SEDIMENTOLOGY AND GEOCHEMISTRY OF THE MIDDLE MIOCENE PLAYA LAKE EVAPORITES IN THE GÜRÜN BASIN (S OF SİVAS), CENTRAL ANATOLIA, TURKEY

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ABSTRACT: The Gürün basin is a half graben filled by alluvial, fluvial and playa-lake deposits of the Gürün Formation accumulated under the N-S direction extensional tectonic regime and volcanic rocks.

The Gürün Fomation is divided into four members such as the Kavak, Gökpınar, Çayboyu and Terzioğlu members, and the Çayboyu Member has two different evaporitic occurrences such as selenitic and satin spar. During the first phase of evaporite deposition, selenitic gypsum crystals in 5 to 15 cm thick layer within the dolomitic mudstones were formed. The second evaporitic phase consists of four different levels of cavity filling within the sandstones and shale alternation at the upper part of sequence originated as 5 to 10 cm sized satin-spar gypsum crystals with white colored, partly orientated, fibrous-radial shaped. XRF major, minor and some rare elements analyses (La, Ce, Ta, W and U) and low $^{87}Sr/^{86}Sr$ (‰) and $\delta^{34}S$ (CDT) values indicate that meteoric and volcanic solution occasionally mixed with the lake water.

In addition, low $\delta^{18}O$ (SMOW) values in the continental evaporate could be interpreted as mixing of fresh water with the playa lake environment. Selenitic gypsum in the Çayboyu Member of the Gürün Formation was precipitated from ground water-brine water rich in humic acid during periodic desiccations of in the shore-lake plain.

Keywords: evaporite; geochemistry; sedimentology; isotope; Gürün Basin; Central Anatolia

INTRODUCTION

The Neogene Gürün Basin located in the eastern Taurus Region, is bounded by the Suçatı and Şuğul Faults in the east and the north, respectively. The basin approximately occupies 100 km^2, filling by fluvial, alluvial and lacustrine sedimentary and volcano-sedimentary rocks. The middle Miocene sedimentary sequence is interpreted by two formations, such as the Gürün Formation and the Karadağ Volcanic. The Gürün Formation is divided into four members as the Kavak, Gökpınar, Çayboyu and Terzioğlu members (Fig. 1) (Önal et al. 2001). The Gürün Basin has been investigated by general geology, hydrogeology, mineralogy and biostratigraphy (Akkuş 1971; Erkan et al. 1978; Kurtman 1978; Aziz et al. 1979, 1982; Aziz and Erakman 1980; Granit 1990; Atabey et al. 1994; Ceyhan et al. 2000; Yalçın 2001; Önal et al. 2004). Recently, several papers dealing with the industrial minerals such as trona and bituminous shale were published (Helvacı 2001; Önal et al. 2004, 2006). Also the lithofacies of the Gürün Formation is interpreted as playa-lake type deposits similar to that of Eugster and Surdam (1973), Yağmurlu and Helvacı, (1994), Helvacı (1998) and Varol et al. (2005). Playa-lake deposition of the Green River Formation has been discussed and supported by various workers (Eugster and Hardie 1975; Surdam and Wolfbauer 1975; Lundell and Surdam 1975; Surdam and Stanley 1979). There has been many investigation about playa lakes deposits and their geochemical properties (Friedman and Sanders 1978; Hardie et al. 1978; Eugster and Hardie 1978; Lowenstein and Hardie 1985; Talbot and Kelts 1990; Bellanca et al. 1992; Johannesson et al. 1994). The aim of this paper is to present sedimentological and geochemical properties of the playa lake evaporites in the Gürün Basin.

MATERIAL AND METHODS

Samples were collected from gypsum bodies in the Çayboyu Member of the Gürün Formation. These samples were petrographically analyzed using polarizing microscopy, as in the study of Mandado and Tena (1986). Detailed trace elements analyses including isotope analyses ($\delta^{18}O$, $^{87}Sr/^{86}Sr$ and $\delta^{34}S$) of host rock (carbonate and dolomite) and gypsum were carried out using XRF (Philips PW-1400 X-ray Fluorescence Spectrometer) (Acme Lab., Canada) and MS (Finnigan MAT 261-8 Mass Spectrometry) (Act Labs., Canada). XRF samples were powdered in an agate mortar and the material passed through a 200-mesh sieve. Then that material was quartered, and 15 g of it was used to produce pellets. XRF studies were using the standards of Norrish and Chappel (1977) and USGS standards for F, Li, Ba, Pb, and Cu (Gladney et al. 1983) was to determine the analytical precision. In the sample preparation for $\delta^{18}O$ stable-isotope analyses, we followed the procedures described by Longinelli and Craig (1967). In order to obtain the SMOW value from the measurements of $\delta^{18}O$ PDB, the procedures of Craig (1961) and Friedman and O'Neil (1977) were followed and a value of 7.26 ‰ was added to the previous value. The gypsum samples were analyzed for $^{87}Sr/^{86}Sr$ using heavy liquids. The NBS 987 $^{87}Sr/^{86}Sr$ isotope ratio (0, 710265 ± 12) was used as a standard during measurement. In addition to the $\delta^{34}S$ CTD measurements,

