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# SODIUM SULFATE (GLAUBERITE-BLOEDITE) - HALITE ASSOCIATION in the TERTIARY (UPPER MIOSENE-PLIOCENE) KATRANDEDETEPE FORMATION, EREĞLİ-BOR BASIN, TURKEY

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Research Article

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#### ABSTRACT

This study covers the investigations related to the glauberite-halite minerals detected in Neogene deposits of the Ereğli-Bor Basin in the Central Anatolia. The basin consists of Paleozoic basement rocks, the unconformably overlying Paleocene-Eocene-Oligocene marine sedimentary and volcano-sedimentary rocks, and the Lower Miocene-Pliocene lake deposits at the top which unconformably overlie all underlying layers. In the study, core drillings related to the determination of geological characteristics and investigation of the mineral potential of buried salt deposits were carried out in the Ereğli-Bor basin. As a result of drillings carried out, glauberite-bloedite, halite and bituminous shale horizons, which possess significant thickness and grade values, were cut for the first time in the Konya-Ereğli-Bor basin. Glauberite minerals were observed in three different structures as; 1- the Glauberite Mineral intercalated with High Graded, Bedded Clays, 2- the Glauberite Mineral intercalated with Halites. Bloedite minerals are mostly observed with halite. It was detected that the economical evaporitic formations in the Konya-Ereğli-Bor Basin had occurred within the Upper Miocene-Pliocene Katrandedetepe formation which represents the playa-lake environment.

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## 1. Introduction

The purpose of the study is to explore probable burial type evaporitic industrial raw material deposits in the Ereğli-Bor Basin and their affordability.

As it is known, evaporitic basins are natural chemical deposits and accepted as the source of various industrial raw material. The Ereğli-Bor Basin is an important basin when the characteristics of geological and depositional environments are taken into consideration in terms of chemical sedimentary raw materials (sodium sulfate, halite, gypsum/anhydrite etc.) and other raw materials (lignite, bituminous shale etc.). Therefore; several investigations have been carried out in the region.

Studies, which are generally related to the investigation of the regional geology in the basin, were carried out by Türkünal, 1972; Oktay, 1982; Yoldaş, 1973; Demirtaşlı et al., 1986; Ayhan et al., 1986 and Ercan et al., 1992. The preliminary study in this region on evaporites belongs to Özgüner et al. (1989). The

authors mentioned about 20 billion tons of apparent operable pure anhydrite reservoirs in their studies, which they had carried out to explore evaporitic salt, and related sedimentary sulfide deposits in the Ereğli-Bor Basin. The investigators also stated that the hydrothermal fluids, which were the final products of the Upper Eocene island arc volcanism during the formation of anhydrite, provided ions that would supply salts to the depositional environment, and also the cherts located within these anhydrites had supported this formation. Later, Murat (1996) studied the distribution and the economic potential of celestines located in the limestone lenses among Ereğli-Ulukışla Tertiary units.

Other studies have also been carried out in Turkey in similar Tertiary basins. Helvacı et al. (1987), stated that the Neogene deposits in the Western Anatolia consisted of significant lignite, bituminous shale, uranium and borate deposits. Altay (2010) studied the mineralogical-geochemical features of the Neogene sedimentary units in Bor-Ulukışla Basin. Önal et

\* Corresponding author: Sa'ad Zeki A.kader Al-Mashaikie, magnesite2006@gmail.com http://dx.doi.org/10.19111/bulletinofmre.298685 al. (2004) specified that the trona occurrences were intercalated with bituminous shale, mudstone and tuffs inside the Terzioğlu Member of the Gürün formation, in the article of "The Geology and the Trona Potential of the Middle Miocene Gürün Basin (Sivas) in the Central Anatolia". The similar studies have been carried out also in the Beypazarı Basin (İnci et al., 1998; Helvacı et al., 1988; Yağmurlu and Helvacı, 1994; Helvacı, 1998; Gündoğan and Helvacı, 2005).

The most significant one of the similar basins in the world is the Green River Basin located in the northwest of Wyoming and hosts the biggest trona deposit of the world. According to Burnside and Culbertson (1979), trona deposits are located within the Wilkins Peak member of the Eocene Green River Formation. They emphasized that this member was composed bituminous shale, marl, claystone, trona, trona-halite, limestone and tuffs. Orti et al. (2007) on the other hand, who investigated Eocene-Lower Oligocene lacustrine evaporites in the southeast of the Ebro basin in NW Spain, implied that the shallow lake environment was controlled by a series of factor such as; 1-tectonical structure, 2- meteoric waters, 3- semiarid climate and 4- alluvial fans.

## 1.1. Study Area

The study area is located in the Ereğli-Bor Neogene Basin, the southern and southeastern parts of the Tuz Gölü Basin in the Konya province (Figure 1).

## 1.2. Method of Study

Evaporite minerals easily dissolve and do not generally crop out at the surface. They should be embedded and preserved by cover deposits (clays) in order to form a deposit.

Among the material and methods for embedded mineral exploration, the drilling method was used to explore evaporite deposits which do not crop out in the Ereğli-Bor Neogene Basin. The geological map (1/25000 scale) of the basin was generated using previous studies. Using satellite data of M32 and M33 sheets (1/100 000 scale), the basin margin faults were investigated extracting lineaments of the basin.

Both previous local and foreign geophysicalgeological investigations carried out in the region, the cuts excavated for various purposes and drilling wells were studied on the site. Oil, irrigation and potable water drillings made by TPAO, DSI and private people were correlated with drill logs in the project, and environments of the basin were interpreted. The age and chemical contents of volcanic activities in the basin and their contact relationships with lake units were studied, so the basin was interpreted by correlating with the Beypazarı basin. All drillings in the basin were carried out at right angle. Both clastic and cored advances were made in drills and put into plastic drilling boxes. Samples were taken from the mineralized zone (halite, glauberite, tenardite, bloedite, bituminous shale), evaporitic zone (gypsum, anhydrite) and non-mineralized both for general and detailed analyses. Samples were collected by the radioactive decay method from drills both for mineralized and evaporitic zones, and the remaining samples were left in the drill box. Solid samples were dried under the temperature of 105°C. Samples were analyzed under the salt program of RIX 3000 model XRF device (Rigaku brand). The other samples were studied under IQ+ (nonstandard program) of the AXIOS model XRF device (Philips brand).

