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

19th National Clay Symposium (Clay'2023) Sprecial Issue 2023

2023, Vol.24, pp. 17-32, DOI: 10.18038/estubtda.1369882

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

Türker YAKUPOĞLU [1, *], Kerem ERDOĞANLI [2]

[1] Department of Geological Engineering, Faculty of Engineering, Van Yüzüncü Yıl University, Van, Türkiye
[2] 11th Regional Directorate of Highways, Van, Türkiye

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

*Corresponding Author: turkery@yyu.edu.tr
Received: 02.10.2023 Published: 29.11.2023

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])

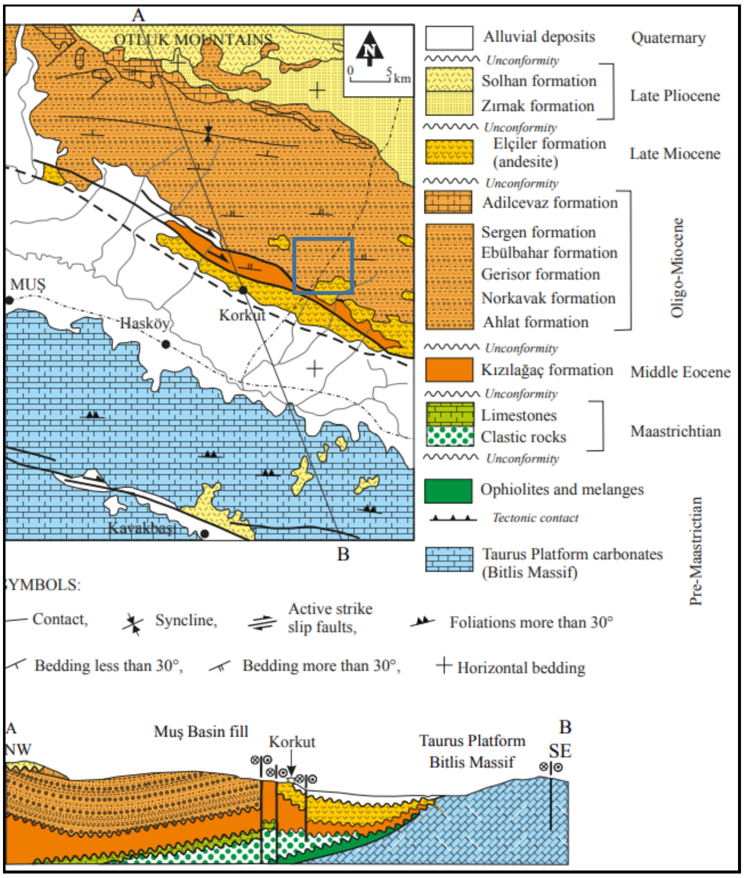


Figure 2. General geological map and cross-section of the Muş basin [1] (The blue square indicates the study area)

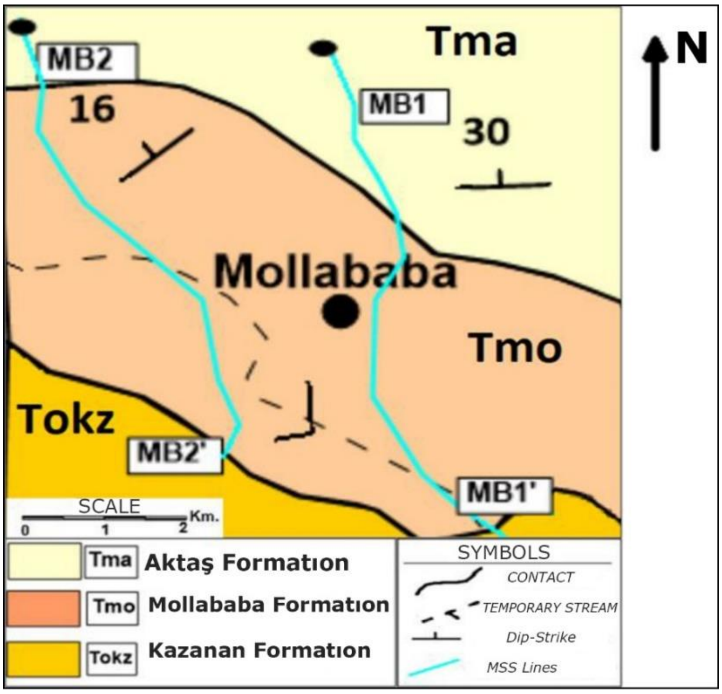


Figure 3. Geological map of the study area and measured stratigraphy section (MSS) routes (Tokz: Chattian, Tmo: Aquitanian, Tma: Burdigalian, MB1: Mollababa 1 MSS, MB2: Mollababa 2 MSS) (edited from [8])

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).