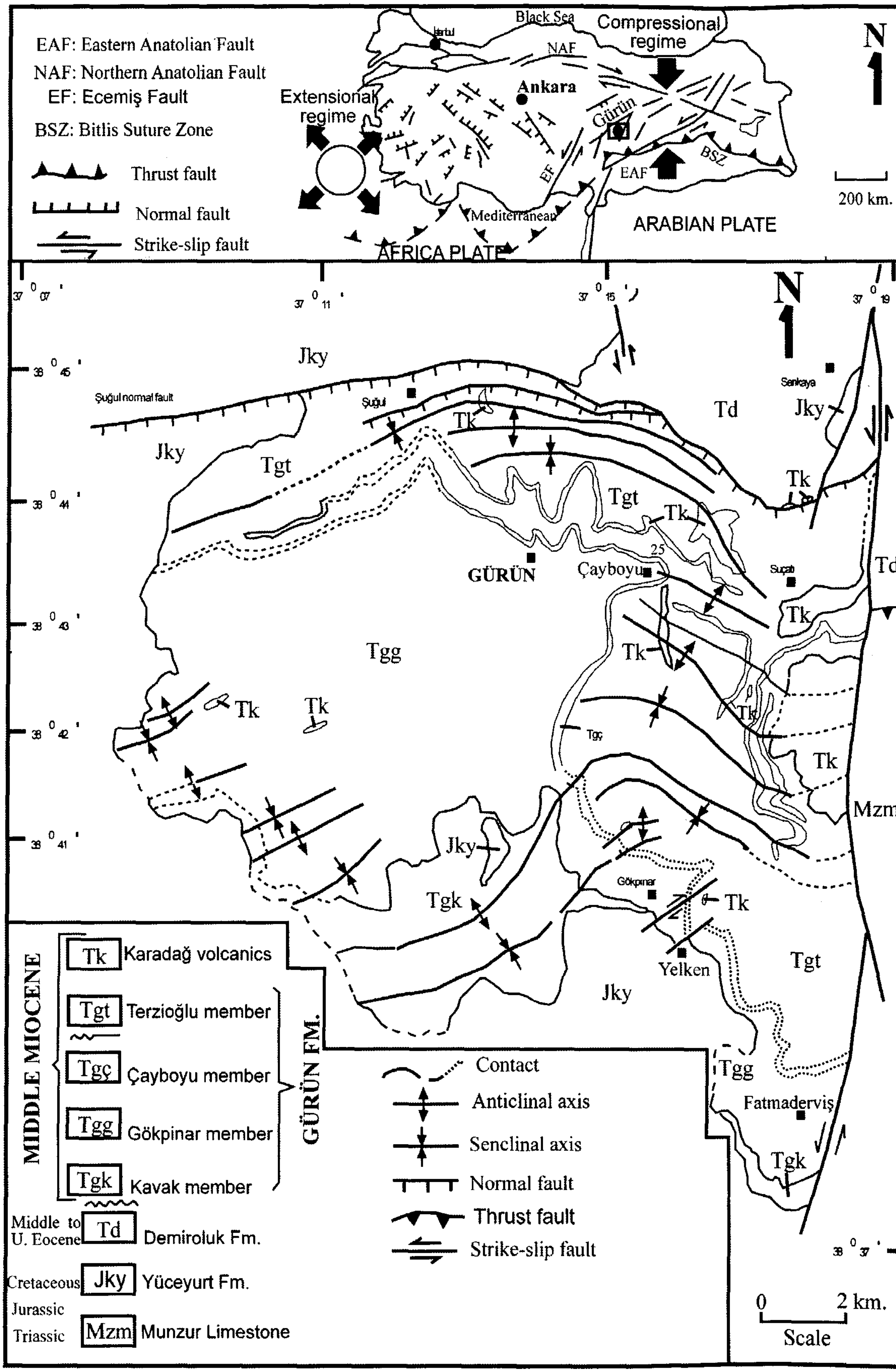

Figure 1. Locality and tectonic structures of the Gürün basin and the major neotectonic features of Turkey (after Önal et al. 2004).

the gypsum samples were dissolved, treating them first with NaOH, and later $BaSO_4$ was obtained by reacting them with $BaCl_2$ at pH=2. The $^{18}O/^{16}O$ and $^{34}S/^{32}S$ isotopes of that precipitate (i.e., $BaSO_4$) were identical to those of gypsum (Hoefs 1987).

