

## Stratigraphy, Geochemistry and Depositional Environment of the Celestine-bearing Gypsiferous Formations of the Tertiary Ulaş-Sivas Basin, East-Central Anatolia (Turkey)

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**Abstract:** Celestine-bearing evaporite mineralization is widespread in the Tertiary evaporitic units of the Ulaş-Sivas Basin, east-central Anatolia. The oldest deposition of gypsum, which is of laminated character, occurred in a shallow inner-lagoonal environment or in depressions during Late Eocene regression. Thick gypsum and overlying beds composed of alternating bedded, nodular gypsum and sandstone developed in coastal sabkhas and abandoned channels within a meander-river complex during Oligocene time. The last occurrence of evaporitic units, namely massive and bedded gypsum alternating with sandstones and fossiliferous limestones, resulted from limited marine transgression of an Early Miocene sea along the southern margin of the Sivas Tertiary Basin.

The celestine deposits are predominantly found within the gypsum beds throughout the Tertiary basin and in subordinate amounts in the limestones of the uppermost Eocene and as open-space fillings in gypsum, and as nodules in the some of the Oligocene fluvial sandstone, claystones and massive gypsums. Large-scale lenses of celestine occur within Early Miocene massive gypsums. The celestine samples were studied by scanning electron microscopy (SEM), ore microscopy, and electron-microprobe (EMP), fluid-inclusion, selected trace-element (XRF)  $^{18}\text{O}/^{16}\text{O}$ ,  $^{34}\text{S}/^{32}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope geochemistry. Field observations and analytical results indicate that the celestine did not develop via primary sedimentary processes. Rather, high-temperature conditions prevailed during late-diagenetic or epigenetic celestine formation.

**Key Words:** Celestine, Gypsum, Geochemistry, Uluşla-Sivas Basin, East-Central Anatolia

### Tersiyer Ulaş-Sivas Havzasında Sölestin içeren Jipsli Formasyonların Stratigrafisi, Jeokimyası ve Çökme Ortamları, Doğu-Orta Anadolu (Türkiye)

**Özet:** Doğu-Orta Anadolu bölgesinde yer alan Tersiyer yaşlı Sivas-Ulaş evaporit havzasında yaygın olarak sölestin içeren evaporit oluşumları bulunmaktadır. Bunlar başlıca üç zona ayrılabilir.

Birincisi Geç Eosen yaşlı ve lamine bir karakter sergileyen jipslerdir. Bu tip jipsler Eosen sonundaki regresyona bağlı olarak oluşan sığ karakterli iç lagünlerde mineralleşmişlerdir. Bunları üzerleyen ikinci jips zonu ise Oligosen yaşlıdır ve başlıca iki tip fasiyes sergilemektedir. Bunlar kalın ve masif karakterli jips fasiyesi ile kumtaşı ara tabakalı nodüler jips fasiyesidir. Oligosen'in birinci tip fasiyesi sığ sahil sabkhalılarında, ikinci tip fasiyesi ise menderesli akarsuların terk edilmiş kanalları içerisinde oluşmuşlardır. Havzadaki üçüncü ve son evaporit zonu ise Erken Miyosen yaşlı masif ve tabakalı jipslerdir. Bunların tabakalı olanları fosilli kireçtaşları ve kumtaşları ile yer yer ara tabakalıdır. Bölgedeki bu en genç evaporit mineralleşmesi, Sivas Tersiyer havzasının Üst Miyosen başında güneşten gelen sınırlı bir denizel transgresyonun ürünüdür.

Bu üç evaporit zonundaki sölestin mineralleşmeleri ise Sivas-Ulaş Tersiyer baseninde oldukça yaygındır. Sölestinler havzada en üst Eosen yaşlı kireçtaşları ve jipsler içerisinde çatlak-karstik boşluklarda dolgu türü tarzında, Oligosen'in flüvyal kumtaşı ve kilttaşları ile masif jipsleri içerisinde yumrular şeklindedir. Üst Miyosen'in masif jipsleri içerisinde ise büyük boyutlu mercerler biçiminde yer alırlar. Sölestinlerde yapılan arazi, elektron mikroskobu (SEM), cevher mikroskobisi, elektron mikroprob, sıvı kapanım, iz element (XRF) ile  $^{18}\text{O}/^{16}\text{O}$ ,  $^{34}\text{S}/^{32}\text{S}$  ve  $^{87}\text{Sr}/^{86}\text{Sr}$  izotop çalışmaları sedimanter-sinjenetik kökenli bir mineralleşmeyi desteklemektedir. Buna karşılık yüksek sıcaklık koşullarının etkili olduğu epijenetik ve/veya geç diyajenetik oluşum şeklini işaretlemektedir.

**Anahtar Sözcükler:** Sölestin, Jips, Jeokimya, Ulaş-Sivas Havzası, Doğu-Orta Anadolu

## Introduction

Many studies have shown that some celestine occurrences and deposits of economic importance are associated with evaporitic sediments (e.g., Müller 1962; Evans & Shearman 1964; Usdowski 1973; Rickman 1977; Olausen 1981; Kesler & Jones 1981; Brodtkorb *et al.* 1982; Martin *et al.* 1984; Kushnir 1985; Carlson 1987; Decima *et al.* 1987). It was reported in most of those works that celestine occurrences are present in Tertiary massive-gypsum units and were deposited in different ways.

The Tertiary Sivas basin contains the most important celestine deposit known in Turkey. There are at least 25 celestine occurrences in the basin; of these, only one (Körtuzla mine) is a major deposit. A total of 20 million tonnes of celestine has been produced from the Körtuzla mine by the open-pit method. Celestine-bearing layers in the Körtuzla mine have lengths of up to 850 m and widths of up to 100 m, and are observed as lenses in three different zones. The average grade of the deposit is 55.2 % SrO. Celestine occurrences in the basin are generally present within gypsiferous units (Tekin 1995). Gypsum deposits of the region (300 km long and 40-50 km wide) extend from Şarkışla in the west to Refahiye in the east (Figure 1a, b). In the Sivas basin, there are places where the evaporitic rock units experienced extensive tectonism and diapirism. The massive gypsum deposits are mostly bounded by structural features, including imbricated thrusts. However, the age of the massive gypsum deposits is still controversial, but these deposits are considered to be Oligo-Miocene in age by many workers (Kurtman 1961; Baysal & Ataman 1980; Gökten 1983; Gökçen & Kelling 1985; Gökçe & Ceyhan 1988). Owing to extensive tectonism and diapirism, primary structural and textural features of many of the massive gypsum deposits have been destroyed. This situation creates considerable difficulty with regard to the interpretation of depositional environments.

