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GLAUBERITE-HALITE ASSOCIATION IN BOZKIR FORMATION (Pliocene, Çankırı-Çorum Basin, Central Anatolia, Turkey)

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Keywords:
Çankırı-Çorum Basin, fossil evaporite, glauberite, halite, Pliocene, playa lake, sabhka.

ABSTRACT

Tertiary Çankırı – Çorum Basin is one of the biggest basin covering evaporitic formations in the Central Anatolia. During borehole drills carried out in Bozkır Formation which contain Pliocene aged evaporites in the basin, a thick rocksalt (halite, NaCl) deposit was detected that consisting of glauberite ($Na_2Ca(SO_4)_2$) interlayers (sabhka) synchronous with sedimentation. Rocksalt bearing layers in Bozkır formation which was deposited in playa-lake – sabhka environment, where seasonal changes are effective, were first defined as Tuz member in this study. Bozkır formation was divided into three zones in drillings carried out in sabhka – playa -lake transitional environment. From bottom to top, these are ordered as claystone-less anhydrite zone, rock salt-claystone-anhydrite-glauberite zone (Tuz member) and claystone-gypsum-less anhydrite zone. Rocksalt was cut in thicknesses reaching 115 meters within Tuz member. Rocksalt (playa-lake) which is mostly bedded and white, pale/dark gray colored is conformable with sedimentation and is low dipping. The level at which glauberite deposition within Tuz member is observed the thickest was defined as glauberite-mudstone zone. Glauberite mineral which is observed as disc and rosette shaped individual forms within mudstone dominant matrix was formed as a diagenetic mineral in saline mudflat environment (sabhka). In geochemical analyses carried out (XRD, XRF, SEM) it was detected that glauberite mineral had been crystallized following anhydrite mineral within matrix that includes complex crystal forms in sabhka environment, halite mineral had grown on glauberite mineral and it was sometimes observed in the form of fracture and crack infill. The glauberite mineral deposition which does not have an economical thickness is of great importance in terms of the existence of fossil Na-sulfate deposition scientifically in Çankırı-Çorum Basin.

1. Introduction

The study area is located in Çankırı-Çorum Basin which is one of the biggest Tertiary depositional basins of Turkey in the Central Anatolia, 25 km to the southeast of the Çankırı (Figure 1). New lithological findings were obtained during borehole drillings carried out in Bozkır formation which contains Pliocene evaporites in the basin.

Bozkır formation is generally represented by the alternation of claystone, gypsum/anhydrite and was deposited in playa-lake environment. During drillings in the formation thick rocksalt (halite, NaCl) deposition was detected which consists of glauberite ($Na_2Ca(SO_4)_2$) interlayers which were deposited in sabhka environments synchronous with sedimentation. These halite (NaCl) bearing layers were first defined as Tuz member in this study.

The purpose of this study is to reveal Na-sulfate (glauberite)-NaCl (halite) association which was first detected in Bozkır Formation in the basin, to establish evaporitic characteristics of the formation, to make

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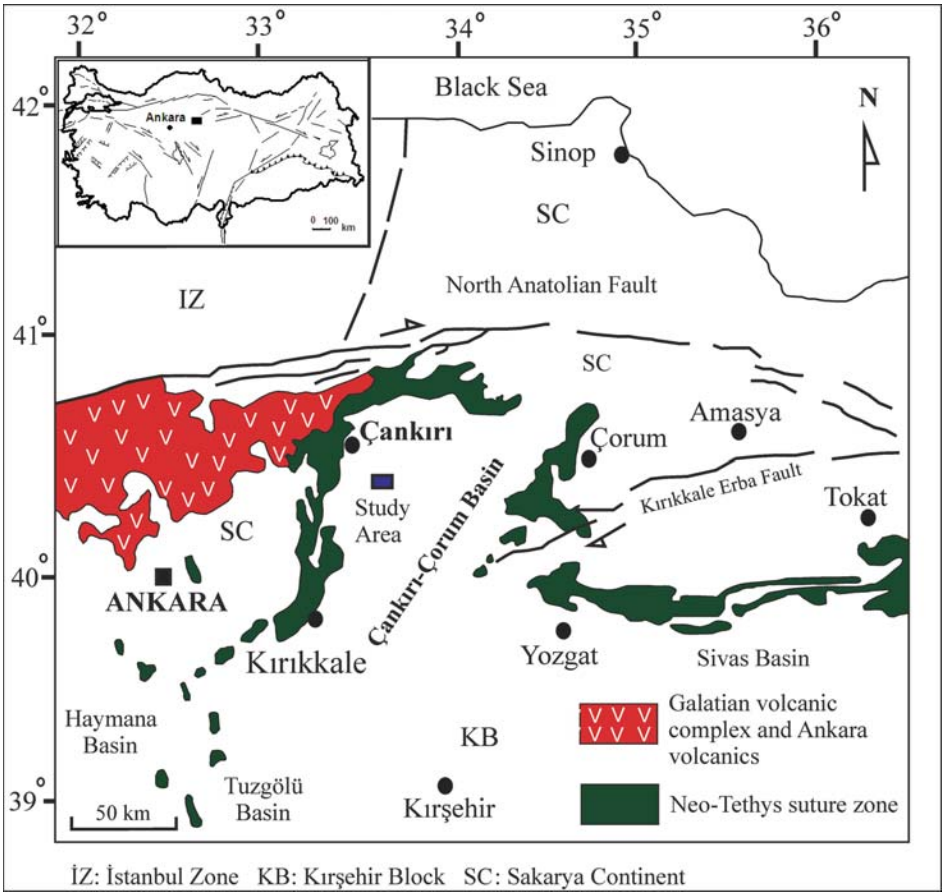


Figure 1- Location map of the study area (Karadeniz et al., 2004).

contribution for the interpretation of the basin and the production of new data in Na-sulfate explorations.

Na-sulfate form several minerals in nature but the most economical and mineable ones are; mirabilite $(Na_2SO_4).10H_2O$, thenardite (Na_2SO_4), glauberite $(Na_2Ca(SO_4)_2)$ and bloedite $(Na_2Mg(SO_4)_2.4H_2O)$. Na-sulfate minerals have hardness values in between 2-3, are colorless in pure state, transparent, easily dissoluble in water, bitterly and saline, with densities ranging between 1.49-2.8 gr/m^3. These occur in continental environments and cannot be well preserved in atmospheric conditions.

Rocksalt which is odorless, dissoluble in water, easily crumbled substance is formed by Na^+ and Cl^- ions, and is crystallized in the form of cubic crystallography. Although it is colorless in pure state it may appear in gray, yellow, red, and even green and blue colored in nature. The hardness of the halite mineral which shows plastic character under high pressure is 2.5 and the specific weight varies in between 2.10-2.55 gr/cm^3. The melting and boiling points of the mineral are 800°C and 1412°C, respectively.

Salt resources which have economic importance are divided into two categories as; solid and liquid. The salt exists in sea, lakes and in saline water resources as in liquid, but occurs as solid in the form of embedded rocksalt deposits. The seas form the biggest salt reservoirs of the world.

The presence of rocksalt in the basin has been known for many times and it was produced in solid form by room-pillar method (Çankırı Salt Cave, Potuk Salt). These operated halite mines are the salts which moved upward (i.e. salts that reached the surface by diapirism) before Pliocene. The rocksalt cut in Bozkır formation does not indicate any diapirism, compatible with sedimentation, as bedded and is in low dipping.

Operated rocksalt which emerged the surface as a result of diapirism is located in north of the study area. Quite steep slopes are observed in northern parts of the study area, in Bozkır formation and in southern part of the operated salt mines (Figure 2). This slope increase occurs due to the deformation controlled by rocksalt tectonics which was generated by pre-Pliocene halite that had risen upward as a result of diapirism.

It was first determined both mineralogically and petrographically that Na-sulfate layers (glauberite) within Bozkır formation in Çankırı-Çorum Basin had turned into secondary gypsum minerals at or near the surface. Similarly; halite minerals which had also been substituted by the secondary gypsum mineral and textures that had formed with this special transformation was published (Gündoğan and Helvacı, 1999; Gündoğan and Helvacı, 2001; Helvacı and Gündoğan, 2008; Gündoğan and Helvacı, 2009). Gündoğan (2000) stated in his study that in geochemical analyses of these pseudomorphic secondary gypsums which were observed in some layers of the formation and formed as a result of glauberite alteration (Figure 3) contained Na_2O less than 1%. He also emphasized that special textures observed in petrographical studies were in the character of key data in Na-sulfate exploration.

Besides; the actual deposition of bloedite ($Na_2Mg(SO_4)_2.4H_2O$) was determined, which is another significant Na-sulfate mineral in the basin, in a seasonal lake environment and as a result of analyses carried out it was detected that this deposition was associated by thenardite and halite and gypsum in few amounts (Sönmez, 2010).

Çayırhan (Ankara) deposit in Beypazarı Basin located in the Central Anatolia is an example for sedimentary embedded Na-sulfate deposit which exists in small numbers in the world (Çelik et al., 1987). The deposit is located among layers of gypsum of the Kirmir Formation which deposited in Upper Miocene playa-lake environment. Na-sulfate exists as glauberite and thenardite in the deposit (Helvacı et al., 1989; Orti et al., 2002). It was observed that Na-sulfate occurrences in the formation mostly consisted of euhedral glauberite, and thenardite minerals which were observed among them bonded glauberite minerals by substitution and/or cementation (Gündoğan, 2000; Gündoğan and Helvacı, 2001; Helvacı and Gündoğan, 2008; Gündoğan and Helvacı, 2009).

In western Mediterranean region (Spain and France) evaporitic Na-sulfate bearing formations take place in different basins in Oligocene and Miocene ages. The association of glauberite-halite minerals was detected; especially, in Lower Miocene Lerin (Menduian et al., 1984) and Zaragoza Gypsum formations (Salvany et al., 2007) and in Oligocene Falce Gypsum formation in Ebro Basin (Spain), and in Lower Miocene saline unit in Madrid (Tajo) Basin (Ordonez and Garcia del Cura, 1994). In addition, this association was also encountered in Oligocene aged

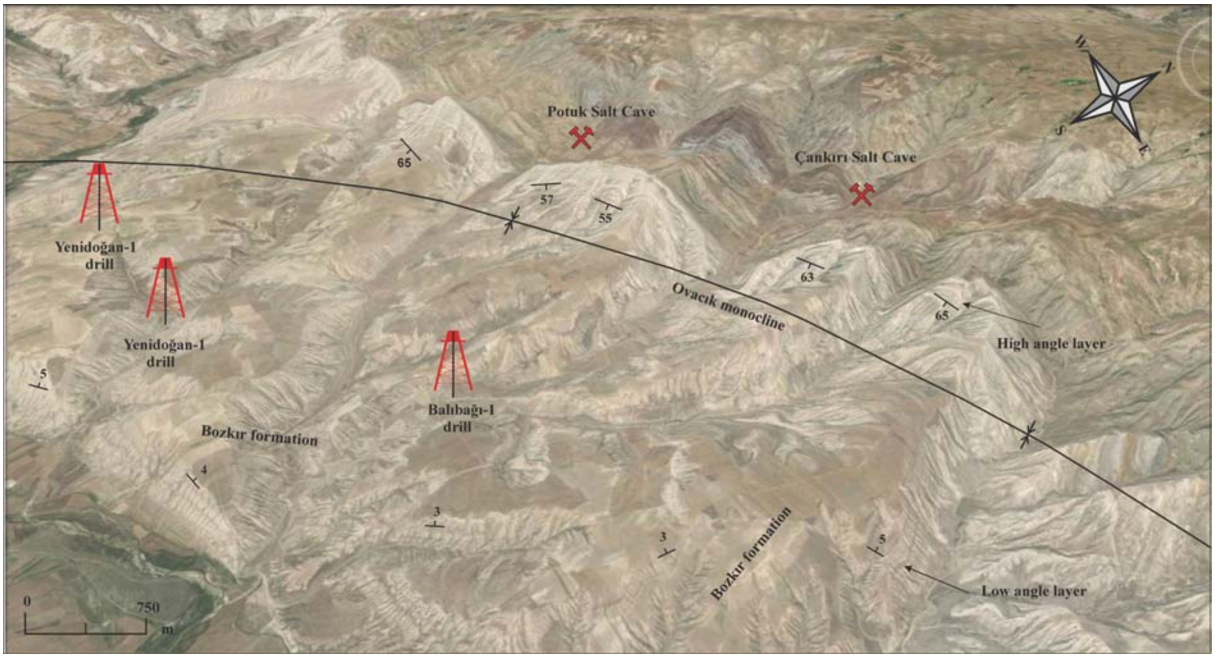


Figure 2- Pre-Pliocene salt quarry in the north of the study area (image taken from Google Earth).

