Sodium sulphate deposits of Neogene age: the Kirmir Formation, Beypazari Basin, Turkey

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Abstract

The Evaporite Member of the Kirmir Formation was deposited in shallow lacustrine environments during the upper Miocene. The most soluble minerals of this member can be currently observed in the Çayırhan mine. The Evaporite Member, which is composed of secondary gypsum at outcrop, can be subdivided into a bedded lower unit and a massive upper unit. In the bedded lower unit, most of the gypsum throughout the basin can be identified as having been transformed from glauberite. In the glauberite layers of the Çayırhan mine, some glauberite textures ('clear glauberite') suggest a primary, subaqueous, free precipitation on a depositional floor. More common, however, are the glauberite textures indicating an interstitial growth within a clayey-magnesitic matrix. In the thenardite layers accompanying the glauberite in the Çayırhan mine, some disruption structures can be assigned to synsedimentary dissolution. These structures together with the textures of the thenardite suggest that the original sodium sulphate was mirabilite, thenardite being a secondary phase, which formed during early to moderate burial diagenesis. The massive upper unit, in which evidence of sodium-bearing minerals is absent, is characterized by laminated to banded gypsum and nodular gypsum in the marginal areas of the evaporitic basin, whereas thick, clast-supported gypsum breccias prevail in the northern, deeper part of the basin. The brecciation of these calcium sulphate layers occurred as a result of synsedimentary, gravitative slumping under tectonic control. Although the sulphur isotopic values (δ34S) of the sulphates of the Kirmir Formation suggest a marine-derived brine supply, the oxygen isotopic values (δ18O) and the strontium ratios (87Sr/86Sr) do not support such a supply. The origin of the mother brines, the glauberite genesis, the depositional model of the sodium sulphates, and the salinity evolution are discussed.

Keywords: Evaporites; Lacustrine; Glauberite; Thenardite; Gypsum; Turkey

1. Introduction

A number of nonmarine water bodies in modern evaporitic settings belong to the sodium sulphate type (Eugster and Hardie, 1978). Gypsum (CaSO4·2H2O), anhydrite (CaSO4), glauberite (Na2SO4·CaSO4), mirabilite (Na2SO4·10H2O), thenardite (Na2SO4), halite (NaCl), and bloedite (Na2SO4·MgSO4·4H2O) are the main minerals precipitated from these brines. In this paragenesis, mirabilite and thenardite are the minerals with most industrial interest, but also the economic importance of glauberite has been emphasized (Grokholvskii, 1978; Ordóñez et al., 1991; Ortí and Salvany, 1991). Mirabilite forms thick beds in recent lacustrine environments, whereas thenardite layers prevail in ancient (mainly Neogene and Pleistocene) formations.
Various genetic aspects of the sodium sulphate deposits remain poorly understood, in particular (1) the precipitating conditions of glauberite (primary or secondary?); (2) the formation of syndepositional dissolution structures in the mirabilite/thenardite deposits; and (3) the late diagenetic conversion of mirabilite-to-thenardite. Although it is common knowledge that glauberite forms by the replacement of precursor gypsum and mirabilite transforms into thenardite with burial, detailed descriptions of these changes are scarce. For instance, the presence of thenardite or glauberite pseudomorphs after mirabilite has not been documented in ancient deposits, despite being common in modern environments (Smoot and Lowenstein, 1991).

In the Evaporite Member of the upper Miocene Kirmir Formation of the Beypazari Basin (Turkey), there is a sodium sulphate deposit near the town of Çayırhan, which has been mined since 1994. Earlier reports on this deposit (Yagmurlu and Helvaci, 1994; Helvaci and Yagmurlu, 1995; Ortı and Helvaci, 1995) assumed a lacustrine origin. In recent years, further mining work in the Çayırhan mine has allowed us to complete the sedimentological/diagenetic study of this deposit. One aim of this paper is to discuss the depositional modes of glauberite, mirabilite and thenardite in this Neogene occurrence as well as the diagenetic processes and associated textural transformations undergone by these precipitates. Another aim is to highlight the possibilities of identifying in outcrop the glauberite formations which have been largely transformed into secondary gypsum. There can be no doubt that this identification has important implications in the geological prospecting of ancient sodium sulphate deposits.