GEOLOGICAL SETTING

Turkey is located within the Alpine-Himalayan orogenic belt at the geological margin between the African-Arabian and Eurasian plates. The Anatolian region consists of a mosaic of fragments of continental crust originally scattered all over the Tethys region. The differential plate motions are responsible for the young, east and west Anatolian volcanic activity. Block faulting and North Anatolian transform movements apparently began in the mid-Miocene (ca.15 Ma). The Anatolian orogenic belts have been shortened by thousands of kilometers since the Late Cretaceous (Campanian-Maastrichtian) to the Miocene-Pliocene (McKenzie and Yılmaz 1991).

The study area is probably an integral part of the Central Anatolian Plain provinces and strike-slip basins of eastern Turkey (Şengör et al. 1985). The Gürün Basin is a fault-wedge basin (Fig. 1) with symmetrical and asymmetrical folds (Önal et al. 2001) normal (the Şuğul Fault) and strike-slip faults (the Şuçatı Fault) (Atabey et al. 1994). During the middle Miocene, sedimentary sequences in the Gürün (south of Sivas) Basin were deposited under the control of growth fault. The Gürün Basin was first affected by the extensional tectonic regime, and than was changed to a compressional regime during the late-Miocene time. During this new tectonic phase, NE-SW compressional regime occurring in the region probably originated from the movement of the East Anatolian Fault (EAF) (Fig.1) (Önal et al. 2004).

The rock sequence of the study area is divided into two main groups: pre-Miocene basement rocks and middle Miocene units (Figs. 1 and 2) (Önal et al. 2004). The pre-Miocene basement rocks are Triassic-Jurassic-Cretaceous and middle-late Eocene in age and consist of limestone (the Munzur Limestone) and flysch like sediments (the Yüceyurt and Demiroluk Formations). The middle Miocene units generally consist of siliciclastic, calcareous, bituminous, and evaporitic sedimentary rocks (the Gürün Formation) and volcanic rocks (the Karadağ Volcanics). The Gürün Formation was deposited in fluvial, alluvial, lacustrine and playa-lake environments, and its total thickness exceeds 1220 m. It is divided into the Kavak-Gökpınar-Çayboyu-Terzioğlu Members (Fig. 2) (Önal et al. 2001).

The Kavak Member begins with basal conglomerates on the erosional surface of the basement rocks in the southern part of the Gürün Basin, consisting of reddish-brownish interbedded sandstone-mudstone alternations (Figs. 2, 3, 4A,B) (Ceyhan et al. 2000). Its sedimentologic features indicate that the deposition took place in alluvial, fluvial and mud-flat environments.

The Gökpınar Member is composed mainly of bituminous shale; conglomerate, clayey limestone and siltstone interbedded with limestone and mudstone alternations (Figs. 4C,D) (Ceyhan et al. 2000). The Gökpınar Member is approximately 270 m thick, and rests with gradational contact on the Kavak Member. Its lithologic features and fossils content indicate that it was deposited in a lacustrine environment.

The Çayboyu Member is composed mainly of sandstone, siltstone, tuff, gypsum, lignite and bituminous shale interbedded with mudstone. Gypsum layers were formed as lenticular beds (10–25 m) within the mudstones -bearing dolomites, and include selenitic (5–15 cm) and stain-spar (5–10 cm) crystals (Figs. 4 E, F) (Ceyhan et al. 2000). Bituminous shale and gypsum were probably deposited in shallow, brackish-water playa-lake environment during seasonal flooding. Sandstones are reddish-brownish, lenticular beds (2–8 cm) within the mudstones. The unit includes a regressive sequence, and is vertically and laterally gradational with the underlying Gökpınar Member. The spore and pollen found locally within the lignite (2-25cm) (*Laevigatosporites haardti* (R. POTONIE and VENITZ), *Tricolporopollenites microreticulatus* PFLUG and THOMSON, *Triatripollenites coryphaeus* (R. POTONE) THOMSON and PFLUG, *Tricolporopollenites densus* PFLUG in THOMSON and PFLUG) suggest the age of the unit to be middle Miocene (Önal et al. 2001). Its lithologic features and fossils indicate that it was deposited in a playa-lake environment (Önal et al. 2001).

The Terzioğlu Member is mainly composed up of micritic lacustrine limestone and locally clayey limestone, silicified limestone, bituminous shale, agglomerate, tuff, intraformational conglomerate and siltstone interbeds with Na-carbonate minerals (such as trona) occurrences (Figs. 4 A-C) (Ceyhan et al. 2000; Önal et al. 2004). Micritic limestones yield locally gastropod fossils in the upper parts of the sequence. Clayey limestones in the lower parts of the unit include ostracods and desiccation cracks. Silicified limestones occur in the upper parts of the unit. The unit includes a transgressive and regressive sequence, and its contact with the underlying Çayboyu Member in the deep parts of the basin (distal part) is gradational, but in the shallow parts of the basin (namely proximal area), the contact with the same member is accompanied by a local unconformity. The lithologic features and fossils indicate that the member was deposited in playa-lake and lacustrine environment. The bituminous shale levels were deposited under anerobic lake conditions (Önal et al. 2001, 2004)

