					
Çincavat	TÇ-19	Siltstone	++	acc	acc	++			acc	+	
Çincavat	TÇ-20	Siltstone	++	acc	acc	+			acc	++	
Çincavat	TÇ-21	Siltstone	++	acc	acc	++			acc	+	
Turabi	TÇ-31	Claystone	++	acc	acc	++				++	
Turabi	TÇ-33	Sandstone	+++	++						acc	
Turabi	TÇ-35	Marl	++	acc	++	+			acc	acc	acc

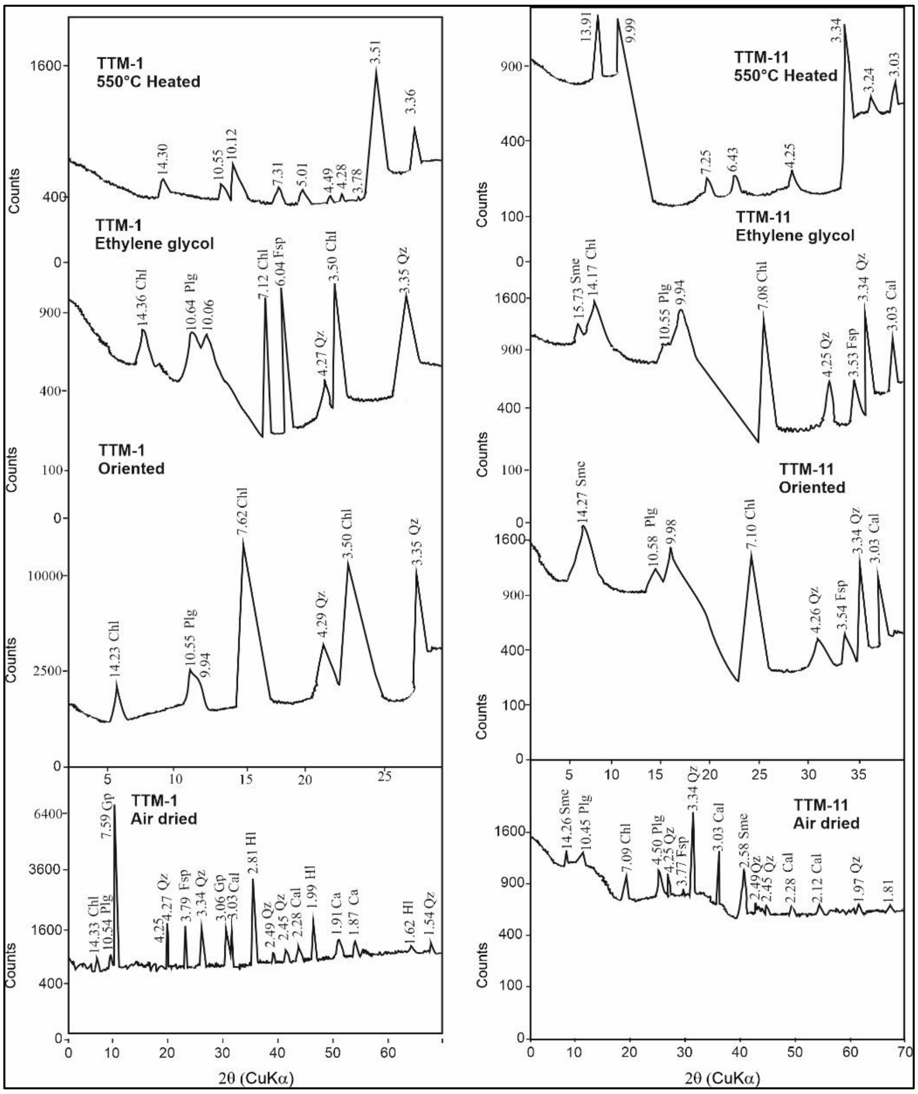


Figure 6. XRD diffractograms of TTM-1 and TTM-11 samples of the Tuzluca Formation (see explanations of Table 1 for abbreviations)

3.3. SEM-EDS Study

Scanning electron microscopy (SEM) and microchemical analysis (EDS) studies were performed on four samples. Among these samples, TTM-1 (Tuzluca) is gypsum, TTM-6 (Tuzluca) and TTM-11 (Tuzluca) are claystone, and TÇ-3 (Çincavat) is mudstone. SEM microphotographs of these samples with numbers and lithologies of them are given in Figure 7.

Gypsum mineral has a prismatic-looking structure. EDS analysis shows Ca (31,49%) and S (21,06%) (Figures 7a, b).

The feldspar grain appears to be surrounded by blocky, well-developed, planar outgrowths. EDS analyses show Si (34,93%) and Al (11,69%) values. In SEM analysis, prismatic-shaped gypsum minerals surrounded the smooth-edged feldspars (Figure 7b).

Chlorite mineral (EDS analysis Si (24.21%), Al (8.96%), Mg (3.07%), Fe (30.54%)), which is an accessory mineral, has developed around the cubic halite mineral (EDS analysis Na (13.28%), Cl (10.47%)) (Figure 7c).

There are calcite minerals (EDS analysis Ca (58.90%), O (30.47%)) around the smooth-edged quartz grain (EDS analysis Si (38.79%), O (52.76%)) (Figure 7d).

The smectite mineral, which consists of leafy plates and has a honeycomb appearance, is seen together with the fibrous palygorskite mineral (Figure 7e, f). While the EDS analysis results of the smectite are Si (24.48%), Al (8.79%), Mg (5.01%), Fe (27.90%), those of the palygorskite are Si (24.72%), Al (9.62%), Mg (6.17%), Fe (7.75%)).

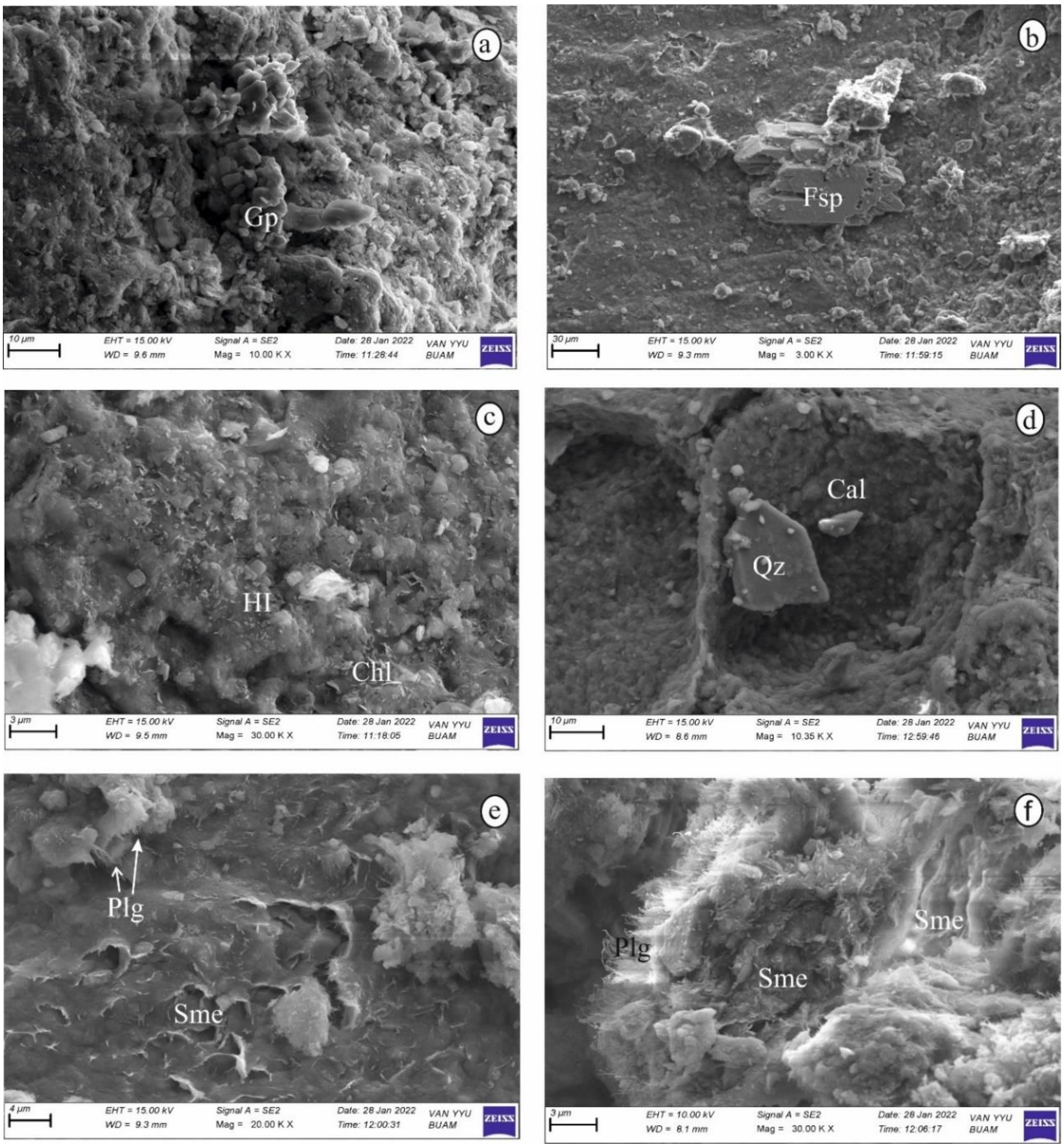


Figure 7. SEM microphotographs of samples **(a)** TTM-1, gypsum **(b)** TTM-1, gypsum **(c)** TTM-1, claystone **(d)** TÇ-3, mudstone **(e)** TTM-6, claystone **(f)** TTM-11, claystone

3.4. Geochemistry

Major oxide and trace elements results of samples of the study area are put in Table 2.

Table 2. Major oxides (% weight) and trace elements (ppm) contents of the samples (Gp: Gypsum, Clst: Claystone, Mdst: Mudstone, Sltst: Siltstone, Ss: Sandstone)

	Tuzluca Formation					**Çincavat Formation**				**Turabi Formation**			
Major oxide (% weight)	**TTM-3 (Gp)**	**TTM- 10 (Clst)**	**TTM-12 (Clst)**	**TTM-14 (Gp)**	**Avg.**	**TÇ-6 (Mdst)**	**TÇ-14 (Mdst)**	**TÇ-18 (Sltst)**	**Avg.**	**TÇ-31 (Clst)**	**TÇ-33 (Sst)**	**TÇ-35 (Marl)**	**Avg.**
SiO_2	25.73	25.42	46.85	30.14	32.0	52.44	55.84	54.76	54.34	54.62	59.65	50.36	54.88
Al_2O_3	5.83	4.39	11.82	7.53	7.39	14.4	13.35	13.47	13.74	15.61	10.9	8.99	11.83
Fe_2O_3	3.62	3.28	6.86	3.43	4.30	8.54	7.26	8.21	8.00	7.07	5.47	4.73	5.76
MgO	3.69	10.15	7.28	4.02	6.28	3.75	2.93	2.55	3.07	2.13	2.22	1.39	1.92
CaO	26.2	27.23	7.72	14.12	18.31	2.42	1.92	2.30	2,21	1.18	1.33	13.8	5.43
Na_2O	0.07	0.05	0.73	0.10	0.20	0.80	1.59	1.01	1.14	0.94	3.27	2.33	2.18
K_2O	1.53	1.23	2.72	1.94	1.85	1.61	1.79	1.71	1.70	1.40	2.31	2.88	2.20
TiO_2	0.35	0.23	0.54	0.42	0.39	0.64	0.73	0.71	0.69	0.63	0.41	0.43	0.49
P_2O_5	0.13	0.09	0.13	0.11	0.12	0.10	0.12	0.11	0.11	0.09	0.14	0.09	0.11
SO_3	15.75	4.54	5.36	19.09	11.18	0.70	0.20	2.03	0.98	2.66	2.38	1.14	2.06
Cr_2O_3	0.01	0.06	0.02	0.01	0.01	0.01	0.02	0.09	0.01	0.01	0.03	0.01	0.01
V_2O_5	0.01	0.01	0.02	0.01	0.01	0.02	0.03	0.02	0.02	0.02	0.01	0.01	0.01
CI	0.26	0.17	0.59	0.17	0.30	0.45	0.62	0.015	0.36	0.27	1.13	0.01	0.47
MnO	0.07	0.14	0.07	0.03	0.081	0.09	0.16	0.10	0.12	0.01	0.04	0.10	0.05
Al_2O_3/TiO_2	16.6	19.00	21.8	17.9	18.9	22.5	18.2	18.9	19.9	24.7	26.5	20.9	24.0
LOI	14.82	21.83	9.83	16.3	15.69	13.82	13.83	12.93	13.52	13.82	10.83	13.93	12.86
Total	99.36	99.24	99.34	99.32	99.32	99.22	99.24	99.76	99.40	99.24	99.26	99.32	99.27
Trace elements (ppm)													
Co	14.0	27.8	42.4	39.9	31.02	39.6	50.3	32.3	40.43	41.9	49.7	30.5	40.7
Ni	106.2	71.3	235	160.1	143.15	86.2	75.3	83.8	81.76	20.7	79.4	25.7	41.9
Cu	24.0	19.0	24.2	49.4	29.15	71.3	29.4	69.2	56.63	35.8	45.9	17.2	32.9
Zn	33.0	27.6	59.9	37.2	39.42	78.3	76.6	91.7	82.2	51.5	64.5	32	49.3
Ga	7.0	6.8	12.3	9.8	8.97	17.7	15.8	18.8	17.43	19.3	13.4	12.1	14,9
Ge	0.4	0.8	0.7	0.4	0.57	1.8	1.1	1.5	1.46	0.9	1.6	0.5	1.0
As	9.8	20.2	5.6	5.0	10.15	5.6	4.5	5.2	5.1	2.7	9.9	4.8	5.8
Se	0.8	0.3	0.3	0.5	0.47	0.5	0.2	0.3	0.33	0.6	1.4	0.3	1.2
Br	4.6	12.6	7.1	4.3	7.15	20.5	12.8	1.8	11.7	6.7	26.2	1.1	11.3
Rb	29.9	25.2	52.2	32.6	34.9	62.7	53.9	67.5	61.3	67.2	57.3	51.9	58.8
Sr	5051	316	1021	213	1650	235	213	233	227	145	308	233	228
Hf	3.6	2.7	3.0	3.4	3.17	3.8	2.9	3.7	3.46	4.1	3.1	2.4	3.2
Zr	95	52.4	113.6	47.6	77.3	138.7	174.1	147.2	153.0	143.2	104.9	102.8	116.9
Nb	6.6	5.7	11.1	6.7	7.52	14.1	17.7	14.3	15.36	11.7	5.5	11.0	9.4
Mo	3.7	4.5	3.4	4.1	3.92	4.3	7.6	3.5	5.13	2.1	3.1	3.5	2.9
Cd	0.8	0.9	0.8	0.8	0.82	0.8	1.1	0.8	0.9	0.8	0.7	0.6	0.7
In	0.9	0.8	0.9	0.8	0.85	0,9	0.9	0.8	0.86	0.8	0.7	0.9	0.8
Te	1.2	1.2	1.3	1.2	1.22	1.2	1.2	1.2	1.2	1.1	1.2	1.3	1.2
I	1.9	1.7	2.1	3.6	2.32	2.2	2.1	2.2	2.16	2.1	2.3	3.5	2.63
Cs	3.5	3.5	3.6	6.7	4.32	3.7	3.6	3.7	3.66	3.6	3.7	3.7	3.66
Ba	358	76.5	465.9	91.3	248.7	522.1	298.1	538	452.7	410.6	874.2	488.1	590.3
La	7.2	7.5	13.8	15.8	11,07	21.4	24.5	24.3	23.4	7.4	13.8	13.6	11.6
Ce	10.0	26.4	28.0	20.0	21.1	52.2	31.3	52.4	45.3	26.6	26.4	23.5	25.5
Y	0.7	7.8	10.8	6.1	6.35	19.6	20.1	24	21.23	8.6	15.2	13.1	12.3
Ta	4.4	3.0	3.8	4.3	3.87	4.5	3.2	4.6	4.1	3.3	3.7	3.2	3.4
W	3.6	2.4	3.5	3.0	3.12	2.7	6.4	2.7	3.93	2.2	40.7	40.3	27.7
Hg	1.0	0.7	0.8	0.7	0.8	0.7	0.7	0.7	0.7	0.7	0.9	0.8	0.8
Tl	1.0	0.8	0.8	0.7	0.82	0.8	0.6	0.8	0.73	0.7	1.3	0.8	0.93
Pb	12.6	8.2	3.4	4.3	7.12	11.3	10.1	14.3	11.9	9.6	9.7	9.5	9.6
Bi	0.7	0.6	0.6	0.6	0.62	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Th	2.8	2.5	2.1	2.2	2.4	9.9	6.5	8.5	8.3	8.7	5.3	5.4	6.46
U	13.3	14.1	17.7	8.4	13.7	8.8	16.9	8.9	11.12	7.2	6.8	7.7	7.23
Sr/Ba	14.08	4.13	2.19	2.33	6.65	0.45	0.71	0.43	0.50	0.35	0.35	0.47	0.38

In samples with high SiO_2 content, quartz accompanies clay minerals.

The increase in Fe/Al oxide ratios is noteworthy in the rock analysis of the Çincavat Formation. These increases indicate the input of terrestrial sediments, and the resedimentation under high energy conditions during maximum flooding [24].

The lower amounts of Na 1.09% and the more common Mg 4.01% in all samples prove that an ancient playa lake developed. Mg-salts or Mg-Al silicates such as palygorskite have been reported from various paleo-lakes [25].

SiO_2 has positive correlations with Al_2O_3 (R^2=0.74), Fe_2O_3 (R^2=0.63), Na_2O (R^2=0.56), TiO_2 (R^2=0.53), while has a negative correlation with MgO (R^2=0.36) (Figure 8).