2. Geological and stratigraphical setting

The Neogene Beypazari Basin (Fig. 1) is located in the Pontids region, in central Anatolia (Turkey). The pre-Neogene basement in the basin ranges in age from Paleozoic to Eocene and comprises metamorphic, granitic, ultrabasic, carbonaceous and clastic rocks in the southern part of the basin, and carbonate and flysch assemblages in the northern part. Paleogene assemblages consist of terrigenous clastics and tuff deposits. The Neogene sedimentary sequence filling the Beypazari Basin integrates middle to upper Miocene clastics, carbonates, evaporites and volcanogenic units, with a thickness of 1200 m. This sequence has been subdivided into a number of stratigraphic units, which were deposited in alluvial, fluvial and lacustrine environments (Inci et al., 1988). The youngest of these units, the Kirmir Formation, reaches a thickness of 250 m in the central part of the basin (Yagmurlu and Helvaci, 1994; Helvaci and Yagmurlu, 1995). This formation has been subdivided into three members, i.e. the basal Gypsiferous Claystone Member, the intermediate Evaporite Member, and the Claystone Member at the top (Fig. 2(A)). The Gypsiferous Claystone Member, up to 100–150 m thick, consists mainly of bedded claystone and gypsum layers with subordinated sandstone and conglomerate beds, which accumulated in playa and saline mudflat settings. The Evaporite Member, up to 100 m thick, comprises thenardite-glauberite layers at the base and crystalline gypsum at the top. A representative section of this member in the area near the Çayırhan mine (section 7, in Fig. 1) is shown in Fig. 2(B). The Claystone Member is up to 50 m thick although it has been eroded locally. In the margins of the basin, the Kirmir Formation interfingers with alluvial fan deposits.

3. Materials and methods

Field studies, stratigraphic observations, facies analysis, sampling, and detailed mapping of particular areas in the Kirmir Formation were carried out at outcrop and mine galleries. Borehole material was also studied. About 100 samples of gypsum, glauberite, thenardite, carbonate and borate rocks were studied petrographically in large-sized thin sections, and analysed by XRD.

The samples were powdered in a tungsten carbide ring mill to provide fine powder for whole rock mineralogy. Diffractograms were run between 2 and 60° 2θ on a Siemens D500 X-ray diffractometer using Cu Kα radiation at scan speed 1° 2θ/min.

The petrographic collection of evaporites was performed as follows. Small pieces of rock samples were cut with an oil-refrigerated cutting machine (DISCOPLAN TS) using a low viscosity oil and a
In the case of soft samples, the material was previously indurated by means of impregnation with a polyester resin under vacuum (RESIPOL 9944, diluted at 50% with monomer styrene in order to obtain a rather fluid liquid). The thin sections were stuck on 5.5 cm² glasses using a glue (LOCTITE 358 for glass/glass) which cures at room temperature rapidly, i.e. in about 1 min, when exposed to UV light (under a UV lamp).

Special attention was paid to distinguish between the secondary gypsum rocks which result from the glauberite transformation, and those resulting from the hydration of anhydrite. This identification was done on the basis of both macrotextural and microscopic criteria.

In 10 representative samples of gypsum, glauberite and thenardite, isotopic determinations of oxygen ($\delta^{18}O$) and sulphur ($\delta^{34}S$) were carried out in order to account for the origin of the mother brines. Moreover, in some of these samples of glauberite and gypsum, isotopic determinations of strontium ($^{87}Sr/^{86}Sr$ ratios) were carried out. The oxygen and sulphur isotopic analyses were performed in the Servicio General de Análisis de Isótopos Estables of the University of Salamanca (Spain), and the strontium isotopic analyses were performed in the Laboratorio de Geocronología y Geoquímica Isotópica...
4. Units of the Evaporite Member