SEDIMENTOLOGY

In this part, the detailed sedimentological properties of the

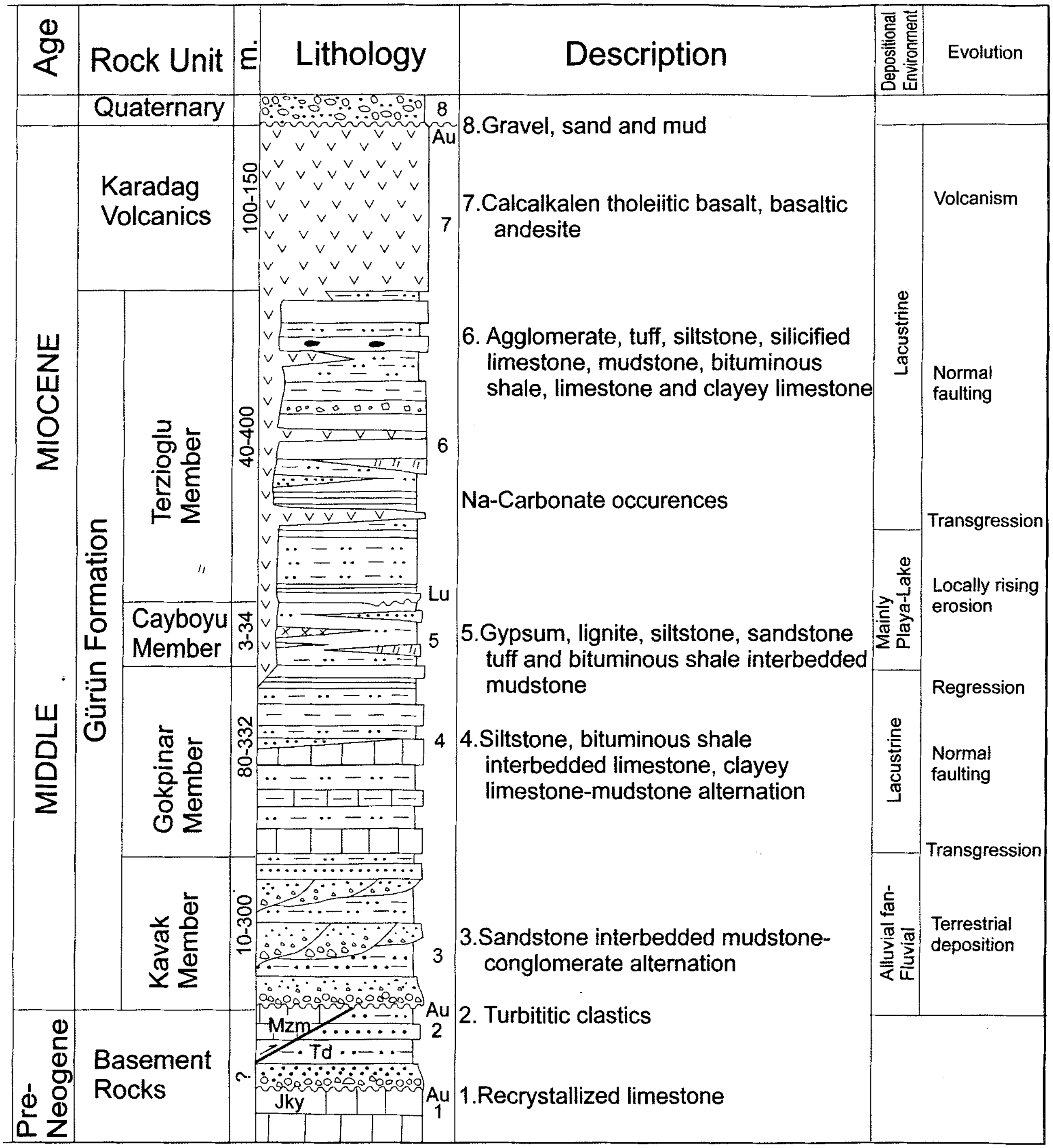

Figure 2. Generalized stratigraphic sequence of the study area (Jky: Yüceyurt Fm., Td: Demiroluk Fm., Mzm: Munzur Lim., Au: Angular unconformity, Lu: Local Unconformity) (after Önal et al. 2004).

middle Miocene of the Çayboyu Member are presented. This Member crops out in a east-west direction within the study area (Figs. 1 and 4 E, F) (Ceyhan et al. 2000). The Type section was measured at Çayboyu village (Fig. 3) (K38-d2; from N 89.250, E: 47,425; to N 89.00; E: 47.250). Mudstone is characterized by light green and red-brown color, medium to thick bedding, rare lamination and bearing plant debris. Mudstones are interbedded with lignite (2 cm to 25 cm), bituminous shale (2 cm to 2 m), gypsum (3 mm to 15 cm), sandstone (2 mm to 8 cm) and siltstones (2 mm to 6 cm), and its thickness is varied (Fig. 3). The Çayboyu Member is gradational vertically and laterally with the underlying Gökpınar Member.