The polygon method was used as the reservoir estimation method. The polygon method is an important reservoir estimation method especially used in the formation of sedimentary deposits, and it generally gives reliable results. The reliability of the method increases depending on the number and interval of drillings performed on the field. The coordinates of drillings performed on the field in order to calculate the sodium sulfate reservoir in the study area were plotted on 1/10 000 scale map, then low angle triangles were formed from drill locations, which are close to each other. Polygons were then formed by drawing the centroid of each triangle. The polygonal area of each drilling was estimated and the reservoir amount of each polygon was separately calculated being multiplied by the mineral thickness, density and factor of safety. The estimated reservoirs were then summed up and total apparent reservoir was obtained.

In grade estimations, Na<sub>2</sub>O and NaCl values were taken as the basis for glauberite and halite, respectively. As it is understood from drillings carried out, the rock salt and sodium sulfate transitions are present in the field. Therefore, the percent amount of



Figure 1- Location map of the study area.

sodium in the body, which combines with chlorine and sulfate, were detected one by one using basically their stoichiometric coefficients. Later on, the grade of  $Na_2SO_4$  was estimated by multiplying the constant of 2.29 which is the stoichiometric coefficient of the percent  $Na_2O$  value that combines with sulfate.

#### 2. Regional Geology

The oldest units of the region, where the Ereğli-Bor Neogene basin is located, are formed by the metamorphic rocks of the Lower Paleozoic Niğde massive (Figure 2). The metamorphics of the Niğde massive, which is generally represented by gneiss, marble, quartzite and amphibolites, were separated as Gümüşler, Kaleboynu, Aşıgediği formations and gathered under the name of "Niğde Group" by being interpreted as group (Atabey and Ayhan, 1986). The Gümüşler formation is composed of units of gneiss, quartzite, calc-silicate, marble and biotitic gneiss. The Kaleboynu formation consists of marble, quartzite and gneiss units. However, the Asıgediği formation is formed by coarse crystallized marble units with amphibolite, gneiss and quartzite bands. The rocks of the Niğde group were occasionally cut by the Upper Cretaceous Sineksizyayla Metagabbro (varying from amphibolite to gabbroic pegmatite) and Üçkapılı Granodiorite (granite with aplitic and pegmatitic veins) (Göncüoğlu, 1981a,b).

The basement units are overlain by the Paleocene-Eocene Ulukışla-Camardı Group in the region (Atabey and Ayhan, 1986). The volcanics are represented by agglomerate, pillow lava, tuff, dacites, syanite and trachy andesite, and they are occasionally composed of limestones blocks. The Sansartepe formation consists of Upper Paleocene monzonitic shallow intrusions (trachy andesite) and pillow lavas with compositions of basalt-olivine-dolerite and sporadically consists of thin limestone interlayers. The Serenkaya formation is composed of shale, conglomerate, siltstone, sandstone with volcanic materials and blocky coarse conglomerates in places, and it overlies the Sansartepe formation (Figure 3). This formation is cut by the Köyderesitepe trachyte. The Upper Paleocene-Eocene (Reefal nummulitic limestone) Başmakçı limestone overlies the Serenkaya formation. All these units are cut by the Lower Eocene Cehritepe syanite.

This unit is then overlain by the nummulitic limestone with coral, gastropod and lamellibraches (much fossilliferous) (Karatepe limestone) (Oktay, 1982). The volcanic activity ended in Middle Lutetian, and the Güney formation began to deposit (Figure 3). The bottom of the Güney formation begins with mudstone and continues with the alternation of gray claystone, beige-brown fine-thick layered calciturbiditic sandstone with volcanic elements and shale in upward. The orogenic movements,



Figure 2- Regional geological map of the Ereğli-Bor Neogene Basin (modified from 1/500.000 scale geological map of MTA).



Figure 3- The generalized stratigraphical section of the Ereğli-Bor basin (modified from Oktay, 1982) (not to scale).

which developed in Upper Lutetian, form an angular unconformity between these rocks and overlying units.

In the Upper Eocene-Oligocene basin, the Zeyvegediği anhydrite, which forms an evaporitic succession (the product of a shallow marine-lagoon environment) was deposited. The Zeyvegediği anhydrites begin with white and layered anhydrite at the bottom (Figure 3), and then continue with brown, thin layered sandstone-limestone and green marl in upward. It is composed of white, layered anhydrite and brown clayey gypsums. Lacustrine units were deposited following the evaporitic succession.

Orogenic movements that developed in Middle Miocene form an angular unconformity between the units deposited in the Middle-Upper Miocene lake and evaporitic and molasses type deposits. The Kızılbayır formation was formed by clastic materials which had been transported from eastern and southern parts, and it is in the form of alternation of red and green sandstone and claystone. Inside, gypsum veins, which were created by the gypsum bearing groundwaters are present (Oktay, 1982). It begins with red, green, pebbly clays in the Kızılbayır locality and then continues with lensoidal-cross bedded sandstone-conglomerate interlayers. It then grades into Katrandedetepe formation with the increase of marl and limestone in upwards (Figure 3). Later on; the formation is overlain by fine clastics and limestone-marl alternation due to the deepening of lake waters.

The abundance of living creatures in this period has caused much organic material to be transported into the lake. The transported organic materials have generated bituminous shales in the anaerobic environment where the lake becomes deep (Katrandedetepe formation). The Katrandedetepe formation begins with green, white marls and is generally alternates with clayey limestone and marl. It sometimes consists of bituminous shale layers which intercalate with evaporitic units.