A number of stratigraphic sections distributed throughout the basin were studied (Fig. 1). The correlation between the most representative of these (sections 1–6) is shown in Fig. 3(A). Outstanding features resulting from this correlation are the following: (1) the secondary gypsum rocks derived from glauberite transformation form bedded facies in the lower part of the evaporite sequence; (2) the secondary gypsum rocks resulting from anhydrite hydration constitute large volumes of brecciated facies in the...
upper part of the evaporite sequence; and (3) the stratigraphic boundary between these two facies is variable, grading from irregular to sharp. Accordingly, two main units were distinguished in the Evaporite Member: (A) a bedded lower unit, which is always present in the centre of the basin and predominates in the marginal zones. This unit is characterized by marked layering and includes the sodium sulphate deposits of the Çayirhan mine. A representative section of this lower unit in this mine is shown in Fig. 2(C); and (B) a massive upper unit, with poorly defined layering and prevalence of thick gypsum breccias. These breccias, however, are present only to the south of the Çayirhan-Beypazarı monoclinal fold (Fig. 1), whereas in the rest of the basin only laminated and nodular gypsum facies are observed. In the marginal sections of the basin (sections 1, 6, 8, 9 and 10, in Fig. 3), the precise boundary between the

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**Fig. 3.** Lithologic logs of the sections studied (see their location in Fig. 1). (A) Stratigraphic correlation of the units distinguished in the Evaporite Member along an E to W profile (sections 1–6). Datum: top of the massive upper unit. (B) Sections in marginal positions (8–10), not included in the former profile.
lower and upper units is difficult to identify. Moreover, in some marginal sections (sections 6 and 9, in Fig. 3) a cyclicity is present, which cannot be observed in the central sections of the basin.

5. The bedded lower unit: evaporite facies and petrology

5.1. Sodium-bearing sulphate facies

In the vicinity of Çayırhan, drilling information indicates that the glauberite layers cover an area larger than that of the thenardite beds, which are intercalated within the glauberite layers. Moreover, the thickness of the glauberite layers may reach 30 m, whereas the thenardite layers attain only a thickness of 3 m. This sodium sulphate deposit is regularly bedded, and layering oscillates from 1 mm to 1 m in thickness. The glauberite and thenardite layers were studied in the Çayırhan mine and in some borehole samples (Fig. 2(C)). Thenardite, glauberite and anhydrite were recognized microscopically and by XRD, whereas other evaporites commonly associated with this paragenesis, such as halite and bloedite, were not observed.

The glauberite layers are characterized by the alternation of two different lithofacies (Table 1; Fig. 4(A)): (1) laminated to banded glauberite, which is composed of fine-grained (< few mm long) glauberite crystals (Fig. 4(B)); and (2) massive glauberite, which comprises coarse-grained (few mm to few cm long) crystals and an abundant matrix, which is made up of a clayey-carbonaceous mixture. In the two lithofacies the main crystal habits of glauberite are euhedral (prismatic to tabular), lenticular, and sub/anhedral

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<th>Table 1</th>
<th>Petrographic characteristics of glauberite and thenardite in the Çayırhan mine</th>
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<td><strong>Glauberite lithofacies</strong></td>
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<td>Laminated to banded glauberite: this lithofacies is formed by dark-coloured laminae (1 mm to 1 cm thick) and bands (1 cm to 1 dm thick) with limited amounts of lutitic-carbonaceous matrix and forming consistent layers.</td>
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<td>Massive glauberite: this lithofacies is formed by light-coloured, massive beds (&gt; 1 dm thick) which are rich in clayey-carbonaceous matrix and form less compact layers.</td>
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<td>In the two lithofacies, a weak tendency to differentiate irregular masses of glauberite and flattened, nodular-like glauberite features is observed. The matrix is composed of clay, micritic magnesite and minor micritic dolomite. The carbonaceous matrix can replace the glauberite crystals along their boundaries. Other components of the glauberite textures are: fan-shaped aggregates, shear-like aggregates and raft-like aggregates. Fine-grained glauberite (50–500 μm) is also present.</td>
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**Types of laminae in the laminated to banded glauberite lithofacies**

*Matrix-rich laminae*: the crystalline fabric ranges from decussate (unoriented) to subvertical; the matrix content is variable and the glauberite crystals usually contain matrix-rich cores.

*Transparent laminae*: the crystalline fabric ranges from decussate to subvertical; the habit of the crystals is commonly anhedral; glauberite crystals can be referred to as ‘clear glauberite’.