The first type of gypsum deposits within the Çayboyu Member occur as free growing selenitic gypsum crystals 5 to 15 cm sized in the mudstones-bearing dolomites. Petrographic studies show that these crystals are displacive

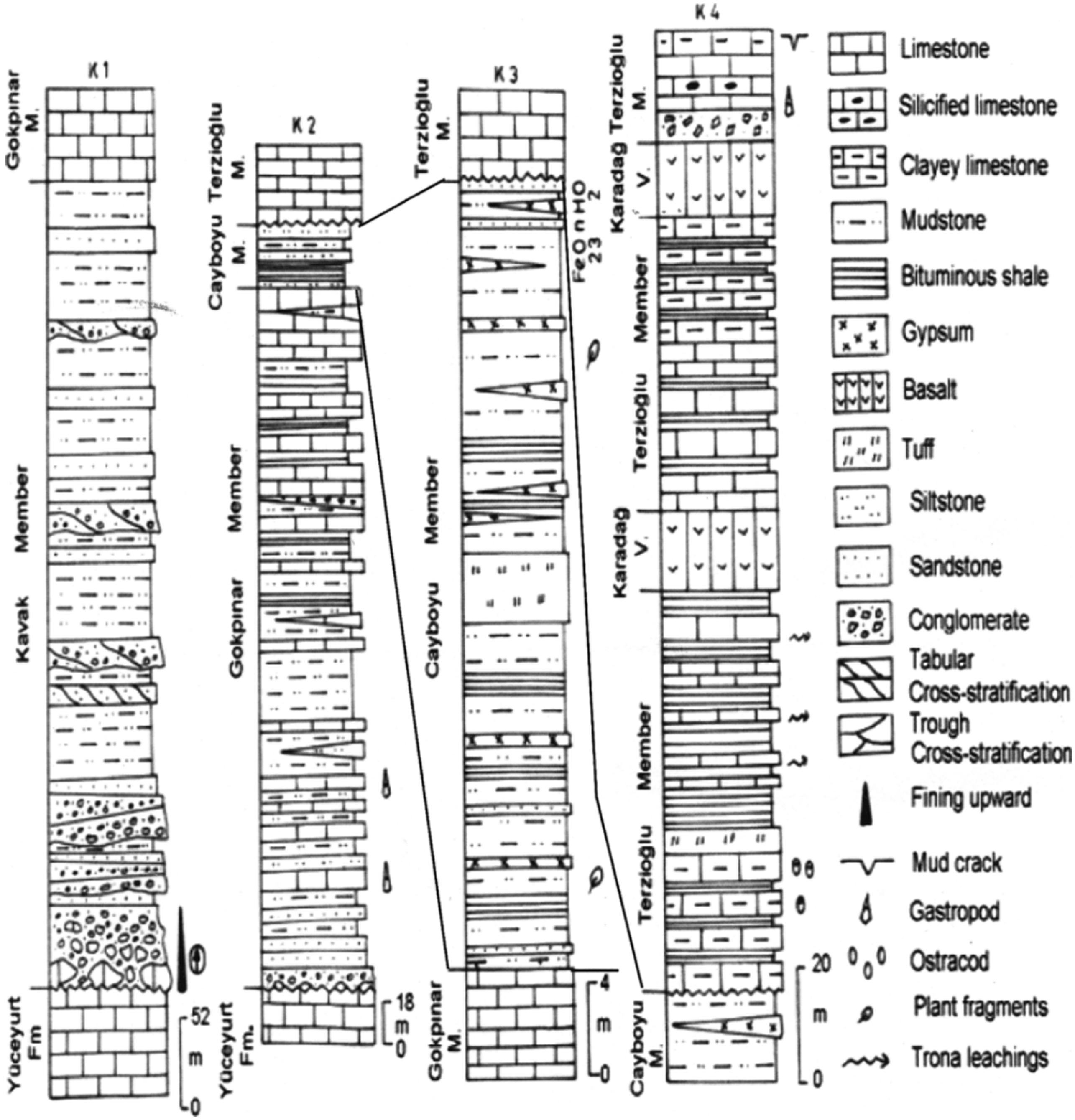

Figure 3. Type sections of the member of the Gürün Formation (after Önal et al. 2004).

gypsum (Fig. 4 G). The discoidal gypsum could be deposited from exhumation during diagenesis. The second type of gypsum occurrences was observed as satin-spar. They are 5 to 10 cm long crystal size, white color; fibrous-radial shaped, partly oriented and showing zoned growing in cavity (Fig. 4 H). Field study observation and petrographic and paleontologic data indicate that these sequences were deposited in flood plain of shore-lake and/or rarely too within coastal swamp environments (Bain 1990; Magee 1991; Salvany and Orti 1997; Türkmen 2004).