The celestine deposits in the Sivas basin have been investigated by many researchers since 1970, but there is no consensus on the origin of these deposits. To date, three different genetic interpretations have been proposed: (a) sedimentary-syngenetic (Çubuk *et al.* 1992), (b) epigenetic mineralization as product of the hydration of anhydrite (Ceyhan 1996) and (c) epigenetic mineralization formed at high temperature (Gundlach 1959; Strübell 1969; Brower 1973; Usdowski 1973;

Bischoff & Seyfried 1978; Barbieri & Masi 1984; Glynn & Reardon 1990; Dove & Czank 1995).

The goal of this paper is to set forth new sedimentological and geochemical data for the celestine-bearing Tertiary evaporites and to provide a new approach to this much-debated mineralization.

## Regional geology

The Sivas Basin in east-central Turkey is one of the three major sedimentary basins of Central Anatolia that collectively lie in a curvilinear belt following a peripheral remnant basin along the Inner-Tauride suture zone (Görür *et al.* 1983; Erdoğan *et al.* 1996). The Inner-Tauride suture zone marks the site of collision between the Tauride carbonate platform to the south and the Central Anatolian Crystalline Complex to the north, and ophiolitic fragments that are remnants of the Inner-Tauride ocean (Neotethyan branch) occur along this suture zone (Figure 1a). The Sivas basin evolved from marine to lacustrine and fluvial environments between the colliding crustal blocks as the intervening Inner-Tauride ocean closed during Tertiary time. The volcanic and sedimentary rocks in the center of the basin rest on an ophiolitic basement. They consist, from bottom to top, of Palaeocene-Eocene siliciclastic, volcanogenic and carbonate flysch deposits with shallow marine limestone and marl-gypsum intercalations and olistoliths of various lithologies; Oligocene fluvial sediments and gypsum; massive Miocene gypsum, fluvial sediments, basaltic lavas, lacustrine limestone and carbonaceous mudstone. The Eocene and younger sedimentary rocks of the basin onlap the deformed rocks of the Tauride carbonate platform to the south and the Akdağ metamorphic massif to the north (Gökten 1983; Gökçen & Kelling 1985; Cater *et al.* 1991; Tekin 1995).

## Materials and methods

In this study, grab and line samples were collected from gypsum occurrences in the Tertiary series of the Ulaş-Sivas evaporitic basin. These samples were then subjected to petrographic analysis using a polarizing microscope, as in the study of Mandado & Tena (1985). Thirty celestine-bearing samples were chosen for microtextural study using a JEOL JSM-840A scanning electron microscope (SEM), and for EDS studies using a Tracor TN-5502 instrument.

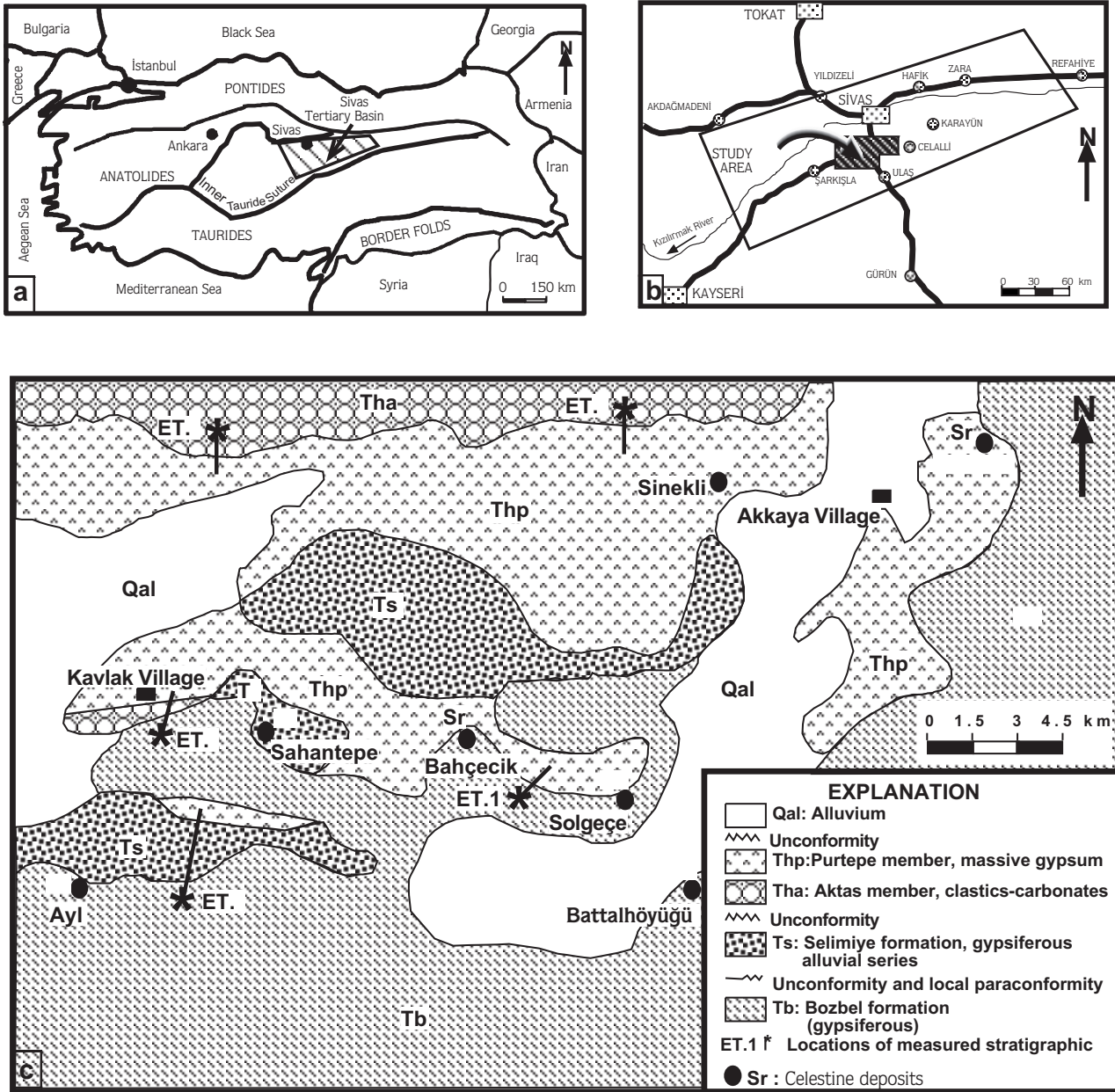


Figure 1. (a) Location of the Tertiary Sivas basin in Turkey. (b) Location map of the study area. (c) Simplified geological map of the study area showing the location of the celestine beds.

Twenty-six gypsum samples were selected and analysed on a Philips PW-1400 X-ray fluorescence spectrometer using the standards of Norrish & Chappel (1977). The samples were powdered in an agate mortar and the material passed through a 200 mesh sieve, that material was then quartered, and 15 g of it was used to produce pellets. USGS standards for F, Li, Ba, Pb, and Cu

(Gladney *et al.* 1983) were used to determine the analytical precision of the XRF studies.