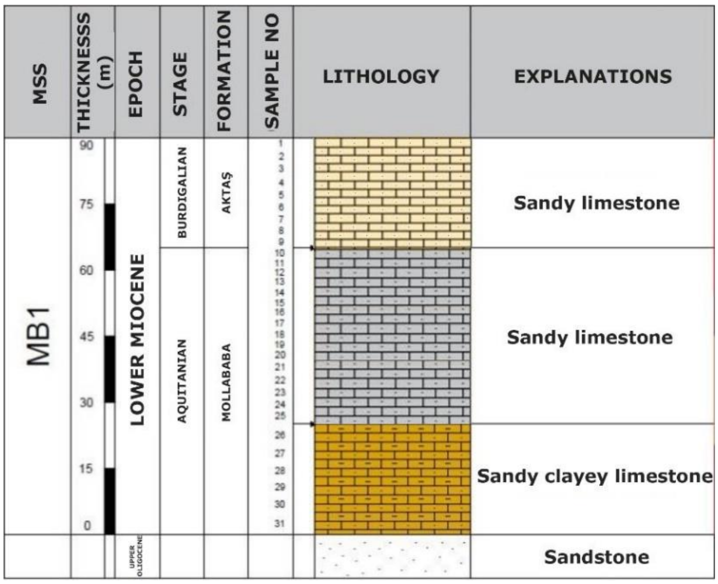


Figure 5. Mollababa 1 (MB1) measured stratigraphic section

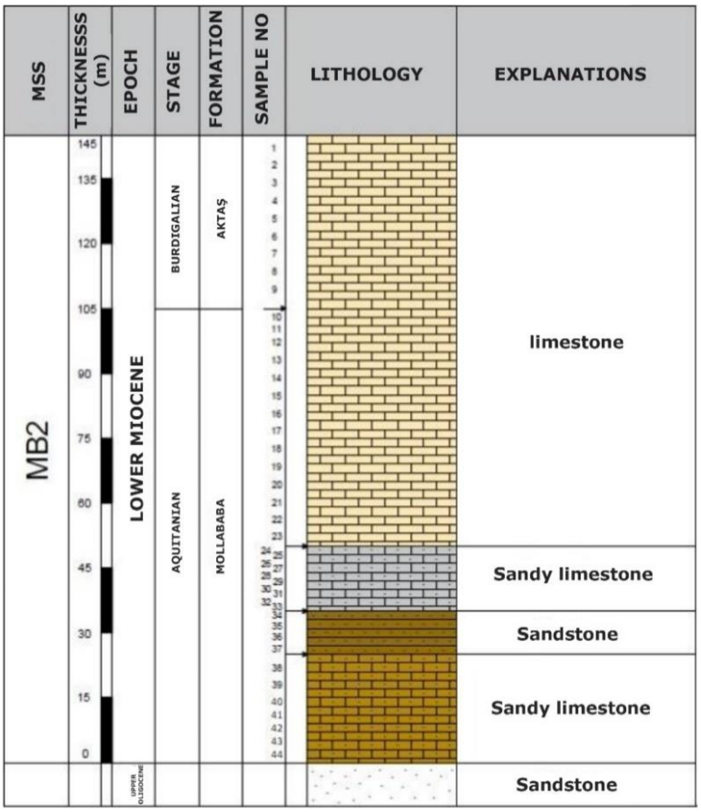


Figure 6. Mollababa 2 (MB2) measured stratigraphic section

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 4º-70º MTA General Directorate Mineral Analysis and Technology Department XRD laboratory. Normal, ethylene glycol, 300ºC and 550ºC heat treatment diffractograms (between 4º-30º) 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	+	+	+	+	-