Clayey limestones are white to dirty white, hard, fine and regularly bedded. However, marls overlying the clayey limestone are greenish gray, with mussel shell fragments. Coarse clastics such as; conglomerate and sandstone, were formed by the re-shallowing of the lake (Beştepeler formation) (Oktay, 1982). The formation, which begins with green sandstone intercalating with conglomerate, is in the form of alternation of sandstone-claystone-conglomerate intercalated with clayey limestone. The uppermost part is represented by the coarse limestone and pebbly conglomerate. Sandstones are occasionally in the form of lenses within conglomerate layers. These were followed by vertical movements affected in Pliocene.

In north, a series of volcanic activities have occurred over the sediments of the Tuz Gölü Basin starting from Upper Miocene-Pliocene to Quaternary and affected the basin in terms of salinity. The calcalkaline type Melendiz and Hasandağı volcanisms, which developed along big tectonical lines in Upper Miocene-Pliocene, form heights on the plain. Augite-Andesite, Pyroxene-Andesite type lavas of the Melendiz volcanics were followed by the Hasandağ volcanism in Andesite-Basalt type in Quaternary and finally by the alkaline type volcanism on the plain (Dönmez et al., 2003).

## 3. Geology of the Study Area

The study area, which is located within basin, has a flat topography and is formed by thick Neogene lacustrine deposits and covered by Quaternary alluvial deposits (Figure 4). The Katrandedetepe formation outcropping in south, which was determined as the target formation for chemical salt explorations, is buried by deep seated fault on basin margins on the plain. Lithological characteristics of formations determined by the study of outcrops and the cores of drills in the study area are given below.

## 3.1. Güney Formation (Tg)

The Güney formation was first defined by Oktay (1982) as a formation, and it is observed in the Güney village, the southern part of the study area and in its close vicinity. It corresponds to the Koçak Formation of Ketin and Akarsu (1965) and the Bozbeltepe member of the Hasangazi formation of Demirtaşlı et al. (1986). It outcrops in southern and southeastern parts of the study area, around Güney, Altay, Kolsuz, Eminlik and Başmakçı villages, between Gökbez-Karacaören villages, in Karakava Tepe and Bozbel Tepe. It mainly strikes in the form of bands in E-W directions. The unit laterally exhibits different thicknesses and developed concurrently from north to south. Therefore, it is observed in different facies and ages in its type locality and southeast of Ulukışla. The bottom of the unit begins with mudstone and



Figure 4- Geological map of the study area.

then continues with alternation of gray claystone, beige to brown, fine to thick layered calciturbidtic sandstone with volcanic materials and shale. To these regions, the clastic material, which was derived due to the erosion of sections of volcanic islands above water and erosion of the land in west of the basin, was rapidly deposited (Oktay, 1982). The Güney formation conformably overlies the Serenkaya formation around Güney village. It is cut by Tayhacı andesite and Dikmenderetepe trachyte, which are the final stage products of the Ulukışla island arc volcanism outside the study area in southwest. It is overlain by fluvial and lake deposits, which was formed by three conformable lithostratigraphical units in lake environment, with an angular unconformity.

The age of the formation was given as Lutetian due to the presence of *Globorotalia* cf., *Discocyclina* sp., *Orbitolites* sp., *Assilina* sp., *Alveolina* sp., *Locharitia* sp., *Halkyardia* sp., *G. mekanna*, *G. aragonensi*, *Globogerina* sp., *Globorotalia* fossils described in different lithological units within the Güney formation by many investigators, who carried out several studies in the study area and its close vicinity (Demirtaşlı et al., 1986; Oktay, 1982; Ketin and Akarsu, 1965; Çevikbaş and Öztunalı, 1992).

#### 3.2. Kızılbayır Formation (Nkb)

This formation was first defined by Oktay (1982) and its type locality is the Kızılbayır locality in SW of the Altay village. It is the first sedimentary deposit which extends in NE-SW directions between Hacıbekirli and Altay villages and formed under lacustrine and fluvial conditions. It exhibits a wide distribution around Gelinkayaları in north of Hacıbekirli, east of Katrandedetepe, south of Bohcadikmentepe, east of Şahingüzmesi Ridge and Altay village (Oktay, 1982).

It begins to deposit with red to green, coarse pebbly clays in Kızılbayır locality and continues with lensoidal, cross bedded sandstone-conglomerate interlayers. It then grades into the Katrandedetepe formation with the increase in marl and limestones in upward (Figure 5).

In the Hacıhüseyinler Obası locality (M32-c4), it begins to deposit with red to green pebbly clays, loose cemented, pink, white to black conglomerate layers which consists of recrystallized limestone and volcanic pebbles at the bottom. It is then overlain by the alternation of brown colored, by mostly cross bedded sandstone and red to green claystone.



Figure 5- The contact relationships of the Güney formation (Tg), Kızılbayır formation (Nkb) and the Katrandedetepe formation (Nkd).

Within this deposit, coal layers with thicknesses varying between 0-20 cm are observed between 3-5 m thick to medium bedded limestone layers. However, this layer is lensoidal and has not any lateral continuity. Claystones inside the formation are unlayered and fragmented in the form of mussel shell. The thickness is approximately 200-250 m. It discordantly overlies Zeyvegediği anhydrites at the bottom. However, there is a tectonical contact relationship with the Serenkaya formation in east of Altay village. It is conformably overlain by the Katrandedetepe formation.

The grains in the Kızılbayır formation, which formed in lake and fluvial environments, are poorly sorted and not well-rounded, as the environment is tidal and transportation is in short distance. There was not found any paleontological data to age the Kızılbayır formation. However, the conformably overlying Katrandedetepe formation to be in Upper Miocene makes us consider that this formation could be Middle-Upper Miocene, too. The thickness of the formation is nearly 300 meters according to drillings carried out in the study area.