Microprobe studies were performed on selected three samples using a JEOL JXA-8600 electron microprobe and spectrophotometer. For this study, up to 0.2 mm-thick slices were prepared and both sides polished, then coated

with carbon. ZAF, 20.00 kV, and 40.0 degree settings were used.

In addition, five gypsum samples and four celestine samples were selected for <sup>87</sup>Sr/<sup>86</sup>Sr isotope studies and were analyzed using a MAT 261 Mass Spectrophotometer. Celestine was concentrated from these samples using heavy liquids. The NBS 987 <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio (0.710265 ± 12) was used as a standard during measurement. In the sample preparation for δ<sup>18</sup>O stable-isotope analyses, we followed the procedures described by Longinelli & Craig (1967). In order to obtain the SMOW value from the measurements of δ<sup>18</sup>O PDB, the procedures of Craig (1961) and Friedman & O'Neil (1977) were followed and a value of 7.26 ‰ was added to the previous value. As for the <sup>34</sup>S CTD measurements,

the gypsum samples were dissolved, treating them first with NaOH, and later BaSO<sub>4</sub> was obtained by reacting them with BaCl<sub>2</sub> at pH=2. The <sup>18</sup>O/<sup>16</sup>O and <sup>34</sup>S/<sup>32</sup>S isotopes of that precipitate (i.e., BaSO<sub>4</sub>) are identical to those of gypsum (Hoefs 1987).

**Stratigraphy**

The stratigraphy of the celestine-bearing evaporite sequence in the study area is given in Figure 2, and the distribution of this sequence is summarized in Figure 1c. The age of the evaporite deposits, developed on the Palaeocene basement, ranges from Late Eocene to Early Miocene. Gypsum deposition of three different ages and celestine enrichments in three different zones have been identified.

ERA	SYSTEM	SERIES	AGE	THICKNESS (m)	FORMATION	MEMBER	LITHOLOGY	EXPLANATION	DEPOSITIONAL ENVIRONMENT	FOSSIL CONTENT	
											QUATERN.
CENOZOIC	QUATERN.	Pleistocene	Late	0-30	Karatepe	Qal		Alluvium	Terrestrial		
								Unconformity			
	TERTIARY	Miocene	Early-Middle	150-800	Hacıali	Th	Purtepe Thp		CELESTINE (Massive) (3rd zone) Massive gypsum and claystone	Shallow lagoon	
									Unconformity		
									Sandstone, marl and fossiliferous limestone	Shallow shelf	Miolepidocyclus sp., Miogypsina sp. Cibicides sp., Byroldina sp., Mactra indani Terebratalia bidentata (GRATELOUP) Tympenotonus calcaratus (GRATELOUP)
		Oligocene	Oligocene	100-600	Selimiye	Ts	Akkas Tha		Red mudstone and claystone	Coastal sabkha - alluvial	
									Nodular and massive gypsum	Unconformity and locally paraconformity	
									CELESTINE (Nodular) (2nd zone)		
		Eocene	Middle-Late	200-1000	Bozbel	Tb			Laminated gypsums	Shallow shelf - lagoon	Halkyardia cf. minima (LIEBUS) Fabiania cassis (OPPENHEIM) Asterigerina sp. (A. cf. rotula KAUFMAN) Nummulites uranensis de la (HARPE) Nummulites galensis (HEIM) Globigerina senmi (BECKMANN) Acartinia bulboroki (BOLL) Coccolithus formosus (KAMPTNER) Reticulofenestra bisecta (HAY) Reticulofenestra coenura (REINHADT) Sphaerolithus radians (DEFLANDRE)
									CELESTINE (Vug filling) (1st zone)		
Paleocene								Carbonate flysch	Deep sea		
Paleocene							Reefal Carbonates	Platform			

Figure 2. Generalized columnar stratigraphic section of the study area.

The lowermost laminated (1-4 cm) gypsum beds with white claystone alternations comprise the uppermost part of the Bozbel Formation, which is Middle-Late Eocene in age. These may be referred to as "balatino gypsum", based on the definitions of Ogniben (1955) and Hardie & Eugster (1971). Celestine mineralization in laminated (balatino) gypsum and sandy limestones generally developed in "zebra-type" (Brodtkorb *et al.* 1982), and void-and fracture-filling types; also, some biogenic fragments have been partially or completely replaced by celestine (Figure 3a, b).

The second type of celestine-bearing gypsum deposition occurs at the base and/or at intermediate levels of the Oligocene Selimiye Formation, which unconformably or locally paraconformably overlies the Bozbel Formation. The gypsum in the Selimiye Formation is of two different facies. The first is white to cream-coloured massive gypsum, 10-20 m thick, located at the base of the formation. This gypsum is transitional with the laminated gypsum of the underlying Bozbel Formation and contains compact anhydrite interbeds. The second Selimiye gypsum is composed of light gray, extremely compact, nodular gypsum (with nodules 20-40 cm in diameter), and occurs in alluvial-fan deposits that make up the middle to upper parts of the Selimiye Formation (Figure 3c). In some places, gypsum and anhydrite-bearing celestine nodules (60-90 cm across) are present within the nodular gypsum beds. This type of nodular deposition is typical in the excavations of the Sahantepe celestine deposit (Figure 3c).

The third zone of celestine-bearing gypsum occurs within the Purtepe member of the Hacali Formation of Early Miocene age (Figures 1 & 2). The Purtepe member was deposited as chemical sediments in the northeastern part of basin, and concordantly overlies the Aktaş member, composed of shallow-marine clastic and carbonate deposits. The Purtepe massive gypsum is approximately a few hundred meters thick and its lateral extent is up to a few kilometers (Figure 3d). Economic celestine deposits in the region occur as lenses in the Purtepe member. Such lenses commonly have lengths of 700-900 m and widths of 100-200 m; the SrO contents of these celestine deposits are in the range of 52.0-55.2 %. Brecciation is typical at the contact between celestine lenses and gypsum layers. Claystone alternations, karstic-type dissolution, voids, and 3-5 m thick compact carbonate or anhydrite bands also occur within the celestine beds (Figure 3e).

The Purtepe member also contains a zone of large (2-20 cm) and transparent gypsum crystals that are mainly twinned gypsum prisms with near vertical growth upon fine, crystalline, massive gypsum. The selenite crystals are present as dome-shaped structures, 70- to 80-cm-long and 70- to 100-cm-thick. The crystals exhibit vertical orientation of their c-axes, involving zig-zag (saw-tooth)-shaped laminations (cf. Schreiber & Friedman 1976). The zig-zag surfaces have been draped by very thin dolomite laminae, likely indicating that periodic environmental changes (from saline to brackish) occurred during growth of the selenite gypsum in a shallow lagoonal area (Figure 3f). Detailed lithofacies descriptions of this evaporite sequence are given in the measured stratigraphic sections (ET. 1 to 5) (Figure 4).