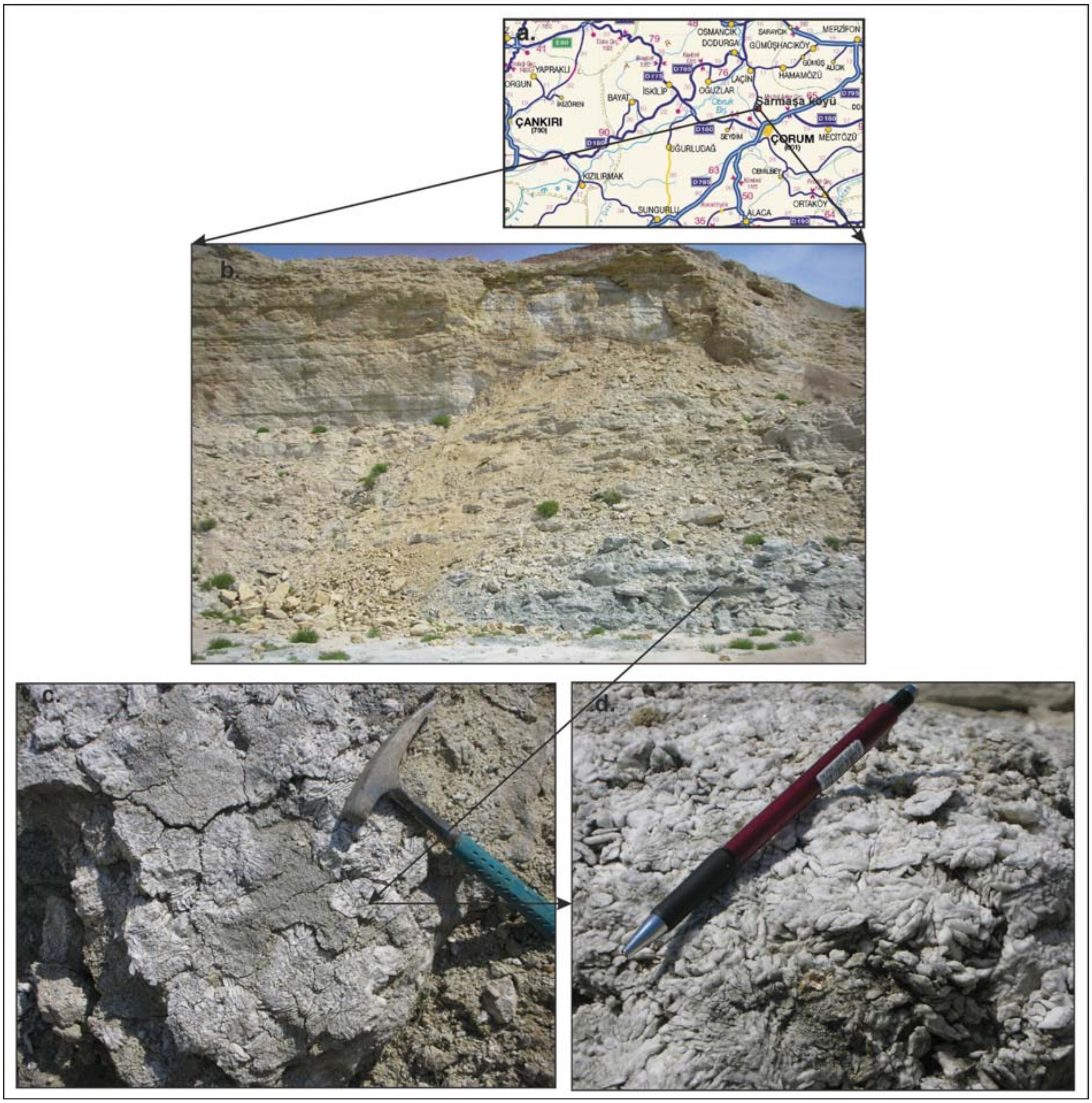


Figure 3- a-b) Gypsum quarry, Çorum Sarmaşa village; c) glauberite pseudomorphs which turned into gypsum; d) close up view.

Upper Evaporite formation in Valence Basin (France) (Dromart and Dumas, 1997).

1.1. Previous Studies

The study area is located in Çankırı-Çorum Basin which is one of the biggest sedimentary basins of Turkey. The basin is situated in the Central Anatolia between longitudes of 33.5°-35° and latitudes of 39.5°-41° (Figure 1).

When looking at previous studies it is seen that several investigations were carried out at different topics in the basin. Norman (1972) determined the recharge of Lower Tertiary sediments in addition to the stratigraphy of the basin in his study and stated that Çankırı basin was divided by faults in ENE-WSW directions, synchronous with the sedimentation. Şenalp (1974 *a, b*) in his study specified that the basin was characteristically in narrow and deep oceanic basin from Early Cretaceous to Middle Eocene, though most of the area was covered with terrigenous sediments. Studies related to Tertiary geology and stratigraphy have continued by Birgili et al. (1975), Akyürek et al. (1982), Yoldaş (1982) and Hakyemez et al. (1986). New findings related to the tectonism and stratigraphy basin were obtained by Koçyiğit (1991). Tüysüz and Dellaloğlu (1994) in their study asserted that Early Tertiary paleogeographical evolution of the Çankırı Basin and its surround in the Central Anatolia had been controlled by a compressive regime which caused the closure of the Neotethys Ocean and continued even after that event. Kaymakçı (2000) discussed the tectonics and stratigraphy of the basin and presented new findings. Seyitoğlu et al. (1997, 2001) discussed fault systems which are effective in basin tectonics from a different point of view. Furthermore; evaporitic environments and its sedimentology in the basin starting from Middle Late Eocene were interpreted by Ergun (1977), Karadenizli (1999), Karadenizli and Kazancı (2000), Gündoğan (2000), Gündoğan and Helvacı (1999, 2001), Varol et al. (2002), Karadenizli et al. (2004). Moreover; exploratory studies of drilled industrial raw material were carried out between the years 2006-2010 by MTA and new data were extracted in the basin.

2. General Geology

Çankırı-Çorum basin is the biggest depositional area of the Central Anatolia in Tertiary time in terms of widespread area and bedding thickness. The basin like other Central Anatolian basins was formed by the convergence of Sakarya Continent and the Kırşehir Block located within Anatolide between Cretaceous-Eocene time intervals (Şengör and Yılmaz, 1981). It is the largest Tertiary basin in the Central Anatolia (Haymana, Tuz Lake, Sivas) (Figure 1). All these Central Anatolian Basins were defined as the collapse basins among rising plates (Görür et al., 1984).

Çankırı-Çorum Basin is located at a complex zone in which it was formed by Sakarya and Kırşehir continents with Ankara-Erzincan suture. Units belonging to Sakarya-Kırşehir continent and İzmir-Ankara-Erzincan Suture zone constitute the units at the bottom of basin. The basin is surrounded by the ophiolitic mélange at west and by the Kırşehir massive at south.

Mesozoic ophiolites located at the bottom of basin are unconformably overlain by Paleocene-Eocene flysch deposit consisting of sandstone-shale alternation. This flysch deposit is cut by basaltic Eocene volcanites (Bayat formation). All these units are then overlain by Oligo-Miocene deposits (Birgili et al., 1975).

A very thick sedimentary deposit takes place in the basin ranging from Cretaceous to Pliocene. Rocks until Oligocene were deposited in marine environment, however rocks which were deposited in and after Oligocene belong to continental environment.

Evaporitic units in Tertiary aged Çankırı-Çorum Basin occurred in four different geological times. In Late Eocene (Kocaçay formation) in which the first evaporitic deposition took place, shallow marine environment has become dominant. However, in evaporites of Oligocene (İncik formation), Miocene (Bayındır formation) and Pliocene (Bozkır formation) totally the lake environment has been dominant.

All rock units in the basin were deposited in fluvial and alluvial fan environments and is unconformably covered by Plio-Quaternary Değim formation.

The oldest unit located in the study area is Oligocene aged İncik formation (Figure 4). This formation consists of rock units which formed in fluvial and lake environments. Conglomerate, sandstone and mudstones of the formation take place within the study area. Bayındır formation which represents Miocene aged evaporites overlies İncik formation. Bayındır formation is then overlain by Upper Miocene Kızılırmak formation consisting of sediments of meandering and braided river environment and flood plain deposits associated with those environments. Then Bozkır formation which contains Pliocene evaporites covers Kızılırmak formation with regional unconformity.

Topuzsaray anticline which was developed by the effect of Upper Miocene compression in western part of the basin is an overturned anticline orienting in NE-SW directions and is located in NE part of the study area. Oil exploration drilling has also been carried out by TPAO on this anticline (Usta, 1992). Furthermore; in the study area, the Ovacık monocline (forced fold) is observed which was developed by the diapirism effect of pre Pliocene rocksalt (Figure 2 and 4).

3. Methodology

Within scope of the project of Central Anatolian Industrial Raw Material Explorations (2010-32-13-05.1) executed by MTA, the revision of 1/25.000 scale geological map, the measurement of the

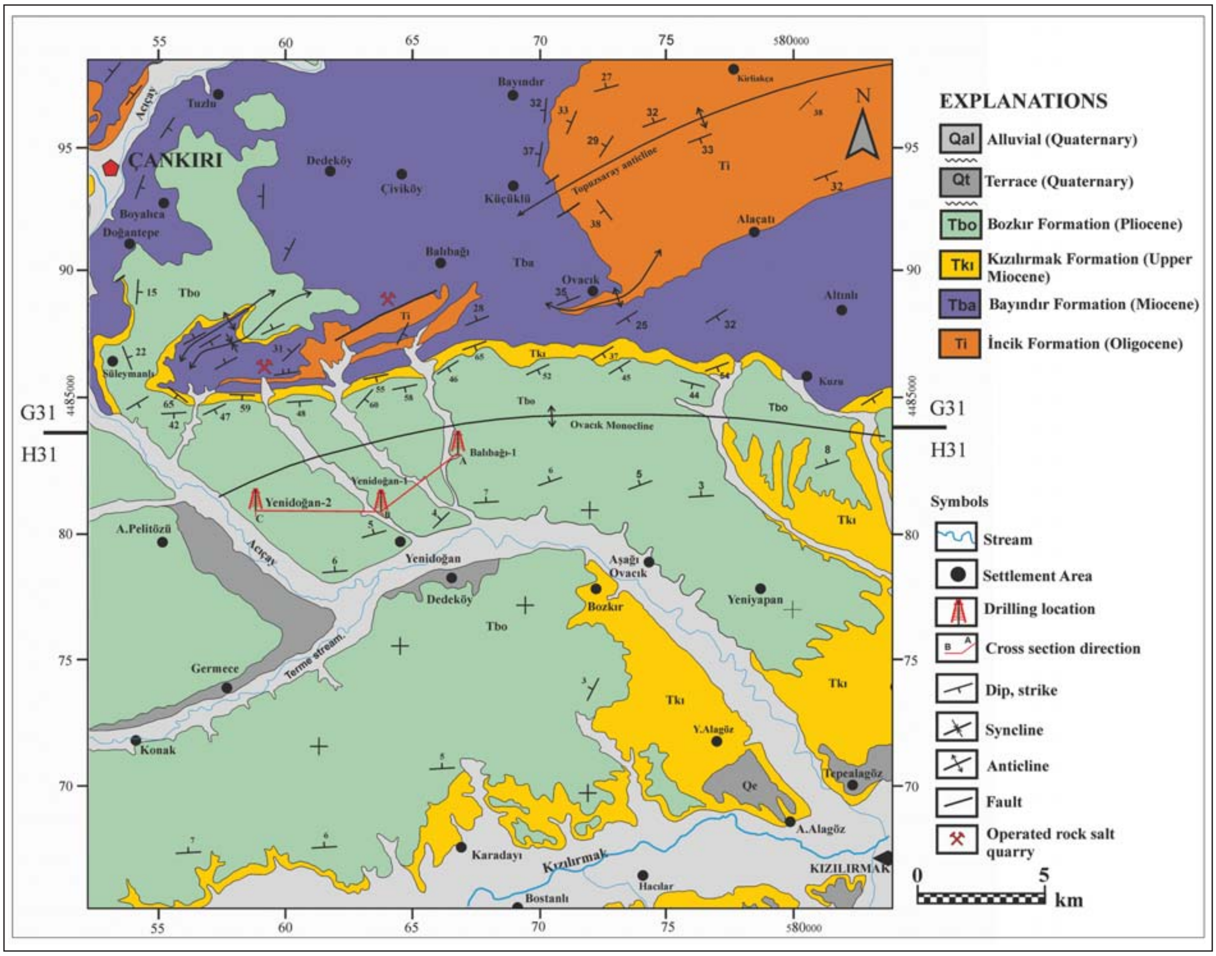


Figure 4- Geological map of the study area (from Birgili et al., 1975).

stratigraphic section and intense field observations were performed. Besides, total of 2068 m. exploratory borehole drillings were carried out at three locations in order to control embedded deposits (Table 1).