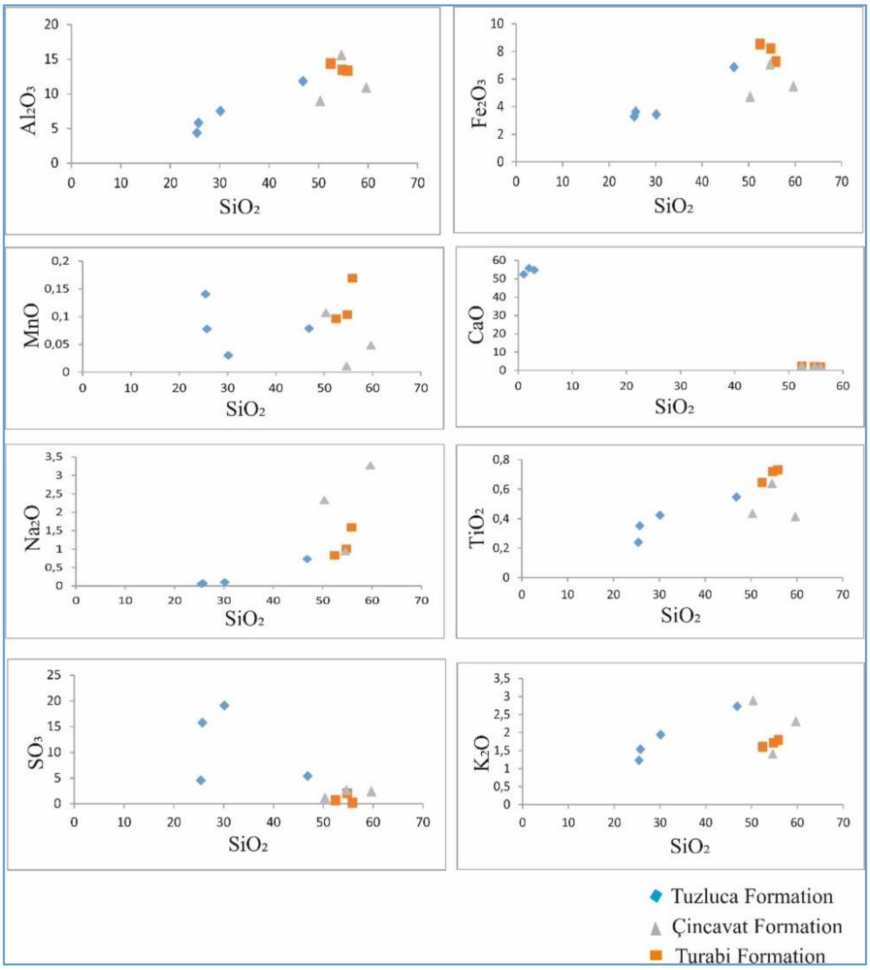


Figure 8. Correlation plots of SiO_2 versus Al_2O_3, Fe_2O_3, MnO, CaO, Na_2O, TiO_2, SO_3 and K_2O

In the chemically analyzed samples, trace elements Sr (avg. 227.4-1650.3 ppm), Ba (avg. 248.0-590.9 ppm), Rb (34.9-61.3 ppm), Co (31.02 ppm). 40,7 ppm), Ni (41.9-143.1 ppm), Cu (34.9-58.8 ppm), Zr (77.3-153.3 ppm), Zn (39,2-82,2 ppm) percentage rates were determined to be high (Table 2). The reason why these values are high is due to the influence of factors (hydrothermal solutions, ground-surface water and confined-closed reducing environment conditions, etc.) affecting the mineralogical and geochemical character of the lake water in different regions (lake shore, lake plain and deep lake area, etc.) during the evaporation of the region [27, 28, 30; 23].

Correlation plots of Al_2O_3 vs. Rb, Th, Zr and Fe_2O_3 vs. Zn values were drawn for the samples where elemental determination was made (Figure 9). The high positive correlation between Al_2O_3 and Rb, Th, Zr indicates that there were siliciclastic inputs into the depositional environment [30-33; 12]). The high positive correlation between Al_2O_3 and Rb (R^2=0.88), Th (R^2=0.65), Zr (R^2=0.73) in the analyzed samples and the feldspar and quartz minerals detected in XRD and SEM images support this view. The presence of a high positive correlation (R^2=0.80) between Zn and Fe_2O_3 indicates that the Zn element is of biological origin. In addition, Zn, Cu, Ni and Co elements and their high concentrations indicate the presence of microorganisms in the environment and the high activity of these organisms [12].

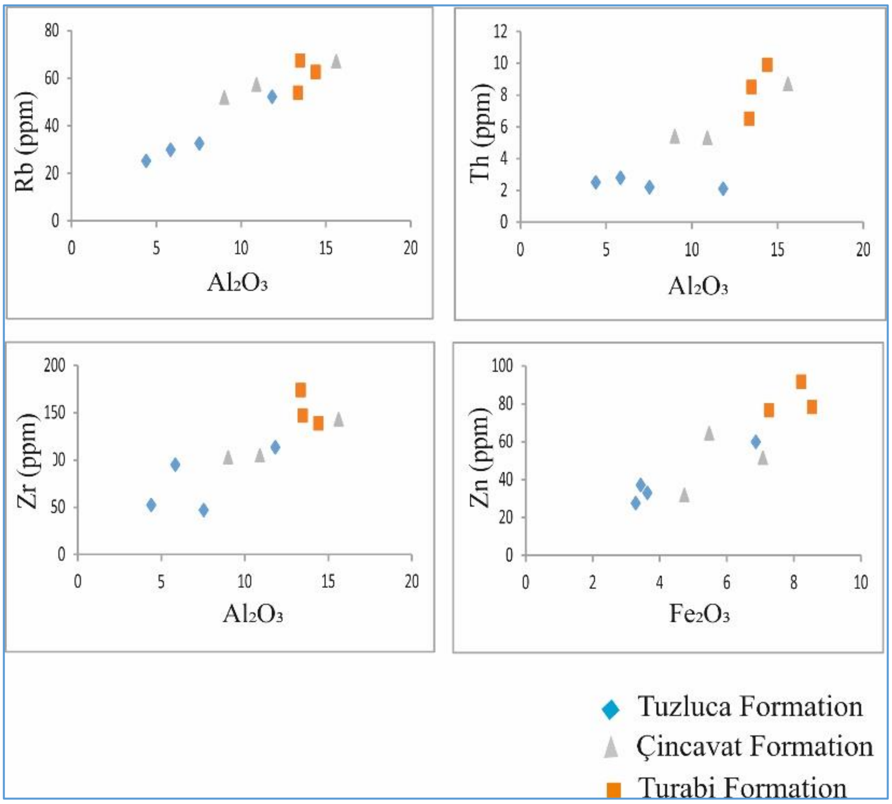


Figure 9. Correlation plots between specific trace elements and major oxides

4. DISCUSSION

In previous studies, it was interpreted that the rocks that constitute the subject of this study were formed in continental environments. While evaporites formed in marine environments have a Sr content of 1000-3000 ppm [34], evaporites in terrestrial environments have a Sr content of 50-200 ppm [35]. In the elemental analyses, Sr content shows values between (an average of 228.8-5051 ppm) (Table 2). Abdioğlu et al. [34] point out that simultaneous volcanism around the basin can increase Sr input into the environment and cause much higher Sr content than normal seawater. In addition, Sr content is also affected by hydrothermal solutions. The fact that there was no simultaneous volcanism during the period when the rocks were formed was interpreted as the excess in Sr content due to the effect of hydrothermal solutions.

Because low MgO values indicate detrital origin [36] the XRF results of samples of Turabi and Çincavat Formations show that the clay minerals (except smectite) are of detrital origin.

Carbonate precipitation is common in areas subject to frequent evaporation and solution concentration [37-39]. Calcite and dolomite are often the first minerals to precipitate during the concentration process. Dolomite has not been identified in the basin rocks. Calcite usually contains less than 5% mol $MgCO_3$. This is because it precipitates from more dilute solutions with low Mg/Ca ratios [40]. In the Tuzluca Formation, the Mg/Ca ratio is the lowest and the calcite ratio is higher.

Clay mineral assemblages are primarily a function of climate, and these minerals are affected by weathering time, slope, water-rock ratio, and water chemistry [41-45]. The fact that smectite is the dominant clay mineral in all three formations is related to an advanced degree of hydrolysis and shows that the climate is generally hot and humid [41-43]. However, the observation of illite and chlorite along with smectite in the Turabi Formation indicates that the environment was occasionally under cold and/or dry conditions [46]. In the Çincavat Formation, the dominance of smectite and the presence of trace amounts of chlorite indicate that the climate is warmer and more humid. It is interesting that palygorskite and magnesium smectite were identified along with gypsum in the Tuzluca Formation samples. The formation of fibrous clay forms such as palygorskite along with Mg-smectite in saline lake environments requires a hot climate, severe hydrolysis and evaporation. While high salinity primarily causes the formation of various salts, high alkalinity in the volcanic environment mostly causes the formation of zeolites [41]. The fact that volcanic material and zeolite minerals were not determined in this study was interpreted as the absence of volcanism in the basin during the period when the studied formations were formed.

The Sr/Ba ratio is an important indicator of paleosalinity [47, 48]. The classification is as follows: Sr/Ba <0,5 indicates brackish water, 0,5 <Sr/Ba <1 indicates a brackish lake, and Sr/Ba >1 indicates a saline water environment [49]. Tuzluca Formation Sr/Ba ratio (mean:6,65) indicates a saline water environment, Çincavat Formation Sr/Ba ratio (mean: 0,5) indicates a brackish lake environment and a brackish water environment, Turabi Formation Sr/Ba ratio (mean:0,38) indicates a brackish water environment.

5. CONCLUSIONS

In this study, the Miocene lithostratigraphic units (Turabi, Çincavat and Tuzluca formations) outcrop in the Tuzluca section of Neogene Kağızman-Tuzluca Basin were studied. The units are represented by evaporitic, carbonate and clayey rocks. Evaporites are common in Tuzluca Formation. Quartz, feldspar, mica, calcite, gypsum and halite minerals were determined in whole rock compositions of the samples. Smectite, illite, chlorite and paligorskite minerals were found in the clay fractions. Because of low MgO values and the increase in Fe/Al oxide ratios of the Çincavat Formation, clay minerals (except smectite) are interpreted as detrital origin. Palygorskite was only detected in the clay fractions of the samples of the Tuzluca Formation. Gypsum, halite, calcite and palygorskite are interpreted as authigenic while chlorite, illite, quartz, feldspar and mica were detrital. These minerals were formed in terrestrial environments without volcanic contribution. The high positive correlation between Al_2O_3 and Rb, Th, Zr indicates that there were siliciclastic inputs into the depositional environment. Clay minerals (smectite, chlorite, illite, palygorskite) suggest that the environmental conditions were alkaline. Smectite is the dominant clay mineral in the rock samples and indicate that the conditions were generally hot and humid. It also shows that there was severe hydrolysis throughout the basin. In addition, the presence of illite in the Turabi Formation signifies that cold and/or dry conditions developed in the basin sometimes. Palygorskite which is only detected in rock samples of Tuzluca Formation implies that the climate conditions were semi-arid from time to time during the period when this formation was formed. Sr/Ba ratios suggest a saline water environment for the Tuzluca formation, both a brackish lake environment and a brackish water environment for Çincavat Formation and a brackish water environment for Turabi Formation. The presence of a high positive correlation ($R^2=0.80$) between Zn and Fe_2O_3 signifies that the Zn element is of biological origin. In addition, Zn, Cu, Ni and Co elements and their high concentrations suggest the presence of microorganisms in the environment and the high activity of these organisms.

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Türker YAKUPOĞLU and Enver KARASU contributed to the study conception and design equally. All authors read and approved the final manuscript.

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THE ROLE AND IMPORTANCE OF MEERSCHAUM-TYPE SEPIOLITE IN THE PROMOTION OF TÜRKİYE

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ABSTRACT

The main factors in the recognition and promotion of countries, cities and regions can be summarised as economic strength, sports achievements, cultural accumulations, underground resources, and scientific and technological developments. Within the scope of underground resources, meerschaum-type sepiolite continues to be used in the production of ornaments, jewellery and souvenirs, and the display of items made of this type of sepiolite in showcases and museums in areas where other types of sepiolite cannot be used continues to ensure the recognition of the countries and cities where it is produced and processed. The meerschaum-type sepiolite is a magnesium-based clay mineral that has played an important role in the recognition and promotion of our country in the world for centuries. The role and importance it plays in the recognition and promotion of Türkiye is considered to be the work of its attributive properties based on its formation mechanism. Many of these unique features have enabled it to find more and more usage areas, turn into a work of art, and be recognised. This first recognised type of Turk sepiolite is described as an ambassador of culture and peace, as it has served as a bridge between our country and some countries for centuries. The quality of the Turk meerschaum-type sepiolite based on its superior properties, the fact that it has maintained this quality throughout the reserve for a long time, and the very important works created by valuable craftsmen and artisans are other points that play an essential role in the recognition of our country. In addition to training meerschaum masters and artisans when processed, it also creates significant added value. The export of raw meerschaum was banned in 1972 due to its importance in recognising and promoting our country by creating significant added value and training meerschaum masters and artisans. Meerschaum-type sepiolite has given birth to an important business line and a branch of art in Eskişehir. Meerschaum processing workshops, which are intensively visited by local and foreign tourists coming to Eskişehir, and the Meerschaum Museum in Odunpazarı district will accelerate the better explanation and promotion of this vital clay and the abandonment of the name "Vienna Stone".

Keywords: Clay, Sepiolite, Meerschaum, Promotion

1. INTRODUCTION

There are fundamental elements that are effective in the recognition and promotion of countries, cities and regions. These fundamental elements are stated under the following headings: (a) economic strength, (b) diversity and achievements in sports, (c) cultural accumulations (history, religion, beliefs, customs, art and artists), (d) scientific and technological developments and scientists, (e) tourism activities, diversity and achievements, (f) underground resources and wealth, (g) leaders and businessmen recognised by the world. The development, expansion and continuity of each of these topics makes a significant contribution to the promotion of a country, city or region. Each country's unique underground resources, such as mines, oil and natural gas, are promotional tools. Each of these underground resources is an important promotional tool for the country concerned and a natural resource that appeals to foreign countries. Meerschaum-type sepiolite is a very important mineral that has continuously fulfilled the most important role for centuries within the scope of underground resources and richness for our country [1-3].

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This study aims to emphasise that the richness and quality of Türkiye's underground resources can be promoted more effectively abroad, to draw attention to the attributes of meerschaum-type sepiolite, which has historical importance, and to offer solutions to the problems experienced (such as lack of domestic and foreign promotion, production, insufficient support).

2. TYPES AND PROPERTIES OF SEPIOLITE

2.1. Definition of Sepiolite

Sepiolite is a type of clay mineral that is composed of magnesium hydrosilicate. It belongs to the sepiolite-paligorskite (atapulgite) clay group. The most significant magnesium-based speciality clay is a type of sepiolite known as meerschaum. Experts suggest that it can be classified into two different models [4, 5].

(a) $Si_2Mg_9O_{30}(OH)_6\ (H_2O)_4\ .6(H_2O)$
(b) $Si_{12}Mg_8O_{30}(OH)_6\ (H_2O)_4.8(H_2O)$

Sepiolite in the theoretical (hence meerschaum-type sepiolite) has the following proportions:

SiO_2 / MgO ratio is 2.22, SiO_2 = %55.60 and MgO=%24.99

Mainly, though;

SiO_2 = % 53.90 ± 1.9
MgO = %21-25 [4, 5]

2.2. Types of Sepiolite

Three types of sepiolite formation have been identified in our country in terms of scientific studies, local nomenclature and matching definitions in the literature. These three types of sepiolite have been scientifically called "sepiolite clay" worldwide since the middle of the 19th century (1847) as a result of the examinations and research carried out by German Mineralogist E.F. Glocker. It is also known as "sepiolite" in Türkiye. The sepiolites of Türkiye are mainly divided into three subtypes (types) in terms of geological aspects brought about by the formation environment and shape, physical properties and other features:

(a) Meerschaum-type sepiolite (meerschaum, Eskişehir Meerschaum, lumpy/tuberous sepiolite, alpha (α) sepiolite, para sepiolite, white gold sepiolite),

(b) Sedimentary-type sepiolite (stratified/layered sepiolite, industrial sepiolite, industrial sepiolite, beta (β) sepiolite, Sivrihisar (Eskişehir) Sepiolite),

(c) Volcanic-type sepiolite (sepiolite of volcanic origin, hydrothermal sepiolite, Kıbrıscık (Bolu) sepiolite, aluminium sepiolite)

All of the economically exploitable deposits of meerschaum-type sepiolite formations, which are the subject of this study known for centuries, are located in the Eskişehir region in Türkiye. In the region, meerschaum-type sepiolite was formed in different areas of different sizes in the form of nodules independent of each other. Apart from the Eskişehir region, meerschaum-type sepiolite formations are encountered in a few regions of our country (Yunak-Konya, Gelendost-Isparta, Çanakkale, Kütahya) [5-9].

2.3. Properties of Meerschaum-Type of Sepiolite

The importance and value of meerschaum-type sepiolite for centuries and its role in promoting countries have emerged depending on its unique properties (attributes). These properties (mineralogical, physical, colloidal, rheological, catalytic, thermal, chemical, sorptive, etc.) have given this sepiolite type of our country a distinct privilege, superiority, quality and advantage. These attributive properties (completely specific to the meerschaum type) that determine the value of this type of sepiolite can be summarised as follows [2, 4, 6-8]:

(a) It is resistant to heat and fire, doesn't shrink, expand, crack or disintegrate, and can withstand temperatures up to 3800°C.
(b) Floats in water when dry, softens when wet/moist, becomes slippery, does not swell and does not disperse.
(c) It has a fibrous structure and good interlocking of its fibres provides resistance and the property of not dispersing in water.
(d) It does not crack, lightens, hardens and increases its strength when it loses its water/moisture/dries. It has the feature of absorbing nicotine, gas and water, it does not undergo deformation and keeps its volume the same.
(e) It does not crumble, crumble, break, crack or disperse when dropped/thrown on the ground.
(f) Microscopically, it does not contain foreign mineral and rock fragments, and capillary veinlets are not seen.
(g) It is slippery like soap, soft, easy to cut, chipped, processed and shaped in its original state. It also does not pollinate.
(h) It has a porous structure. This porosity provides lightness and natural moisture and increases the absorption feature.
(i) If the cigarette/tobacco smoke turns yellow when it absorbs nicotine, it can be whitened again by wiping it with cologne cotton.
(j) Even the dust and trimmings can be utilised for different purposes by pressing without wasting, leaving no waste/waste.
(k) Since it is suitable for making many ornaments based on its light weight (0.988–1.279 g/cm^3) and hardness (2-2.5), it is the most utilised metal in every respect.
(l) It can be polished, painted and lacquered, but its natural white colour is generally preferred.
(m) It occurs in compact, massive nodules and is predominantly uniform in colour (white).
(n) Non-transparent/opaque in appearance, pure, clean, characterised as a symbol of simplicity, peace and sincerity.
(o) After the final product is made, it gains a new appeal if the exterior is varnished/waxed to provide protection and shine.
(p) The homogeneous distribution of the components in terms of volume enables easy chipping and obtaining a spotless, white and smooth surface.
(q) It is an alkaline clay and when wetted and rubbed like soap, it dissolves and cleans the dirt on hands and clothes.
(r) When the pipe absorbs nicotine, if it is rested for a while (7-10 days) without being used, it vomits the nicotine absorbed.
(s) It can be coloured in all kinds of colours by wrapping it with special paper (marbling paper) and burning it, and it keeps its colour, it is permanent.