GEOCHEMISTRY

Detailed geochemical results are presented in Table 1 and 2 respectively. In Table 1, the gypsum of the Çayboyu Member major element values are SiO_2 % 3.20, Al_2O_3 % 0.61, Fe_2O_3 % 0.23, MgO % 0.30, CaO % 34.2, Na_2O % 0.22, K_2O % 0.12, TiO_2 % 0.13, P_2O_5 % 0.10, AK % 24.3, and $SO^{=3}$ % 39; some rare/trace elements values are Co 16 ppm, Ni 39 ppm, Cu 20 ppm, Zn 6 ppm, Rb 6 ppm, Zr 12 ppm, Mo 6 ppm, Ba 25 ppm, Sr 70 ppm, and rare earth

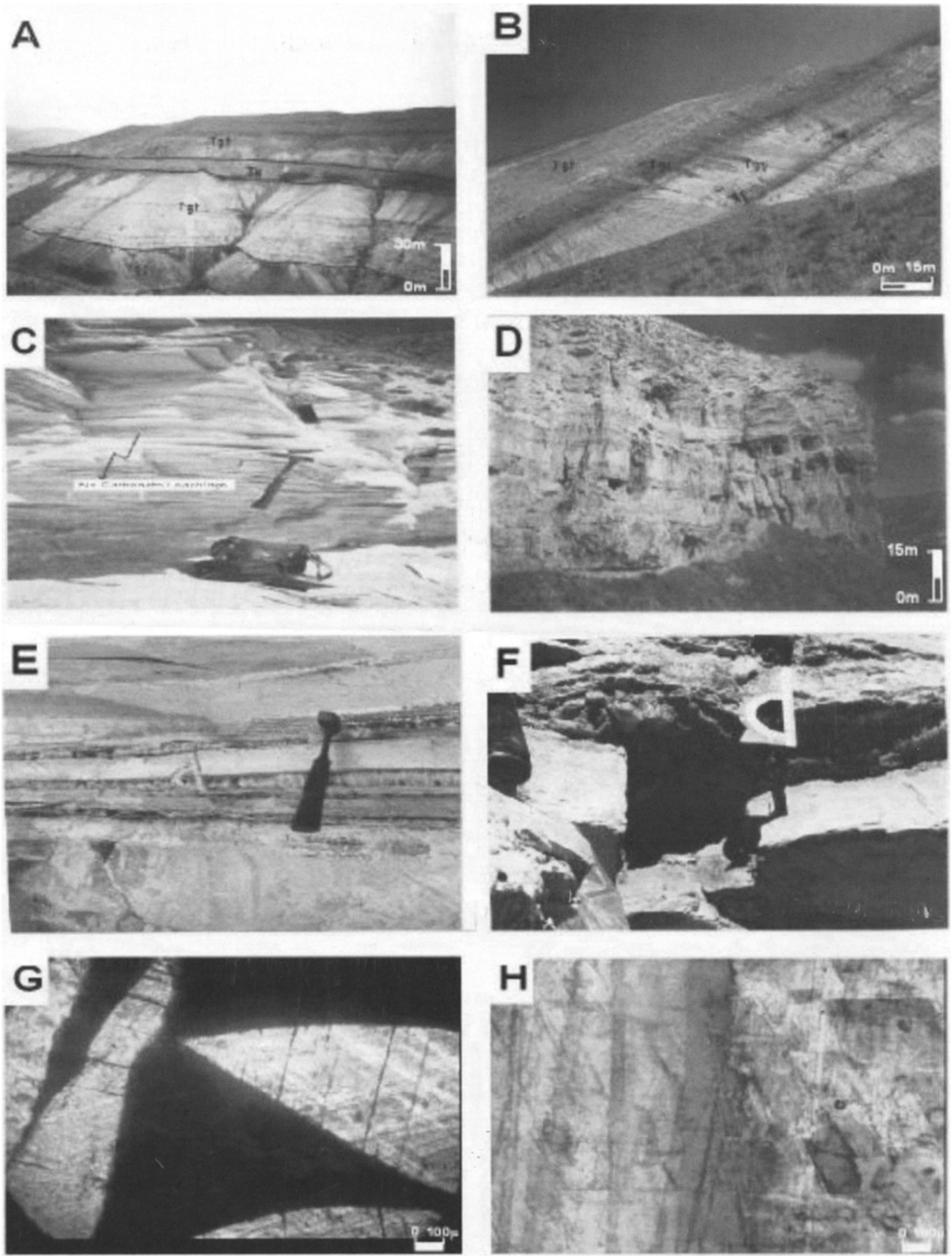

Figure 4. A) Photograph showing the members of the Gürün Formation (Tgk: Kavak M., Tgg: Gökpınar M., Tgç: Çayboyu M., and Tgt: Terzioğlu M.). B) Photograph showing the members of the Gürün Formation (Tgg: Gökpınar M., Tgç: Çayboyu M., and Tgt: Terzioğlu M.). C) Photograph showing Na-carbonate leaching within the bituminous shales in the middle parts of the Terzioğlu member (after Önal et al. 2004). D) Photograph showing limestones in the upper parts of the Terzioğlu member. E) Photograph showing satin-spar gypsum crystals between sandstones and shale layers of the Çayboyu member (Tgç) F) Photograph showing selenitic gypsum crystals between mudstones layers of the Çayboyu member (Tgç) G) Photograph showing displacive gypsum. H) Photograph showing fibrous-radial shaped and zoned gypsum growing in cavity.