#### 3.3. Katrandedetepe Formation (Nkd)

Its type locality is the Katrandedetepe location in Tepeköy village (Niğde-Ulukışla). That is why it was named under this nomenclature (Oktay, 1982). It corresponds to the Ulukışla formation of Yoldaş (1973). The formation can easily be distinguished by its dirty white color over the red-green Kızılbayır formation. It spreads in the form of banding parallel to the Kızılbayır formation. To the north; it outcrops in east of Gücük Tepe (M32-c2), in Boztepe, the north of Çakmaktepe, around Beştepeler, and to the south; in Karakayatepe, Katrandedetepe (M32-c3) and Tozlu Tepe (M32-c4), then it wedges out in Çayhan Valley in west of Hacıbekirli.

The formation starts to deposits with green to white marls and generally alternates with clayey limestone and marl. It also includes bituminous shales in occasion (Figure 6). Bituminous shale layers alternate with evaporites. Clayey limestones are white to dirty white, hard and horizontal bedded. The marls overlain by clayey limestones are greenish gray colored with fragments of mussel shell. The evaporite ore minerals such as; halite, bloedite, loweite, tenardite in the basin were formed within this formation.

In places, where the bituminous content of the formation increases, the color becomes dark brown, blackish and laminated. The maximum thickness measured on the outcrop is 200 m. However, it was determined that the formation thickness varied in between 235-1400 meters in drillings performed and the thickness increased due to the sinking of the basin.

Many trenches excavated within bituminous shales were studied, and it was observed that these alternated occasionally with dolomites and green illitic clays. It was seen that bituminous shales turned into the view of wet carton when they dried up losing their moisture. The Katrandedetepe formation conformably overlies the Kızılbayır formation and underlies the Beştepeler formation and remains below the Ereğli-Bor plain with a gentle slope.



Figure 6. View from units of the Katrandedetepe formation in a trench excavated in Ulukışla-Tepeköy-Karakaya Tepe.

Yoldaş (1973) dated the formation definitely as Upper Miocene according to spores and pollens in samples collected from bituminous layers. Oktay (198) dated the unit as Lower Pontian according to Ostracoda fauna present in green marls underlying the unit. The age of the formation was accepted most probably as Upper Miocene due to Ostracoda and Gastropoda shells and Chara sp in samples collected from clayey limestones. The Katrandedetepe formation has the characteristics of lacustrine-playa environment because of evaporitic interlayers it includes. The thickness of the formation is approximately 350 meters according to drillings carried out in the study area.

#### 3.4. Beştepeler Formation (Nb)

It is best observed in Beştepeler locality that is why it was named under this nomenclature (Oktay, 1982). This is the last formation deposited in fluvial and lake environments in the Ereğli-Bor Basin and overlies the Karadedetepe formation with a distribution in NE-SW directions. It spreads over a very wide area in north starting from Gücük Tepe-Bögelek Tepe, Beştepeler (M32-c2), southeast of Tepeköy (M32-c4), Şeyhömerli, Çayhan, north of Hacıömerli and north of Bozdağ to the plain.

The formation, which begins to deposit with green sandstones intercalated with pebbles in

north, is in the form of sandstone-conglomerate alternation intercalating with clayey limestone. It is fully represented by loose conglomerates at the top and continues with alternation of clayey limestoneconglomerate in north of Hacıbekirli and around Cayhan. The sandstones are occasionally in the form of lenses within conglomerate layers. The conglomerates are fine to medium in north, medium to thick in west and are loose cemented. It easily disperses since it is loose cemented, and forms pebble piles. Pebbles are well rounded. The formation is conformably overlies the Katrandedetepe formation and remains below the alluvial of the Ereğli-Bor plain with a gentle slope. There was not encountered any fossils to date the formation. As the age of the Katrandedetepe formation, which conformably underlies the formation, is Upper Pliocene the age of this formation is considered to be Upper Pliocene-Miocene or younger in age. The depositional environment of the formation is fluvial and fresh water lake. The dominant fragmental material indicates that this formation formed in shallow and energetic environment. The thickness of the formation is approximately 300 meters in the study area according to drillings performed.

#### 3.5. Hasandağı Ashes (Qhk)

It is observed as widespread in northwest of the study area. It is grayish white, beige, gray and milky white colored. Volcanic rock fragments are observed in ash and tuff. Dönmez et al. (2003) dated the unit as the Lower Quaternary.

## 3.6. Alluvial (Qal)

Quaternary deposits, which outcrops in east-west directions in the central part and in wide regions in northwest of the study area, are formed by alluvial (Qal) and talus (Qym). Alluvial deposits mainly consist of pebble, sand and clayey materials. However, talus consists of angular limestone talus in variable sizes belonging to the Güneydağı formation (Tg) in western part of the Güneydağı. In drilling carried out in the Ereğli-Bor Basin the thickness of the alluvial cover was determined between 3-18 meters. The alluvial thickness in the study area is approximately 10 meters according to the drillings made.

## 4. Economical Geology

Yeniköy sodium sulfate deposit is located in 30 km northeast of Ereğli (Konya), approximately 25 km northwest of Ulukışla (Niğde), 27 km southwest of

Bor (Niğde). Ankara-Adana auto road passes through the study area.

The major mineral of the sodium sulfate deposit is glauberite and it is a burial chemical sedimentary type deposit. Another sodium sulfate mineral, which is frequently encountered in the deposit, is the bloedite mineral that accompanies with halite (Figure 7). The sodium sulfate deposition alternates with bituminous shale and rock salt within evaporite zone of the Upper Miocene-Pliocene Katrandedetepe formation, and it is formed from the association of glauberite, halite, magnesite, bloedite and anhydrite.

Below the sodium sulfate deposition the grayish black, laminated bituminous shale, which generates liquid petroleum, is encountered. However, inside the deposition the alternation of pale gray siltstoneclaystone which consists of fiber like gypsum and nodules of anhydrite and dolomitic layers in occasion are observed (Figure 8).