XRD samples were taken at certain intervals during borehole drilling studies performed in Bozkır formation. Chemical analyses were performed from rocksalt samples in halite-claystone-anhydrite-glauberite zone which is defined as the Tuz (halite) member. Interlayers of glauberite were used as for the XRD and XRF analyses. Representative samples were collected from glauberite interlayers and glauberite-mudstone zone where the glauberite mineralization is the thickest and observed the best within Tuz member. Then, SEM studies were done in order to understand the mineral associations and their crystal morphology. Besides, XRD and XRF analyses were carried out in samples taken from claystones within Tuz (halite) member.

Mineralogical analyses were performed by Philips PW XRD instrument in laboratories of the Dept. of Mineral Analyses and Technologies in MTA. Diffractograms were obtained using Cu-K radiation between 2.5°-70° and within 2θ interval. Samples were dried at 105°C during chemical analyses. Analyses were carried out in XRF instrument in IQ+ mode (unstandardized program) in the same laboratories.

Using four samples selected in SEM analyses, total of 40 secondary electron detector (SE) image and 15 EDS (Energy Dispersive X Ray Spectrometer) point analysis results were taken under FEI Quanta 400 MK2 model scanning electron microscope. EDS point analyses are the results of unstandardized, semi quantitative elementary and oxide analysis by EDAX Genesis XM4I model EDS detector. Elementary point analyses were made under kV:25.00 Tilt:0.00 Take-off:34.94 AmpT: 102.4 Det Type:SUTW, Sapphire Res:130.54 Lsec:10 detector conditions.

Table 1- Drilling studies carried out in Bozkır formation.

Drilling name	Elevation (m)	Drilling depth (m)	Tuz member entrance-exit (m)	Tuz member thickness (m)	Rocksalt thickness (m)	Glauberite-mudstone zone thickness (m).
Balıbağı-1	622	920	85-430	345	70	2,85
Yenidoğan-1	620	658	45-406	361	115,40	2,20
Yenidoğan-2	670	490	100-404	304	115,80	3,20

4. General Characteristics of Bozkır Formation

Bozkır formation which consists of evaporitic layers was first defined by Tanrıverdi (1973) and Birgili et al. (1975). The age of the formation is upper Miocene according to Tanrıverdi (1973) and Birgili et al. (1975). The age of the formation was determined as Upper Micene-Pliocene according to Kaymakçı (2000) and as Early Pliocene by Karadeniz et al. (2004).

Bozkır Formation was deposited in evaporitic lakes where palustrine conditions are observed in which seasonal changes are effective (Varol et al., 2002). Formation occurs by four main lithofacies groups as sulfates, carbonates, siliciclastics and chlorites (NaCl). Bozkır formation consists of massive bedded gypsum, halite, glauberite, anhydrite, gypsum arenite, individual gypsum crystals, thick claystone, dolomite and ooidic limestone. The thickness of the unit reaches 700 m. The basin has low dipping, widespread area in general (Figure 5).

Although there were carried out several studies in the formation, borehole drilling was first time performed within this project. Mainly, three lithological zones were observed in drillings (Figure 6). These are from bottom to top as; claystone-less anhydrite zone, halite-claystone-anhydrite-glauberite zone and claystone-gypsum-less anhydrite zone. Rocksalt bearing zone was named as Tuz (halite) member. As for the layers deposited in sabhka environment where the glauberite mineralization observed the thickest within this zone was named as glauberite-mudstone zone. In drillings lateral continuity was also detected in these zones (Figure 7).

The formation unconformably overlies Upper Miocene Kızılırmak formation and older units on margins of the basin, and is unconformably overlain by Plio-Quaternary Değim formation which was deposited in alluvial fan environment.

Bozkır formation was divided into three main depositional environments based on the measured section studies taken from different parts of the formation by Varol et al. (2002). These are alluvial, lake shore and lake center environments.

Figure 5- General view of the Bozkır formation (looking at N-NW from Çankırı-Çorum highway).

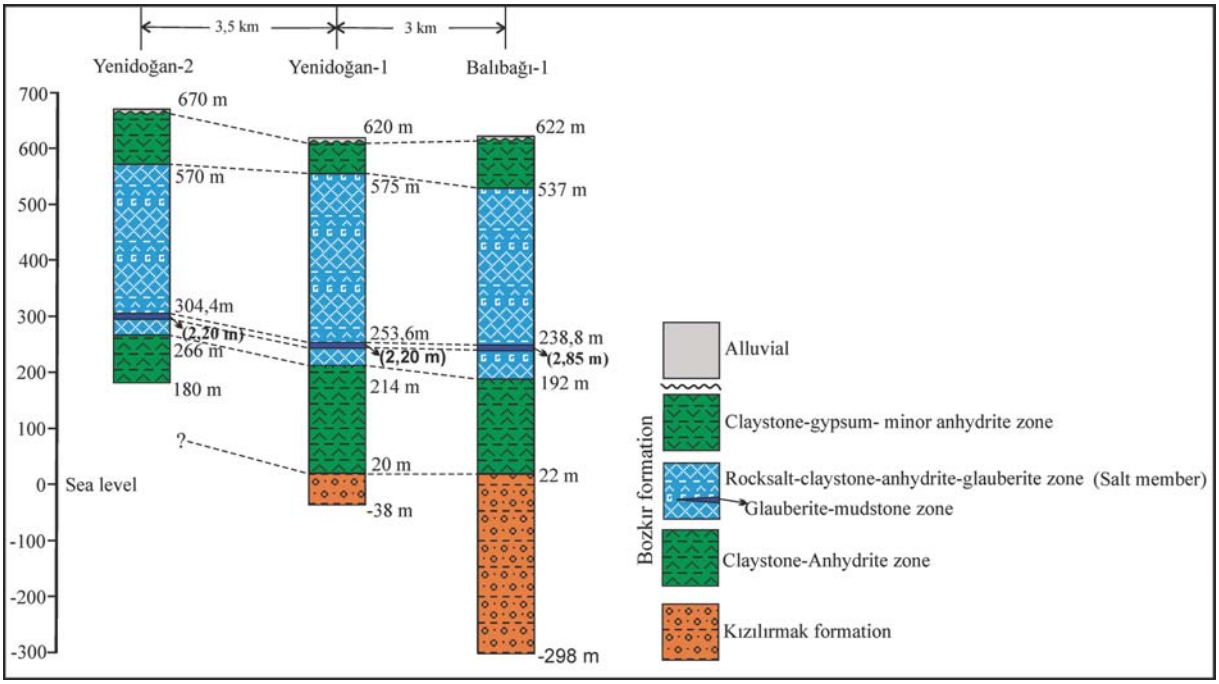


Figure 6- Drillings made in Bozkır formation.

Gündoğan (2000) in his study defined depositional environments of sulfate facies in Bozkır formation as wavy, transient, shallow, saline lake and sabhka. It was emphasized that nodular anhydrite and discoidal gypsums within claystones were formed as associated with variations in water level in sabhka environment and existed as intercalating within main lake deposits (selenitic gypsum and gypsum arenite).

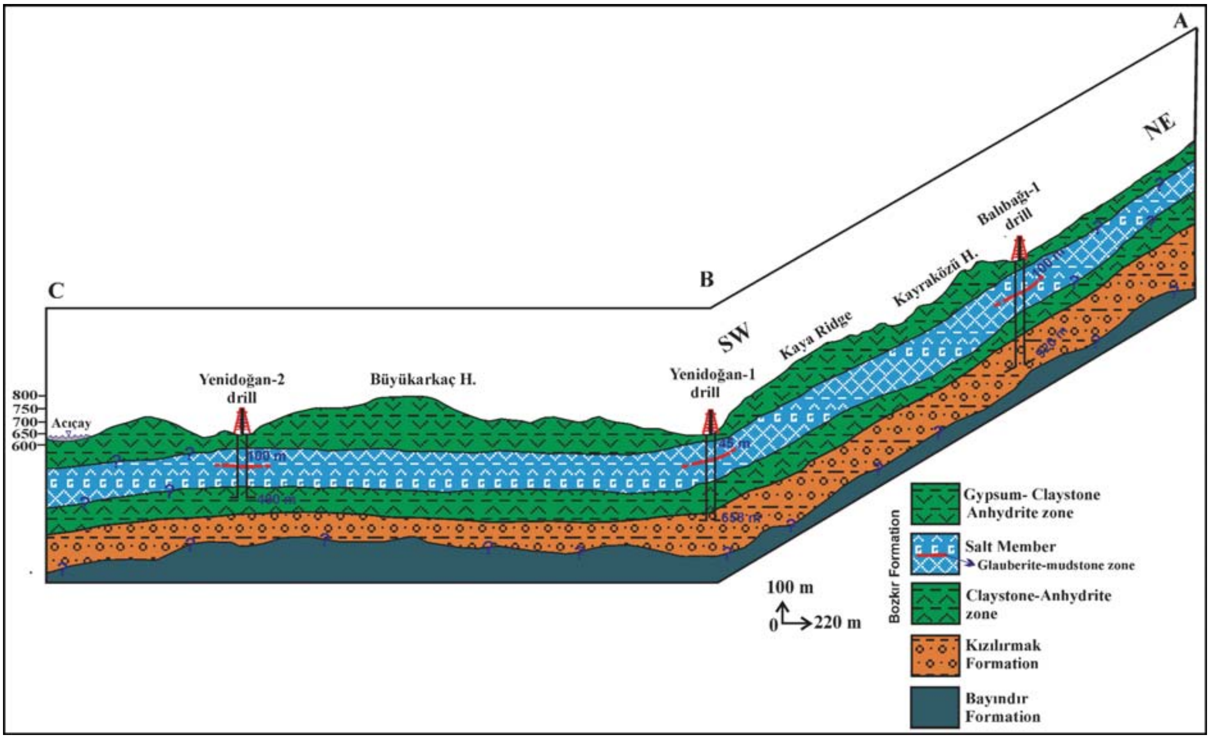


Figure 7- ABC cross section through drillings.

4.1. Tuz Member (Bozkır formation)

Tuz (halite) member which was detected in borehole drillings was performed in sabhka playa-lake transition in the Bozkır formation and is formed by rocksalt, claystone, anhydrite alternation consisting of glauberite interlayers (Figures 8 a, b, c, d). The member was deposited when the formation had been hydraulically isolated and in period when arid climate conditions had been prevalent.

In drillings, rocksalt was cut in thicknesses reaching 115 m within Tuz member which was observed the most in 362 m thickness. Rocksalt (playa-lake) which is mostly bedded and white, pale/dark gray colored is conformable with sedimentation and is low dipping (Figure 9).

The zone in which glauberite bearing layers, interlayering within playa-lake in Tuz member, is the thickest were defined as glauberite-mudstone zone and it was encountered at thicknesses of 3.2 m in drillings (Figure 10). Glauberite mineral which is observed as disc and rosette shaped individual crystals within mudstone dominant matrix was formed as a diagenetic mineral in saline mud plain environment (sabhka). In drillings carried out in sabhka- playa-lake transition zone, it was determined that sabhka deposits intercalated with playa-lake deposits (Figure 11). In addition to glauberite mineral which was formed within mudstone dominant matrix in saline mudflat environment, individual growths of halite mineral with nodular gypsum and anhydrite were also encountered (Figure 12).

Detritic minerals are observed as; various clay minerals, magnesite, quartz, feldspar group mineral and serpentine group mineral within the matrix from which it is formed by the mixture of several minerals.