Besides these properties of meerschaum-type sepiolite, it is also desired to be of a certain size (dimension). This size feature is one of the criteria determining the quality. Criteria such as size, colour and processing quality are primarily sought. The size of the stone guides the master/craftsman. The size of the stone, which can be transformed into which product (artefact), is determined during the smoothing process in the chipping process.

In the Eskişehir region, seven sub-dimensions (group, type) are used in raw production and sales (Table 1). The ornaments, jewellery and souvenirs to be produced are also adjusted according to this size and selected from this size. The most important factors affecting the value of meerschaum-type sepiolite are perfection and size. A defect in the colour or texture of the nodule of this type of sepiolite, even if it is rare, greatly reduces its value. The classification and naming of meerschaum-type sepiolite is based on centuries of habit, experience and tradition rather than scientific criteria.

Table 1. Nomenclature of meerschaum-type sepiolite according to size [5].

Type/size	Explanation/comprasion
Sıramalı	4-5 pieces Pamuklu
Birimbirlik	2 pieces Pamuklu
Pamuklu	Suitable for making 1 pipe
Daneli	½ piece Pamuklu
Orta	¼ piece Pamuklu
Dökme/cılız	It consists of 300-400 pieces and is evaluated by the sack (weight is 40 kg.)

Pamuklu has an average weight of 200 grams. Very rarely, larger lumps (pieces) called "omuzlama" and "budama" can be produced. Approximately 15% of meerschaum-type sepiolite belongs to the first four sizes (sıramalı, birimbirlik, pamuklu, daneli), while approximately 85% belongs to orta, dökme, and cılız [5].

2.4. The Nomenclature of Meerschaum-Type Sepiolite

Meerschaum-type sepiolite is known by many different names in the world and Türkiye. These different names have increased and continue to increase the production centre, importance and value of meerschaum-type sepiolite for centuries. Lûle is derived from the Persian word "Lûle" meaning pacifier, mouthpiece for smoking tobacco. Lûle, tobacco stick, pipe and hookah are also called the "nest" that allows tobacco to be placed on the ends of products such as pipe and hookah. In science (geology); as a result of the naming of mineralogist A. F. Glocker, it has been named as sepiolite since 1847, in Europe as königin (queen) or king (king), and in Vienna (Austria) as Vienna Stone (Wiener stein). German: meerschaum (sea foam), English: sea foam/sea foam, Italian: schiuma di mare, French: Écume de mer, Latin: spuma maris, Latin: sepiolite, Helen: halos hachne, Greek; sepion (cuttlefish), Czech; mořská pena, Swedish; sjöskum, Finnish; merenvaha, Portuguese; espuma de mar, Spanish; sepiolita (for all types of sepiolite).

Meerschaum-type sepiolite has also received various local names in our history. For example; Old Uyghur Turk; Tolay kopugu, Ottoman Turk; derya kopugu, among the people and in different regions of our country; meerschaum, Eskişehir Lületaşı, Eskişehir Taşı, Aktaş, Patal, Patal Taşı, Soap Foam, Sea Foam, White Gold, Lûle Lülü (mouthpiece, stick, peace stick) (Nusret Güngör's personal interviews with meerschaum producers and artisans and domestic and foreign experts on various dates).

3. RECOGNITION, IMPORTANCE, AND REASONS FOR PREFERRING MEERSCHAUM-TYPE SEPIOLITE

3.1. The Importance of Promoting a Country: A Historical Perspective on Awareness

Archaeological excavations show that meerschaum-type sepiolite has been known in the world for about 5,000 years and has been used for various purposes. This sepiolite type of the Eskişehir region can be dated as the oldest. This point can also be confirmed by some archaeologists.

Eskişehir, which is an important region in terms of meerschaum-type sepiolite, has economic potential in terms of agriculture, industry and trade. Mineral deposits within the provincial borders play an important role in this potential. The main minerals important for Eskişehir are meerschaum-type sepiolite, magnesite, boron, manganese, perlite and chromium. Meerschaum-type sepiolite is considered to be the oldest of these mines according to its historical development [10].

The work by Ali Bin Abibakr Al-Haravi, who travelled around Anatolia in 1173, is considered to be the first source in which meerschaum is mentioned. However, in this work, the author did not give any information about the use of meerschaum [11, 12]. Meerschaum-type sepiolite became a mineral that Europe recognised and started to demand, especially after the 1850s. The Austro-Hungarian Empire was the main buyer of meerschaum and the country that both made the main profit from meerschaum and introduced it to Europe and the world. Detailed information on the export of meerschaum and the Austro-Hungarian connection can be found in Viennese sources. In a report published on June 3, 1886, by Das Handels-Museum, it was stated that Vienna had a history of over half a century in the meerschaum industry. In other words, it is seen that Vienna's connection with Eskişehir goes back to the 1830s [11].

Charles Texier stated that in 1834 meerschaum-type sepiolite was monopolised by the Ottoman Empire. At that time, meerschaum was sold only in the general warehouses in Eskişehir and its export was carried out by the Ottoman Empire and a chest of meerschaum was purchased for 1.500 kuruş, i.e. 625 francs. This price is a good monetary value according to the conditions of that day and corresponds to 30 gold coins according to the Ottoman market [10, 13]. In the absence of roads and vehicles developed to today's standards, one of the most important problems was the transport of the ore rather than its export. Until the advent of railway transport, the transport of meerschaum-type sepiolite purchased in Eskişehir was carried out by merchants through animals (camel caravans). This road between Eskişehir and İznik was named "Meerschaum Road" by A. Reinhardt. Meerschaum-type sepiolite, which reached İstanbul from İznik, was shipped to Belgrade and Budapest and from these centres it passed into the hands of Viennese merchants. Since no customs tax was levied on meerschaum-type sepiolite by Austria, Vienna became the centre of its exploitation and trade. In other words, the meerschaum-type sepiolite trade was almost entirely dominated by Viennese merchants in the 19th century [10, 14].

Meerschaum-type sepiolite, which has been more recognised in the world for centuries, especially in Europe, is still known and promoted as "Vienna Stone" abroad, although not as much as in the past. However, the fact that this sepiolite, which is of the highest quality and used in any field, belongs to Türkiye (Eskişehir) has not been explained and promoted knowingly or unknowingly. This type of sepiolite has been recognised in our country for about 550 years, and has been better known and continues to be better known for the last 250 years. However, the awareness and recognition of this sepiolite type is not sufficient for our country. It is known that as a result of being smuggled abroad for centuries and being marketed as raw or processed, it has caused the depletion of important quality reserves.

Researchers agree that Ali Osman Denizköpüğü, one of the meerschaum veterans, was the person who started the meerschaum business in the Republican period. He was given the surname Denizköpüğü because of the award he won as a result of a competition organised in Italy [12]. The first workshop was opened in the bazaar with Ali Osman Denizköpüğü, whom Ataturk met and guided, and many masters and craftsmen were trained. The apprentice-master relationship continues, although not at the desired level.

Festivals have been organised to promote this type of sepiolite both domestically and globally. The "International White Gold Festival" organised every year in September-October between 1988-1991, the first of which was in 1988, was aimed to make this natural quality in Eskişehir more aware, to promote it more comprehensively on a global scale, to train masters and artisans/craftsmen and to better explain its economic value. Significant progress has been made in this regard in the years mentioned.

In addition to being used in ornaments, jewellery and souvenirs, meerschaum-type sepiolite has been used in state protocol, homes, guesthouses, showcases and museums for a long time in areas where other types of sepiolite cannot be used. This situation has enabled the country and especially the cities where it was produced and processed to be promoted in history. This first recognised type of Turk sepiolite is essentially an ambassador of culture, tourism and peace for our country. It is known that it has fulfilled and has been fulfilling the duty of a bridge between our country and some countries for centuries. Meerschaum-type sepiolite, a special clay mineral that has played this role naturally and without any effort for centuries, continues to increase its importance and value both in the world and in our country, although not enough [5, 15, 16].

When its raw exports were stopped in 1972, especially after this year, meerschaum-type sepiolite provided the birth and survival of both an important business line and a branch of art in Eskişehir. The quality of the Turk meerschaum-type sepiolite based on its superior properties, the fact that it has maintained this quality throughout the reserve for a long time, and the very important works of valuable masters and artisans/craftsmen within the scope of semi-precious metal/stone play a very important role in the recognition of our country [5, 7].

The first museum in the world dedicated to only one type of a mineral was established independently in the early 1990s by the Governorship of Eskişehir. In the following years, this museum was moved to the Kurşunlu Kulliye established by Odunpazarı Municipality in 2008 (Figure 1). The precious crafted products exhibited in this museum are the works of craftsmen and artisans from Eskişehir. The artefacts were donated during the establishment of the museum to explain the importance and promotion of meerschaum-type sepiolite, which is an important value for Eskişehir. This mini museum is an important step in the recognition of meerschaum-type sepiolite, but it is not enough. More visual promotion should be made through public service announcements to be made with the media (mass) communication tools and exhibitions to be established especially in schools for the final products. Odunpazarı Municipality also continues its national promotions under the title of "sea foam".

Figure 1. Views from the meerschaum museum in Odunpazarı/Eskişehir) (The images are taken from the web page of Türkiye Cultural Portal)

3.2. The Reasons for Preference

Meerschaum-type sepiolite, sometimes exported in raw form and sometimes smuggled during the Ottoman Period, was processed in Europe, especially in Austria, and gained an important commercial value for a long time and was used in the promotion of some countries and is still being used. The reasons for this uninterrupted preference abroad can be summarised as follows [5]:

(a) The quality of Turkish meerschaum, made from sepiolite, is superior due to its advantageous properties. Formation in the form of tubers, lightweight and size suitable for smuggling (in raw form),
(b) In the first years, the reserves at levels closer to the surface can be produced more easily in a shorter time and manually (manually),
(c) It is easy to process and transform into different works of art due to its rarity,
(d) As countries are introduced to Turkish meerschaum-type sepiolite, the commercial revenues for those countries increase continuously,
(e) Light, durable, easy to transport (can be carried by hand),
(f) The fact that its importance and value were not sufficiently known in Türkiye, especially in the the region where it was formed before the Republic of Türkiye,
(g) The fact that it has been well known, recognised, marketable and providing added value abroad for centuries,
(h) Colour (white) homogeneity, purity, cleanliness, simplicity and the ability to be formed and obtained in seven different accepted sizes,
(i) Every piece of particles and dust can be pressed without waste and can be commercially utilised for different purposes,
(j) Good awareness abroad of the continuous increase in the commercial value of the finished (crude) and especially the final product after processing,
(k) Being one of the first minerals exported abroad and being heavy in cost when processed,
(l) The fact that the apprentice-apprentice-master relationship was established centuries ago and continues uninterruptedly,
(m) Creating employment and being adopted as an important branch of art and advertising and promoting their countries.

3.3. The Main Regulations and Criteria for Meerschaum-Type Sepiolite

The export of meerschaum-type sepiolite was originally authorised in 1960. In the Ministerial Decree No. 7/3812 published in the Official Gazette of Türkiye dated 14.2.1972 and numbered 14099, its export was prohibited with the provision "... unprocessed Eskişehir Meerschaum and all kinds of trimmings" in the minerals section of the list of goods whose export is subject to licence. 06.06.2006/Export 2006/7 numbered Communiqué on Goods whose Export is Subject to Registration is also prohibited with "raw meerschaum and draft pipe". In this way, the prohibition of exporting raw meerschaum has led to the revival of meerschaum craftsmanship in Eskişehir and the opening of many workshops. Accordingly, meerschaum masters and artisans/craftsmen were trained in greater numbers in a certain period. On 27.10.1997, as a result of the application (no: C 97/02) made by Eskişehir Chamber of Industry, the Turk Patent Institute issued a "geographical indication registration certificate" as "Eskişehir Meerschaum" with registration number 26 on 07.01.1999. Everyone and every sector has important duties for the quality required by this certificate, traditionalism, belonging to a certain region, having products that have gained a certain reputation, protection, transferring them to future generations, and more promotion in the world, especially in our country.

Meerschaum-type sepiolite, briefly known as "meerschaum", is included in the "precious and semiprecious stones" section of Group V in the mineral groups listed in Article 2 of the Mining Law no. 3213, and is processed and evaluated as "semi-precious Stones". In this group of stones, there is an international "4C rule" which determines the properties and quality of the stone. The 4C rule consists of the initials of four characteristics in English. These characteristics are (a) colour, (b) carat weight, (c) cut, and (d) clarity. In addition to the characteristics of the 4C rule, "4 basic criteria" are sometimes taken into account. These criteria are; formability, cutability, workability, and polishability. Meerschaum-type sepiolite fully complies with the 4 basic criteria and partially complies with the 4C rule (approximately 2/4 = colour and cut predominantly).

3.4. Transition from Underground Resource to Final Product/Value and Problems Experienced

The process of discovering and utilizing meerschaum-type sepiolite as an underground resource can be broken down into several stages. Firstly, the material was sourced from underground, and then it was mined and transformed into industrial raw material. Afterwards, it became clay and eventually became magnesium-based clay. From there, it became sepiolite and was refined into meerschaum-type sepiolite, also known as meerschaum. The next step was to produce it using a shaft-wheel-skip system, which resulted in a semi-finished product. This product was then turned into final products and exported or marketed domestically for commercial gain. Finally, the product was promoted to increase sales.

Meerschaum-type sepiolite is subjected to some processes in order to become semi-finished products after it is produced from the quarry. These processes can be counted as beating, counter-scaling, roughing, chipping technique, embossing technique, sanding, polishing, tandooring, wet aba, oil aba, polishing, sorting and boxing (crating). In addition, in the decoration of products made of meerschaum-type sepiolite, embossing technique, milling technique, soaking in wax, burning technique, marbling paper painting, and painting technique processes are applied [17].

The mining method of meerschaum-type sepiolite has been carried out for centuries without much change until today. After the 1960s, within the scope of modernisation in the mines, the production of a method called the spinning wheel method was changed to the skip method. In this method, there is an electric winch placed at the mouth of the mine pit, a compressor used from time to time in digging operations and motor pumps used to discharge the groundwater accumulated in the pit out of the pit. The quarries where meerschaum, also called wells, are operated can be classified as dry and wet wells according to the water status. Water can accumulate at the bottom of the quarries where water income is available. The water accumulated at the bottom affects the working environment and makes working conditions difficult. In these quarries, problems may be encountered in terms of operational safety. However, meerschaum produced from these quarries is of higher quality [12].

The problems encountered in mining in general (lack of financing, bureaucracy, lack of coordination, environment, property permit, transportation, lack of qualified personnel and expert engineers and fuel costs etc.) are also valid for meerschaum-type sepiolite. In addition to these general problems, there are also special problems related to this mine.

These problems can be summarised under the following headings (Nusret Güngör's personal interviews with meerschaum producers and artisans and domestic and foreign experts on various dates) [2]:

(a) Difficulty of raw (raw) production-mining-cooking water (groundwater) problem,
(b) Problems related to processing (producer, intermediary, master-artisan relations),
(c) Discontinuity of training, failure to train new masters and craftsmen,
(d) Lack or errors in marketing and promotion,
(e) Operational safety in terms of production activities and occupational health and safety for employees (especially spinning, shaft spinning, skip methods),
(f) Problems of organisation and lack of unity,
(g) Lack of literature, inventory, reports and scientific studies on informality,
(h) Other problems (local problems, labour, insufficient incentives... etc.).

3.5. Usage Areas of Meerschaum-Type Sepiolite

The areas where meerschaum-type sepiolite is utilised (used) are increasing day by day. There are thousands of patents in Spain and Japan for direct and indirect technological uses of sepiolite. In general, sepiolite is currently used in more than 100 fields. However, this type of sepiolite is used in specialised areas such as decorative household items, stationery products, clothing accessories and tobacco products, based on its superior properties, scarcity, diminishing reserves and the fact that it is the most suitable natural raw material/specialised clay for the production of many works of art only from this type. In addition, it is among the raw materials preferred in recent years in spaceships and factory chimneys [5, 15, 16]. Meerschaum-type sepiolite can also be used in areas where other sepiolite types are used. However, due to its low reserves and the increase in the known reserves of sedimentary-type sepiolite as a result of research, it is only used in areas with high added value. In addition, other types of sepiolites cannot be used in areas where meerschaum-type sepiolite is used.

Tobacco products: Pipe types, cigar mouthpiece, cigar mouthpiece, cigarette mouthpiece, hookah mouthpiece, tobacco box, tobacco tray, hookah, tamper.

Decorative household items: Magnet, incense holder, candle holder, panel, candlestick, table clock, jewellery box, prayer, picture frame, Ottoman/Turk head figures, famous/leading human figures, trinket, animal figures, sugar bowl, spice holder, napkin holder, different purpose box, chess set.

Clothing accessories: necklaces, bracelets, bangles, wristbands, buckles, earrings, rosaries, eyeglasses, strings, brooches (pins), thimbles, anklets, beads, key rings, walking sticks, pocket watches, belts, etc.