Above the sodium sulfate bearing zone, again grayish black, laminated bituminous shale, in which



Figure 7- Bloedite-halite alternation cut in the drilling KEY-09/05 excavated in Konya-Ereğli-Yeniköy study (x: 4177106, y: 612493).



Figure 8- Bituminous shale core with liquid petroleum indications cut at 462 m in Yeniköy drilling KEY-08/02 (x: 4176100, y: 613550).

between laminae the liquid petroleum generates, anhydrite and dolomitic layers, in which pores and fractures are occasionally filled with liquid petroleum, are located (Figure 9).

Sodium sulfate bearing zone generally begins with gray, discoidal gypsum, liquid petroleum bearing dolomite and thin laminated bituminous shales at the bottom. Within bituminous shales, prismatic, layer like glauberite crystals with 2-3 cm in size are much observed. The thickness of glauberite crystals increases much more in upper layers. Pale gray – dirty white glauberite minerals disintegrate in the air and are broken into small pieces like flavor by whitening and swelling. The thickness of glauberites, which are the major mineral of the deposit, varies between 0.60 – 14.40 m. The number of glauberite bearing layers shows variation between 4 to 11 (Table 1).

In drillings KEY-09/02 and KEY-09/03 carried out in the eastern part of the study area two glauberite zones were cut as being different than other drills. In both drillings glauberite minerals in the upper zone are located in halite-anhydrite alternation with interlayers of siltstone-dolomite between 407-429 m. However, the glauberite zones located below were deposited within alternation of oil producing shale-halite and anhydrite as it had been in other drillings.



Figure 9- Liquid petroleum infilling the pores of dolomites cut in Yeniköy drill KEY-08/04 (371 m).

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Drilling No	Mineralization Interval (m)	Number of layer	Total Thickness (m)
KEY-08/02	447,30-572,70	8	30,95
KEY-08/04	403,40-438,80	4	19,90
KEY-09/01	437,00-510,80	8	16,30
KEY-09/02	407,00-601,00	5+5	16,70
KEY-09/03	407,00-676,30	3+8	19,80
KEY-09/04	499,30-629,80	5	30,00
KEY-09/05	518,60-668,40	4	27,70
Mean	403,40-676,30	Different	23,05

Sodium sulfate deposit is at the depth of 404-528 m from the surface and in the form of a zone of which its thickness varies between 16.30-30.95 m (Table 2). As a result of drillings made in the study area, it was detected that the sodium sulfate deposit dispersed over a wide area (13.59 km<sup>2</sup>) and generally possessed a sub-horizontal slope.

Determined grades of the Yeniköy sodium sulfate deposit vary between 27.39% and 42.16%  $Na_2SO_4$ . On the other hand; the mean sodium sulfate grade of the deposit was determined as; 33.34%  $Na_2SO_4$ , bloedite grade as; 28.19%  $Na_2SO_4$ , and halite grade as; 80.25% NaCl.

#### 5. Mineralization

## 5.1. Ore Minerals and Mineral Association

NaCl salt is obtained in nature in two different ways as; marine and terrestrial environments. The

main economical source of the salt is oceans in the world. On lands, it is obtained from rock salts and salt lakes. However, mainly the rock salt (halite), anhydrite, gypsum and glauberite were observed in drillings in the study area (Table 4). Major ore minerals though in fewer amounts are accompanied by magnesite, dolomite, hydro glauberite, quartz, illite/mica group clays, starkeyit, zeolite group (clinoptilolite, heulandite and analcim-C) minerals, chlorite group minerals and amorph materials.

In addition that sodium sulfate salts form many minerals in nature, its most significant minerals are mirabilite, tenardite, glauberite, bloedite and glaserite in terms of economy and workability. These salts are deposited in contemporary alkaline lakes and playa lakes. Ereğli-Yeniköy sodium sulfate deposit is also a playa type deposit and covers wide areas. In drillings made in this basin, glauberite-bloedite and halite minerals were cut. The correlation of the mineralized zone based on drillings is shown in figure 10.

Table 2-	Yeniköy	sodium	sulfate	deposit	(Mineralization	ation thi	icknesses	with respect t	o drillings)
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Drilling No	Drilling Name	Mineral	Total Thickness (m)	Mean Tenure (% Na2SO4) and (% NaCl)				
		GLAUBERITE	30,95	35,66				
1	KEY-08/02	BLOEDITE	6,00	18,08				
		HALITE	16,00	89,29				
		GLAUBERITE	19,90	42,16				
2	KEY-08/04	BLOEDITE						
		HALITE						
		GLAUBERITE	16,30	27,39				
3	KEY-09/01	BLOEDITE	3,75	36,85				
		HALITE	17,05	93,07				
		GLAUBERITE	16,70	31,97				
4	KEY-09/02	BLOEDITE	2,60	43,66				
		HALITE	21,10	45,50				
		GLAUBERITE	19,80	35,39				
5	KEY-09/03	BLOEDITE						
		HALITE	31,30	64,15				
6		GLAUBERITE	30,00	28,03				
	KEY-09/04	BLOEDITE						
		HALITE	35,80	85,50				
		GLAUBERITE	27,70	20,05				
7	KEY-09/05	BLOEDITE						
		HALITE	45,40	93,08				