Due to seasonal changes, Bozkır playa-lake has been recharged by both groundwater and surface waters. The bedded rocksalt has been deposited as a result of evaporation from lake water due to ionic enrichment in lake (Na^+, Cl^-) during arid periods

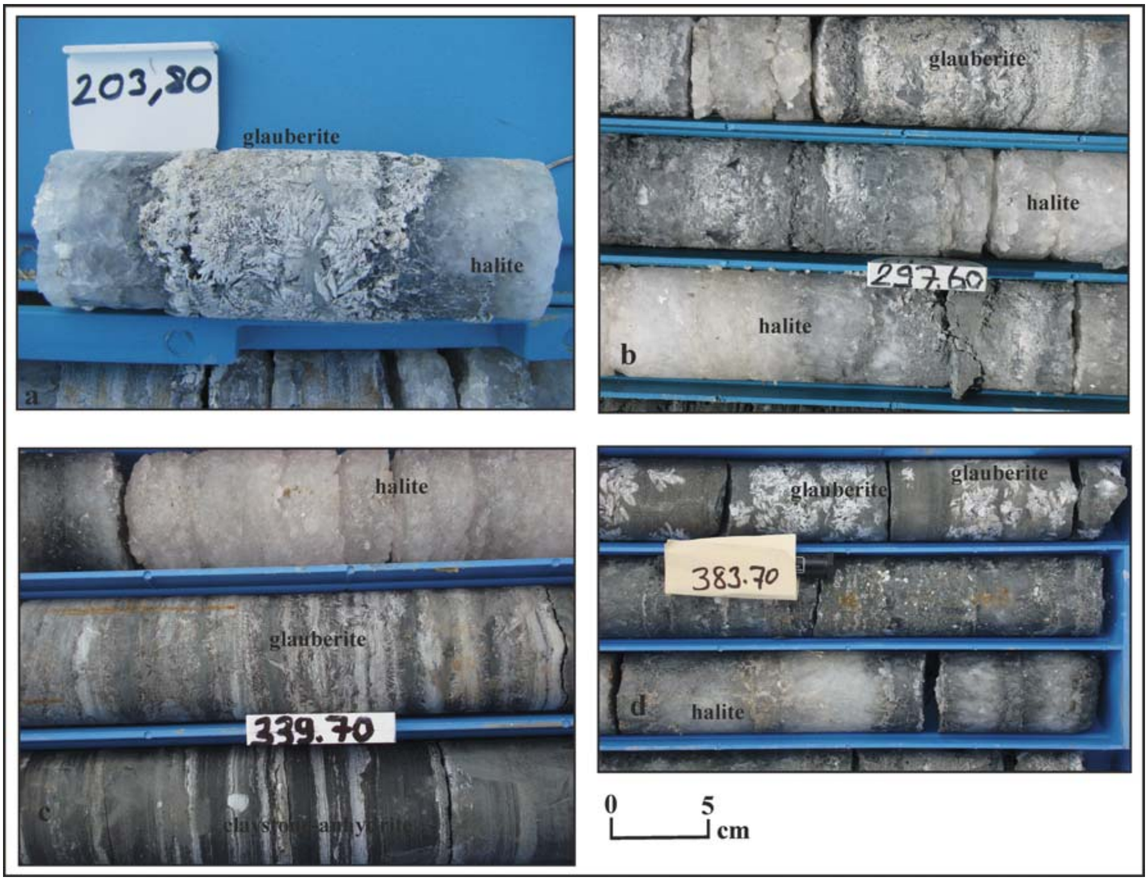


Figure 8- Glauberite interlayers and halite layers within Tuz member, a) Yenidoğan-2 drill, b) Balıbağı-1 drill, c, d) Yenidoğan-1 drill.

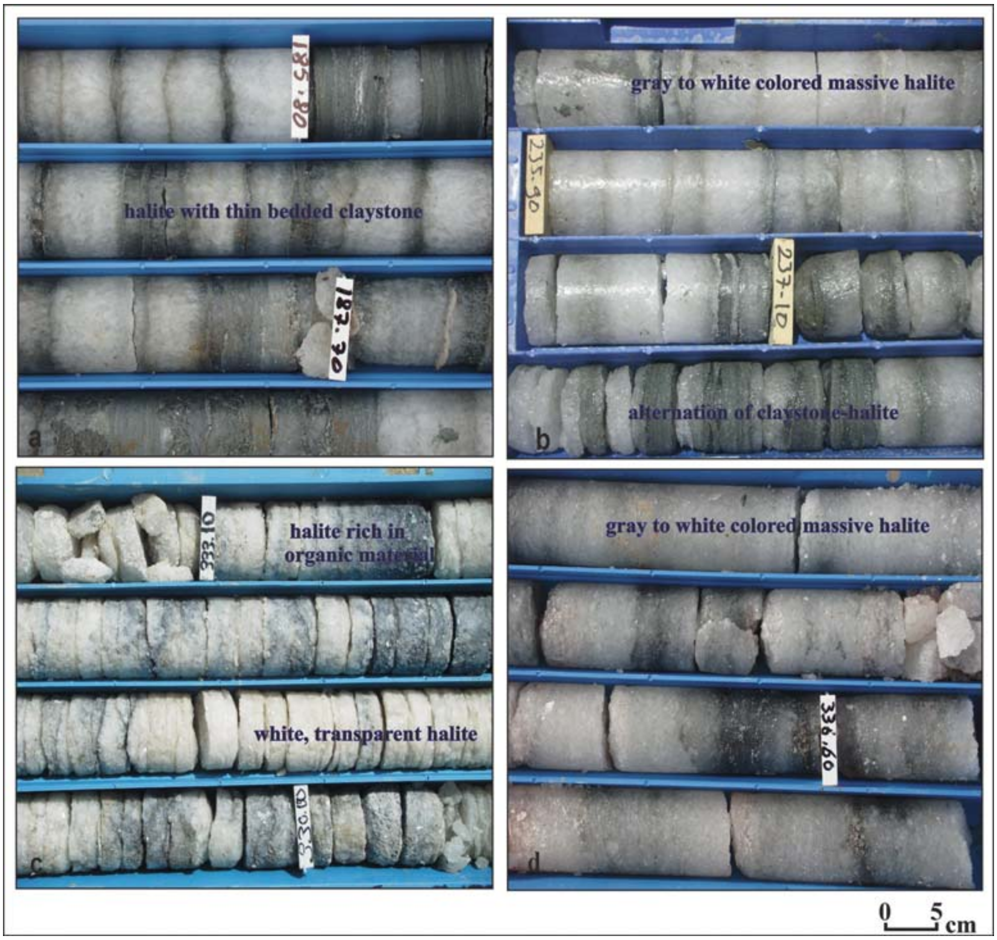


Figure 9- Rocksalt layers cut within Tuz member, a) Yenidoğan-1 drill, b) Balıbağı-1 drill, c) Yenidoğan-2 drill, d) Yenidoğan-1 drill.

where the playa lake has been hydraulically isolated (Figure 11).

When the lake passed into hydraulically open conditions in short and long terms, claystones have been mostly deposited. Varve lamination which occurs as a type of lamination due to seasonal changes is observed in claystones (Figure 13). The successive deposition of anhydrite, gypsum and halite on the other hand occurs due to chemical and temperature variations as a result of seasonal and/or climatic changes (Figure 14).

Moreover; rocksalt which was most probably deposited diagenetically between claystone and anhydrite in drillings was also detected as a different observation (Figure 15).

There are still discussions regarding the depositional source of the glauberite mineral whether it is primary or diagenetic in formation. Many studies related to actual and fossil Na-sulfate deposits indicate that glauberite was formed as a diagenetic mineral in saline mud-flat environment (Smooth and Lowenstein, 1991). In addition to that, it was suggested in some studies that some layers of the glauberite deposition were primarily deposited in subaqueous environment (Mees, 1999; Orti et al., 2002). Investigators who consider the primary origin for glauberite formation is less than the ones who consider that it had originated from an early diagenetic mineral (Salvany et al., 2007) as this mineral turns into gypsum at or near the surface.

4.2. Mineralogy

In geochemical analyses of the samples taken from rocksalt layers within Tuz member in Bozkır formation which is formed by the alternation of halite-claystone bearing interlayers of glauberite, Na^+ and Cl^- ratios were detected high and K_2O ratio was detected low (Table 2).

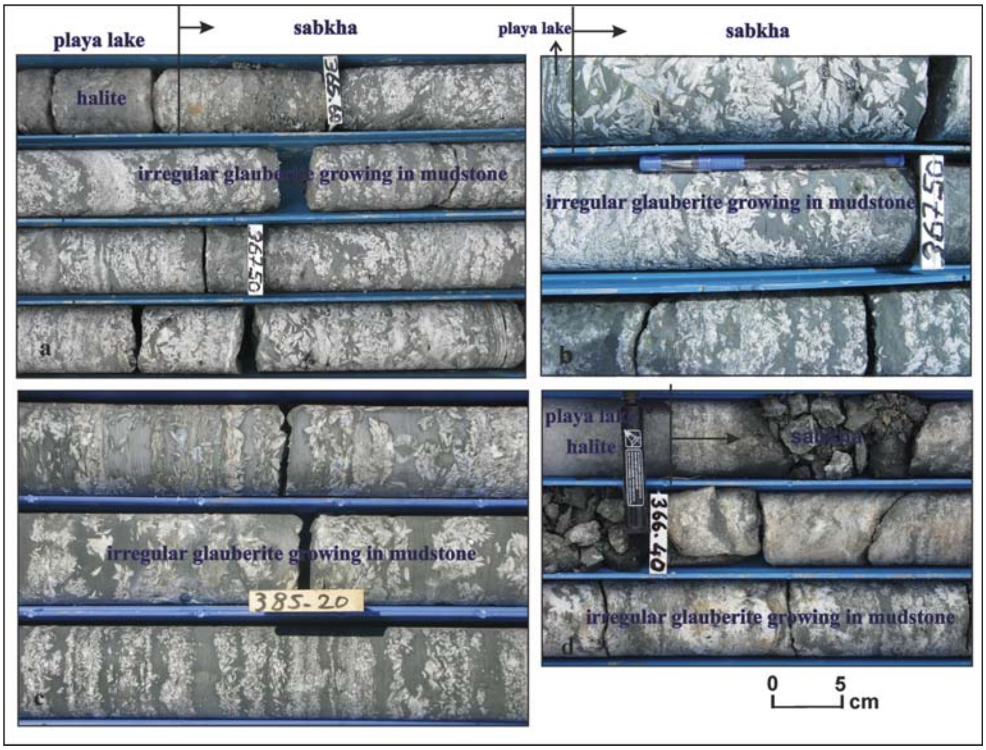


Figure 10- Glauberite-mudstone zone distinguished among playa-lake deposits in Tuz member; a, b) Yenidoğan-2 drill, c) Balıbağı-1 drill, d) Yenidoğan-1 drill.

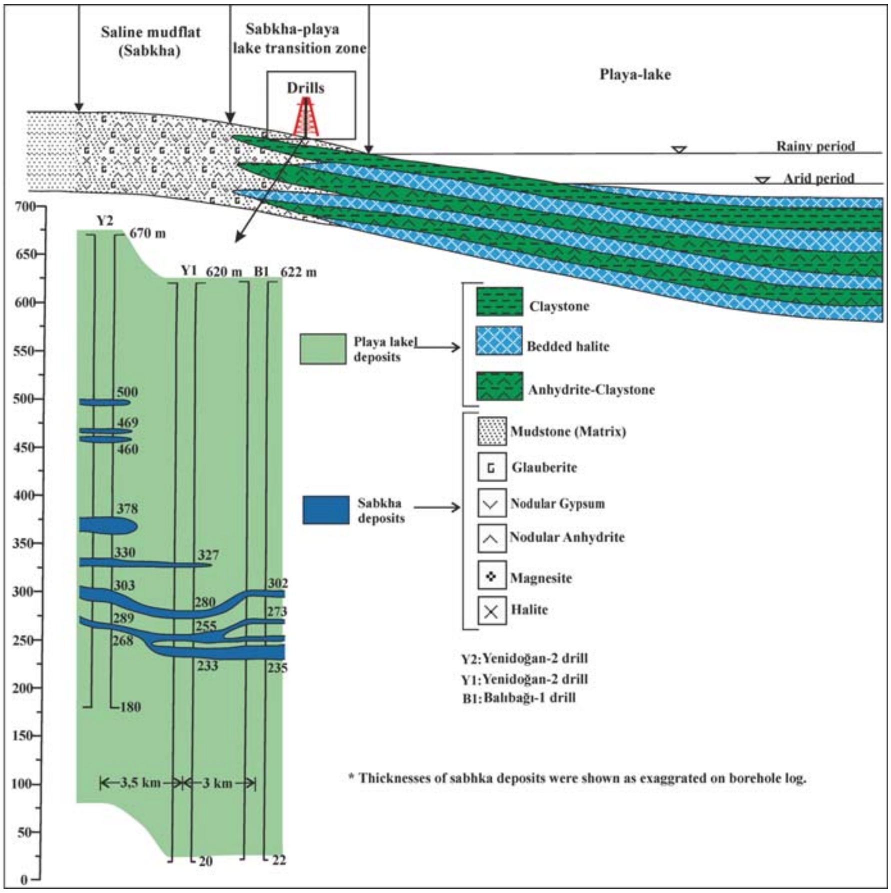


Figure 11- Schematic section showing the depositional environment of the Bozkır formation.