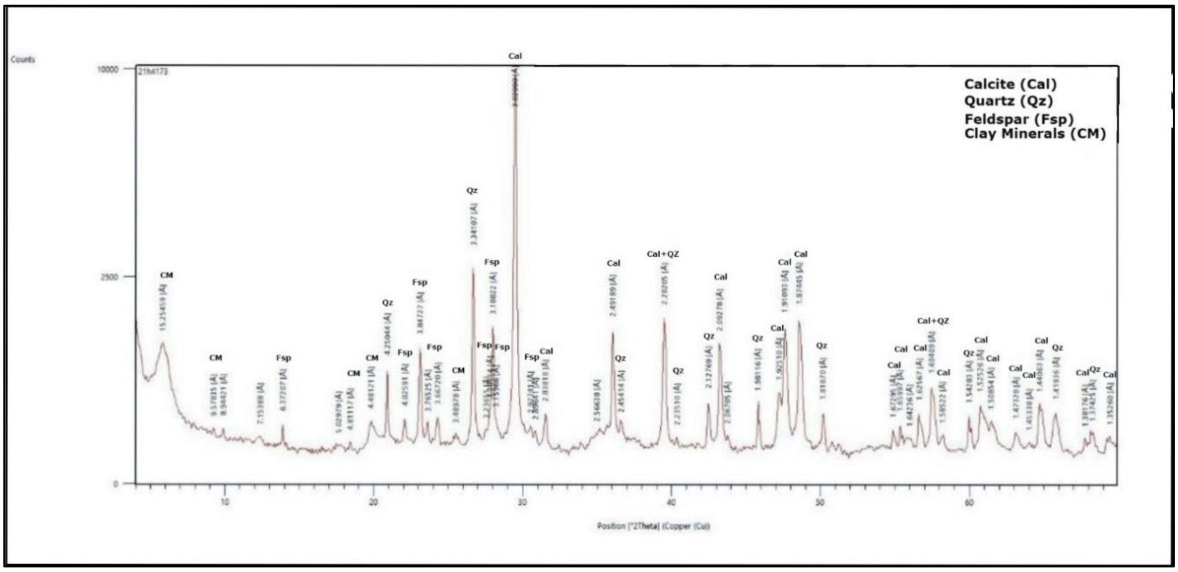


Figure 7. X-ray (WR) diffractogram of MB1-4 (Aktaş Formation) sample

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	+	+	+	+	-

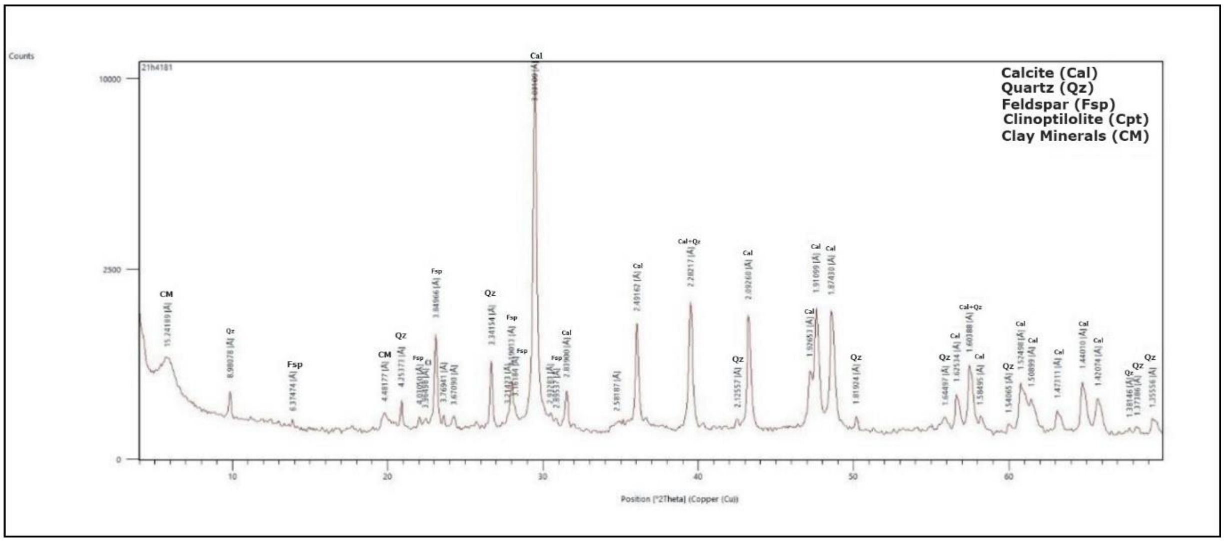


Figure 8. X-ray (WR) diffractogram of MB1-12 (Mollababa Formation) sample

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.