Table 1. Whole-rock analyses of major oxide, selected trace elements and some rare earth elements of gypsum (selenitic and satin-spar) samples in the Gürün Formation.

MAJOR OXIDE (%)											
Gypsum Type	SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	$SO^{=3}$
Selenite	3,23	0,70	0,32	0,33	33,8	0,23	0,13	0,17	0,13	23,8	38,24
Satin-Spar	2.17	0.52	0.13	0.28	34.6	0.21	0.10	0.9	0.6	24.7	39.7

TRACE ELEMENTS (ppm)										RARE EARTH ELEMENETS				
Gypsum Type	Co	Ni	Cu	Zn	Rb	Zn	Mo	Ba	Sr	La	Ce	Ta	W	U
Selenite	20	60	21	6	7	13	9	37	102	15	10	7	5	9
Satin-Spar	12	18	19	5	4	11	3	13	35	21	8	3	9	7

Table 2. Isotope analyses results ($^{87}Sr/^{86}Sr$ ‰, $\delta^{34}S$ CDT and $\delta^{18}O$ SMOW) of gypsum (selenitic and satin-spar) samples in the Gürün Formation.

SELENITE GYPSUM			SATIN - SPAR GYPSUM		
$^{87}Sr/^{86}Sr$	$\delta^{18}O$	$\delta^{34}S$	$^{87}Sr/^{86}Sr$	$\delta^{18}O$	$\delta^{34}S$
(‰)	(SMOW)	(CDT)	(‰)	(SMOW)	(CDT)
0,710361±8	0,5^{+}	13,8	0,710269±9	3,8	14,7*

* from Ceyhan et al., (2000) and Palmer et al., (2004)
\+ from Ceyhan et al., (2000)

elements values are La 18 ppm, Ce 9 ppm, Ta 5 ppm, W 7 ppm and U 8 ppm. High values such as SiO_2, Sr, Ba, Co, Ni and Cu and low values of La and W can be important for sulphate bearing water origin. In Önal et al. (2004), high Sr, Ba, Co and Zr values were determined from carbonates of the Gürün Formation, and positive correlations between these elements were determined. In addition, it was observed that there is similar parallelism between some major and minor elements in the Miocene evaporite of the Sivas-Ulaş basin (Tekin 2001; Tekin et al. 2002) and the Gürün Basin evaporites.

In Table 2, selenitic and satin-spar gypsum isotopic values are presented as ($^{87}Sr/^{86}Sr$ (‰) 0.710361± 8, $\delta^{18}O$ (SMOW) 0.5 and $\delta^{34}S$ (CDT) 13.8 for selenitic gypsum, and for satin-spar are $^{87}Sr/^{86}Sr$ (‰) 0.710259± 9, $\delta^{18}O$ (SMOW) 3.5 and $\delta^{34}S$ (CDT) 14.7. On the other hand, these isotope geochemistry results are not similar to Sivas-Ulaş Miocene evaporites data (Tekin et al. 2001; Tekin 2001). Therefore, the low $\delta^{18}O$ (SMOW) data of the selenitic gypsum are important to determine origin of evaporates, which this probably to be marked origin of reduction environment conditions and here biological activity or clastic transported from basement rocks (Faure 1986; Palmer et al. 2004).

CONCLUSIONS

The middle Miocene Gürün Basin was characterized by alluvial, fluvial, flood plain, shore -lake and playa deposits under an extensional regime (Fig. 5). It was observed that some economic occurrences that are bituminous shale-lignite levels and Na-carbonate (trona) are present in the basin. The Sr values (mean 35-100 ppm) of evaporates (selenitic and satin-spar types), presented in Table 1, are lower than those of the middle Miocene massive marine gypsum Sr values (mean 1500-5000 ppm) in the neighboring Sivas-Ulas Basin. Therefore, celestite mineralization could not occur together with the gypsum. However, due to determination high Sr content in the carbonates and volcanic rocks, it would be necessary to work on celestite mineralization in the future.