Figure 12- Individual growths of anhydrite and halite minerals in sabhka environment between playa lake; a, b) Yenidoğan-2 drill, c) Balıbağı-1 drill, d) Yenidoğan-1 drill.

Figure 13- Varve lamination in claystones a) Yenidoğan-1 drill, b) Balıbağı-1 drill.

Glauberite mineral which was crystallized from an evaporitic surface water as a diagenetic mineral in the form of individual growths in saline lake mud-flat environment were detected in XRD analysis of the samples collected (Figure 16). Anhydrite and gypsum are other individual minerals crystallized in halite matrix (Figure 17). In analyses it was seen that magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)_2$), halite (NaCI) and calcite ($CaCO_3$) minerals were observed within cryptocrystalline matrix which possessed a quite complex mineral assemblage and these are the other minerals observed in evaporitic environment (Figure 18).

Mg mineral which exists as a result of the alteration of ophiolitic rocks located at the bottom of the basin may be transported into the environment by surface and groundwaters and deposited from the lake water which its Mg^{+2}/Ca^{+2} ratio increases. Halite mineral both crystallizes individually in sabhka environment and exists in the matrix. Besides, it is deposited in aqueous environment by evaporation from lake water as bedded halite (Figure 9).

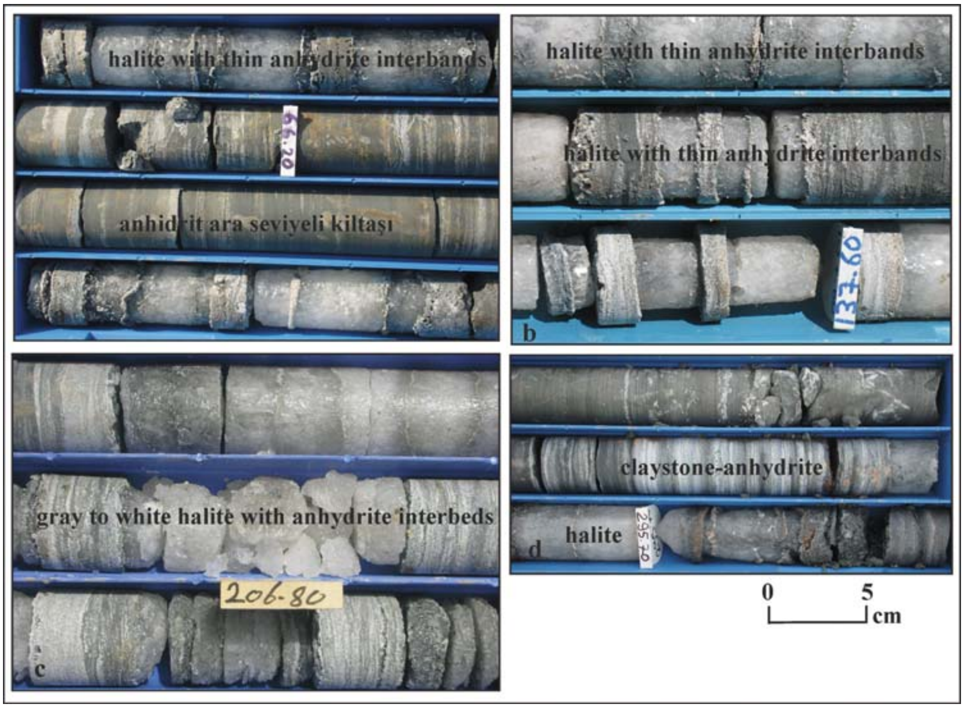


Figure 14- Alternation of rocksalt-anhydrite-claystone; a) Yenidoğan-1 drill, b) Yenidoğan-2 drill, c) Balıbağı-1 drill, d) Yenidoğan-1 drill.

Figure 15- Rocksalt which was deposited into sediment; a) Balıbağı-1 drill, b) Yenidoğan-1 drill.

Table 2- Chemical analysis of samples taken from drills (Oxide values were given in weight %)

Drilling name	Meter	Na	Cl	MgO	Al_2O_3	SiO_2	CaO	K_2O	Fe_2O_3	SrO	Br	Li	I	SO_3
Balıbağı-1	97.4	37.5	61.8	0.4	<0.1	0.3	0,1	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01	<0.01
Balıbağı-1	264.6	37.5	60,2	<0.1,	<0.1,	0.2	1.0	<0.1	<0.1	0.03	<0.01	<0.01	<0.01	1.17
Balıbağı-1	319,1	38,1	61,4	0.2	<0.1	0.2	<0,1	<0.1	<0.1	0.02	<0.01	<0.01,	<0.01	0,07
Balıbağı-1	427.4	37.9	59,3	<0.1	<0.1	0.3	1.1	<0.1	<0.1	0.02	<0.01	<0.01,	<0.01	1.38
Yenidoğan-1	59.8	38,6	59,2	0.1	0.1	0.2	0,7	<0.1	0,2	<0.01	<0.01	<0.01	0.22	0,02
Yenidoğan-1	216,5	39,1	60,3	6 0,1	0.1	0.2	<0,1	<0.1	0,2	<0.01	<0.01	<0.01,	<0,01	0,01
Yenidoğan-1	339,4	39,1	59,8	0,1	0.1	0.2	0,2	<0.1	0,1	<0.01	<0.01	<0.01	<0,01	0,01
Yenidoğan-1	390,1	38,5	59,4	0,1	0,1	0,2	0,8	<0.1	0,1	0,06	<0.01	<0.01	<0,01	0,02
Yenidoğan-2	102,4	40,0	58,4	0,2	0,3	0,8	0,1	<0,1	0,3	0,11	<0.01	4 ppm	<0,01	0,01
Yenidoğan-2	211,4	33,6	45,9	1,9	2,9	9,2	2,4	0,4	3,2	0,01	<0.01	6 ppm	<0,01	0,01
Yenidoğan-2	310,4	40,4	58,8	<0,1	0,1	0,2	0,4	<0,1	0,1	0,01	<0.01	<1ppm	<0,01	0,01
Yenidoğan-2	399,0	40,0	59,0	0,1	0,2	0,4	0,2	<0,1	0,1	0,03	<0.01	<1ppm	<0,01	0,01

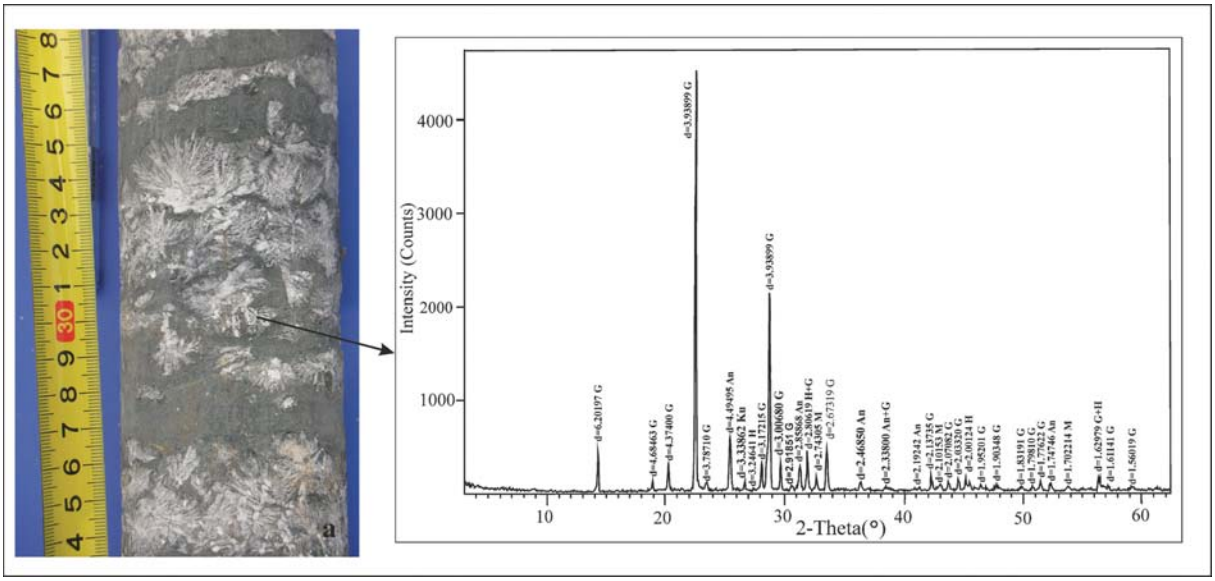


Figure 16- Interlayer of glauberite, a) Balıbağı-1 (340-340.15 m), b) XRD diffractogram of the sample taken from level which has disk like minerals, H: halite, G: glauberite, M: magnesite, An: anhydrite, Q: quartz.

Other minerals which were detected as a result of analyses in saline mudflat environment are palygorskite and zeolite group minerals (analcime, heulandite-clinopilolite) (Figures 18 and 19).

There is sodium enrichment due to evaporites (especially NaCl) in mudflat environment and this helps Na-rich clays to crystallize authigenically. Zeolites which are aqueous aluminum silicates (Na-K-Ca-Al aqueous silicates) occur as a result of the reaction between volcanic materials (tuff) with saline lake water. The source of the volcanic effect in Bozkır formation is considered as volcanic ash flows which occur due to Galatian massive on the western margin of the basin (Figure 1) and is transported into the environment by wind systems as the formation was deposited.

Palygorskite mineral $(Mg,Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ which is aqueous magnesium-aluminum silicate composite clay mineral was detected within a matrix in XRD analyses (Figures 18, 19). Arid climates, saline alkaline lakes, environments in which pH is greater than 7 and where sources that supply Si and Mg into the basin are the most significant places of formation of this mineral (Weaver, 1989). In the study area where all these conditions are supplied, palygorskite formation in the environment indicates the increase of Al fetch in addition to Mg and Si enrichments.

Other minerals observed in samples collected from the matrix of glauberite bearing zone are detritic minerals which were transported into the basin such as; quartz, mix layered clay mineral, illite/mica group mineral, kaolinite group mineral, chlorite group mineral, talc group mineral, serpentine group mineral and feldspar group mineral.

Chemical analyses of samples which were taken from the differentiated zone as glauberite-mudstone in Tuz member are given in table 3. High Cl^-, MgO, Al_2O_3 and SiO_2 values in analysis originate from minerals in the matrix. Also, high Na_2O and low Cl^- ratios originate from higher glauberite content than halite content.

In claystones (Figure 14) which intercalate with bedded halite in subaqueous environment in Tuz member were detected evaporite minerals in low rate (anhydrite, halite), zeolite group mineral (analcime, heulandite-klinoplilolite), palygorskite and transported detritic minerals (quartz, illite/mica group minerals, chlorite group minerals, amorphous material, talc group mineral, serpentine group mineral, feldspar group mineral, amphibole group mineral, mix layered clay mineral) in analyses.

Although claystones have similar mineralogy with the matrix of the environment consisting of glauberite mineral in mudflat (subaerial), they have low Na_2O ratio and high MgO, Al_2O_3, SiO_2 ratios compared to glauberite bearing layers in chemical analyses (Table 4).