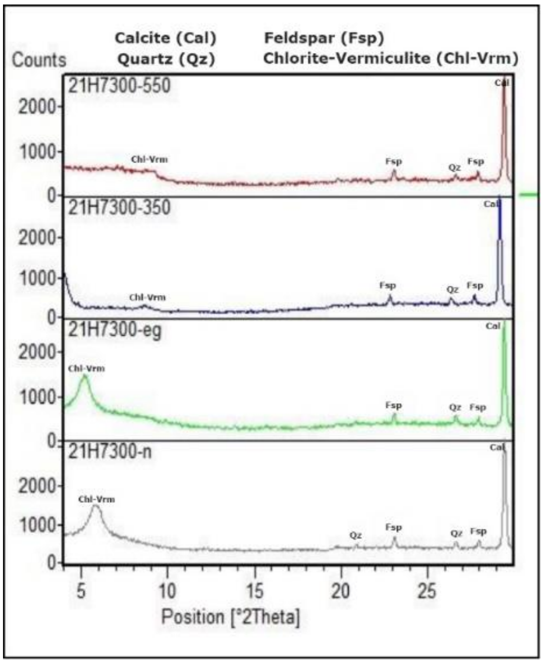


Figure 9. X-ray (CF) diffractograms of MB1-4 (Aktaş Formation) sample

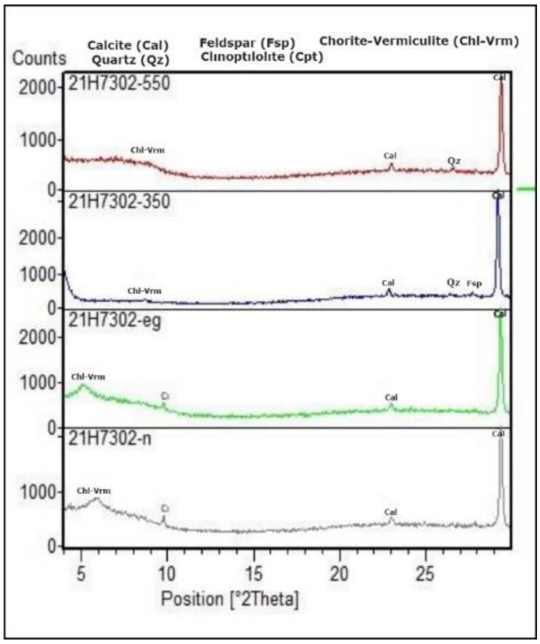


Figure 10. X-ray (CF) diffractograms of MB1-12 (Mollababa Formation) sample

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.