Table 3- Grade and reservoir conditions of the Yeniköy sodium sulfate deposit.	
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Drilling No	Reservoir Based Polygon Areas (m <sup>2</sup> )	Mineralizaton Thickness (m)	Specific Gravity (ton/ m3)	Factor of Safety	Apparent Reservoir (Ton)	GLAUBERITE Values of Weighted Mean Analysis (%)						TE				
	1	2	3		5=1x2x3x4	Na	Cl	Na <sub>2</sub> O	SO <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	$Na_2SO_4$
KEY-08/02	2.840.000	30,95	2,77	0,7	170.434.222	13,96	3,72	18,82	40,23	5,72	0,83	4,69	0,21	15,86	1,08	35,66
KEY-08/04	2.140.000	19,90	2,77	0,7	82.574.254	13,76	0,16	18,55	42,87	5,80	0,61	5,18	0,17	16,53	1,15	42,16
KEY-09/01	2.640.000	16,30	2,77	0,7	83.439.048	10,71	2,84	14,43	44,72	7,98	0,09	5,00	2,60	8,64	1,15	27,39
KEY-09/02	2.150.000	16,70	2,77	0,7	69.619.795	13,27	4,49	17,88	37,61	7,89	0,68	4,72	0,24	16,64	1,31	31,97
KEY-09/03	1.670.000	19,80	2,77	0,7	64.114.974	13,62	3,33	18,36	38,54	7,41	0,18	4,49	0,23	17,44	1,26	35,39
KEY-09/04	2.150.000	30,00	2,77	0,7	125.065.500	10,30	1,88	13,88	44,32	6,45	0,77	3,48	0,15	19,43	0,86	28,03
		TOTAL			595.247.793											
VALUES OF	WEIGHTED	MEAN ANAL	YSES (FI	ELD)		12,59	2,76	16,97	41,60	6,64	0,59	4,53	0,53	15,95	1,10	33,34
Drilling No	Reservoir Based Polygon Areas (m <sup>2</sup> )	Mineralizaton Thickness (m)	Specific Gravity (ton/ m3)	Factor of Safety	Apparent Reservoir (Ton)	Values of Weighted Mean Analysis (%)				BLO	BLOEDITE					
	1	2	3		5=1x2x3x4	Na	Cl	Na <sub>2</sub> O	SO <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	$Na_2SO_4$
KEY-08/02	2.840.000	6,00	2,25	0,7	26.838.000	23,72	27,58	31,98	28,40	6,60	0,02	0,23	0,01	0,64	0,07	18,08
KEY-09/01	2.640.000	3,75	2,25	0,7	15.592.500	13,34	2,16	17,98	51,58	9,48	0,01	0,95	0,02	3,44	0,28	36,85
KEY-09/02	2.150.000	2,60	2,25	0,7	8.804.250	28,27	21,80	38,10	32,10	7,40	-	0,20	0,20	-	-	43,66
		TOTAL			51.234.750											
VALUES OF WEIGHTED MEAN ANALYSES (FIELD)			I	21,34	18,85	28,77	36,09	7,61	0,01	0,44	0,04	1,38	0,12	28,19		
Drilling No	Reservoir Based Polygon Areas (m <sup>2</sup> )	Mineralizaton Thickness (m)	Specific Gravity (ton/ m3)	Factor of Safety		Values o	Values of Weighted Mean Analysis				<u> </u>	<u> </u>	<u> </u>	I	IALI	TE
					Apparent Reservoir (Ton)											
	1	2	3	4	5=1x2x3x4	Na	Cl	Na <sub>2</sub> O	SO <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	NaCl
KEY-08/02	2.840.000	16,00	2,17	0,7	69.023.360	35,06	54,18	47,25	7,95	2,00	0,10	0,26	0,10	0,45	0,10	89,29
KEY-09/01	2.640.000	17,05	2,17	0,7	68.373.228	36,22	56,48	48,82	1,39	0,19	0,04	0,21	0,01	0,52	0,13	93,07
KEY-09/02	2.150.000	21,10	2,17	0,7	68.909.435	27,81	27,61	37,49	23,51	2,04	0,12	0,69	0,10	6,64	0,19	45,50
KEY-09/03	1.670.000	31,30	2,17	0,7	79.399.649	28,18	38,93	37,98	11,50	2,80	0,20	0,40	0,03	0,91	0,13	64,15
KEY-09/04	2.150.000	35,80	2,17	0,7	116.917.430	23,10	51,88	31,13	10,27	2,05	0,11	0,83	0,07	2,67	0,23	85,50
KEY-09/05	1.760.000	45,40	2,17	0,7	121.374.176	36,22	56,48	48,82	1,39	0,19	0,04	0,21	0,01	0,52	0,13	93,08
TOTAL					523.997.278											
VALUES OF WEIGHTED MEAN ANALYSES (FIELD)				30,82	48,70	41,53	8,68	1,50	0,10	0,45	0,05	1,86	0,16	80,25		

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Drilling No	Mineralization Interval (m)	Zone Thickness (m)	Mineral Paragenesis
KEY-08/02	447,30-572,70	125,40	Glauberite halite magnesite bloedite anhydrite
KEY-08/04	403,40-438,80	35,40	Glauberite anhydrite magnesite gypsum
KEY-09/01	437,00-510,80	73,80	Glauberite halite magnesite
KEY-09/02	407,00-429,00 519,00-601,00	22 + 82=104,00	Glauberite halite bloedite dolomite
KEY-09/03	404,20-429,70 547,00-676,30	25,50+ 129,30= 154,80	Glauberite anhydrite halite magnesite
KEY-09/04	499,30-629,80	130,50	Glauberite anhydrite halite magnesite
KEY-09/05	518,60-668,40	149,80	Glauberite anhydrite halite magnesite
MEAN	403,40-676,30	Variable	Glauberite halite magnesite bloedite anbydrite

Table 4- The distribution of ore minerals and paragenesis of the Yeniköy sodium sulfate deposit based on drillings.



Figure 10- Drilling correlation of the Yeniköy sodium sulfate deposit.

Γ

5.2. Mineralization and the Factors Controlling the Mineralization

The Ereğli-Bor Neogene Basin is located in north of the Central Taurus belt, west of the Ecemiş Fault and in southeast part of the Tuzgölü Basin. At the basement structural elements are dominant. These elements were formed by the Alpine orogeny, which caused the closure of the Southern Neotethys Sea and affected in the form of N-S directing compression starting from Upper Cretaceous to Upper Miocene (Şengör and Yılmaz, 1983). The Niğde Fault Zone, which restricts the basin from south, continues until Karaman in the form of discontinues branches. The Niğde fault zone is approximately 170 km long, 5-8 km wide, left lateral strike slip fault with a strike of NE-SW and dipping in NW direction (Kocyiğit, 2000). The northeastern border of the Ereğli-Bor basin is controlled by the branches of the Tuzgölü fault zone (Figure 11).