Stationery products: Pen holders, bookmarks, envelope openers, paper clips, pincushions, eraser holders, etc [5, 15, 16].

4. DISCUSSION

As is the same for all civilised countries, Türkiye faces great loneliness and loss in many areas, mainly economic, cultural and political, if the country is not promoted. In this respect, promotion in every respect is important and necessary for all countries. Some countries have unique underground resources. These resources play an important role in the culture, history, tourism, works of art and civilisation of that country and promote their countries abroad. Among these underground resources (mines) specific to our country, meerschaum-type sepiolite comes first.

From the past to the present, it should be well known that the meerschaum-type sepiolite found in Türkiye is a magnesium-based quality sepiolite clay, which is a mine with a historical past in the world.

This type of sepiolite has been much better known and recognised in Europe than in Türkiye for centuries. The fact that it has been smuggled from Türkiye to abroad for centuries, that research has been carried out on it, that it has been processed and exported to some countries of the world, especially from Vienna, and that it has been known as "Vienna Stone" dates back to ancient times. In this way, Vienna-Austria was both well-known and gained commercial value for centuries. The importance, value and indispensability of meerschaum-type sepiolite in the recognition and promotion of our country has been better understood after the commercial activities of meerschaum-type sepiolite were encouraged after the Republican period and started to be processed by masters and craftsmen from Eskişehir. However, the level reached today is not sufficient. Illegal production and informality, which cannot be adequately controlled, should be completely prevented and severe sanctions should be imposed.

Meerschaum-type sepiolite is among the most important minerals that have been ambassadors of tourism, peace and culture on behalf of our country for centuries. This type of sepiolite should be recognised and declared as a "national mineral" taking into account its historical background, importance and value.

The areas where meerschaum-type sepiolite is formed and the production sites must be taken under protection in terms of security and informality. If possible, geological formations (locations) and locations where this sepiolite is found should not be built.

Some exceptions and incentives should be introduced in the legislation related and related to meerschaum-type sepiolite in terms of production activities and the training of craftsmen and artisans.

The State should provide more support to those who produce and process the processed meerschaum type sepiolite (craftsmen and artisans) rather than those who buy and sell it. This mineral, as a historical mineral in the world, should be granted some more special privileges for it to reach the level it deserves, as it promotes our country as an ambassador of culture, art and tourism.

Since the mining of meerschaum-type sepiolite is related to many disciplines, especially geology, academicians, producers, exporters, craftsmen and artisans who are directly or indirectly involved in the mining of meerschaum-type sepiolite, and those who are responsible for implementing the relevant legislation should ensure that the problems are solved with common sense under a scientific roof. Producer associations should be established through a good organisation in the process, extending from production to marketing and these associations should be guided and supervised by experts.

Since meerschaum-type sepiolite is better known abroad than in our country, it would be appropriate to organise activities such as symposiums, panels and seminars by all institutions, organisations and relevant local administrations to prevent it from being known as Vienna Stone and to make our country better known in this regard. In addition, this important underground resource of ours should be better explained and promoted to our citizens through public service announcements to be made with the media (mass) communication tools and exhibitions to be established for the artefacts made from meerschaum-type sepiolite.

Turkish meerschaum-type sepiolite is very special and important in every respect. This point should be constantly emphasised, and the fact that there is no other mineral/clay that can be substituted for it should be well explained.

Meerschaum-type sepiolite, its quality based on its superior properties, the fact that it is a historical mineral and that it has been exported sometimes as raw since the Ottoman Period and that it has been processed in Europe long before has caused the reserve of this type of sepiolite to be consumed mainly years ago. There is a problem in terms of the reserves that can be obtained by manpower, generally for quality meerschaum-type sepiolite. No significant progress has been made in the operation/production of meerschaum below the groundwater level due to various reasons. Relevant public institutions and organisations should take the necessary initiatives in unity.

Production by the spinning wheel method continued until the beginning of the 1960s, and although the skip method was introduced, problems regarding production and reserves persisted. These problems should be solved by the relevant institutions and organisations with a common mind.

5. CONCLUSION

Every meerschaum is definitely sepiolite. However, every type of sepiolite is not meerschaum.

Türkiye is the only country in the world where three geological and mineralogical types of sepiolite clays have been identified. In terms of known reserves and quality, it ranks first in the world in all three sepiolite types. As can be understood from this, Türkiye is a sepiolite country without hesitation.

Meerschaum-type sepiolite has been economically produced in Türkiye mainly within the borders of Eskişehir province around the villages of Margi (Kozlubel), Beyazaltın (Sepetçi), Karatepe, Gökçeoğlu, İmişehir, Sarısu, Başören, Türkmentokat, Karatokat, Karaçay, Söğütçük, Kümbet, Kepeztepe, Karahoyuk, Yenişehir, Nemli, Gündüzler, Taycılar for about 550 years with mining activities. Sivrihisar-Eskişehir region is also the region with the highest sedimentary/industrial-type sepiolite reserves in Türkiye.

The superior properties of meerschaum-type sepiolite (colour homogeneity, whiteness, lumpy formation in different sizes, lightness, (porosity, easy processing, etc.) and the fact that it was first discovered as the highest quality in the world and based on this quality, it has ensured and continues to ensure that Eskişehir and Türkiye remain in the world market as raw and processed for centuries.

Meerschaum-type sepiolite is a valuable piece of jewellery worn on the body and clothes, which is easy to carry, light in weight, but heavy in value.

CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

The authors contributed to equally in all parts of the article.

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KAOLIN FORMATION IN YATAĞAN (MUĞLA) LIGNITE DEPOSIT

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ABSTRACT

The 30-km-long and 10-km-wide, coal-bearing Yatağan Basin is located in SW Anatolia, close to the eastern coast of the Aegean Sea, Türkiye. The basement consists of Menderes Massif metamorphics in the NW part of this intermontane basin, c. 80-km2-large area (Turgut lignite deposit). The Neogene and Quaternary sedimentary filling comprises fluvioterrestrial, limnic and telmatic sediments which contain a mineable coal seam up to 15 m thick, unconformably overlain the basement. Two fresh and six weathered samples were picked up from the Menderes Massif gneiss outcrops of the catchment area. Eight sedimentary rocks, inorganics over and underlying the coal seam, were obtained from four borehole cores. All samples were examined under the optical microscope; XRD, SEM-EDX and ICP-MS analyses were later performed. This study aims to examine the mineralogical content and geochemical processes of the sedimentary rocks from different formations, namely Sekköy and Turgut Formations, which are over- and underlying the lignite horizon, to assess the clay mineral formations and transformations. Gneiss samples contain mainly quartz, plagioclase, K-feldspar, muscovite and biotite with a lesser amount of tourmaline, chlorite, garnet, apatite, zoisite, zircon and Fe-oxides. The -2 µm fraction consists mainly of illite, with fewer smectite and kaolinite. Sericitizitation of feldspar is the main product in gneisses. Coal over-and underlying sedimentary rock samples contain mainly quartz, plagioclase, K-feldspar, muscovite, and biotite with less pyrite and iron oxides. The -2 µm fraction of the sedimentary rock samples consists of variable clay mineral contents. Kaolin content is higher in acidic conditions with an opposite correlation to smectite occurrences. The geochemistry of Menderes Massif gneisses shows that it gave felsic material to the catchment area, whereas the geochemistry of sedimentary rocks is not coherent in all cases. Geochemical parameters like CIA and PIA proved that weathering processes of the source materials prevailed during the generation of these sedimentary units.

Keywords: Turgut, Sekköy, Illite, Smectite, Kaolinisation

1. INTRODUCTION

Since Neogene times Western Anatolia experienced intercontinental tectonics, which formed NW-SE, NE-SW, and E-W trending basins [1-14]. The NW-SE trending Yatağan Basin is one of them being located in SW Anatolia, close to the eastern coast of the Aegean Sea, Türkiye. The 30 km long and 10 km wide basin is filled with Cenozoic siliciclastic and carbonate deposits [15-19]. In the NW part of Yatağan Basin, the Turgut lignite deposit is hosted, occupying a c. 80-km^2-large area; it contains a mineable coal seam up to 15 m thick. Lignite deposits are studied widely and extensively in the region regarding abundance, operability and priority of supply [20-23]. Feldspar, quartz and marble open-pit mines exist in the surrounding area as well. Moreover, the existence of the antique city Stratonikea in the south of Turgut area points to the economic importance of the region in the past, even in the 3rd century BC (Figure 1).

The economic clay potential is yet to be extensively investigated and interpreted in the study area. In addition, there is no study in the literature in which the clay minerals of these sediments are evaluated in detail in the light of mineralogical and geochemical data, field-wide (horizontal) and depth-dependent (vertical) and correlated with other existing findings. The present study focuses on the petrographic, mineralogical and geochemical compositions of the sedimentary rocks over- and underlying the coal seam. The aim is to research the clay mineral formations and to assess the existence of kaolinisation.

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2. GEOLOGICAL SETTING

The basement consists of Menderes Massif metamorphic rocks. The stratigraphy of the Menderes Massif is divided into two units consisting of the Late Neoproterozoic Pan-African basement and the Paleozoic-Early Tertiary cover series. In the study area, the observed units belonging to the Menderes Massif Pan-African basement are schist and orthogneiss. The units belonging to the Menderes Massif cover series are phyllite, quartzite, marble alternations succession and overlying platform type and pelagic marbles, respectively. The primary contact between these two series is a regional-scale Pan-African unconformity that defines a deep erosion [24-30].

The Miocene sequence, which unconformably overlays the basement, comprises three formations, namely those of Turgut, Sekköy and Yatağan Formations [18, 19, 31-35]. From bottom to top, Turgut Fm includes conglomerate, sandstone, mudstone, limestone, coal, mudstone deposited under alluvial fan, fluvial and lacustrine conditions, whereas Sekköy Fm comprises coal, silty claystone, mudstone, marl and limestone deposited under telmatic/lacustrine conditions. These formations are conformably overlain by the Yatağan Fm, which hosts conglomerate, sandstone, limestone-marl-mudstone deposited under alluvial fan and lacustrine conditions. Quaternary alluvial deposits constitute the Yatağan Fm (Figures 1, 2).

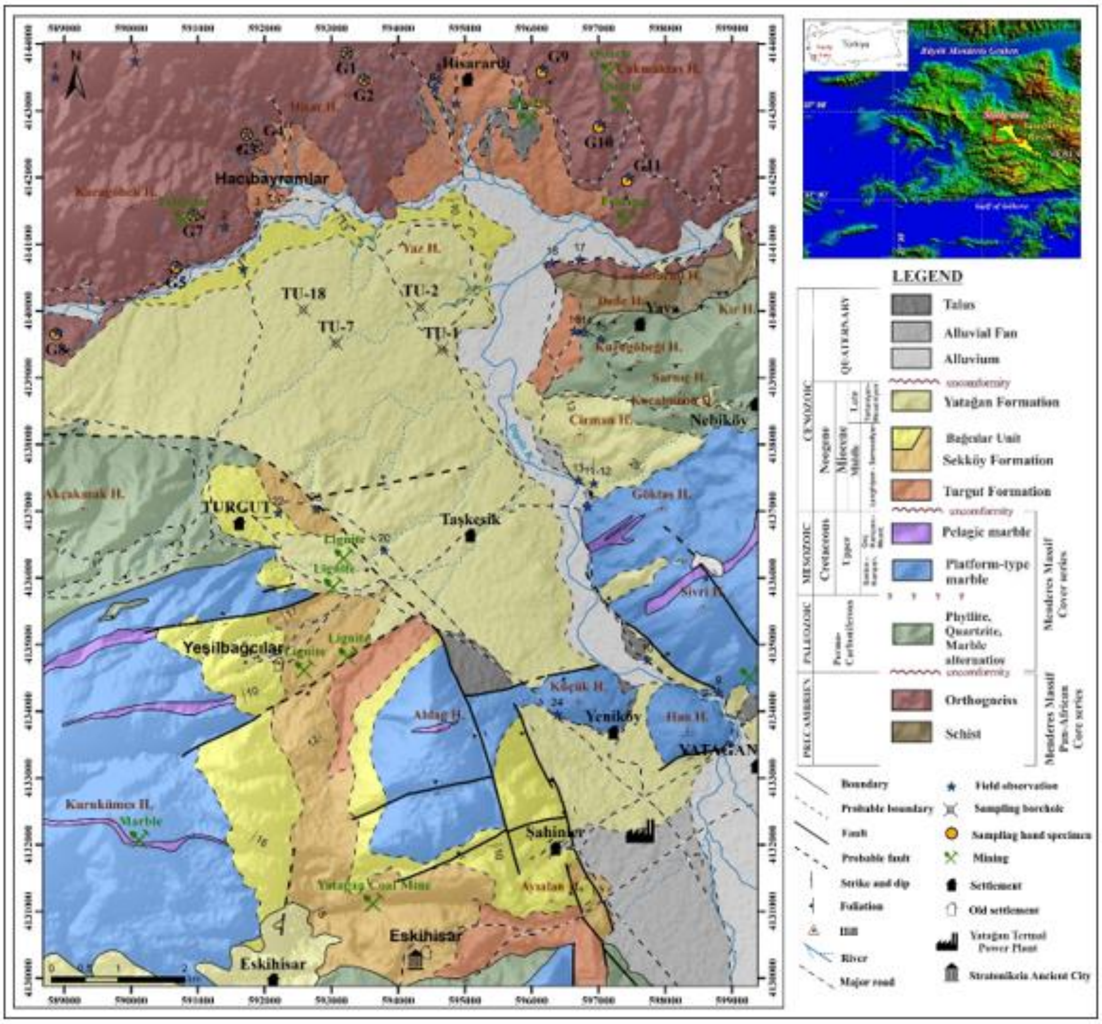


Figure 1. Geological map of Turgut area in Yatağan lignite deposit [18, 27-30].

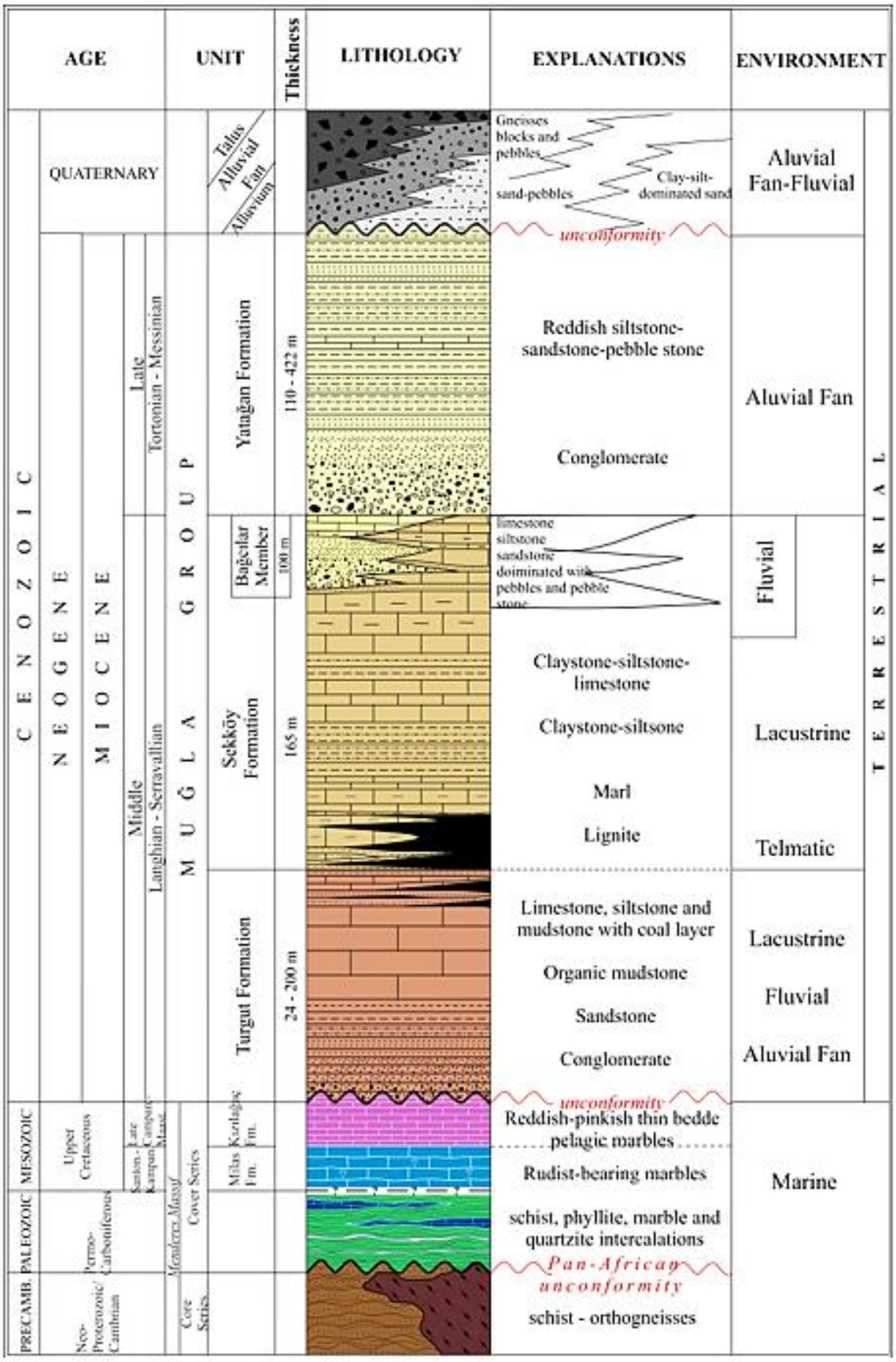


Figure 2. Stratigraphic column of Turgut area in Yatağan Basin [18, 19, 27-30].

3. MATERIALS AND METHODS

Based on field work the geological maps of previous studies [18, 27-30] were revised on a scale of 1:25,000. The geological map was digitised using UTM (Universal Transverse Mercator) projection type, WGS 1984 Datum and Zone: 35 in the ArcGIS™ software ArcMap 10.5 application. NASA Earthdata and 30-m resolution elevation data from the Shuttle Radar Topography Mission (SRTM) were used for the digital elevation model (DEM) [36, 37].