*Mixed laminae*: clear glauberite commonly displays palisade (subvertical) fabric at the base and blocky texture in the central part. Fan-shaped aggregates are present. At the top of the lamina, eu/subhedral glauberite with dirty cores predominates; the fabric of this glauberite ranges from decussate to subparallel to bedding.

*Clastic laminae*: a subparallel to bedding fabric of the crystals is predominant; a mixed crystalline texture both in habit and size is present.

**Glauberite textures: particular features**

The fan-shaped aggregates are composed of more or less curved crystals up to 7 mm long the sheaf-like aggregates are characterized by undulose optical extinction. The zoned growth is marked by the alternation of matrix films and transparent glauberite bands (syntaxial overgrowths). Tubular particles (presumably, faecal pellets) of clay and carbonaceous micrite are present as solid inclusions in the glauberite crystals. Some replacement of glauberite by small dolomite rhombs is present locally.

**Thenardite textures: particular features**

*Massive thenardite*: the thenardite crystals, which commonly have undulose extinction, form an interlocking mosaic in which individuals are difficult to distinguish. In some thenardite layers, an increase in the crystal size from the base to the top is observed.

*Subvertical thenardite*: formed by elongated, crystalline masses (Ortı and Helvaci, 1995).

*Coarse-crystalline thenardite*: the crystals in this texture can grade from a subvertical arrangement to other orientations, or can crosscut several thenardite layers.
(Fig. 4(C)). Furthermore, small rosettes and micronodules of glauberite are present, as well as a number of polycrystalline aggregates: sheaf-like, fan-shaped (Fig. 4(D)), geometric, and raft-like aggregates (Fig. 4(E)). The prismatic to lenticular crystals of glauberite can entrap solid inclusions of the matrix and faecal pellets as well, and can display a zoned growth (Fig. 4(F) and (G)). Very fine-grained glauberite can accompany the larger glauberite crystals, or can be mixed with the matrix. Some of these fine-grained crystals can be found as solid inclusions within the larger ones. Anhydrite relics preserved in the glauberite crystals are present (Fig. 5(A)).

In the laminated to banded glauberite lithofacies, a number of types of laminae are distinguished (Figs. 5(B), 6 and 7). (A) Matrix-rich laminae are composed of eu/subhedral crystals (laminae b and d, in Fig. 6; laminae 3 and 5, in Fig. 7); normal graded bedding can be observed locally (lamina d, in Fig. 6). (B) Transparent laminae are composed of eu/subhedral crystals, anhedral crystals (blocky texture of ‘clear glauberite’: Fig. 5(F); lamina a, in Fig. 6; lamina 2, in Fig. 7), as well as sheaf-like aggregates (Fig. 5(C) and (D)). (C) Mixed laminae show an upward transition from clear glauberite in the lower part to matrix-rich glauberite at the top (Fig. 5(E); laminae c, e, f, g, h, and i, in Fig. 6; lamina 6, in Fig. 7); also normal graded bedding is commonly observed (Figs. 4(C) and 6). (D) Clastic laminae are composed of variably sized, reworked glauberite crystals and aggregates (laminae 1 and 4, in Fig. 7) as well as matrix clasts (Fig. 5(G)).

A common feature to all these glauberite laminae is the presence of thenardite crystals (Fig. 5(H)) of various habits, ranging from euhedral (almost square, rectangular and rhomboidal sections) to lenticular or anhedral (crystalline plates). In all these habits, slightly undulose extinction is common. Euhedral and lenticular thenardite crystals can be displacive and may show zoned growth. Anhedral plates of thenardite cement the glauberite. All these thenardite crystals replace glauberite to some extent (Figs. 6 and 7). The thenardite crystals in these laminae can attain up to 30% (Figs. 6 and 7).

In the massive glauberite lithofacies, glauberite is coarse crystalline (up to few cm long), eu/subhedral, and displays a zoned pattern. The fabric is commonly decussate, and a significant proportion of matrix is mixed with the glauberite crystals, suggesting an interstitial growth for glauberite. Thenardite crystals are commonly associated with the glauberite texture; these thenardite crystals both cement and replace the glauberite.