The geochemical analysis results show that selenitic gypsum was formed diagenetically from evaporation of SO_4 rich from the point of view meteoric water and groundwater's rich in humic acid during the contraction of the lake plain. They are primary evaporates facies, resulting from growing freely upward between sediments and brine water surface. Low $\delta^{18}O$ (SMOW) and La, W values and observed coaly plant/branch remains indicate this types environments and formation. In addition, low $\delta^{18}O$ (SMOW) values in the continental evaporates could be interpreted as influx densely river water into the playa lake environment (Palmer et al. 2004). In addition, $^{87}Sr/^{86}Sr$ (‰) and $\delta^{34}S$ (CDT) values of the selenitic gypsum were lower than those of marine evaporate. Hydrothermal solution could be originated from

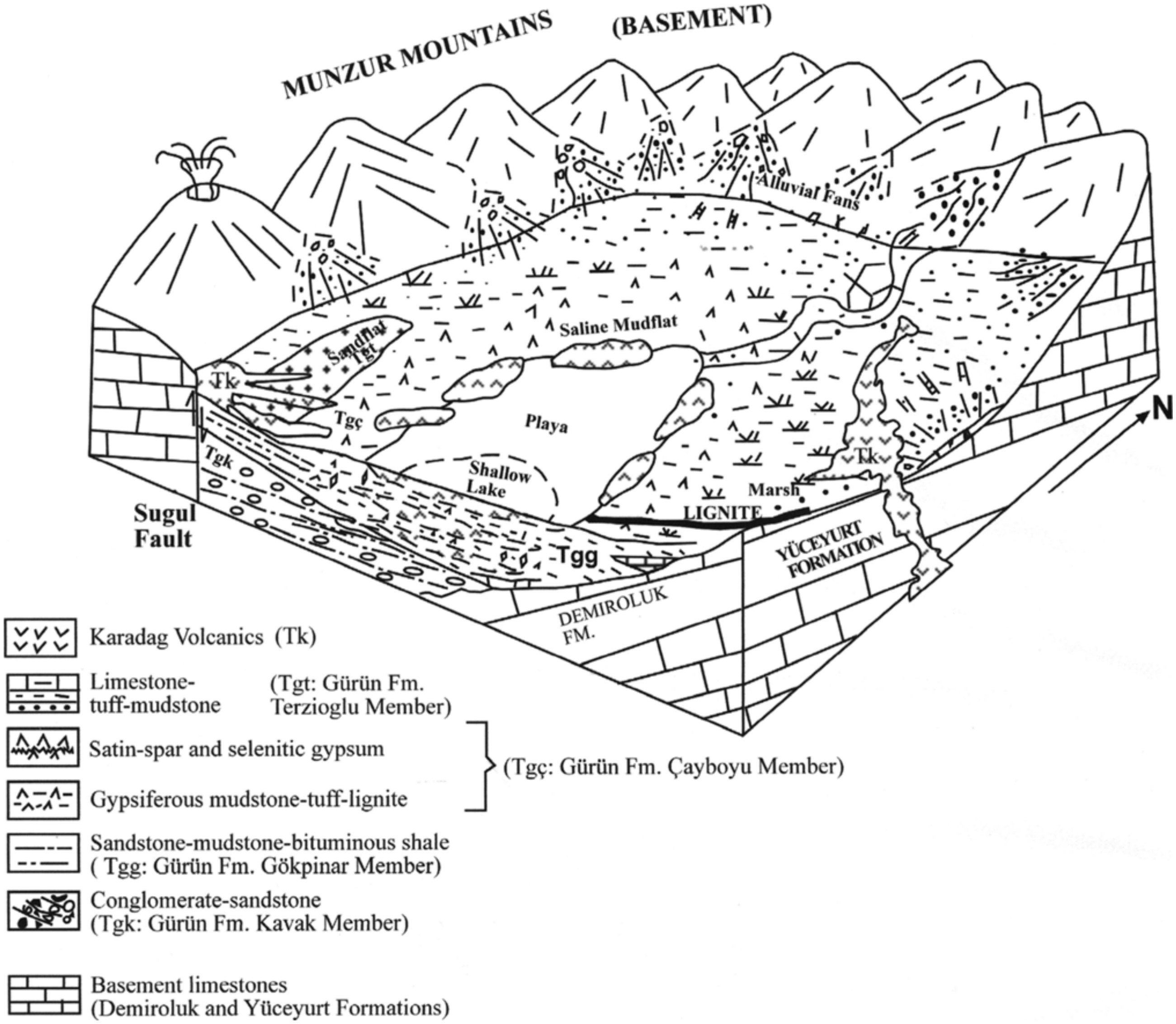

Figure 5. Schematic depositional model for the Neogene deposits of the study area (Not to scale).

Karadağ volcanic activity Sr values of the tuff from Önal et al. (2004) also suggested the similar origin evaporates. On the other hand, it is considered that the vug-filling stain-spar secondary gypsums were crystallized results hydratisation of anhydrite pseudomorphs in the conditions lake plain environment. In the literature, Shearman et al. (1972) and Gündoğan et al. (2005) similarly stated that hydratisation results in cavities are filled by secondary gypsum (satin-spar types) during the transformation from anhydrite to gypsum

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