Two fresh,(G1, G5), eight weathered gneiss samples were collected from outcrops in the north margins of the study basin (Figure 1, 3). Eight sedimentary rock samples were obtained from four borehole cores, namely TU-1, TU-2, TU-7 and TU-18; the samples picked up from the coal-overlying layers received the code A and these from the underlying ones B (Figure 1, 4).

Figure 3. Outcrops of the Menderes Massif, Hisar Hill (see Figure 1).

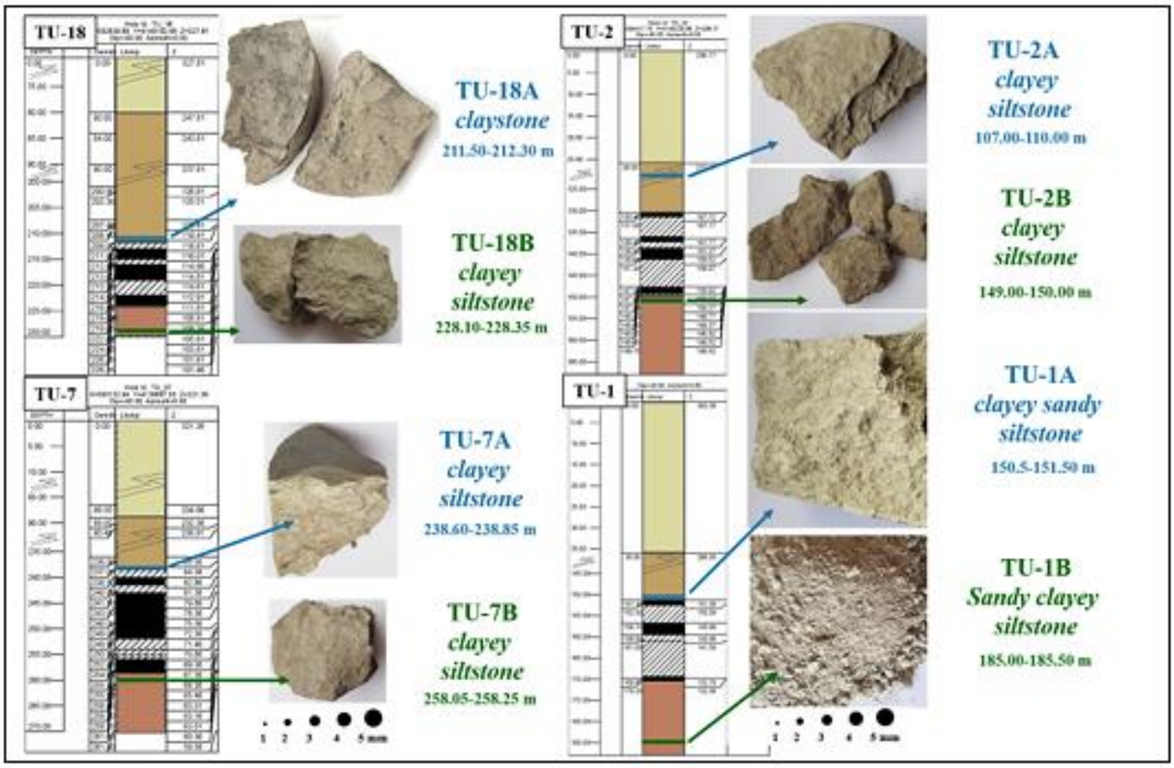


Figure 4. Borehole graphics and the sampled sedimentary rocks.

The gneiss samples were cut perpendicularly to the foliation and examined under the Leica DM750P polarized microscope. The sedimentary rock samples (fraction size > 63 μm) were examined for transformations also under the microscope. The studies were performed at the Department of Geological Engineering, Dokuz Eylül University (İzmir, Türkiye) and the photomicrographs were taken via the Leica DFC 290 HD attachment.

The XRD analysis was carried out on random oriented samples using a Rigaku MiniFlex 600 diffractometer at the Department of Geological Engineering, Dokuz Eylül University (İzmir, Türkiye) using CuKα radiation (k=1.542 Å). The diffractograms were obtained at 33 kV and 15 mA, scanning 2-65° of 2θ with a step size of 2°/min. The clay mineralogical composition was determined after separating the < 2 μm fraction in distilled water by centrifugation. The clay particles were dispersed through ultrasonic vibration for ~15 min. The clay fractions were vacuumed by pipette of the clay suspension and transferred to three glass slides to get oriented preparations. Three different XRD patterns were obtained from three different phases (air-dried, solvated with ethylene glycol at 60°C, and heated at 550°C for 2 h) of each sample at scanning 2-40° of 2θ. Semi-quantitative determinations were obtained by multiplying the intensities of the principal basal reflections of each clay mineral by appropriate factors. The analysing error is 5 wt.% [38]. The crystalline phase identification was carried out using the PDXL2 software package (Rigaku).

Andreasen pipette method was applied to sedimentary rock samples to quantify the < 2 μm fraction of each sample. Each sample was placed in distilled water to get a suspension. In order to prevent the suspended grains from coagulating and flocculating in the liquid, the pH of the suspension was increased by using NH_3, and in order to ensure that the grains were well dispersed in the liquid, the suspension was kept in an ultrasonic bath and mixed in an automatic shaker. The suspension was placed into an Andreasen pipette vessel, a narrow and high cylindrical glass container with a sedimentation column height of 200 mm, which has a 10 ml chamber sealed with glass stopper on the top and designed to draw samples from the bottom. Then the vessel was shaken vigorously and placed on a stable plane. The temperature of the pulp was kept constant at 23°C during the experiment; the pulp was drawn into the 10 ml chamber and taken out of the Andreasen pipette into a weighed beaker at specified time intervals, and the remaining body after evaporation was weighed again. Calculations were made based on Stoke's law and the clay grain size (< 2 µm) content of the sample was calculated according to the DIN 66115 standard [39].

Electron microscope examinations were undertaken on gold-coated gneiss and sedimentary rock samples (particle size > 63 µm) using a Carl Zeiss 300VP Scanning Electron Microscope (SEM) at Central Research Laboratories Research and Application Center (İKÇÜ-MERLAB), Katip Çelebi University (İzmir, Türkiye).

Whole rock chemical analyses were performed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) following a lithium borate fusion and dilute acid digestion of a 0.2 g sample in ACME Analytical Laboratories, Canada.

Abbreviations of the minerals and associated phases in the figures and tables follow the literature, which are listed in Table 1 [40, 41].

Table 1. List of the abbreviations of the minerals and associated phases [40, 41].

Symbol	Mineral Name	IMA status*	Symbol	Mineral Name	IMA status*
Afs	alkali feldspar	GROUP	Jd	jadeite	A
Alp	allophane	G	Kfs	K-feldspar	informal
An	anorthite	GROUP	Kn	kaolin	Group
Ap	apatite	GROUP	Kln	kaolinite	A
Bt	biotite	GROUP	Mca	mica	GROUP
Chl	chlorite	GROUP	Mnt	montmorillonite	G
Cpx	clinopyroxene	GROUP	Ms	muscovite	A
Di	diopside	G	Opq	opaque mineral	informal
Fsp	feldspar	GROUP	Pl	plagioclase	GROUP
Gbs	gibbsite	A	Py	pyrite	G
Grt	garnet	GROUP	Qz	quartz	A
Gp	gypsum	G	Ser	sericite	D
Hem	hematite	A	Sme	smectite	GROUP
Hly	halloysite	G	Tur	tourmaline	GROUP
Hbl	hornblende	GROUP	Zr	zircon	G
Ilt	illite	GROUP	Zo	zoisite	G
Others					
IO	*Iron oxides*				
ML	*Mixed-layer phases*				

* International Mineralogical Association (IMA) abbreviations: A = Approved; D = Discredited; G = Grandfathered (generally regarded as valid mineral name); GROUP = Name designates a group of mineral species.

4. RESULTS AND DISCUSSION

4.1. Petrographical and Mineralogical Investigations

The gneiss of the study area has porphyroblastic texture. The microscopic composition of these samples consists mainly of quartz, plagioclase, K-feldspar, muscovite, and biotite. Sericizitation of the feldspars is widespread, while argillization of K-feldspar is less (Figure 5 (a-d)). Chloritization of biotite is rare and chlorite comprises fibrous bundles (Figure 5 (e, f)). Garnet and turmaline minerals are relatively abundant to apatite, zircon and zoisite (Figure 5 (g-j)).

Major mineral composition of the gneiss samples as detected by XRD analysis are quartz, plagioclase, K-feldspar and mica minerals (Figure 6 (a)) and the relative abundances of these minerals are given in Table 2. Illite is the main clay mineral, while smectite and kaolinite determined in -2 µm fraction of the samples (Figure 6 (b)) and the semi-quantitative results of these clay minerals are given in Table 3.

SEM results show that the main transformation is sericizitation (Figure 7). Smectite formations from opal-CT is shown in Figure 7 (b). Rosette chlorite was determined in the gneiss samples showing the formation of chlorite from biotite. (Figure 8).

In many studies, orthogneisses, which are defined as "augen" or "granitic", have been named in various ways such as to describe the degree of metamorphism (sillimanite gneiss), deformation characteristics (mylonitic gneiss) and the rock of origin (orthogneiss) as well. Additionally, these intrusions are categorized into three groups based on their mineral compositions and classified based on the type and content of mafic minerals in the rock biotite orthogneiss, amphibole orthogneiss and tourmaline leucocratic orthogneiss [42, 43]. Based on their primary textures and mineral compositions, studied samples are biotite orthogneisses which are the most abundant type in the study area.

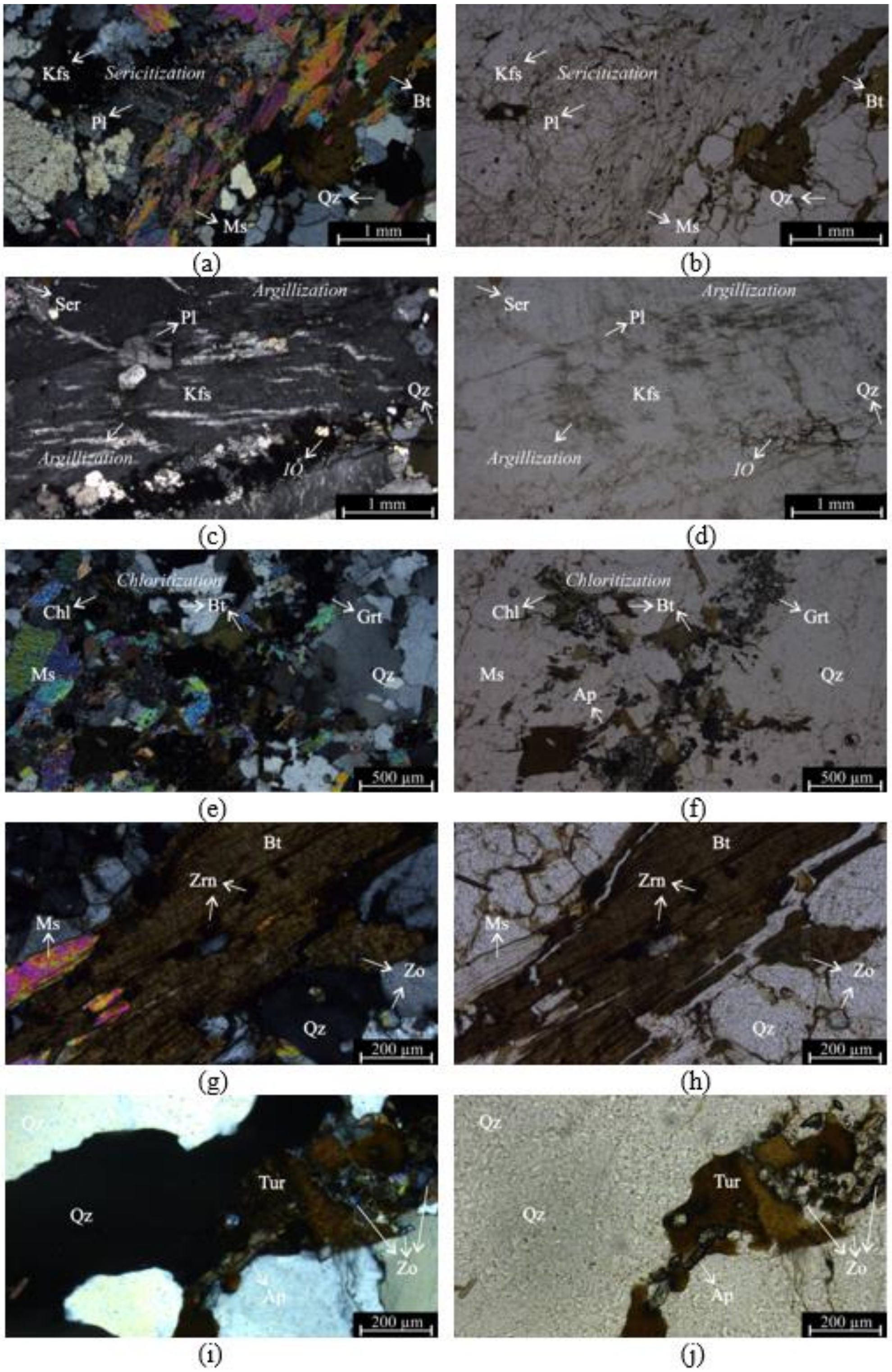
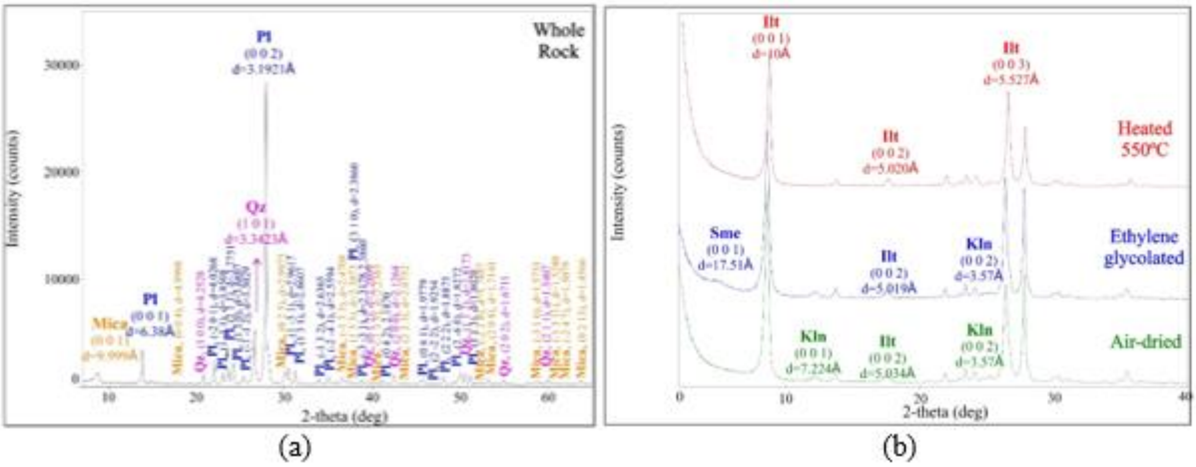


Figure 5. Photomicrographs of the gneiss samples: (a) with crossed polarizers. Sericitization of K-feldspar and plagioclase; (b) in plane polarized light (G9); (c) with crossed polarizers. Sericitization and argillization of feldspar minerals. Pertitic texture of K-feldspar; (d) in plane polarized light (G4); (e) with crossed polarizers. Chloritization of biotite; (f) in plane polarized light (G1); (g) with crossed polarizers. Zircon inclusions in biotite; (h) in plane polarized light (G2); (i) with crossed polarizers. Tourmaline, apatite and zoisite minerals; (j) in plane polarized light (G1).



(a) (b)

Figure 6. X-Ray diffractograms of (a) whole rock mineral compositions; (b) clay compositions of -2 μm fraction of G8 as a representative gneiss sample.

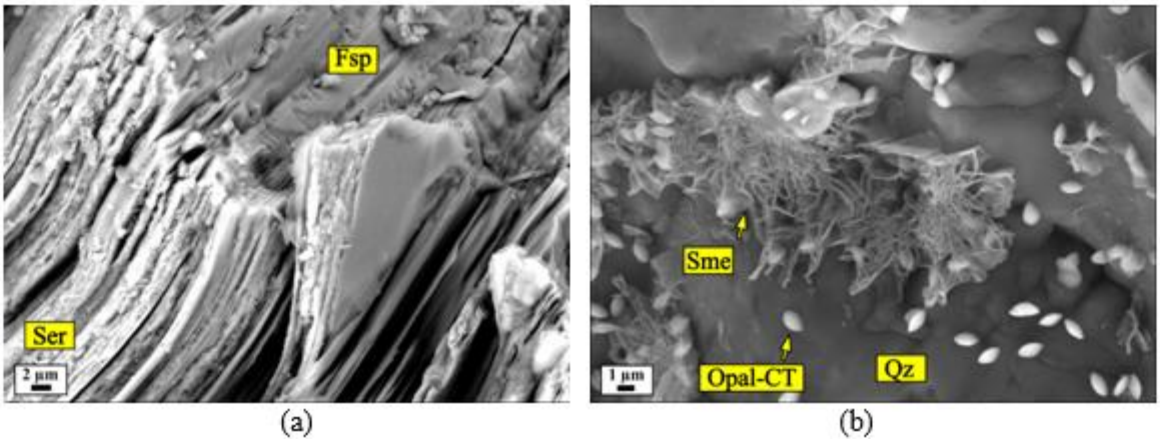
Table 2. Relative abundance* of minerals in the analysed gneiss samples.

	G1	G2	G3	G4	G5	G7	G8	G9	G10	G11
Qz	va	va	va	va	va	va	s	va	va	va
Pl	m	m	m	a	a	a	va	m	a	va
Kfs	vs	?	vs	vs	s	vs	?	?	vs	vs
Mica	s	s	s	m	m	s	vs	s	m	s

* va: very abundant, a: abundant, m: moderate, s: scarce, vs: very scarce.