Central Anatolia is divided into two neotectonic regions. These are; 1- Konya-Eskişehir neotectonic region and 2-Kayseri-Sivas neotectonic region



Figure 11- Simplified neotectonic map of the Central Anatolia and its close vicinity (modified from Koçyiğit, 2000).

(Figure 11). Konya-Eskişehir neotectonic region is the first neotectonic region that remains between the Kesikköprü fault that extends between Kırıkkale in north and Niğde in south, and the area to the east of Tuzgölü fault zone. Konya-Eskişehir neotectonic region is the eastern continuation of the West Southwest Anatolia and the Turkish Lake Land (Göller Bölgesi) horst graben system and characterized by extensional tectonic regime and oblique slip normal faulting. The starting age of the neotectonic regimes characterizing the Central Anatolia is the post-Pliocene (Koçyiğit, 2000). The Ereğli-Bor basin is located in the first neotectonic region, too. This basin has the characteristics of being a semi-graben type depositional basin which developed in and after the Upper Miocene as a result of the pressure release which occurred in the region following the Miocene compressional tectonism (Sengör and Yılmaz, 1983).

In the formation of the Ereğli-Bor Basin, which is a closed lake basin, it is considered that tectonically; an extensional regime became effective and tectonical factors causing the development of basin mediated a volcanic activity in the same period (Middle-Upper Miocene). It was observed that volcanism (Balcı volcanism) derived solutions and other volcanic materials were supplied into the lake environment as the sinking in the basin synchronously occurred with sedimentation (Kadınkız and Pekgöz, 2015).

Tectonic and volcanic activities effective in the basin development, beyond the occurrence of the extensional region, have provided significant volcanism derived solutions that would cause economical mineralization especially to the lake environment. Besides; the Zeyvegediği anhydrite (Upper Eocene-Oligocene) has a great importance for ion supplement into the basin (Figure 12). As sedimentation in the lake environment continues, it is considered that Na, Ca and SO<sub>4</sub> bearing solutions mix into lake water by means of fracture systems (Kadınkız et al., 2015).

Most of the lake deposits exhibit especially well developed bedding, lamination and frequently lateral lithology and color variations. Fresh water carbonates, thin dolomite layers, bituminous shales and evaporites are particular stages and types characterizing the lake environment (Einsele, 1992). It is probable to encounter one or several such rock salts in many lake deposits



Figure 12- Schematic model showing the glauberite deposition in the Ereğli-Bor Neogene Basin in Miocene.

(İnci et al., 1998; Helvacı et al., 1988; Yağmurlu and Helvacı, 1994; Helvacı, 1998; Gündoğan and Helvacı, 2005). When significant salt formation types in closed lake systems are taken into consideration, it is seen that gypsum, halite, glauberite and bloedite minerals in sulfate lakes in which sulfate, chlorine and calcium rich waters are effective, are deposited.

The presence of thin lignite layers located at the bottom indicates that the primary lake bottom started to shape and the environment was a marsh land rich in plant and tree remnants in the first period when the Ereğli-Bor Basin began to open. Parallel to the gradual deepening and the enlargement of the basin, the sediment transportation and depositional process also began to develop. Marl-carbonate and lignite occurrences in the form of thin layers are encountered in sediments deposited in this period. Besides; sodium sulfate and rock salt layers observed within the Katrandedetepe formation and bituminous shales, which form a thick succession in the form of alternations, were deposited in the basin (Kadınkız et al., 2005) (Figure 10).

Bituminous shales deposited in the closed saline lake system of the Ereğli-Bor basin are also important. The presence of bituminous shales alternating with evaporite minerals in the basin shows that some planktonic organisms and plants may increase if there will be high temperature and enough food support although high salinity waters are not rich in organisms. In such environments phytoplankton production and the occurrence of algal accumulations could reach important amounts. However, a few part of this production were deposited with sediments while most of them decayed. These kerogen rich bituminous shales indicate high lake altitude and humid phase. Sodium sulfate minerals and halite layers on the other hand were deposited in a playa lake environment in which organic poor and more arid climate had developed. Bituminous shales have generated liquid petroleum in significant amount and frequency. Bituminous shales of which their kerogen types are suitable to generate petroleum have produced oil by the effect of temperature and pressure that increases with embedding, and by the temperature which increase as a result of hydrothermal solutions originating from Plio-Quaternary Melendiz Mountain volcanisms in the basin. Thus, the primary migration of the petroleum has occurred by the petroleum generation from bituminous shales which are source rocks for petroleum.

When relationships between the bituminous or oily shales and evaporites are studied, it is seen that there is an active transgressive-regressive system in which bituminous shale deposition is followed by the evaporite deposition (Eugster, 1985). It was also determined in late diagenetic stages of highly alkaline isolated saline lakes that siliceous and alkaline zeolites turned into analcime and potassium feldspar (Sheppard and Simandi, 1999). Accordingly; the presence of analcime also in the study area was assessed as data showing that the alkaline amount is high. In humid climates HCO<sub>3</sub> is available more than Ca and Ca-sulfates cannot form, so carbonates are deposited dominantly. During arid periods, in which meteoric input is comparatively low, sulfate minerals such as; gypsum and glauberite are deposited rather than carbonate in case of excess Ca than HCO<sub>3</sub>. Depending on the evaporation and increase in the concentration of salt, Na-Mg sulfate minerals such as; tenardite, mirabilite, epsomite and bloedite are deposited in lakes of alkaline arid regimes (Sinha and Raymahashay, 2004).