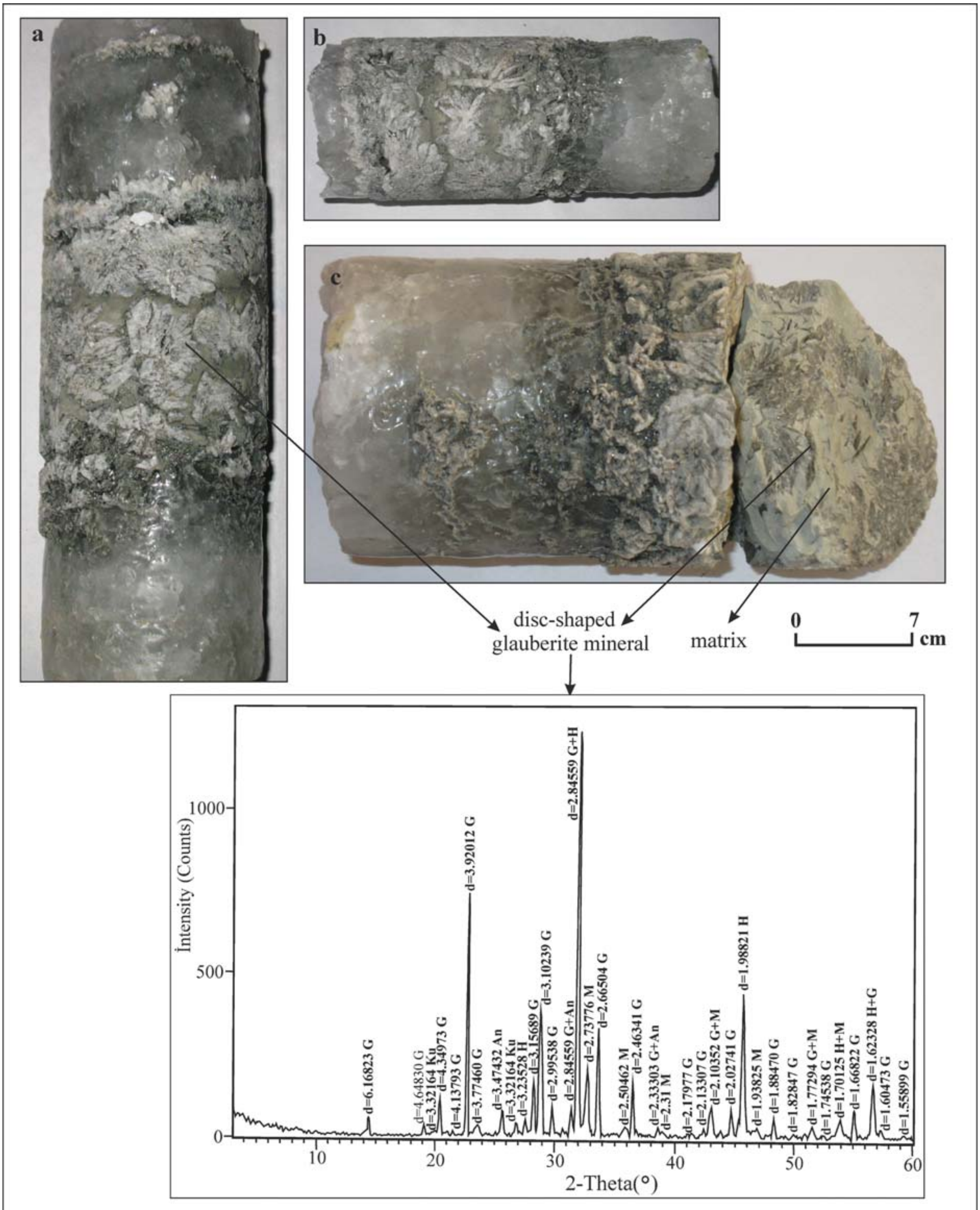


Figure 17- Interlayer of glauberite in rocksalt (Yenidoğan-2 drill, 158-158.35 m). a, b, c) photos of the same borehole, d) XRD diffractogram of the sample, H: halite, G: glauberite, M: magnesite, An: anhydrite, Q: quartz.

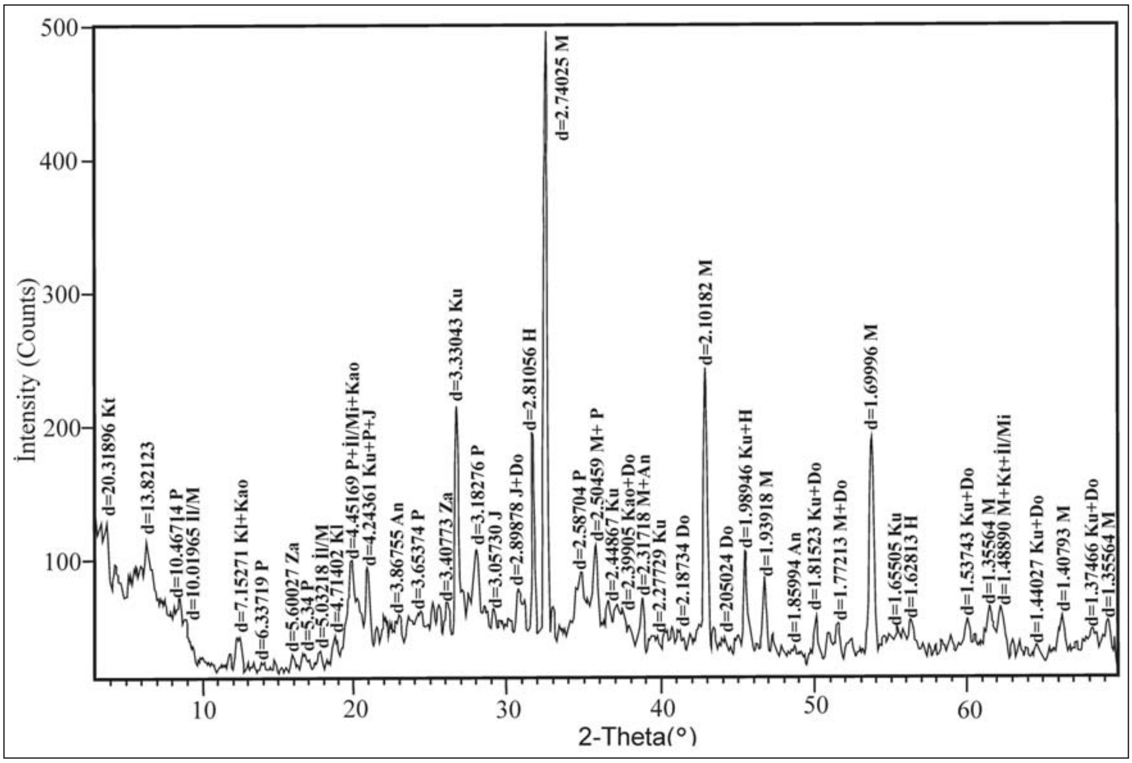


Figure 18- XRD diffractogram of the sample taken from the matrix of glauberite mudstone zone; Kt: mix layered clay mineral, P: palygorskite, İl/M: Illite mica group mineral, Kao: kaolinite group mineral, Za: zeolite (analcime), J: gypsum, An: anhydrite, Q: quartz, Do: dolomite, H: halite, M: magnesite, (Balıbağı-1 drill, 385.30 m).

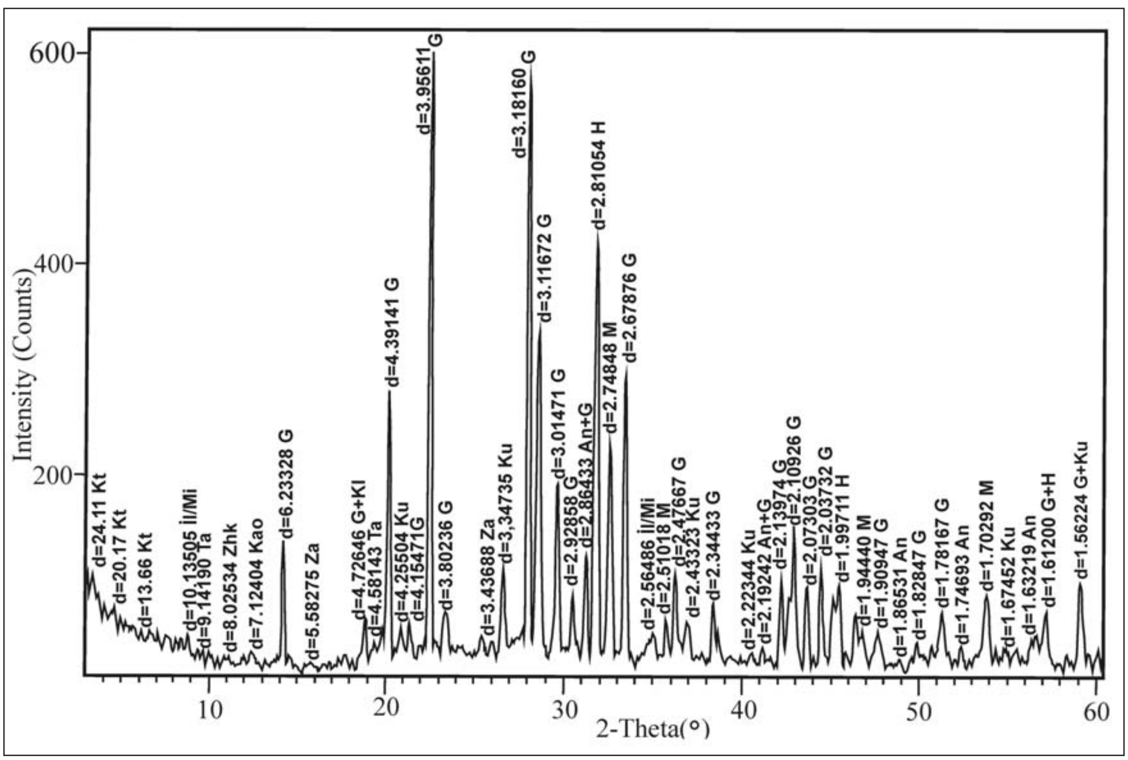


Figure 19- XRD diffractogram of the sample taken from glauberite mudstone zone; Kt: mix layered clay mineral, Ta: talc group mineral, Zhk: zeolite (Heulandite-Clinopilolite), G: Glauberite, P: palygorskite, İl/M: Illite mica group mineral, Kao: Kaolinite group mineral, Kl: chlorite group mineral, Za: Zeolite (analcime), J: Gypsum, An: Anhydrite, Q: Quartz, Do: Dolomite, H: Halite, M: Magnesite (Yenidoğan-2, 366.1 m).

Table 3- Chemical analysis of samples taken from glauberite mudstone zone (Oxide values were given in weight%).

Drilling name	Meter	Na_2O	Cl	MgO	Al_2O_3	SiO_2	CaO	K_2O	Fe_2O_3	A.Z	P_2O_5	TiO_2	MnO	SO_3
Balıbağı-1	385,3	10,8 1	,97	3,6	3,7	13,3	21,7	0,6	2,7	10,25	0,1	0,2	<0,1	30,2
Yenidoğan-1	340,0	16,0	1,82	6,4	3,5	12,1	13,8	0,5	2,1	8,0	0,1	0,2	<0,1	35,3
Yenidoğan-1	367,6	16,5	2,21	3,0	3,3	12,0	17,5	0,6	2,2	8,85	<0,1	0,2	<0,1	35,3
Yenidoğan-2	158,0	21,4	9,17	1,9	3,6	11,4	13,4	0,5	1,6	9,6	<0,1	0,2	<0,1	27,08
Yenidoğan-2	366,1	22,0	2,1	4,1	3,6	13,3	15,3	0,5	1,9	5,05	<0,1	0,2	<0,1	31,73

4.2.1. SEM Studies

SEM analyses were performed on glauberite bearing samples of which their mineralogical description had been carried out by XRD analysis. Secondary electron (SE) detector views of each detected mineral (morphological views) were taken and EDS point analyses were carried out in order to control their elemental contents.

In EDS point analyses carried out on morphological views of samples, euhedral and subhedral glauberite crystals were detected in the matrix (Figures 20 and 21).

Another mineral detected in SEM analyses is anhydrite mineral. These generally occur in euhedral form in cryptocrystalline or associates with glauberite mineral (Figure 23). It was determined that glauberite mineral had been crystallized following the anhydrite mineral (Figure 24).

During studies made in close up SE views of glauberite minerals, it was observed that halite mineral had grown on glauberite mineral and sometimes appeared in the form of fracture and crack infill (Figure 25). Besides, it was detected that halite mineral were developed on glauberite minerals in various crystal forms (Figures 26 and 27).