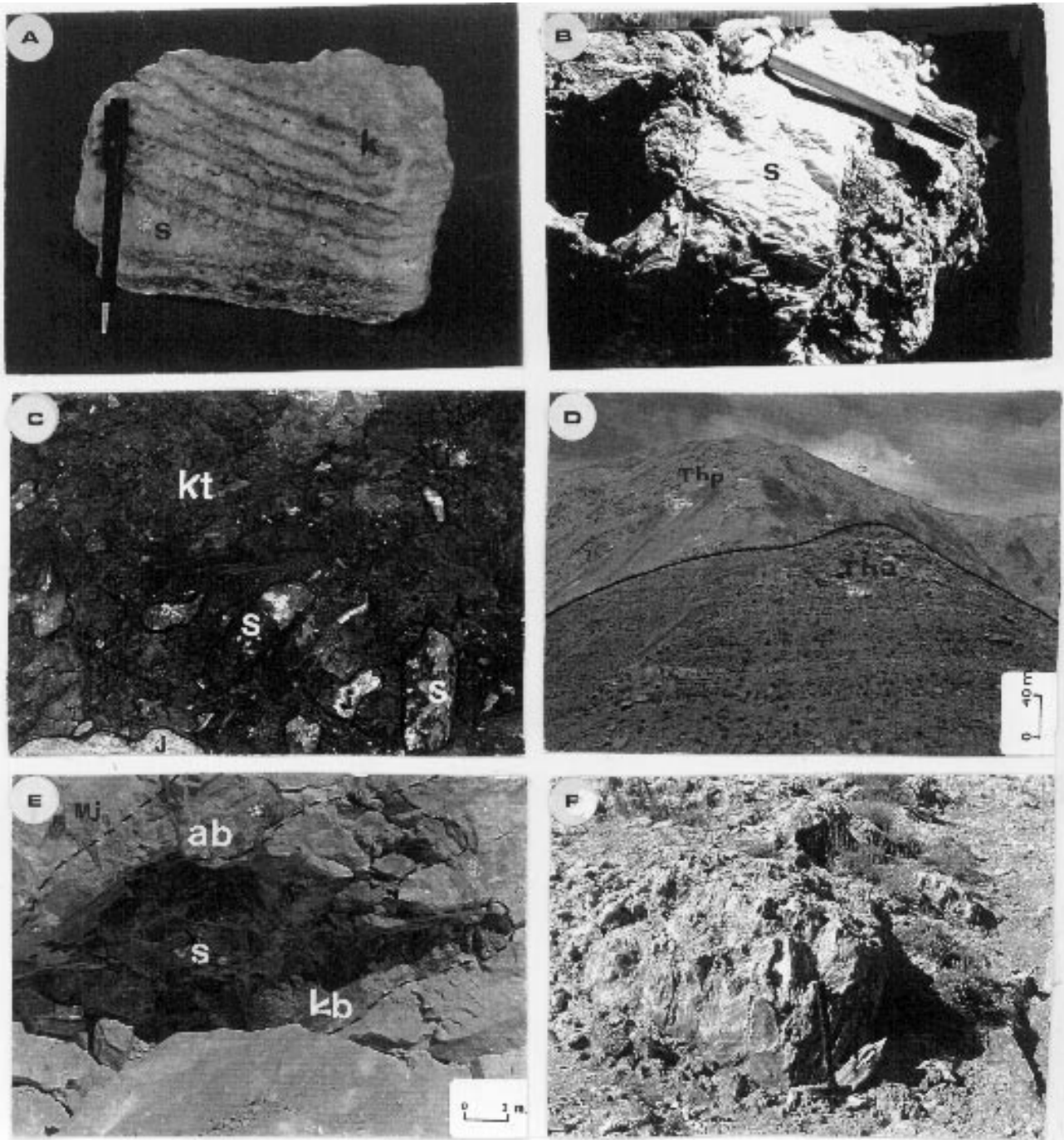
A terrestrial gypsum has also been identified 20 km northeast of the study area; this gypsum formed in a playa-lake environment that lacks celestine mineralization. Its age is likely Late Miocene-Pliocene, and contains a vast amount of associated halite. This gypsum is overlain by Pliocene basaltic volcanic rocks (Gökçe & Ceyhan 1988).

### Petrography

The Upper Eocene gypsum is laminated, made up of fine to medium, euhedral-subhedral forms. This gypsum comprises bands of several centimeters to a few decimeters thick, in claystone and marl rich in organic matter. Their fossil content is extremely low, containing poorly preserved planktonic foraminifers. Also found are the remnants of benthic foraminifers. The claystones contain silt-sized gypsum crystals (reworked fragments) that are dispersed in the clay matrix.

The celestine mineralization in the laminated gypsum and claystone bands is present in economic quantities. This type of celestine mineralization developed in fractures that irregularly cut the laminated gypsum and cm-thick claystone bands. The celestine crystal forms are prismatic and bar-like (Figure 5a). SEM studies revealed that those large, prismatic and bar-like celestine crystals parallel the growth orientation of the gypsum crystals (Figure 5b).

Almost all of the Oligocene and Lower Miocene evaporites consist of secondary gypsum; these are alabastrine-type crystals having microcrystalline nature. Locally, the alabaster is megacrystalline or may have a



**Figure 3.** (a) Photograph of specimen from zebra-type celestine occurrence, Bahçeciktepe celestine deposit, Upper Eocene Bozbel Formation (Tb). k- microcrystalline carbonate band, s- tabular crystalline celestine band. (b) Photograph showing fracture-filling celestine mineralization (white) in the Solgeçe celestine deposit, Upper Eocene Bozbel Formation (Tb). k- limestone, s- fracture-filling celestines. (c) Photograph of celestine-gypsum nodules observed in alluvial fan deposits of the Sahantepe celestine exposure, Oligocene Selimiye Formation (Ts). Celestine-gypsum nodules are irregular and spherical-ellipsoidal shaped. kt- claystone matrix, s- celestine nodule, and j- gypsum nodule. (d) Photograph showing the concordant relationship between clastic-carbonates units of the Aktaş member and the Purtepe massive gypsum member. Thp: Purtepe member of Middle(?) Miocene age, and Tha: Aktaş member of Early Miocene age. (e) Photograph of carbonate-anhydrite bands of the Sinekli celestine deposit in massive gypsum of the Purtepe member. Mj- massive gypsum, ab- anhydrite band, kb- carbonate band, and s- celestine. (f) Photograph of selenite gypsum crystals developed in the upper levels of the massive gypsum of the Purtepe member.