Glauberite in playas and saline lakes occur starting from Na-rich sulfate and chlorine minerals such as; mirabilite, bloedite, tenardite and halite by the effect of Ca-rich groundwater solutions (Grokhovskii, 1978). In this case, the glauberite mineral is located in lower parts of halite and tenardite layers as it is also seen in the study area. Besides; glauberite may form also starting from gypsum by the effect of Narich groundwater solutions (Formula-1) (Hardie, 1968, 1984; Eugster and Hardie, 1978; Smoot and Lowenstein, 1991; Arakel and Cohen, 1991; Orti et al., 2002). Grokhovskii (1978) stated that some primary glauberites in playas were formed by the mixture of Ca-rich groundwater solutions with sodium sulfate solutions.

 $\begin{aligned} & 2\text{CaSO}_{4}2\text{H}_{2}\text{O}_{(s)} + 2\text{Na}^{+}_{(aq)} \iff & \text{CaSO}_{4}\text{Na}_{2}\text{SO}_{4(s)} + \text{Ca}^{++}_{(aq)} + 4\text{H}_{2}\text{O} \text{ (Formül- 1)} \\ & (\text{Gypsum}) \end{aligned} \tag{Glauberite}$ 

Prismatic, layer like glauberite crystals reaching a length of 2-3 cm in bituminous shales are excessively observed. The solubility of mirabilite ( $Na_2SO_4.10H_2O$ ), which is an aqueous sulfate mineral, is quite variable with temperature. As the temperature increases, their solubility also increases. By the increase of temperature up to 35-40°C due to embedding, mirabilite mineral transforms into tenardite ( $Na_2SO_4$ ) (Last, 1999; Helvacı et al., 2013). Tenardite may form with gypsum as a secondary mineral starting from glauberite (*Formula-2*);

#### 6. Results

Sodium sulfate is white, in crystal or powder form, liquid and odorless substance, and used in the production of detergent, paper, glass, textile paint and some chemical materials. In the production of powder detergents, sodium sulfate is used as the infilling material with percentages varying between 16-40%. The sodium sulfate ratio used in the production of detergents determines the cost and its bleaching degree. It is used in the kraft process for cellulose production in paper sector. In glass sector, sodium sulfate has many functions in the formation of Egyptian blue, and it is consumed approximately in 3% in glass production. In textile sector, it helps dye to homogenously diffuse into the fabric. It is also used in the production of some chemical materials (potassium sulfate, aluminum sulfate, sodium silicate).

It is extremely important to extract and put the sodium sulfate mineralization, which has a widespread use both in the world and Turkey, into the country's economy as a result of drillings. In these studies conducted in the Ereğli-Bor Basin, glauberitebloedite, halite and bituminous levels, which possess significant grade and thickness values, were cut the first time. It was also approved by these drillings that the Ereğli-Bor basin, which forms the southeastern part of the Tuzgölü Basin, was an important basin in terms of chemical sedimentary raw material (like sodium sulfate, halite, lithium, nitre and gypsum/ anhydrite) and energy raw material (like lignite, bituminous shale, petroleum, natural gas). In the study area, total of 5197.45 m drilling was made in 7 locations (750 m as clastic drilling and 4447.45 m as core drilling). Based on the geological data obtained by drillings and analyses in the Ereğli-Bor Neogene Basin, it was determined that the evaporitic chemical sedimentation in the basin had formed within evaporite zone of the Upper Miocene Katrandedetepe Formation (playa-lake environment) and sodium sulfate deposit had occurred. Glauberite minerals detected within evaporitic zone in the Ereğli-Bor Basin were observed in three different structures as;

- 1- alternated with bedded clays,
- 2- disseminated crystals within clays and
- 3- alternated with halites (Figures 13, 14, 15).



Figure 13- Glauberite mineralization alternated with high graded clays.



Figure 14- Disseminated, rosette type glauberite mineralization within low graded clays.



Figure 15- Prismatic, high graded glauberite mineralization alternated with halites.

The mineralization is reached at depth of approximately 400 meters from the surface in the Yeniköy sodium sulfate deposit. The approximate thickness of the glauberite mineralization varies between 17-31 meters. Thickness of the halite mineralization on the other hand is in between 16-45 meters. It was observed that the sodium sulfate mineralization deceased towards south but increased towards north.

Besides; there were also detected oil producing thick bituminous shales with approximate thicknesses varying between 40-85 meters in the study area. The correlations of drillings were lithologically made, and the level distribution of sodium sulfate, rock salt and bituminous shale, and layer and thickness variations with depth were shown in Figure 16.

According to the correlation of drillings, it was observed that zones of sodium sulfate and halite took place in major part of the study area and thickened northward (Figure 16).

To make comparison, the reservoir of the Çayırhan sodium sulfate deposit is totally 190 million tons with 33% grade. Sodium sulfate zone is located at depths of 75-100 meters with thicknesses varying between 1.85-20.05 meters. The major mineral of the Çayırhan sulfate deposit is glauberite. The sodium sulfate zone is formed by the association of glauberite-tenardite-gypsum-Brugnatellite ( $Mg_6Fe^{3+}(CO_3)$  (OH)<sub>13</sub>. 4(H<sub>2</sub>O) (Çelik et al., 1987).

Total of 1.8 million tons of sodium sulfate is present in Acıgöl, Tersakan and Bolluk lakes (Alkim AŞ, 2010, oral). According to lake sizes, volumes of water and chemical analyses, our sodium sulfate reservoir in three lakes is estimated at least as 50 million tons (Gündoğan et al., 1995).

However; it was estimated that the Ereğli-Yeniköy sodium sulfate deposit became an important ore deposit in worldwide with its apparent reservoir of 646.482.543 tons. The approximate sodium sulfate and halite grades of the deposit were estimated as; 33.34% Na<sub>2</sub>SO<sub>4</sub> and 80.25% NaCl, respectively (Kadınkız et al., 2015).

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Figure 16- The correlations of drillings 8-4, 8-2 and 9-4 and the locations of mineralization zones.

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