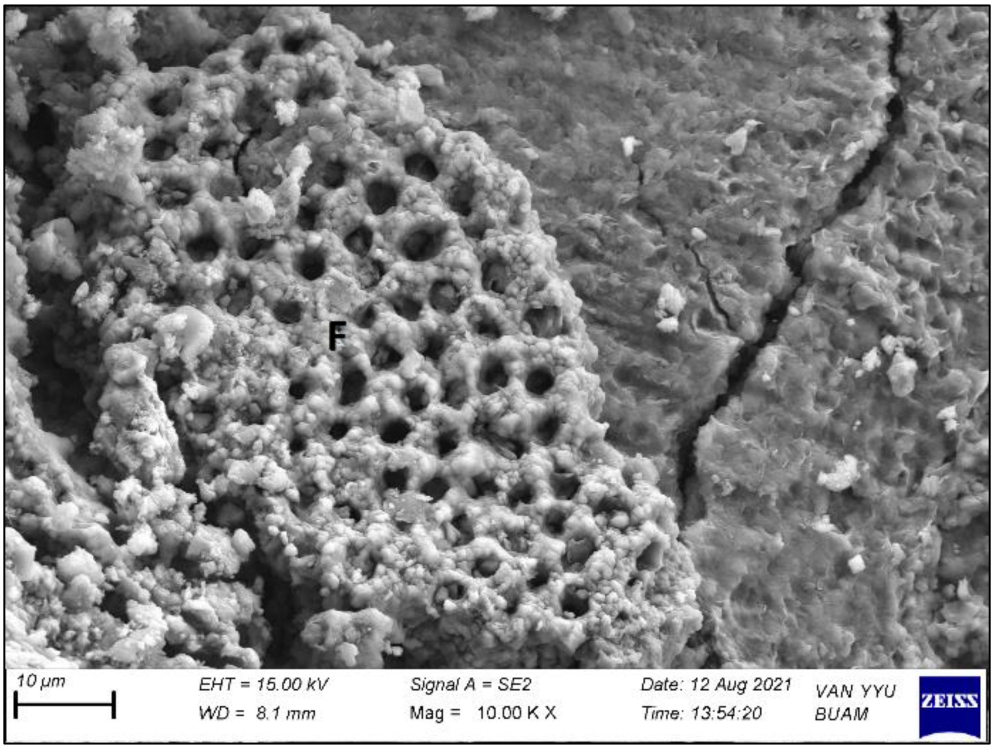
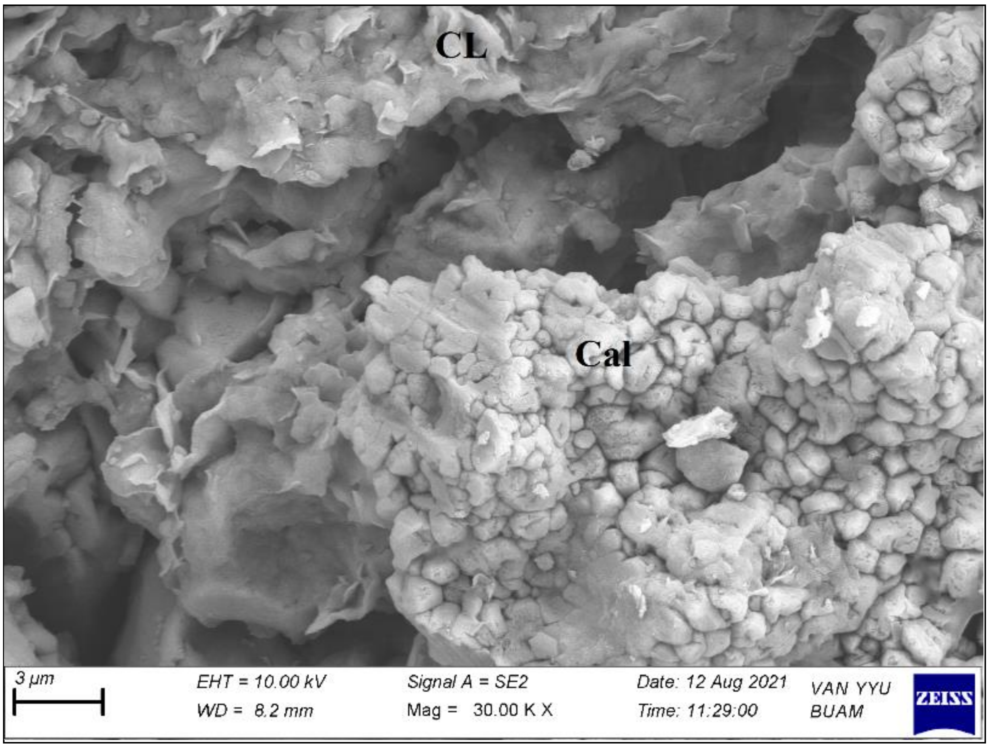