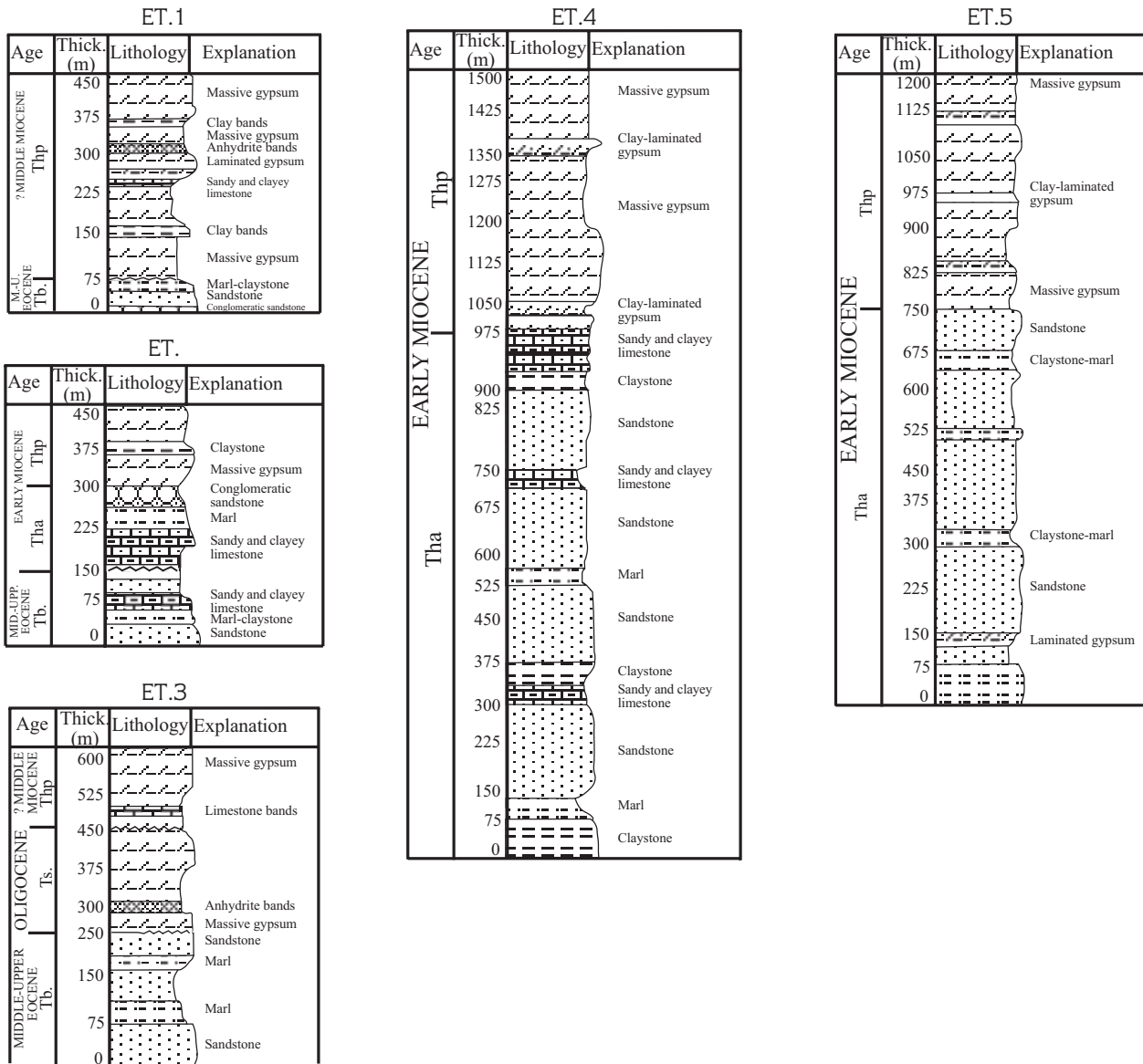
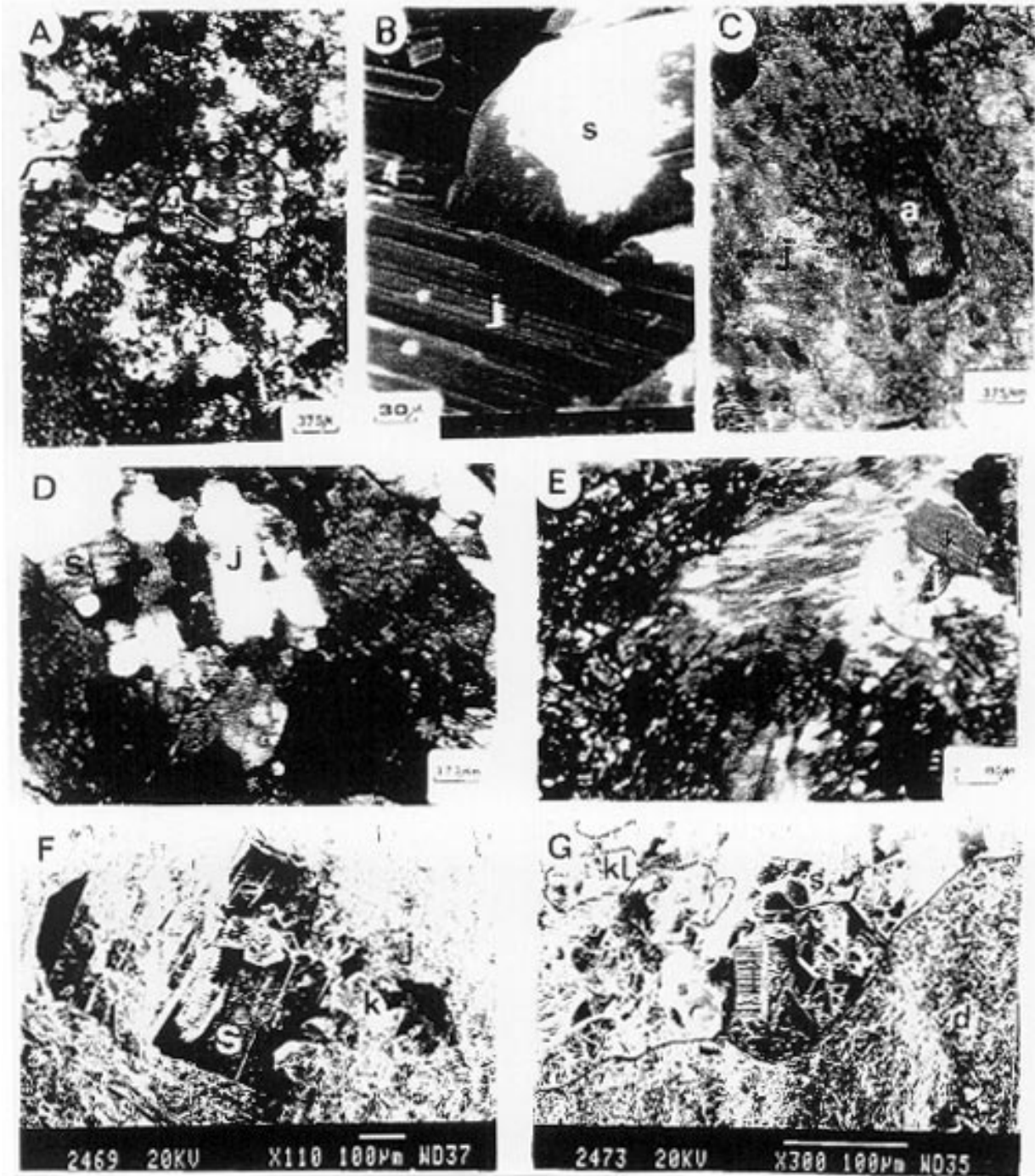