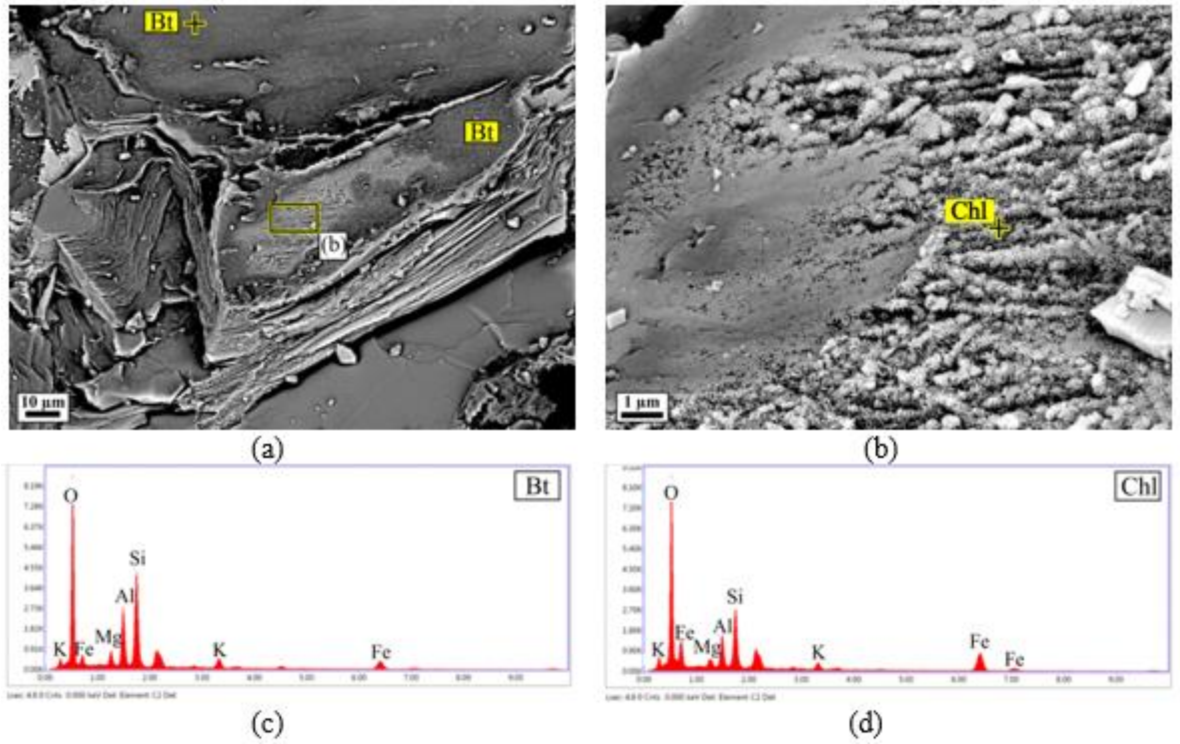
Table 3. Semi-quantitative results of clay minerals in the analysed gneiss samples (percentage of fraction size < 2μm).

	G1	G2	G3	G4	G5	G7	G8	G9	G10	G11
Ilt	100	97.9	100	100	91.7	94.3	94.4	94.3	100	97.1
Sme	-	-	?	?	8.3	?	3.2	?	-	1.9
Kln	-	2.9	-	-	-	5.7	2.4	5.7	-	1.0
Chl	-	-	-	-	-	-	?	-	-	-



(a) (b)

Figure 7. SEM images showing the (a) transformation of feldspar to mica mineral in the process of sericitization at the edges; (b) smectite formations from opal-CT.



(a) (b)

(c) (d)

Figure 8. SEM images (Sample G1) showing the (a) elongated biotite mineral; (b) close-up view of the rectangle that points to the rosette-like chlorite formations from biotite; (c) EDX analysis showing the major elements of biotite; (d) EDX analysis showing the major elements of chlorite.

Thin sections which prepared > 63 µm fraction size of the sedimentary rocks point to different features, except all contain sericitization. Coal-underlying samples mainly consist of sedimentary lithic grains, while overlying samples contain mineral grains, mainly quartz and lesser feldspar, with sericitization at their edges. Some samples have bioclast cavities filled with lithic and opaque particles that point to the ostracods [44] (Figure 10). SEM results show that main transformation is kaolinisation from biotite, while serisitation from feldspar is lesser (Figure 11-13).

Major mineral composition of the sedimentary rock samples as detected by XRD analysis were quartz, plagioclase, K-feldspar and mica. The -2 µm fraction of the samples consists of illite, smectite and kaolinite with a minor amount of mixed-layer species. XRD diffractograms of coal-underlying sample, TU-18B, and coal-overlying kaolin rich sample, TU-18A are given in Figure 14. Illite was determined by (001) peak at 10.00-10.20 Å. Smectite was determined by peak at 12.00-14.00 Å, that expanded to 17.00-17.30 Å following ethylene-glycolation; the intensity of this peak collapsed to 10.05-10.21Å following heating at 550°C. Kaolinite was determined from its (001) peak at 7.00-7.20 Å and (002) peak at 3.57 Å, absence of swelling with ethylene-glycol treatment, and those peaks destroyed at 550°C due to dehydroxylation. The contents of main clay minerals were calculated semi-quantitatively according to the XRD determinations of -2 µm fraction for each sample. These results were re-calculated according to the -2 µm particle size amount of whole rock samples, which were analysed via Adreasen pipette method (Figure 15).

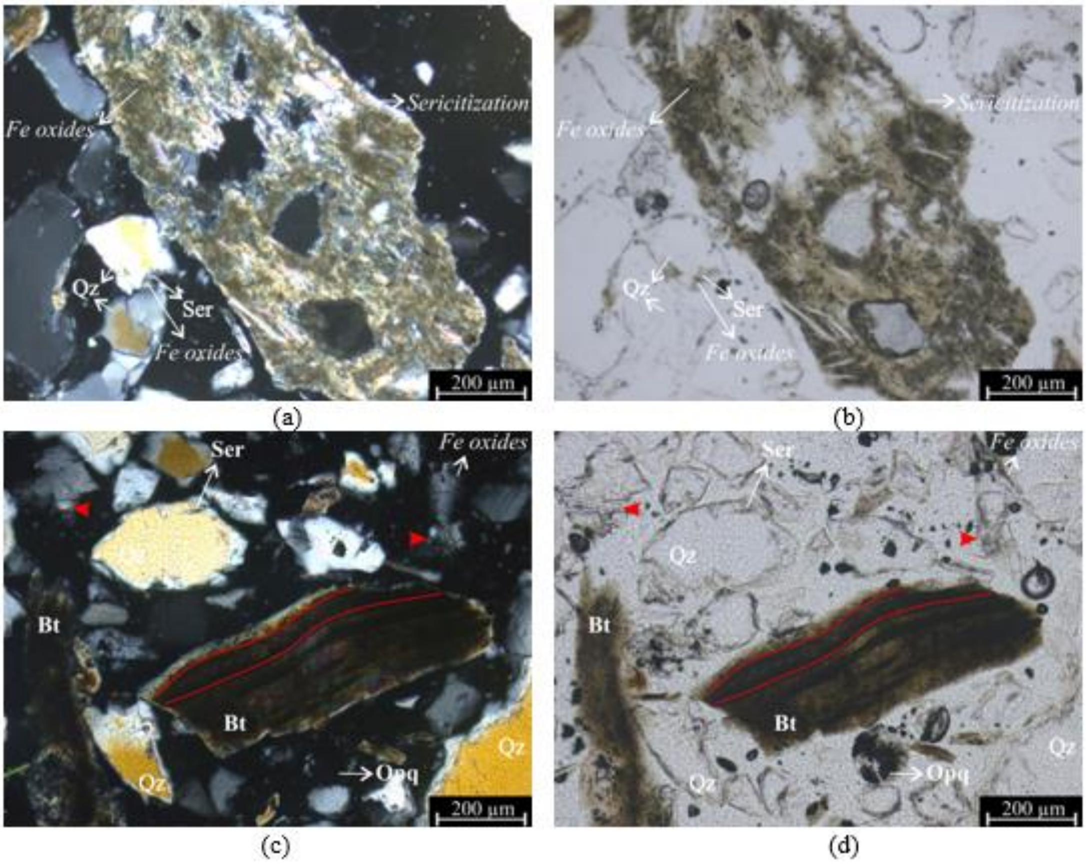


Figure 9. Photomicrographs of the coal-underlying sedimentary rock samples (fraction size > 63 µm): (a) with crossed polarizers. Sericitization and chloritization in detritic grain; (b) in plane polarized light (TU-1B); (c) with crossed polarizers; (d) in plane polarized light (TU-2B).

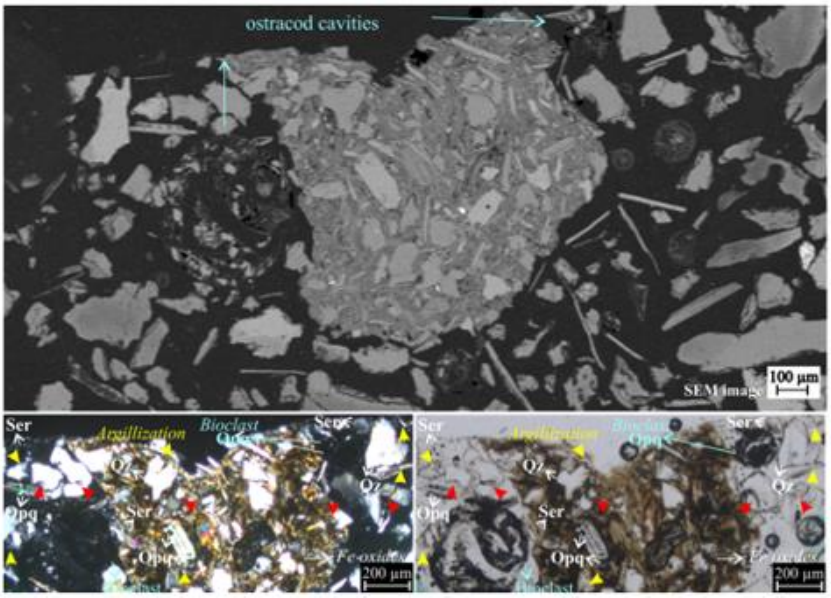


Figure 10. Photomicrographs of the coal-underlying sedimentary rock sample with crossed polarizers and in plane polarized light (TU-2B).

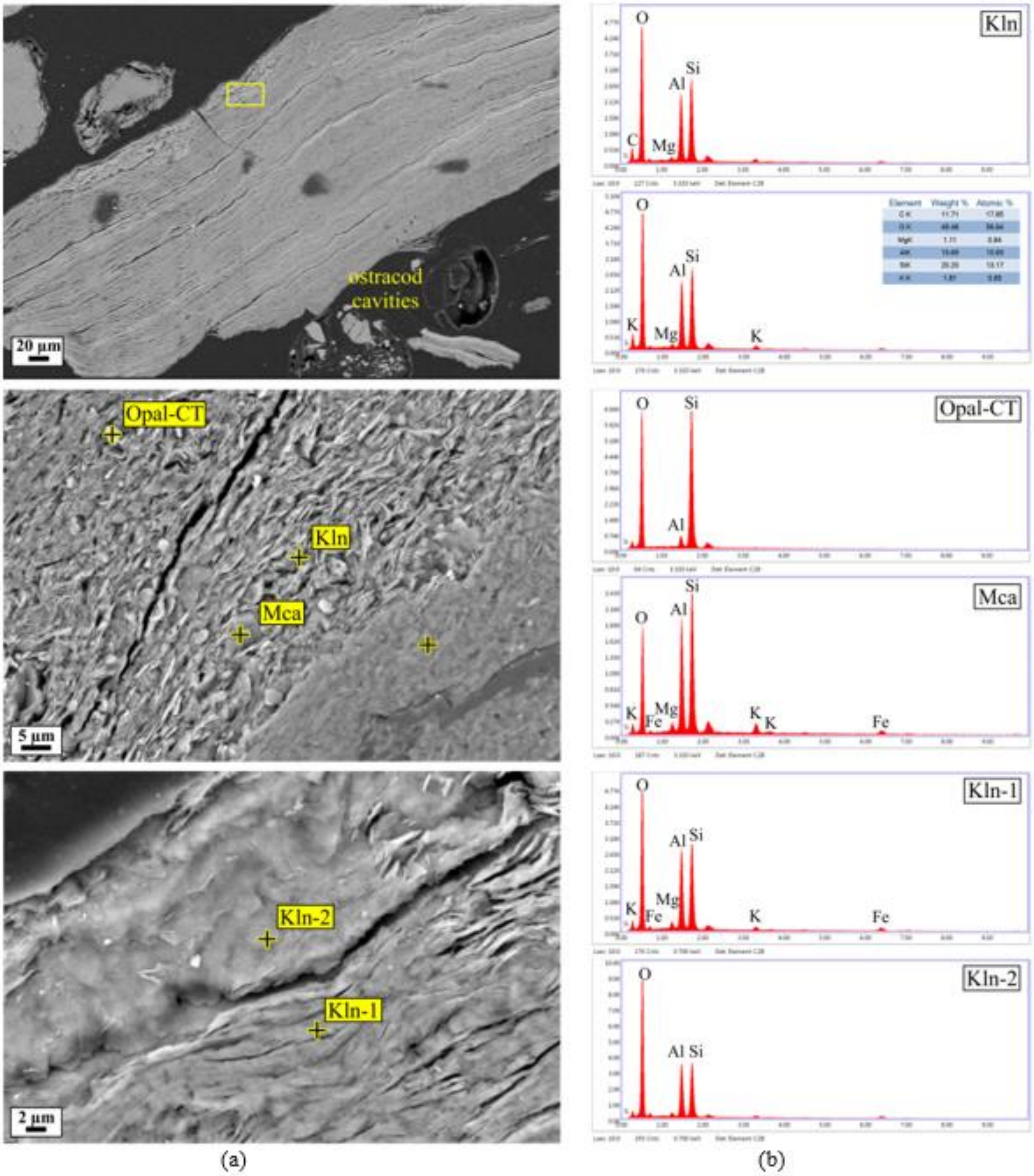


Figure 11. SEM images (TU-2B) showing the the (a) kaolinisation process of mica mineral; (b) EDX analyses showing the major elements of the selected points. This mica is the same pointed in Figure 9.

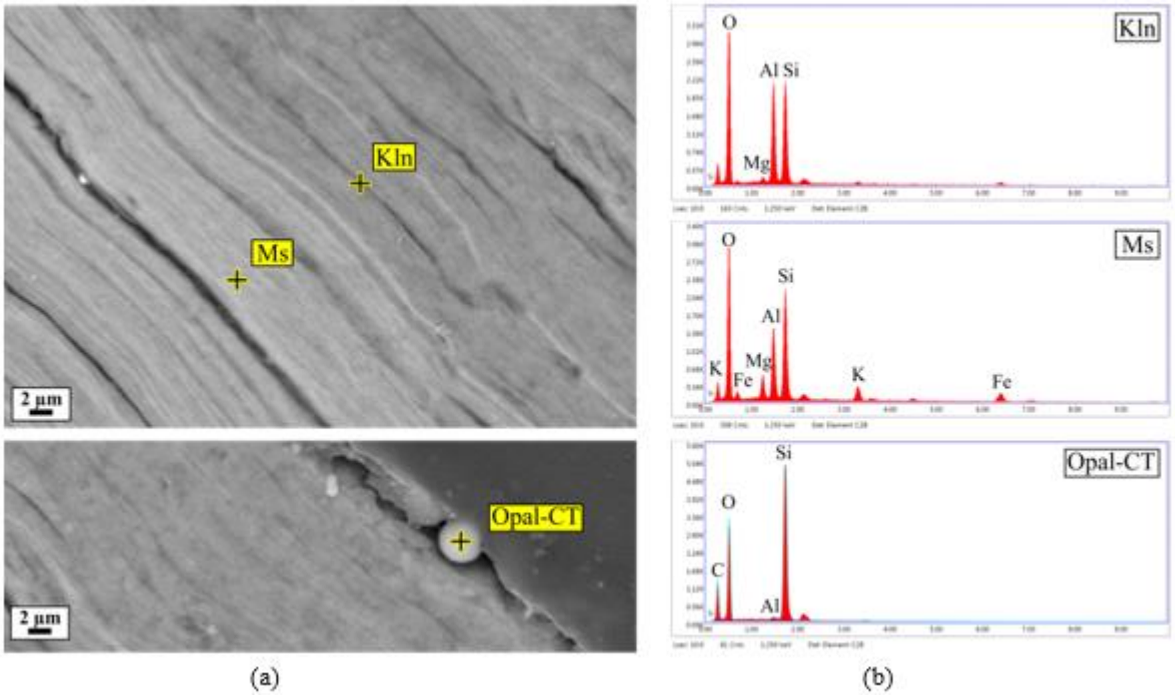


Figure 12. SEM images (TU-18A) showing the the (a) kaolinisation process of mica mineral; (b) EDX analyses showing the major elements of the selected points.

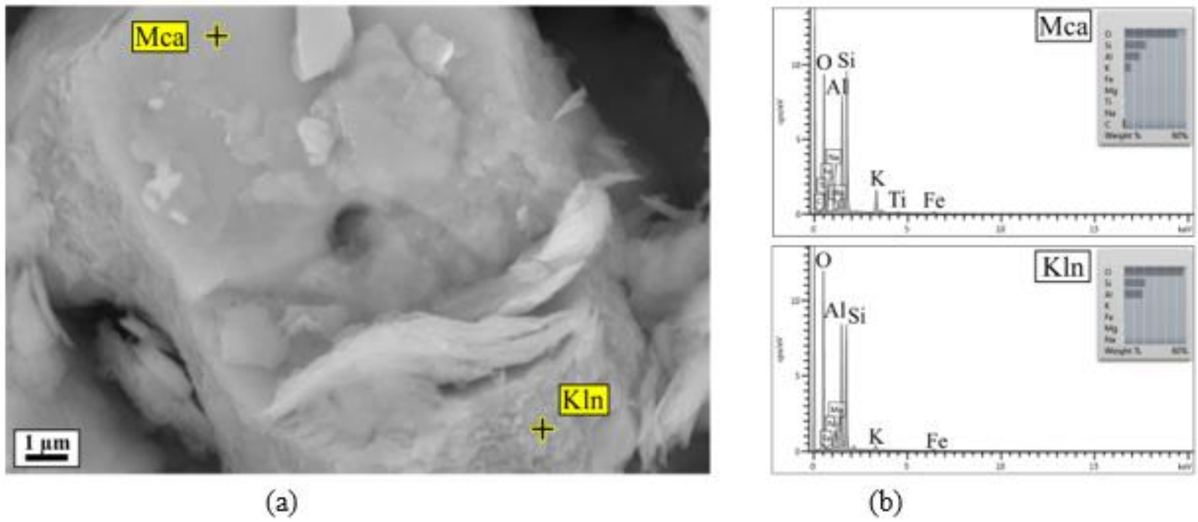


Figure 13. SEM images (TU-2A) showing the the (a) kaolinisation process; (b) EDX analyses showing the major elements of the selected points.