SEM-EDS analyses were performed in order to determine mineralogical characteristics of the cryptocrystalline matrix in which glauberite mineral is situated. In SE views and EDS point analyses, it was seen that the matrix had quite complex crystal

Table 4- Chemical analyses of samples taken from claystones deposited in playa lake within Tuz member (oxide values were given in weight %).

Drilling name	Meter	Na_2O	MgO	Al_2O_3	SiO_2	CaO	K_2O	Fe_2O_3	A.Z	P_2O_5	TiO_2	MnO
Balıbağı-1	269.4	2,1	11,4	5,6	20,7	418,8	0,9	4,9	30,75	0,1	0,4	0,2
Yenidoğan-1	273.0	2,7	5,9	8,4	33,4	220,7 1	,3	6,4	20,04	0,1	0,4	0,1
Yenidoğan-2	273.9	2,7	6,2	7,1	27,8	220,7	1,3	5,7	20,95	0,1	0,4	0,1
Balıbağı-1	280.3	3,3	6,0	10,1	37,2	113,3	1,5	7,4	16,7	0,1	0,6	0,2

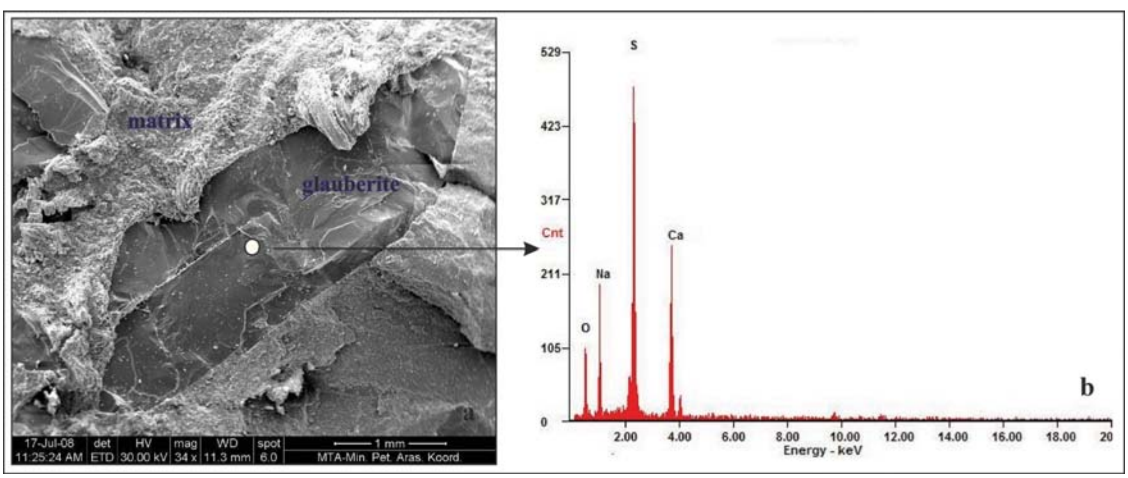


Figure 20- a) Euhedral glauberite crystal within matrix, b) EDS spectrum of the glauberite mineral (o: measurement point of EDS analysis taken on the crystal) (Balıbağı-1 drill, 385.30 m, XRD figure 18).

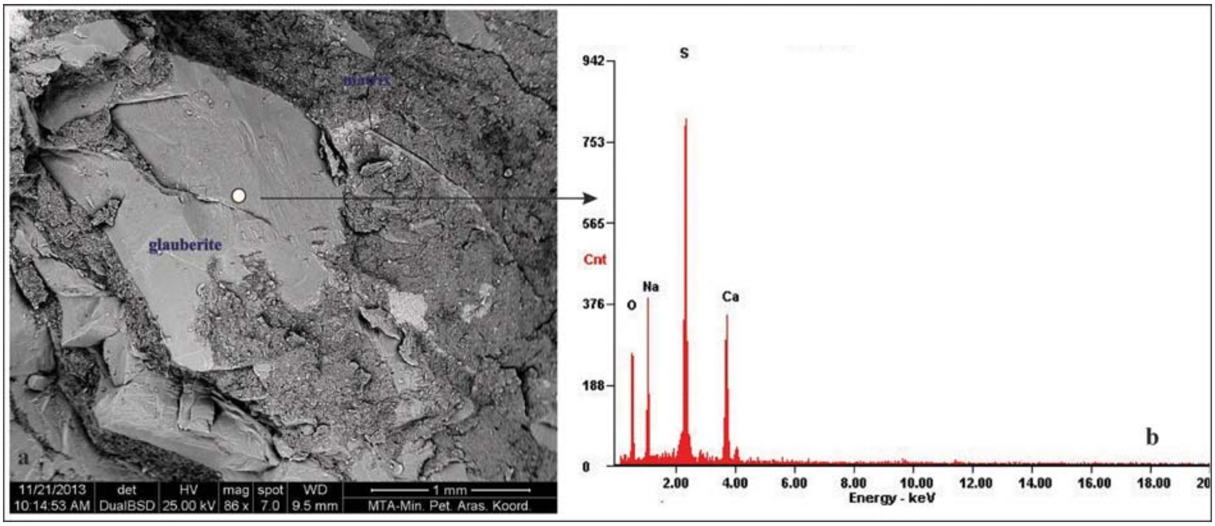


Figure 21- a) Subhedral glauberite mineral within matrix, b) EDS spectrum of the glauberite mineral, (o: measurement point of EDS analysis taken on the crystal). (Yenidoğan-1 drill, 340 m).

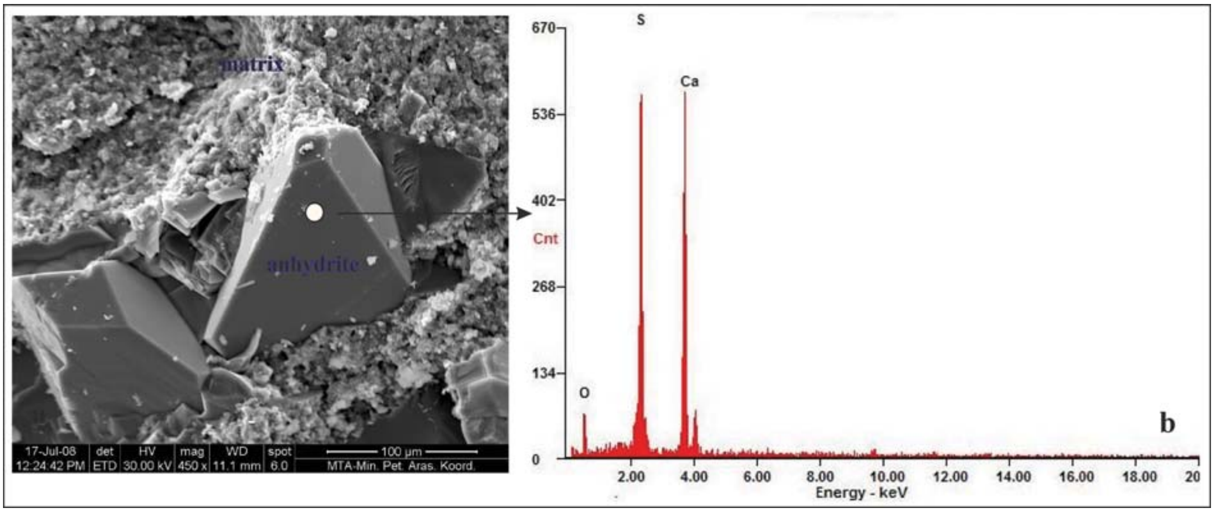


Figure 22- a) Euhedral anhydrite crystal within matrix, b) EDS spectrum of the anhydrite mineral, (o: measurement point of EDS analysis taken on the crystal), (Yenidoğan-2 drill, 366.1 m, XRD figure 19).

forms and elemental content (Figure 28). Quartz, calcite, zeolite group (analcime, heulandite-clinopilolite), palygorskite, illite/mica mineral group, feldspar mineral group were detected within magnesite and halite matrix.

As a result of SEM analyses based on the boundary relationships among minerals, the following occurrences were determined in sabhka environment (saline lake mud-flat). First gypsum and anhydrite minerals were crystallized within cryptocrystalline detritic matrix, then glauberite mineral was crystallized and grew on anhydrite minerals occasionally, and finally; halite mineral was crystallized. And this result is in accordance with evaporitic depositions in sabhka or saline environments in which the chain of formation starts with Ca compound minerals then passes into Na compound minerals.

5. Results

During borehole drillings carried out in Bozkır formation consisting of Pliocene aged evaporitic units in Çankırı-Çorum basin, thick rocksalt (halite) deposition which contain glauberite interlayer was determined.

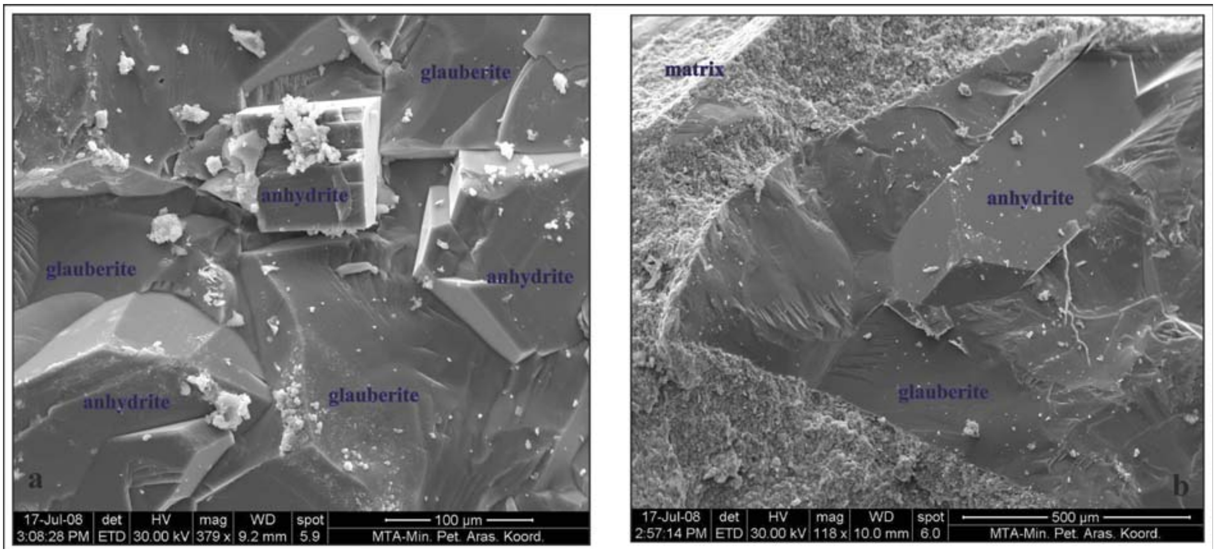


Figure 23- a) SE views of glauberite-anhydrite crystals, b) SE view of euhedral anhydrite mineral within glauberite mineral. (Balıbağı-1, 385.30 m, XRD figure 18).

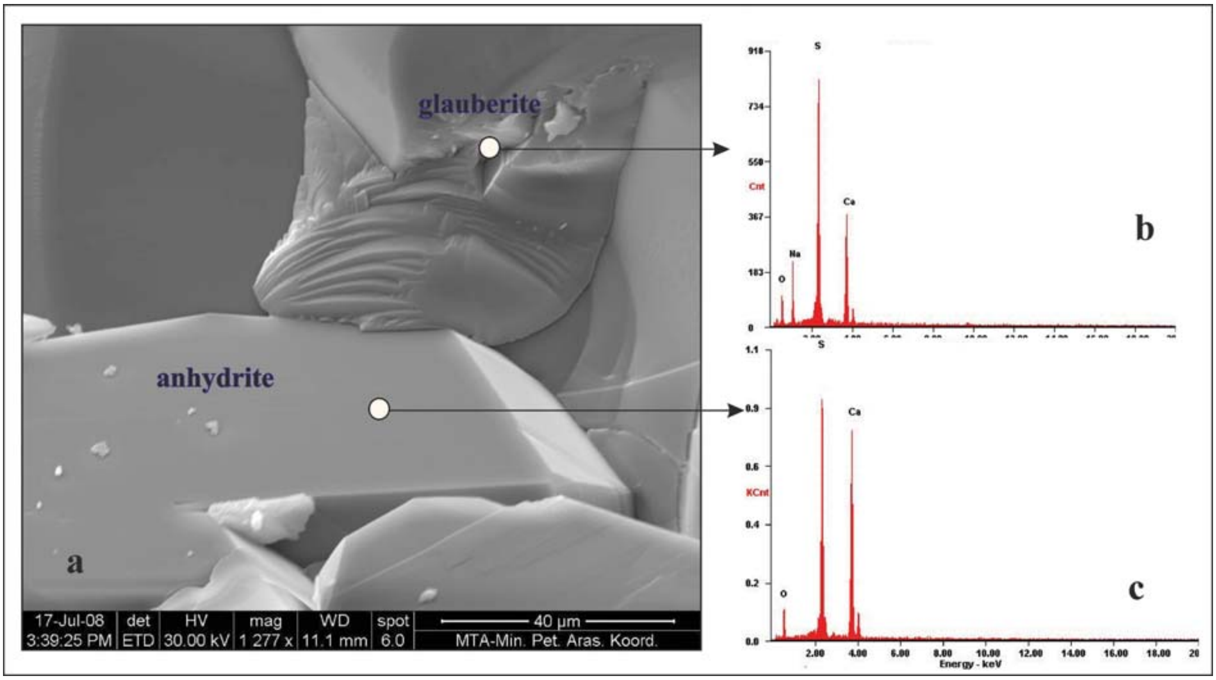


Figure 24- Concoidal fracture surfaces on glauberite mineral grown in anhydrite mineral, (o: measurement point of EDS analysis taken on the crystal) (Balıbağı-1 drill, 385.30 m XRD figure 18).