Figure 4. Measured stratigraphic sections from the studied area.

porphyroblastic texture. Their origin can be attributed to the rehydration of anhydrite during exhumation (Murray 1964; Kinsman 1966). Evidence supporting this conclusion is the presence of anhydrite inclusions and lenses in the secondary gypsum units (Figure 5c). Hence, the transformation has obscured or erased distinctive textures and has altered mineralogy; thus, it may be difficult to recognize their original petrographic character. Another kind of gypsum in the massive evaporites is a porphyroblastic texture; this texture is characterized by fibrous-radial crystals with anhydrite

inclusions having jagged edges. In the field, these layers have a general character similar to the nodular mosaic texture (Holliday 1970; Warren & Kendall 1985).

The celestines in the Oligocene and Lower Miocene gypsums are categorized into three types, based on their petrographical features: (a) prismatic and bar-like, (b) sub-idiomorphic and tabular, and (c) fibrous-radial. The first and third types characterize the Lower Miocene deposits and usually co-exist. The first type is mostly observed in vugs, forming geodic fillings (Figure 5d). The sub-idiomorphic-tabular type on the other hand,



**Figure 5.** (a) Coarse, prismatic celestine crystal within clayey-carbonaceous gypsum matrix. Such inclusions of gypsum crystals in the celestine crystals is typical. j- gypsum, and s- celestine. (b) SEM image of coarse, prismatic, euhedral celestine crystals of displacement type with oriented, fibrous-radial gypsum crystals. j- gypsum, and s- celestine. (c) Anhydrite inclusions within euhedral, prismatic gypsum crystals indicative of hydration-dehydration processes. a- anhydrite, and j- gypsum. (d) Coarse, bounded, prismatic, bar-like gypsum of porphyroblastic texture and prismatic celestine crystals relics. j- gypsum, and s- celestine. (e) Gypsum of alabastrine texture together with coarse calcite and celestine crystal inclusions (replacement type) in the matrix. s- celestine, k- calcite, j- gypsum. (f) SEM image of coarse, prismatic, bar-like, irregularly freely growing celestine crystals within a gypsum matrix (alabastrine texture) together with euhedral calcite crystals. s- celestine, k- calcite, and j- gypsum. (g) SEM image of sub-euhedral celestine crystals developed in a microcrystalline dolomite matrix. Zoned celestine crystal together with surrounding chlorite nodules and dolomite silt in the central part of photograph are distinctive. s- tabular celestine crystals, d- dolomite silt, kl- chlorite ball.



characterizes the Oligocene celestines; these are moderately to coarsely crystalline and are surrounded by gypsum and anhydrite. These celestines are mostly pure, but locally contain various amounts of gypsum relicts (Figure 5e).

The appearance of prismatic- to bar-like celestine in the SEM images is such that their growth is multidirectional in the gypsum matrix, and they are surrounded by euhedral calcite crystals (Figure 5f). In SEM views, the second type of celestine mineralization (i.e., sub-idiomorphic and tabular) has the characteristics of both vug-filling and nodular celestine deposits. They are interpreted to have formed as zonal-growth crystals in the clay- and/or carbonate-dominated matrix (Figure 5g). The last group, the fibrous-radial type, are nearly pure celestines that grew multidirectionally in vugs.

## Geochemistry

### Trace-element geochemistry

Major-oxide values of SrO, CaO, MgO, K<sub>2</sub>O, Na<sub>2</sub>O, and SO<sub>3</sub> obtained from XRF analyses of 26 different gypsum samples were measured weight percentages, whereas the trace elements F, Li, Ba, Pb, and Cu were measured in ppm. These SrO values significantly increase, starting from the Upper Eocene laminated gypsum at the base and continuing upward to massive gypsum of the Lower Miocene Purtepe member (0.10-1.74 %). It is important to note that massive gypsum of the Purtepe member contains about 1.75 % SrO in the crystal lattice. This SrO value is above the normal limit for marine gypsum, and this high Sr<sup>2+</sup> content is attributed to its accommodation into the crystal lattices of the massive gypsum of the Purtepe member, this premise is supported by the results of microprobe analyses. Because seawater contains only 8 ppm Sr<sup>2+</sup> in ionic form (e.g., Turekian & Kulp 1956; Usdowski 1973; Krauskopf 1979; Sonnenfeld 1984), such a high Sr<sup>2+</sup> content is an important factor in primary strontium enrichment. This enrichment may be due to an additional Sr coming from the dissolution of early gypsum (Purtepe member), or from a supply via a syn-sedimentary influx of water. This is finding important for determining the source of Sr<sup>2+</sup> ions for the formation of economically important celestine deposits of the region.

The SrO contents of freely growing-twinned secondary gypsum at the top of the Purtepe massive gypsum member and the laminated-massive-nodular

gypsum of Late Eocene-Oligocene age are within the expected range. The major oxide values of 32.7-38.6 % CaO, 0.1-1.2 % K<sub>2</sub>O, 0.17-0.32 % MgO, and 0.11-0.31 % Na<sub>2</sub>O are consistent with those of gypsum of syn-sedimentary origin (Müller 1962; Turekian 1964; Baysal & Ataman 1980; Hardie 1984; Carlson 1987; Gökçe & Ceyhan 1988).

The F, Li, Ba, Pb, and Cu contents of gypsum samples of varying ages from the Ulaş-Sivas Basin are also instructive. F values are between 3.4-4.8 ppm, Li is 1.6-3.0 ppm, Ba is 0.01-6.5 ppm, Pb is 0.14-2.5 ppm, and Cu is 0.1-2.0 ppm. Thus, the F and Li contents of the 26 samples are very similar, however, their Ba, Pb, and Cu contents are somewhat variable. Tardy *et al.* (1972) attributed low F and Li contents to excess evaporation. Tekin (1995) suggested that the Ba (6.5 ppm), Pb (2.5 ppm), and Cu (2 ppm) contents, which are above the normal values in the Purtepe massive gypsum member and similar contents determined in associated celestine may be indicative of hydrothermal fluids having played an important role in the formation of epigenetic celestines in the region.

A comparison of the trace-element values of the Ulaş-Sivas celestine-bearing gypsum units to those from studies carried out on gypsum from the eastern part of the Tertiary Sivas basin (Baysal & Ataman 1980; Gökçe & Ceyhan 1988) is presented in Table 1. This shows that in the Ulaş-Sivas basin, the F contents are lower and the Sr and Mg contents higher than those reported in other studies, and that the Li values are similar.