Figure 11. Fossil fragment (F) observed in the SEM study of sample MB2-16



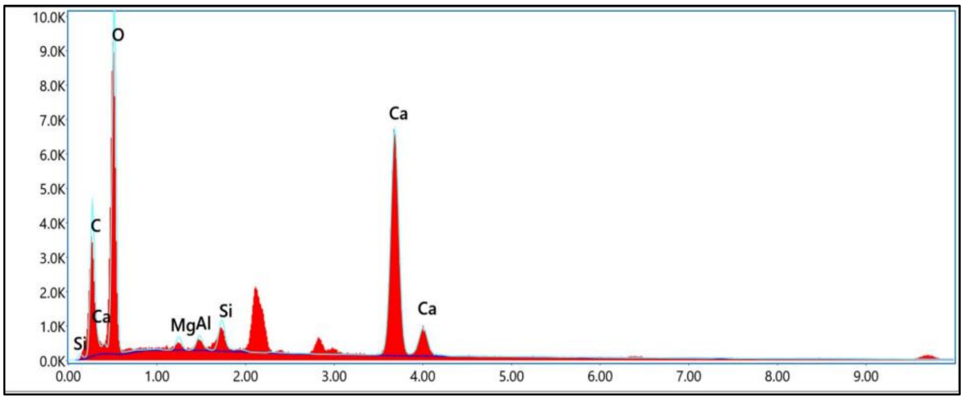
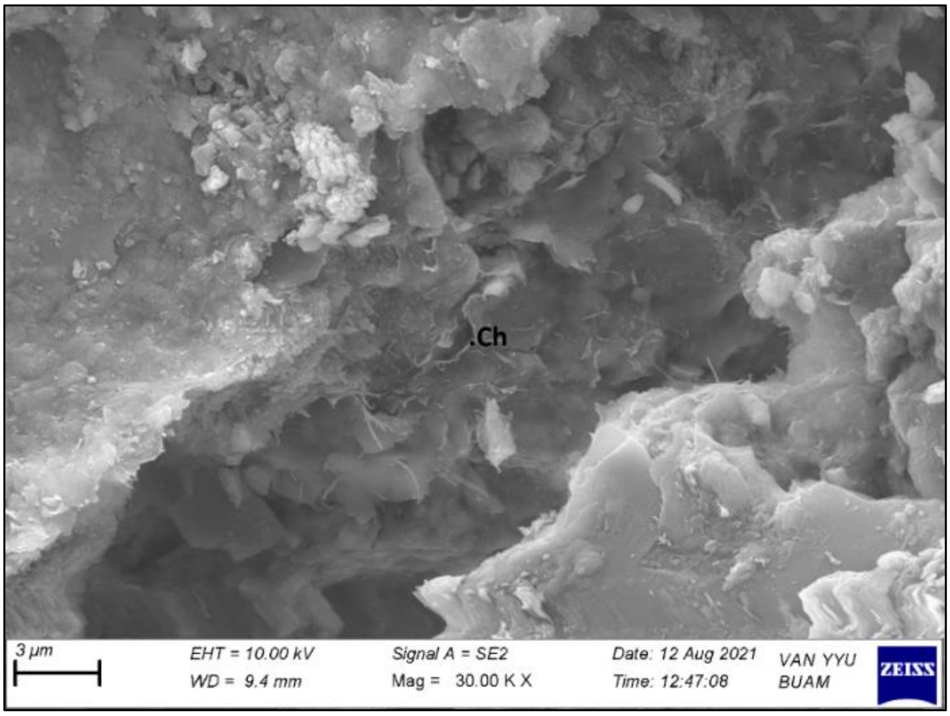


Figure 12. Microphotograph showing the microcrystalline calcite (Cal) and clay leaflets (CL) observed in the MB1-24 sample (above) and microchemical analysis diagram of calcite (below)



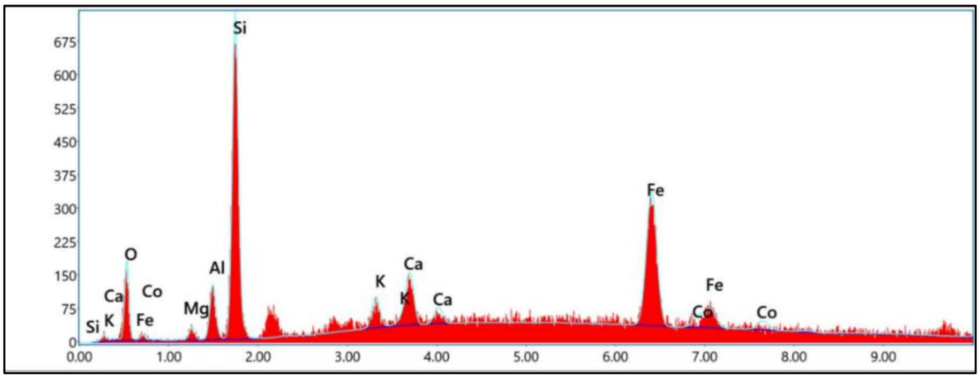


Figure 13. Microphotograph (above) and microchemical analysis diagram (below) of the chlorite (Ch) mineral observed in sample MB1-41