The formation of micas generally is observed within the zone of slightly changed parent rock and locally in the kaolinite-mica zone. Incongruent dissolution of feldspars in these zones leads to the formation sericite and/or illite on their surface. This process takes place under alkaline conditions with the activity of K^+ ions in the solutions. Local formation of sericite is observed at the borders and along cracks of quartz grains, which is formed probably by dissolution of quartz in solutions containing ions of K^+ and

Al^{3+}, the latter being provided by minerals remaining with them in equilibrium [45]. Furthermore, kaolinite is accompanied by feldspar as well as opal-CT and quartz. This indicates that Al is taken up from feldspar during the in-situ conversion to kaolinite via hydration of feldspar [46-48].

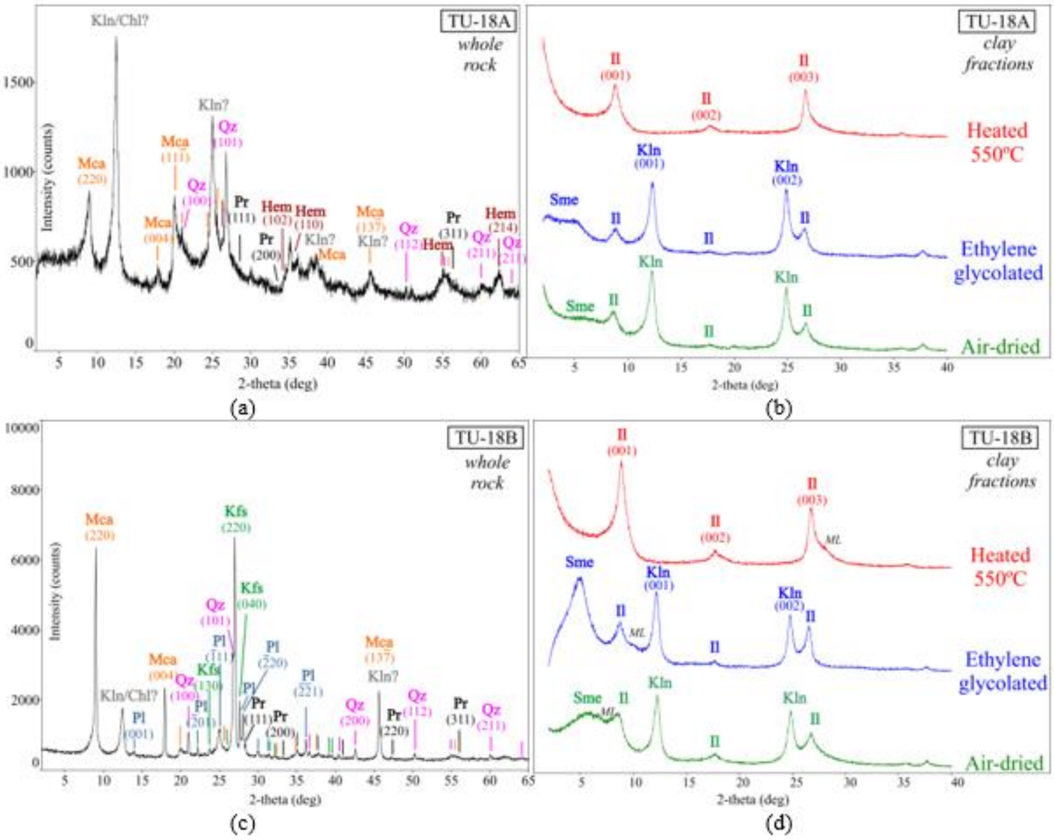


Figure 14. X-Ray diffractograms of the (a) whole rock mineral compositions of coal-overlying sample; (b) clay compositions of -2 µm fraction (TU-18A); (c) whole rock mineral compositions of coal-underlying sample; (d) clay compositions of -2 µm fraction (TU-18B).

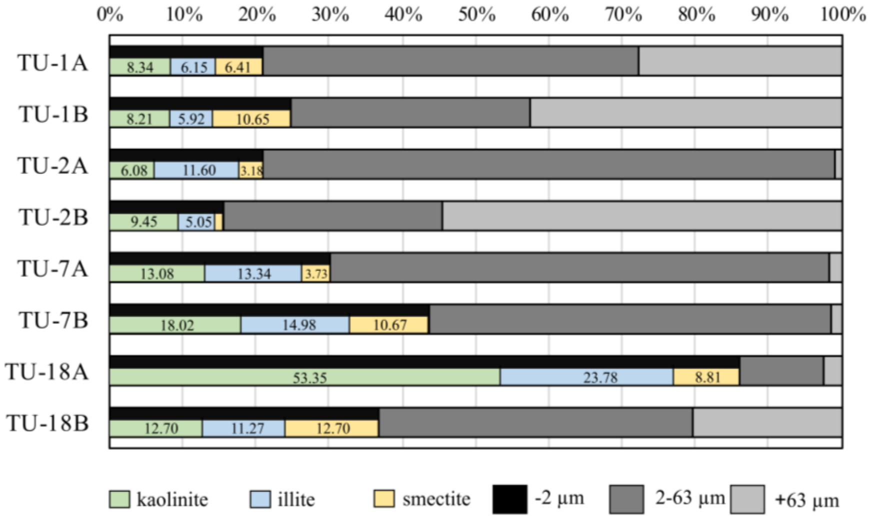


Figure 15. Semi-quantitative results of clay minerals within -2 µm fraction size of the sedimentary rock samples.

4.2. Geochemistry

In order to reveal the main geochemical characteristics of the gneiss samples, classical nomenclature diagrams were applied. The chemical compositions of gneiss and sedimentary rock samples were given in Table 5 and 6, respectively. Orthogneiss samples of study area were consisted of granites [49]. They were classified as calc-alkaline [50, 51] and showed peraluminous composition [52] (Figure 16). Al_2O_3 have negative corelation with SiO_2 element variation with higher amount in coal-underlying samples. The SiO_2/Al_2O_3 is less than two in the samples, that indicates low-maturity of sedimentary rock samples [53] (Figure 17). Chondrite-normalized [54] rare earth element patterns of gneiss and sedimentary rock samples were shown in Figure 18. Negative Eu anomalies of gneiss samples, suggesting the significance of plagioclase fractionation. Sedimentary rock samples also have negative Eu anomalies, suggesting the derivation from these bedrocks. NASC (North American Shale Composite) [55], PAAS Post-Archean Australian Shale) [56], ES (European Shales) [57] and UC (Upper Crust) [58] values are also plotted to the diagram.

Table 5. Major element (wt. %) and REE (Rare earth element) (ppm) concentrations of gneiss samples.

	G1	G2	G3	G4	G5	G8	G9	G10
SiO_2	74.80	74.70	74.23	72.62	69.42	75.89	75.54	76.87
Al_2O_3	13.19	13.34	13.57	14.19	17.29	12.58	13.38	13.08
Fe_2O_3	1.42	1.33	1.43	1.79	0.43	1.33	1.37	0.90
MgO	0.36	0.38	0.28	0.49	1.04	0.26	0.68	0.44
CaO	1.17	0.96	0.90	1.27	0.80	0.60	0.58	0.35
Na_2O	2.72	3.19	2.58	2.89	8.76	2.51	4.46	5.33
K_2O	4.92	4.44	5.45	4.76	0.85	4.97	2.20	1.56
TiO_2	0.19	0.20	0.17	0.24	0.23	0.16	0.19	0.11
P_2O_5	0.12	0.11	0.16	0.18	0.25	0.13	0.16	0.18
MnO	0.02	0.02	0.02	0.02	<0.01	0.02	<0.01	<0.01
Cr_2O_3	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
LOI	0.80	1.10	1.00	1.30	0.80	1.30	1.20	1.00
Sum	99.78	99.79	99.79	99.76	99.86	99.73	99.81	99.83
CIA[1]	60.00	60.83	60.31	61.40	62.42	60.90	64.89	64.37
La	20.10	16.20	17.60	23.20	1.60	12.30	16.90	6.80
Ce	40.60	33.40	35.00	46.50	2.90	32.50	33.30	15.10
Pr	4.59	3.86	3.98	5.40	0.40	3.20	3.99	1.86
Nd	17.10	14.30	15.00	19.80	1.90	11.30	13.90	6.60
Sm	3.86	3.30	3.53	4.60	0.76	3.00	4.04	1.87
Eu	0.66	0.53	0.51	0.78	0.08	0.37	0.52	0.16
Gd	4.11	3.50	3.77	4.59	0.96	3.24	4.05	1.96
Tb	0.86	0.69	0.80	0.87	0.21	0.75	0.84	0.45
Dy	5.92	4.60	5.52	5.73	1.39	5.67	5.61	3.38
Ho	1.31	1.01	1.22	1.23	0.30	1.29	1.24	0.75
Er	4.00	3.06	3.84	3.64	0.95	4.23	3.77	2.64
Tm	0.58	0.43	0.54	0.52	0.13	0.67	0.58	0.41
Yb	3.57	2.56	3.57	3.12	1.00	4.37	3.60	2.91
Lu	0.51	0.36	0.50	0.44	0.14	0.65	0.53	0.39
Eu/Eu*	0.51	0.48	0.43	0.52	0.29	0.36	0.39	0.26
Ce/Ce*	1.02	1.02	1.01	1.00	0.87	1.25	0.98	1.02

[1] $CIA\ (Chemical\ Index\ of\ Alteration) = 100 \times [Al_2O_3 \div (Al_2O_3 + CaO^* + Na_2O + K_2O)]$

$Eu/Eu^* = Eu_N \sqrt[2]{[(Sm_N) * (Gd_N)]}$, $Ce/Ce^* = \sqrt[2]{[(La_N) * (Pr_N)]}$

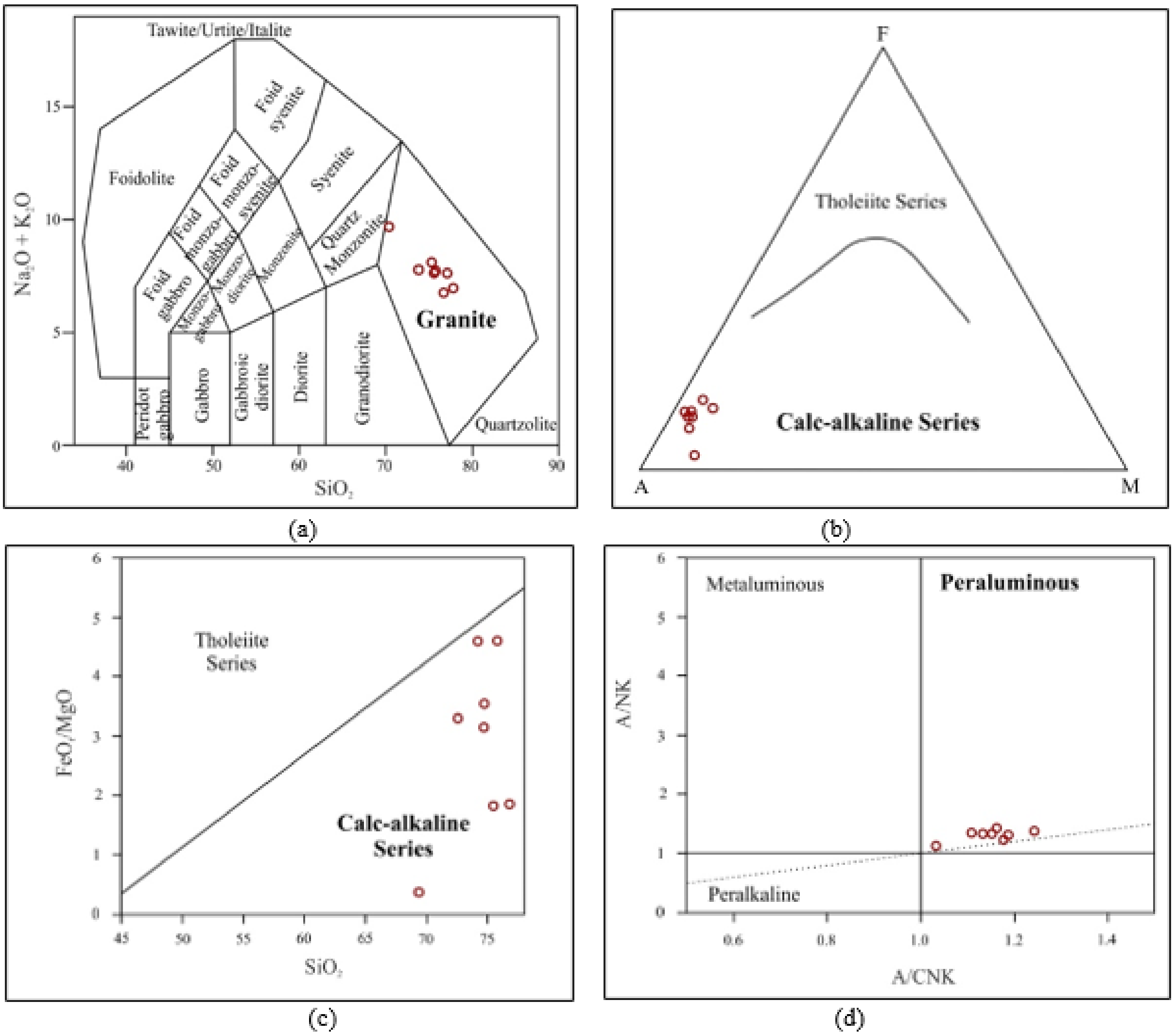
Table 6. Major element (wt. %) and REE (Rare earth element) (ppm) concentrations of sedimentary rock samples.

	TU-1A	**TU-1B**	**TU-2A**	**TU-2B**	**TU-7A**	**TU-7B**	**TU-18A**	**TU-18B**
SiO_2	62.68	54.52	47.53	44.07	65.59	69.26	49.03	57.09
Al_2O_3	19.87	20.30	23.01	27.56	17.60	16.72	25.45	22.05
Fe_2O_3	2.90	5.21	9.82	4.46	3.46	2.09	4.76	4.70
MgO	1.08	1.61	1.69	1.26	0.99	0.78	1.36	1.16
CaO	0.82	0.92	0.73	0.57	0.67	0.60	0.49	0.66
Na_2O	1.44	1.65	0.84	0.14	1.76	2.27	0.58	1.23
K_2O	3.89	3.83	4.12	2.21	3.19	3.02	3.83	3.71
TiO_2	0.61	0.77	0.93	0.87	0.62	0.66	0.89	0.82
P_2O_5	0.26	0.09	0.10	0.09	0.07	0.03	0.08	0.08
MnO	0.02	0.02	0.11	0.02	0.01	0.02	0.02	0.02
Cr_2O_3	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
LOI	6.30	10.90	10.90	18.60	5.90	4.40	13.30	8.30
Sum	99.88	99.84	99.84	99.87	99.88	99.89	99.82	99.86
CIA[1]	76.36	75.80	76.03	73.95	80.17	83.86	90.42	79.75
ICV[2]	0.54	0.61	0.69	0.57	0.79	0.47	0.35	0.56
La	37.70	49.90	65.20	67.90	38.00	31.20	72.40	57.20
Ce	82.30	101.60	128.80	144.90	74.20	58.20	149.60	116.00
Pr	8.54	11.59	15.05	14.99	8.98	7.10	16.96	13.42
Nd	31.70	43.30	56.90	52.60	32.60	27.00	63.10	49.50
Sm	6.99	8.92	11.76	10.95	6.95	5.37	14.32	10.86
Eu	1.23	1.56	1.95	2.01	1.26	0.95	2.28	1.85
Gd	6.58	8.44	11.64	10.63	6.87	5.10	14.15	11.10
Tb	1.14	1.38	1.94	1.75	1.19	0.82	2.46	1.90
Dy	7.17	8.31	11.45	10.16	7.39	4.65	15.42	11.49
Ho	1.48	1.69	2.39	2.11	1.55	0.96	3.12	2.21
Er	4.10	4.98	6.96	5.95	4.40	2.79	8.97	6.46
Tm	0.61	0.67	0.95	0.79	0.65	0.40	1.27	0.90
Yb	3.64	4.13	5.83	4.93	3.97	2.45	7.81	5.33
Lu	0.53	0.58	0.83	0.66	0.57	0.40	1.06	0.73
Eu/Eu*	0.55	0.56	0.55	0.56	0.51	0.49	0.57	0.52
Ce/Ce*	1.10	0.97	1.02	0.94	0.99	1.03	1.09	1.01

[1] $CIA\ (Chemical\ Index\ of\ Alteration\ ) = 100 \times [Al_2O_3 \div (Al_2O_3 + CaO^* + Na_2O + K_2O)]$

[2] $ICV\ (Index\ of Compositional\ Variability\ ) = [(Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2) \div Al_2O_3]$

$$Eu/Eu^* = Eu_N \sqrt[2]{[(Sm_N) * (Gd_N)]},\ Ce/Ce^* = \sqrt[2]{[(La_N) * (Pr_N)}$$



(a) (b)

(c) (d)

Figure 16. Plotted gneiss samples on (a) SiO_2 vs. (Na_2O + K_2O) binary (TAS) diagram [49]; (b) (Na_2O+K_2O) – FeO_t – MgO (AFM) ternary diagram [50]; (c) SiO_2 vs. FeO_t/MgO binary diagram [51]; (d) Al_2O_3/(CaO+Na_2O+K_2O) vs. Al_2O_3/(Na_2O+K_2O) (mol. %) (A/CNK - A/NK) diagram [52]. (wt% of Fe_2O_3 used in the calculations as FeO_t)

Coal over- and underlying sedimentary rocks plotted to the shale area, accept two samples, which contain coarser detritics (Figure 19 (a)) [59]. In the TiO_2/Ni discrimination diagram sedimentary rock samples plotted to magmatogenic rock field showing felsic to medium trend, whereas in the Sr versus Ba diagram they plotted to the mature field, and/or around mudstone area (Figure 19 (b, c)) [60]. Samples plotted ICV-CIA diagram [61], which pointed to mature field, showing trend from weak to intense weathering (Figure 19(d)). TiO_2-Zr contents of the gneiss points to the felsic igneous rock field, while sedimentary rocks point this area with the samples which has coarser lithology (Figure 19(e)) [62]. Samples plotted to felsic-intermediate igneous provence area in discrimination diagram (Figure 19 (f)) [63]. The coal over- and underlying sedimentary rocks of the study area are about one which change around the limit according to the Ce/Ce* values in a typical shale, which is one [61, 64]. Existing fine –grained framboidal pyrite crystals in the samples shows the anoxic conditions [65].