### <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>18</sup>O/<sup>16</sup>O and <sup>34</sup>S/<sup>32</sup>S isotope studies

<sup>87</sup>Sr/<sup>86</sup>Sr, <sup>18</sup>O/<sup>16</sup>O and <sup>34</sup>S/<sup>32</sup>S isotope ratios for selected gypsum samples from the Tertiary Ulaş-Sivas Basin are given in Table 2. There is a dramatic increase in <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>18</sup>O/<sup>16</sup>O and <sup>34</sup>S/<sup>32</sup>S values from the oldest gypsum at the base to the youngest at the top. Similar data was presented by Hoefs (1987) and Utrilla *et al.* (1992). These increases indicate that the Ulaş-Sivas gypsum was derived from Upper Eocene-Lower Miocene marine units. Müller (1962), Turekian (1964), Emery & Robinson (1992), and Faure & Powell (1972) also reported similar <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>18</sup>O/<sup>16</sup>O isotope ratios from various evaporitic basins. However, these values are slightly lower than to the <sup>87</sup>Sr/<sup>86</sup>Sr ratio of seawater reported in the studies of De Paolo & Ingram (1985), Burke *et al.*

**Table 1.** Trace-element contents of gypsum samples from the study area compared to those reported in previous studies. Mean contents in parentheses.

Trace Elements	Zara-Refahiye Region (Baysal & Ataman 1980) (ppm)	Celalli-Karayün and Hafik Region (Gökçe & Ceyhan 1988) (ppm)	Sivas-Ulaş Region (this study) (ppm)	
F	16.1	40	3.4-4.8	(4.1)
Li	2.8	3.1	1.6-3	(2.6)
Sr	783	2450	2526-5368	(3946)
Mg	3741	6528	3158-4768	(4158)
Ba	--	--	0.01-6.5	(0.1)
Pb	--	--	0.14-2.5	(0.3)
Cu	--	--	0.1-2	(0.2)

(1982) and Peterman *et al.* (1970). This situation may have arisen in a variety of ways. In addition, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of samples from four different areas of celestine mineralization are very similar to those of gypsum, which are in range of between  $0.707405 \pm 16$  to  $0.707683 \pm 19$ . The close relationship of the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratios suggests that the Middle Miocene Purtepe massive gypsum member is the most probable  $\text{Sr}^{2+}$  source from the celestines. Trace-element contents and the results of microprobe analyses of gypsum and celestines also support this contention (Tekin 1995).

### Gypsum environments

Depositional-environmental and sedimentologic studies indicate that the uppermost Eocene laminated gypsum was deposited during short periods of evaporitization alternating with clay deposition from suspended material in a shallow inner lagoon, which was periodically isolated from the main sea (marine water) during Late Eocene regression. The presence of red muds enclosing the gypsum also suggest the shallowing stage of a basin (Hardie & Eugster 1971; Sonnenfeld 1984) and an influx of argillaceous matter.

Interpretation of field observations indicates that the massive gypsum of the Selimiye Formation exhibits an

intense and continuous gypsum sedimentation, which probably occurred in depressions left from the Eocene sea. This unit gradually passed upward into gypsum-bearing sandstones, which contain large gypsum and celestine nodules. The lenticular shape of evaporite outcrops within the alluvial sediments suggests that evaporitization occurred in dry channels or ox-bow-lake-type environments. This phase of evaporite deposition closed when meandering rivers deposited by very thick sandstones (Kinsman 1969; Magee 1991).

The Purtepe massive gypsum member overlies the Oligocene units unconformably and has a very complex stratigraphy. The gypsum was deposited both in coastal sabkhas and in shallow lagoons, which were the remnants of Miocene transgression. As a result of this, the marginal areas were continuously flooded by seawater, and later became extremely shallow and finally dried. The environment was temporarily isolated from the main sea. Thus, red claystones and thin-bedded marls were associated with massive gypsum. Most of the gypsum deposits were transformed into anhydrite upon burial, and then into secondary gypsum (mainly alabaster) when they were exhumed. The uppermost layers do not contain relicts of the growth of gypsum to anhydrite (c.f. Schreiber & El Tabakh 2000). The absence of chloride salts (e.g., NaCl, KCl, and  $\text{MgCl}_2$ ) in the massive gypsum

**Table 2.**  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{18}\text{O}/^{16}\text{O}$  and  $^{34}\text{S}/^{32}\text{S}$  isotope analyses of gypsum samples from the study area.  $^{87}\text{Sr}/^{86}\text{Sr}$  Sr values from Tekin & Varol (1997).

Sample No	Age	Types of Gypsum Mineralization	$^{87}\text{Sr}/^{86}\text{Sr}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$	$\delta^{34}\text{S}_{\text{CDT}}$
ET.90/45	Early Miocene	Discoidal and twinned secondary gypsum (Purtepe member)	$0.707819 \pm 9$	18.35	11.6
SY.6		Massive gypsum (Purtepe member)	$0.707733 \pm 9$	16.83	25.1
SH.1	Oligocene	Nodular gypsum (Selimiye fm.)	$0.707546 \pm 9$	15.97	13.9
ET.90/61		Massive gypsum (Selimiye fm.)	$0.707628 \pm 9$	14.47	22.4
ET.90/27	Late Eocene	Laminated gypsum (Bozbel fm.)	$0.707413 \pm 9$	12.68	21.8

is attributed to the leaching of these highly soluble salts and subsequent removal from gypsiferous units in the region (Gökçe & Ceyhan 1988). Gökçe & Ceyhan (1988) also wrote that, considering the presence of salt pans in the Sivas Basin, such a leaching process is still in operation. The absence of chloride salts could also be explained in a different way; perhaps they were simply not deposited because the concentration of the seawater was never high enough to form them. On the other hand, the extreme thickness of the Purtepe massive gypsum member (300 m in places) may be attributable to salt diapirism, continuous feeding from seawater and, particularly, to tectonic control of the basin (e.g., Peryt 1994).

### Origin of Celestines

Several studies were carried out previously on the celestines of the Sivas Basin (e. g., Gökçe 1989-1990; Çubuk *et al.* 1992; Karamenderesi *et al.* 1992; Ceyhan 1996). Gökçe (1989-1990) evaluated the formation of all the celestine deposits (occurrences of vug-fillings and/or veins) in the massive Middle Miocene gypsum beds as well as those in the clastic deposits. The origin of the celestine was explained by Gökçe (1989-1990) thus: the  $\text{Sr}^{2+}$  in gypsum, limestones, marl and claystone was first leached by meteoric water and then formed compounds with abundant  $\text{SO}_4^{2-}$  in the stratigraphic series yielding deposits of  $\text{SrSO}_4$ . Çubuk and others (1992) later asserted that the celestine occurs along bedding planes in the Middle to Upper Eocene flysch facies; they suggested that the celestines first formed syngenetically by chemical deposition and later were transported in solution into the overlying and underlying units.