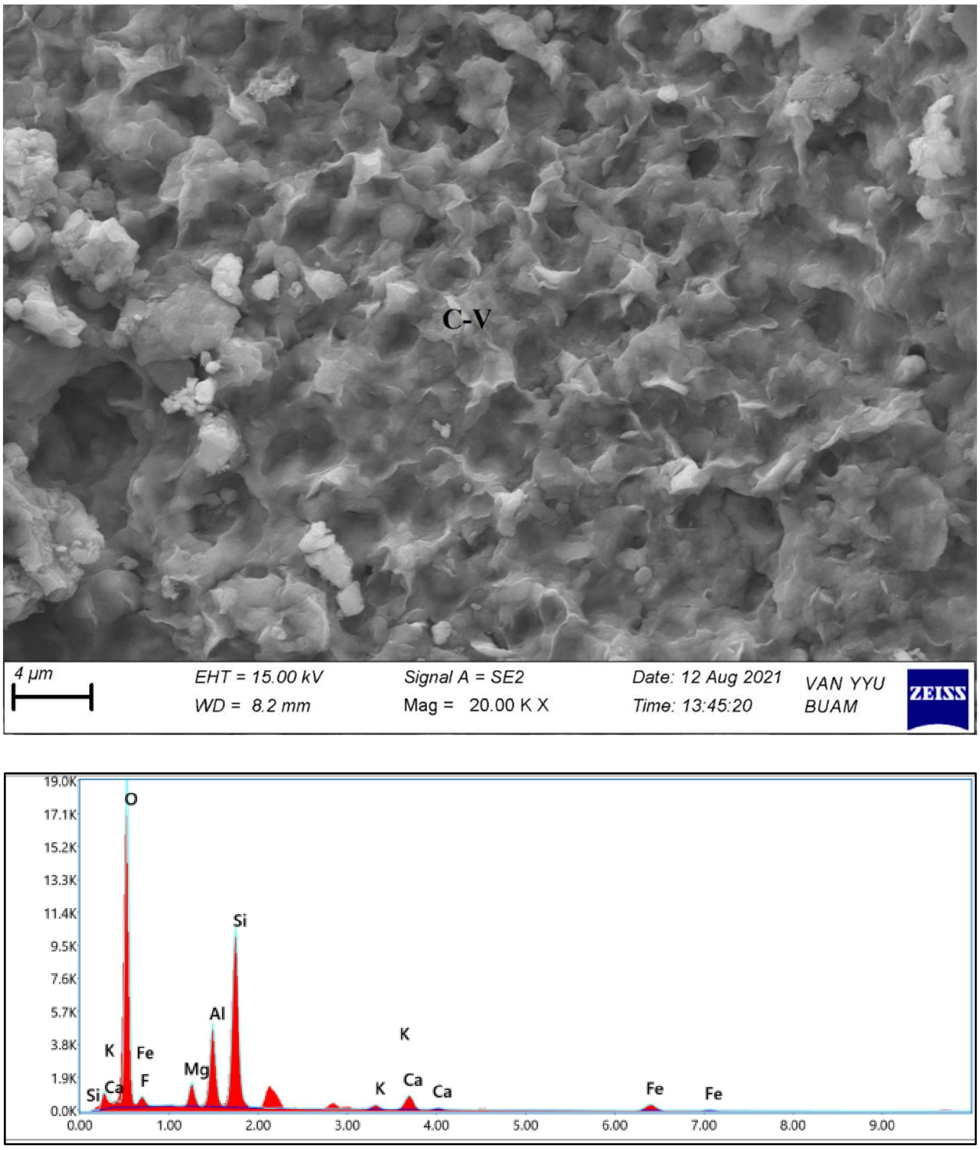


Figure 14. Microphotograph (above) and microchemical analysis diagram (below) of the chlorite-vermiculite (C-V) mixed layer clay mineral observed in the MB2-16 sample.

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

ACKNOWLEDGEMENTS

This paper was prepared by using the second author's master's thesis [24]. The thesis has been supported by Van Yüzüncü Yıl University Scientific Research Projects Coordination Unit under grant number FYL-2021-9280.