Gneiss samples and sedimentary rock samples were plotted on A-CN-K (Al_2O_3-CaO*+Na_2O-K_2O) diagram (Figure 20) [66-68]. The initial trend (early weathering) is sub-parallel to the A-CNK boundry of the triangle gneiss samples and their CIA values pointed to slightly weathering. Sedimentary Rock samples CIA values pointed moderately weathering. Studied sedimentary rocks weathering processes and mechanisms have been similar profiles developed from granitoids of diverse composition display systematic, predictable, compositional weathering trends.

Mainly the coal-underlying sedimentary rocks contain detritic particles, which may be related to the metasediments of the basement. Menderes Massif cover series and Karaova Formation of Lycian Nappes contain metasediments: these of Mg-carpholite-bearing rocks and Fe-Mg-carpholite bearing rocks [69], which do not occupy a surface area in Turgut lignite deposit.

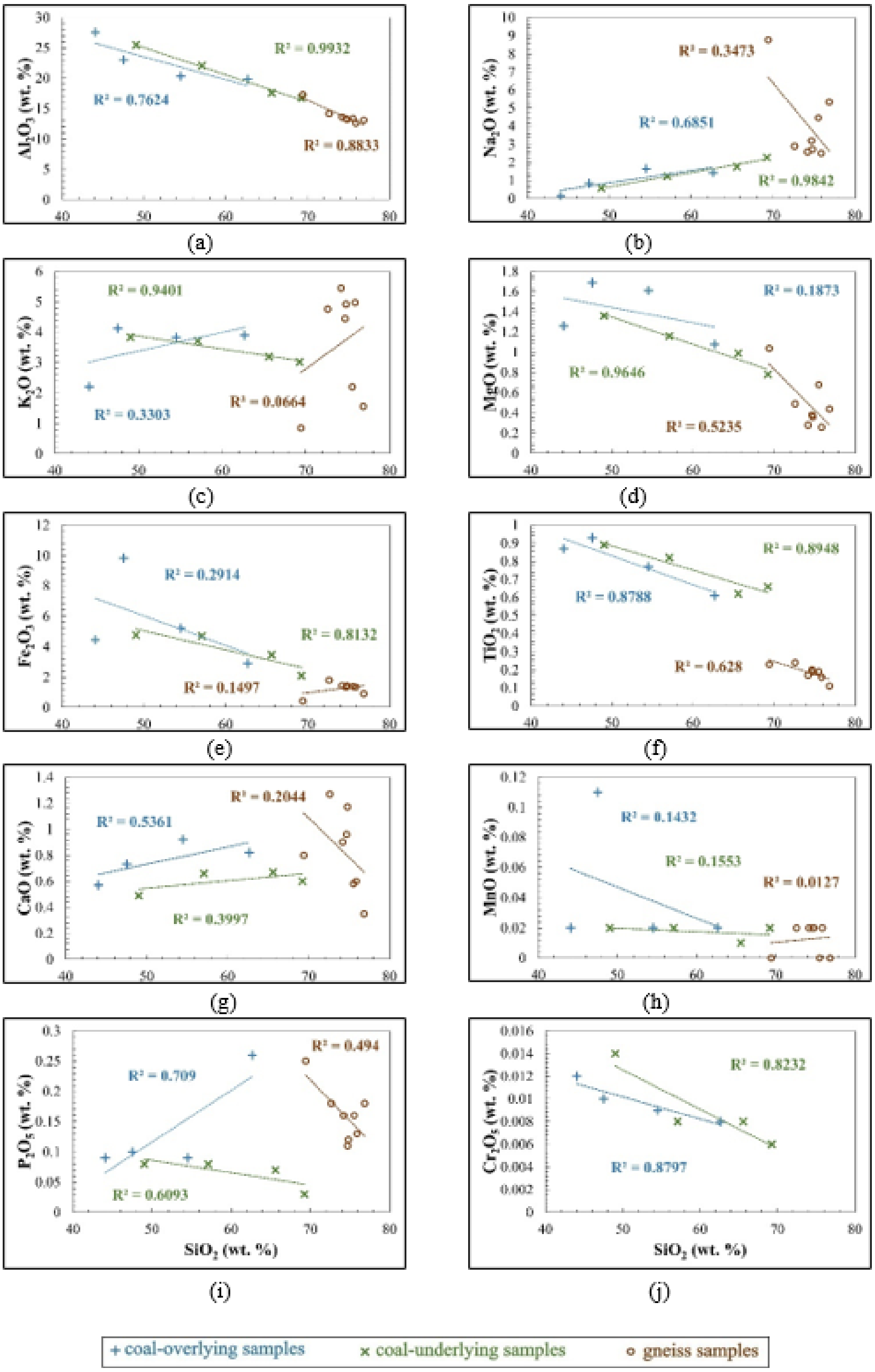


Figure 17. Variation diagrams for (a) Al_2O_3-SiO_2 plot of all samples; (b) Na_2O-SiO_2 plot of all samples; (c) K_2O-SiO_2 plot of all samples; (d) MgO-SiO_2 plot of all samples; (e) Fe_2O_3-SiO_2 plot of all samples; (f) TiO_2-SiO_2 plot of all samples; (g) CaO-SiO_2 plot of all samples; (h) MnO-SiO_2 plot of all samples; (i) P_2O_5-SiO_2 plot of all samples; (j) Cr_2O_5-SiO_2 plot of sedimentary rock samples showing differentiation between concentrations of major oxides.

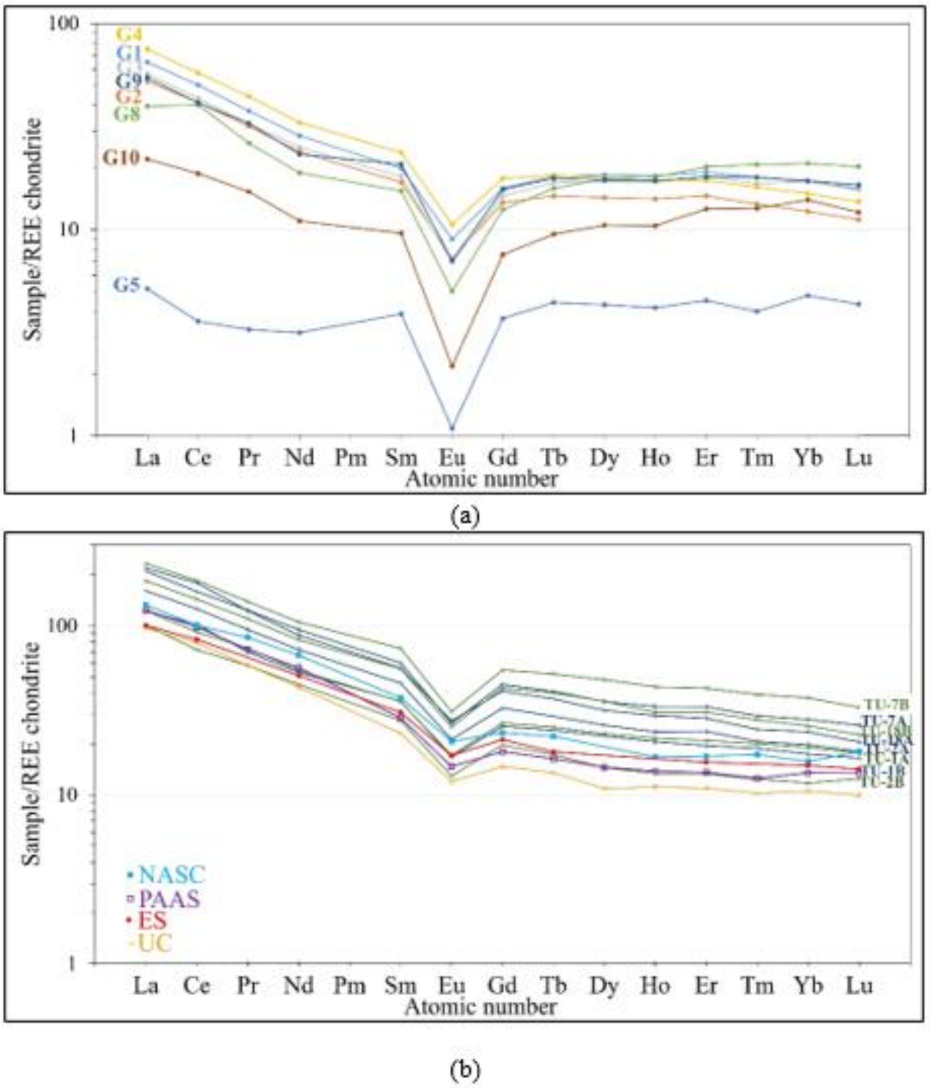


Figure 18. (a) Chondrite – normalized rare earth element (REE) pattern for gneiss samples [54]; (b) Chondrite – normalized rare earth element (REE) pattern for sedimentary rock samples [54]. NASC (North American Shale Composite) [55], PAAS (Post-Archean Australian Shale) [56], ES (European Shales) [57] and UC (Upper Crust) [58] values are plotted for comparison.

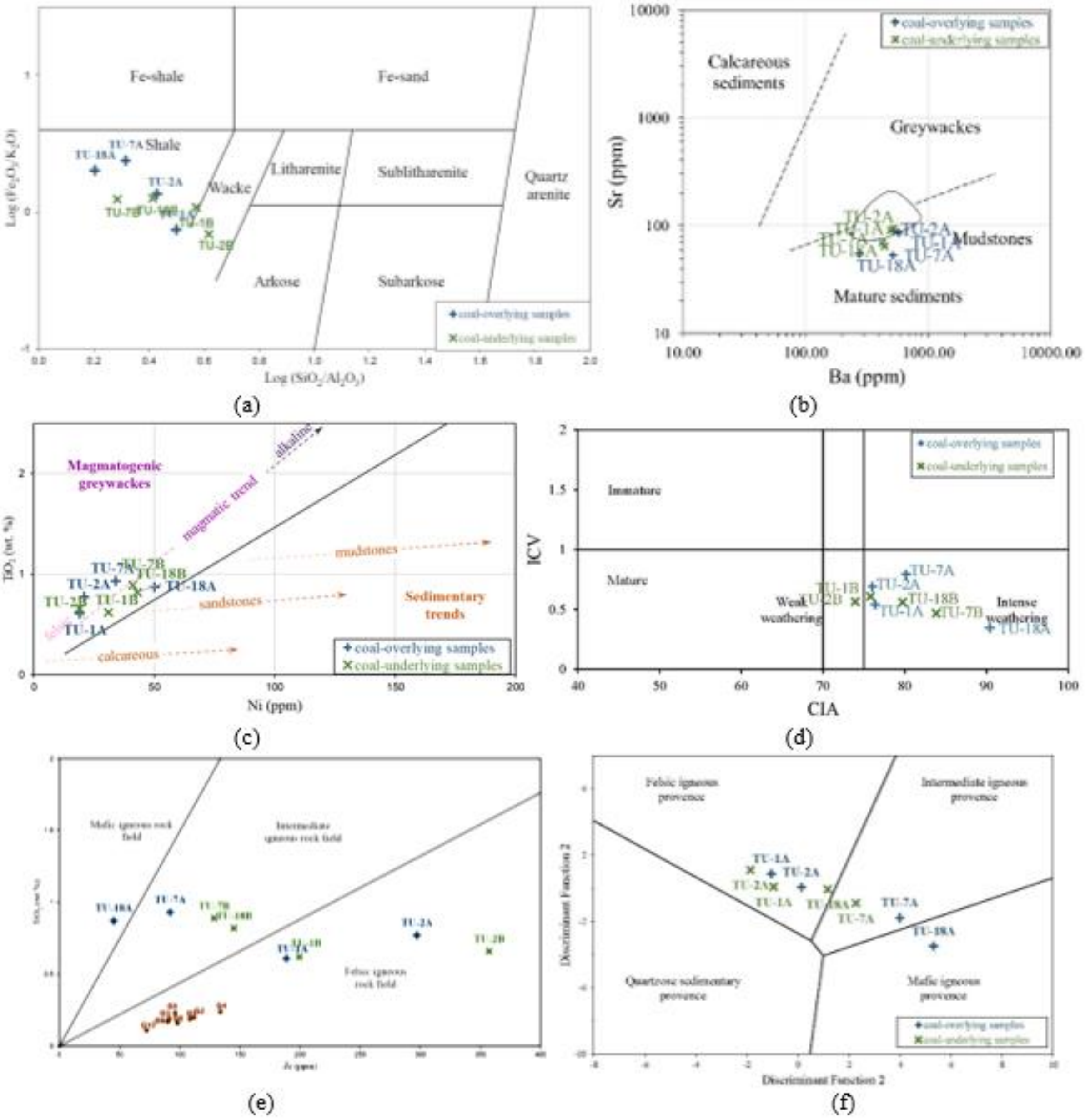


Figure 19. (a) Sand classification diagram [59]; (b) Samples plotted on Sr-Ba diagram showing; (c) TiO_2-Ni plot of sedimentary rock samples showing the magmatogenic greywackes following a trend for asidic rocks [60]; (d) ICV and CIA diagram [61]. (e) TiO_2-Zr contents of the gneiss and sedimentary rock samples [62]; (f) Discriminant plots of sedimentary rock samples [63].

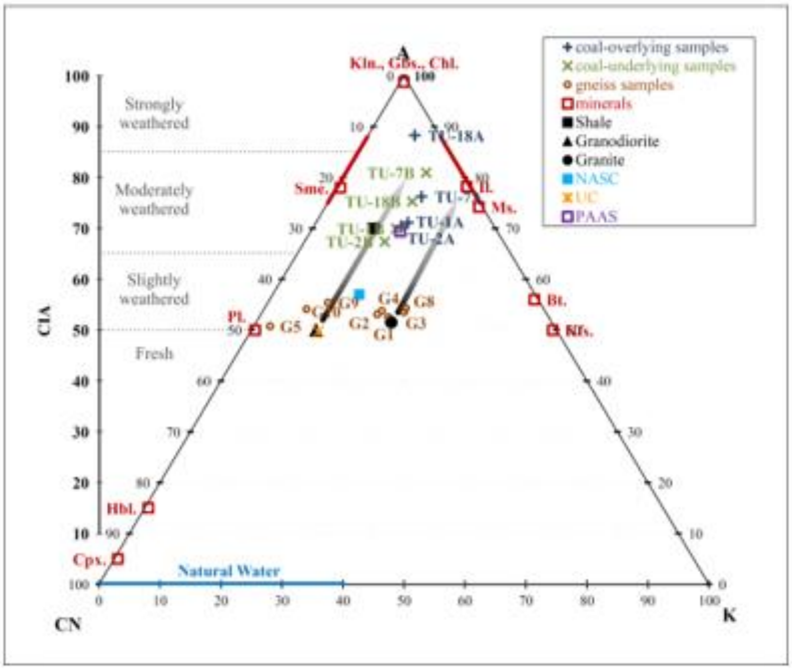


Figure 20. Gneiss and sedimentary rock samples plotted on Al_2O_3-CaO^*+Na_2O-K_2O (A-CN-K) diagram (CaO^* represents CaO associated with the silicate fraction of the sample.) as molar proportions. Granite, granodiorite, shale, NASC, UC, PAAS samples plotted for comparison as molar proportions of the average values. Red squares are idealized mineral compositions. The arrows are the calculated initial trends followed by the leachates during the initial weathering stages [66-68].

5. CONCLUSION

Dominantly siliciclastic deposits characterize the sedimentary record of the Turgut area (Yatağan Basin). Gneiss samples contain mainly quartz, plagioclase, K-feldspar, muscovite and biotite with a lesser amount of tourmaline, chlorite, garnet, apatite, zoisite, zircon and Fe-oxides. The -2 µm fraction consists mainly of illite, with fewer smectite and kaolinite. Sericitization of feldspar is the main product in gneisses. Coal over-and underlying sedimentary rock samples contain mainly quartz, plagioclase, K-feldspar, muscovite, and biotite with less pyrite and iron oxides. The -2 µm fraction of the sedimentary rock samples consists of variable clay mineral contents. Kaolin content is highly acidic conditions with an opposite correlation to smectite occurrences. The clay mineral content of one sample reaches up to 86%. This sample contains about 53% kaolinite. It is suggested that kaolinite-rich levels must be examined in detail for their utilization potential as raw materials. The geochemistry of Menderes Massif gneisses gave material to the catchment area, whereas the geochemistry of sedimentary rocks is not coherent in all cases. More samples must be studied to understand the weathering effect in the basin.

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CONFLICT OF INTEREST

The authors stated that there are no conflicts of interest regarding the publication of this article.

AUTHORSHIP CONTRIBUTIONS

Zeynep Büçkün: Formal analysis, Investigation, Writing-original draft, Visualization, Conceptualization. **Mümtaz Çolak:** Supervision, Investigation, Conceptualization.

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