Karamenderesi and others (1992) proposed that the celestines are the products of buried volcanic and/or intrusive sources, which were active during the latest Miocene-Pliocene. Thus, they interpreted the celestines to be of hydrothermal origin, and supported this view by pointing out that the Sr, Ba, and B contents of modern hydrothermal solutions and the travertine deposits adjacent to the celestine beds are almost identical. Ceyhan (1996) reported three zones of celestine deposition in the Upper Eocene, Oligocene and Lower Miocene carbonaceous, clastic, and evaporitic units. Ceyhan (1996) also claimed that the celestines are of epigenetic origin, having resulted from  $\text{Sr}^{2+}$  released by the dissolution of calcite and gypsum during the dehydration

of anhydrite, forming compounds with the sufficient  $\text{SO}_4^{2-}$  in the environment.

This background information reveals that there is no consensus opinion on the mechanism of formation and the age of celestines in the Sivas Basin. The fact that the celestine deposits that co-exist with carbonate, evaporitic, and terrestrial deposits are not age-dated definitively and the lack of geochemical and isotopic ( $^{18}\text{O}/^{16}\text{O}$ ,  $^{34}\text{S}/^{32}\text{S}$ ) data present significant difficulties with regard to their genesis. The present study provides an approach to the origin and age of the celestines using the following findings from Tekin *et al.* (1994), Tekin & Varol (1997): (1) Hydrothermal alteration zones with Si and Al enrichment, are present in all of the celestine deposits and there is also enrichment in pyrite, stibnite, limonite, siderite-ankerite, and barite at the same localities; (2) There are Fe-oxide stains and iron-bearing silica concretions in celestine beds of the Upper Eocene deposits; (3) The presence of celestines mainly in fractures and karstic vugs; (4) A pyrite-limonite-and stibnite-bearing mudstone level apparently restricted the downward extension of celestine; (5) Extensive  $\text{CO}_2$  release from the Lower Miocene Hacıali Formation; (6) Zonal-growth structures in celestines, oriented gypsum crystals, dolomite inclusions, and secondary micro-scale dissolution structures observed through SEM studies; (7) Bravoite, melnikovite pyrite, marcasite, limonite, siderite-ankerite, native gold, electrum, psilomelane, realgar-orpiment, rutile, sphalerite, and stibnite were observed through ore-microscopy studies. Tiny detrital gold crystals were observed in tabular celestine crystal that displays zonal growth (SEM view); (8) Repetition of Ba and Sr in the form of dark-light zones observed through EMP and EMPAS analyses. Celestine crystals collected from different layers have average Sr and Ba contents ranging from 3645 to 4465 ppm, and 0.020 to 0.041 ppm, respectively; (9) Elevated homogenization temperatures observed through the fluid-inclusion studies on celestines. A decrease in homogenization temperatures, from 360 °C to 200 °C, occurred from the Late Eocene to the Early Miocene. Salinity values are almost constant, in the range of 14-23% NaCl equivalent; (10) Relatively higher values of trace elements, such as Li (3 ppm), Mo (1.8 ppm), Pb (19.39 ppm), W (1.21 ppm), As (1.84 ppm), Zn (3.46 ppm), Cu (7.9 ppm) and Ba (20 ppm), with respect to syngenetically deposited celestine mineralization (from seawater); (11)  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic

ratios of vug-filling, nodular, and massive-lenticular celestines vary between  $0.707405 \pm 16$  and  $0.707683 \pm 19$ , whereas relatively lower isotopic ratios ( $0.706005 \pm 20$ ) characterize the zebra-type celestine.

Based on these findings, the sedimentary origin of celestines of the Sivas Basin should be questioned. In particular, the existence of metal ions and the elevated homogenization temperatures in all the celestines suggest a hydrothermal-epigenetic origin; Scholle and others (1990) suggest that the celestines they studied formed epigenetically. However, the  $^3\text{H}/^1\text{H}$  isotope values of modern  $\text{CO}_2$  exhalations indicate the existence of buried volcanic masses in this region (Emin Teke, personal communication, 1995). Moreover, field observations indicate that the Sivas Basin experienced an extensive volcanic activity during the Tertiary. Based on this evidence, the formation mechanism of the celestines can be outlined as follows:

In the epigenetic stage, the effect of meteoric waters on evaporites caused the release of strontium via dissolution. Sr-rich solutions then were mixed with hydrothermal solutions. I envisage that strontium-bearing hydrothermal solutions in a convective system brought about the deposition of celestine. Strontium enrichment caused by this convective system may also have been promoted by the hydration of anhydrite (Tekin 1995; Ceyhan 1996). Although the literature does not provide a definitive model for celestine formation, models suggesting the high-temperature crystallization of celestine have been proposed (Gundlach 1959; Strübell 1969; Brower 1973; Usdowski 1973; Bischoff & Seyfried 1978; Barbieri & Masi 1984; Glynn & Reardon 1990; Dove & Czank 1995).

## Conclusions

This study yielded the following results: (1) Three types of evaporite deposits of different ages were observed in the Tertiary Ulaş-Sivas Basin. These are: (a) the laminated gypsum in the Upper Eocene Bozbel Formation in the lower part of the sedimentary succession; (b) massive gypsum of the Oligocene Selimiye Formation, located in the middle part of the sequence and conformably overlying the laminated gypsum; and (c) the massive gypsum of the Lower Miocene Purtepe member of the Hacıali Formation in the uppermost part of the succession. Celestine mineralization in these gypsum

occurrences are vug fillings in the Bozbel Formation, nodules in the Selimiye Formation, and massive-pure material in the Purtepe member. The celestine mineralization as large lens-shaped masses in the Lower Miocene massive gypsum of the Purtepe member are economic deposits. (2) Based upon petrographic studies, it was determined that gypsum samples from the evaporitic facies of the region generally have secondary alabastrine and/or porphyroblastic textures. In addition, some of the samples display brecciated mosaic, chicken wire, and granoblastic textures (c.f. Shearman 1977; Schreiber *et al.* 1976; Lowenstein 1987). (3) Major-and trace-element geochemical studies performed on celestine-bearing gypsum samples,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{18}\text{O}/^{16}\text{O}$  and  $^{34}\text{S}/^{32}\text{S}$  isotope ratios from five samples, and paleontological findings show that, based on the classification of Hardie (1984), the water in the gypsum is of marine origin. However, there is a difference between the Oligocene nodular gypsum and freely growing-twinning secondary gypsum crystals of Late Miocene age. Pore water within the claystones is the most probable source for sulfate-rich waters in the gypsum. Cody & Cody (1988), Cody (1991), Lowenstein (1987), and Bain (1990) also suggest that the formation of this type of gypsum units is directly related to evaporated porewater. (4) The origin of celestine deposits within the Purtepe massive gypsum remains debatable. However, our preliminary evidence suggests that the celestine is not sedimentary in origin, but most probably formed at high temperature (200-360 °C) as a product of late-diagenetic replacement.

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