The authors thank the reviewers for their constructive input to the improvement of this article.

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.

REFERENCES

[1] Yılmaz A, Yılmaz H. Structural Evolution of the Eastern Anatolian Basins: An Example from Collisional to Post-Collisional Tectonic Processes, Turkey. Turk J Earth Sci 2019; 28(3): 329-350. https://doi.org/10.3906/yer-1805-20.

[2] Kurtman F, Akkuş MF. Inter-Mountain Basins in Eastern Anatolia and Their Oil Possibilities. Bull Min Res Exp 1971; 77: 1-9.

[3] Şaroğlu F, Yılmaz Y. Geological Evolution and Basin Models in the Neotectonic Period in Eastern Anatolia. Bull Min Res Exp 1986; 107: 73-94.

[4] Akay E, Erkan E, Ünay E. Stratigraphy of the Muş Tertiary Basin. MTA Dergisi 1989; 109: 59–76.

[5] Kurdal S. Analysis and modeling of Muş Basin by using geophysical data. MSc, University of Sivas Cumhuriyet, Sivas, Türkiye, 2019.

[6] Sakınç M, Geology, Biostratigraphy and Paleontology of the Mollababa-Uruman (Muş Province) Area. İstanbul Yerbilimleri 1982, 3 (1-2): 235-272.

[7] Saygılı R. Map of Muş province. http://cografyaharita.com/haritalarim/4l_mus_ili_haritasi.png. 2020.

[8] Eser İ. Microfacies of Aquitanian-Burdigalian (Early Miocene) deposits in east-southeast of Mollababa Village (Muş). MSc, Van Yüzüncü Yıl University, Van, Türkiye, 2019.

[9] Welton JE. SEM Petrology Atlas., USA, The AAPG Methods in Exploration Series; no: 4237, 1984.

[10] Brown G. The X-Ray Identification and Crystal Structures of Clay Minerals. Norwich, GB: Jarrold and Sons Ltd., 1961.

[11] Grim RE. Clay Mineralogy. New York, USA: Mc Graw Hill Book Company, 1968.

[12] Thorez J. Practical Identification of Clay Minerals. Editions G. Lelotte, Dison, Belgium. 1976.

[13] Brindley GW. Quantitative X-ray Mineral Analysis of clays. In: Brindley G.W, Brown, Editors. Crystal Structures of Clay Minerals and Their X-Ray Identification. London Mineralogical Society, 1980. pp. 125-195.

[14] Brown G. Associated Minerals. In: Brindley GW, Brown, Editors. Crystal Structures of Clay Minerals and Their X-Ray Identification. London Mineralogical Society, 1980. 361-410.

[15] Velde B. Clay Minerals: A Physico-Chemical Explanation of their Occurrence. Developments in Sedimentology, 40, Amsterdam, NL: Elsevier Scientific Publication Company, 425. 1985.

[16] Wilson MJ. A Handbook of Determinative Methods in Clay Mineralogy. London, GB: Blackie, 1987.

[17] Moore DM. and Reynolds RC. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford, UK: Oxford University Press, 1997.

[18] Hanawalt JD, Rinn HW, Frevel LK. Chemical Analysis by X-Ray Diffraction. Analytical Chemistry 1938; 10, 475-512.

[19] Serdar S. Investigation of whole rock and clay mineralogy of Oligocene sedimentary rocks outcrop near NE of Korkut (Muş). MSc, Van Yüzüncü Yıl University, Van, Türkiye, 2021.

[20] Mükemre ME. Microfacies of Oligocene deposits in south-southeast of Mollababa Village (Muş). MSc, Van Yüzüncü Yıl University, Van, Türkiye, 2019.

[21] Uygur K. Carbonate Geology. Ankara, Türkiye: T.P.A.O. Arama Grubu Başkanlığı, 1989.

[22] Görür N. Carbonate Rocks-2: Environmental Analysis. Ankara, Türkiye: T.P.A.O. Arama Grubu Başkanlığı, 1982.

[23] Millot G. Geology of Clays. Paris, FR: University of Strasburg, 1970.

[24] Erdoğanlı H. Investigation of whole rock and clay mineralogy of early Miocene sedimentary rocks crop out in the northeast of Korkut (Muş). MSc., Van Yüzüncü Yıl University, Van, Türkiye, 2022.