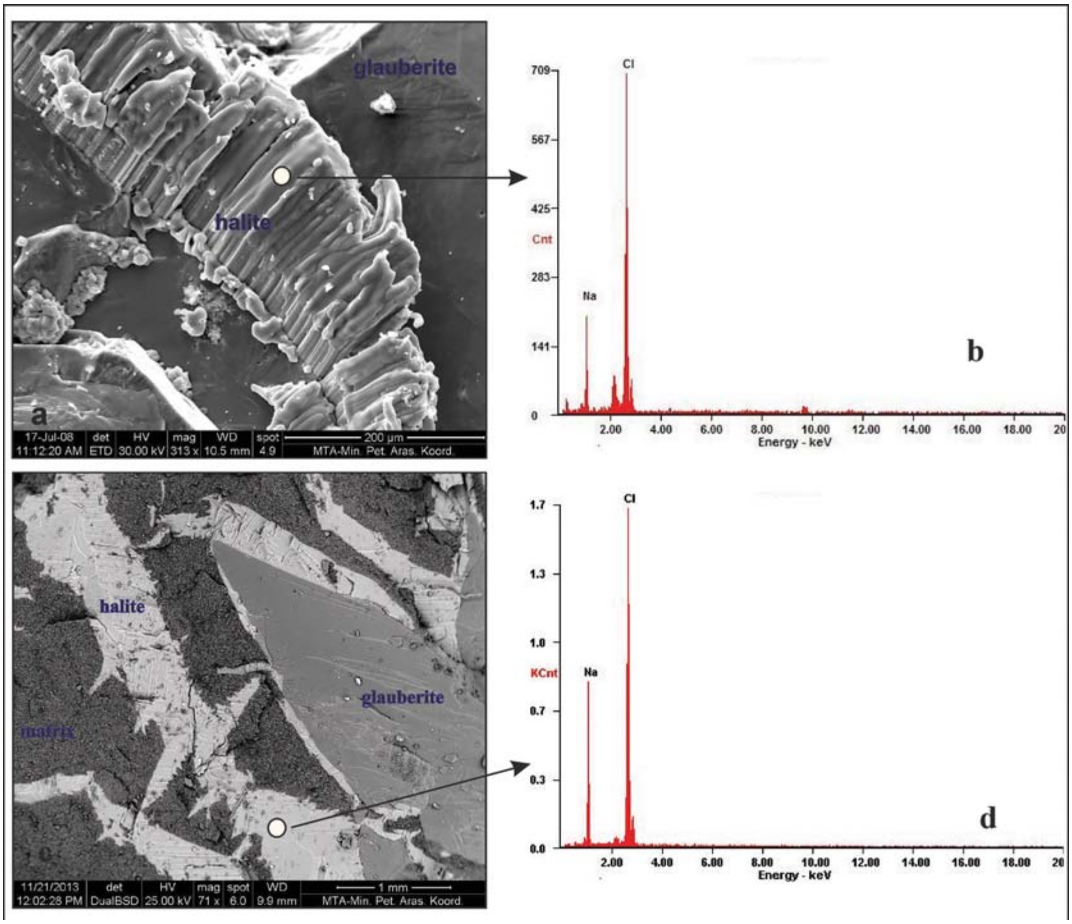


Figure 25- a) SE view of glauberite mineral on which halite mineral has grown (Yenidoğan-2 366,1 m, Figure 2), b) EDS spectrum of the halite mineral, c) SE view of the halite mineral which is observed in the form of fracture and crack infill, d) point of EDS analysis of halite mineral in the form of fracture and crack infill (Yenidoğan-2 drill, 158 m, XRD Figure 17) (o: measurement point of EDS analysis taken on the crystal).

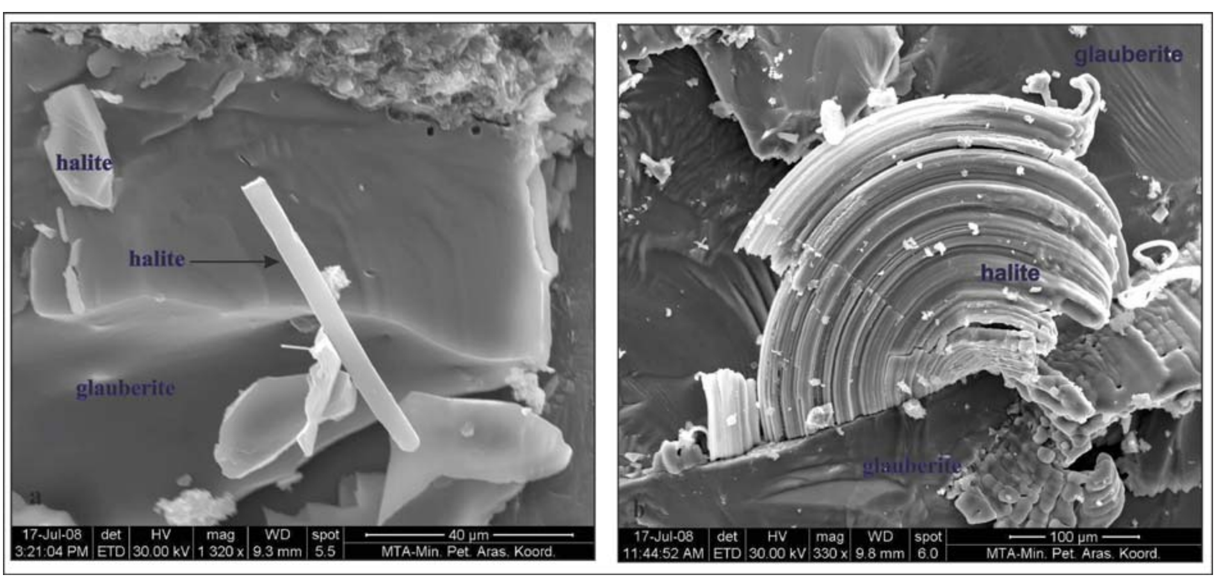
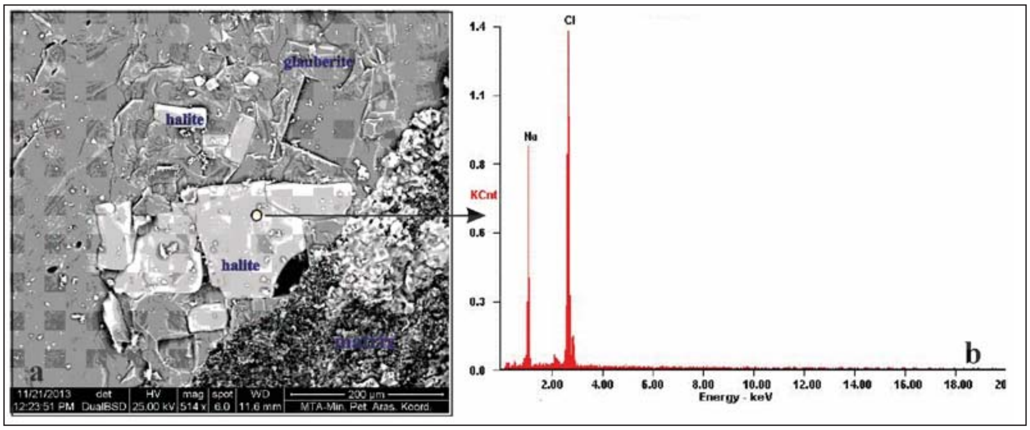


Figure 26- Crystallized halite forms on glauberite mineral, a) rod like halite crystal, b) concentric halite crystal (a, b: Balıbağı-1 drill, 385.30 m, XRD figure 18).



Şekil 27- Globerit minerali üzerinde gelişmiş prismatik özşekilli halit kristalleri, (O: kristal üzerinde alınan EDS analiz ölçüm noktası). (Yenidoğan-2 366,10 m XRD şekil 19).

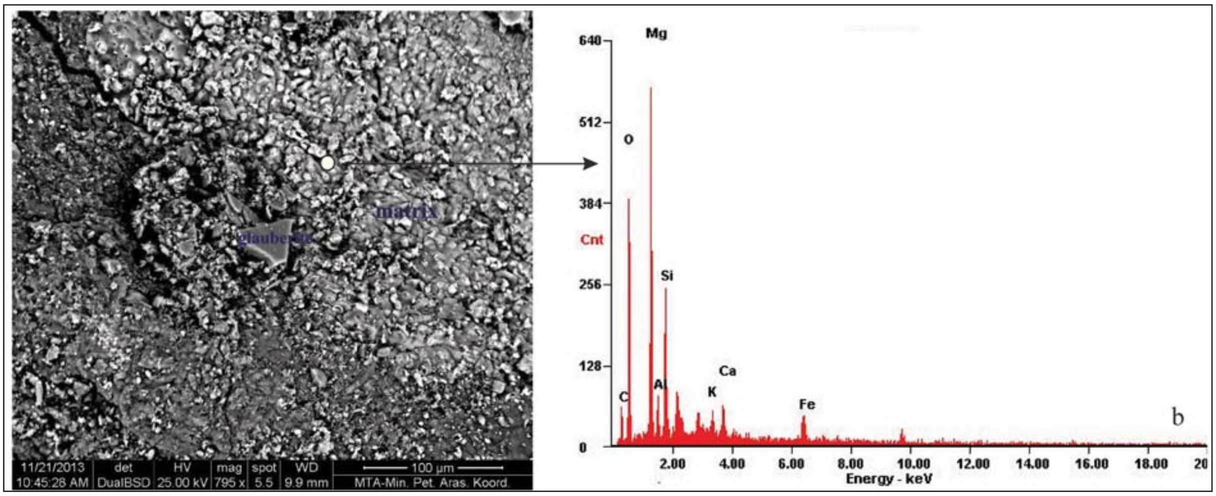


Figure 28- a) General view of the matrix which consists of glauberite layers, b) EDS spectrum of the matrix (o: measurement point of EDS analysis taken on crystal) (Yenidoğan-1 drill, 340 m).

Glauberite interlayers observed in Tuz member were deposited in sabhka environment and located as intercalating with playa lake sediments. Layers where the glauberite containing layers are the thickest were defined as glauberite-mudstone zone and were cut in thicknesses reaching 3.2 m.

In drillings which were performed in Tuz member in playa lake environment, 115 m thick rocksalt was cut which carries an economical potential. Glauberite mineral which does not have economical thickness is also important in revealing scientifically the existence of fossil Na-sulfate deposition in Çankırı-Çorum Basin.

In drilling studies performed at playa lake- sabhka transition zone in Bozkır formation, three lithological zones were detected in general. From bottom to top, these are claystone-less anhydrite zone, rocksalt-claystone-anhydrite-glauberite zone (zone consisting of sabhka interlayers) and claystone-gypsum-less anhydrite zone.

Glauberite mineral which is observed as disc and rosette shaped individual forms within mudstone dominant matrix was formed as a diagenetic mineral in saline mudflat environment (sabhka).

Glauberite mineral which was crystallized after anhydrite mineral in sabhka environment is observed as euhedral and subhedral within saline matrix. It was also detected that halite mineral had grown on glauberite mineral and was observed sometimes in the form of fracture and crack infill.

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