The thenardite layers, which are intercalated between the glauberite beds (Fig. 2(C)), have an individual thickness of up to 1 m. These layers are commonly coarsely crystalline and are relatively pure (Fig. 8(A)). Bedding is parallel, although some irregularities can be observed locally. Several types of crystalline textures are distinguished. The most common is massive, with a transparent to blueish, glassy to milky appearance. This texture is made up of matrix-free, coarse-grained (1 mm to 1 dm long), sub/anhedral, equant to elongated thenardite crystals (Fig. 8(B)), and can contain some coarse euhedral to lenticular glauberite crystals, which are commonly replaced by the thenardite to some extent. A second texture (Fig. 8(C)) is composed of subvertically elongated crystals or crystalline masses. A third texture is formed by remarkably pure, very coarse crystalline masses (up to 1 m long) of transparent thenardite (Fig. 8(D)). The surfaces outlining these masses, however, are often curved or they appear to be cleavage planes rather than crystal faces. Although thenardite and glauberite can form separate layers, they commonly form ‘thenardite cycles’, with an individual thickness ranging between 1 dm and 1 m (Fig. 2(C)). These cycles are constituted by three horizons, with an upward increasing thickness (Fig. 8(C)): (1) dark-coloured lutite at the base (<1 dm thick); (2) intermediate glauberite (<2 dm thick), containing variable amounts of thenardite and lutitic matrix; and (3) thenardite at the top (up to 1 m thick), with minor amounts of glauberite and clay. The glauberite horizon can be locally absent. The glauberite crystals in these cycles can be partly replaced by thenardite.

Some mirabilite is present in the galleries of the Çayırhan mine along fractures and stratigraphic joints as an alteration product of thenardite and glauberite due to meteoric waters (Fig. 8(B) and (C)). In the thenardite samples, a mirabilite film appeared after sampling and exposure to the air. This film displays a millimetric, laminated structure (Fig. 8(E)) formed by subvertically arranged prisms of mirabilite of <0.5 mm in length.
5.2. Calcium sulphate facies: secondary gypsum

In the Kirmir Formation, the presence of secondary gypsum at outcrop is widespread, and no facies composed of primary gypsum were identified. The secondary gypsum developed close to the surface owing to the transformation of preexisting sulphates in contact with meteoric waters. In the Çayırhan mine, the identification of secondary gypsum after (precursor) glauberite is readily made in the external zones of the galleries. In the other sections studied, the identification was based on the presence of (1) macroscopic gypsum pseudomorphs after glauberite, and (2) alabasterine fabrics that are characteristic of the glauberitetogypsum transformation, such as the net-like (reticulated) (Fig. 8(F) and (G)) and acicular fabrics (Ortı et al., 1995; Ortı and Rosell, 2000). The following lithofacies are distinguished: laminated to banded gypsum, massive gypsum, nodular gypsum, nodular-banded gypsum, and enterolithic layers; commonly, these lithofacies display fluid-like, deformational structures (Fig. 9(A)). The following features are differentiated: irregular masses of macrocrystals, rosette aggregates, isolated nodules (Fig. 9(B)), and veins filling mud cracks (Fig. 9(C)). Both the laminated to banded and the massive gypsum lithofacies seem to correspond to the same lithofacies described in the glauberite of the Çayırhan mine. In contrast, the nodular and nodular banded lithofacies, the deformational structures affecting the various lithofacies, and the nodules and rosette aggregates are only present in sections removed from the mine area. The rosette aggregates present at the top of the Gypsumiferous Claystone Member were assigned to syngenetic gypsum by Yagmurlu and Helvaci (1994). The petrographic study, however, allows us to identify them as secondary gypsum pseudomorphs after glauberite rosettes (Fig. 9(D)). Similar rosettes are recorded in borehole samples preserved as (unchanged) glauberite (Gündogan, 2000). The habit of the crystals comprising these rosettes is characteristic (Fig. 10), and also corresponds to the macroscopic, euhedral prismatic crystals of the Çayırhan mine, and to most of the pseudomorphs preserved in secondary gypsum.

The identification of secondary gypsum after (precursor) anhydrite is based on the presence of microscopic relics of anhydrite and some characteristic textures, such as the alabastrine, the megacrystalline and the porphyroblastic textures (Shearman et al., 1972; Ortı, 1977). These lithofacies are distinguished: laminated gypsum (laminae are < 1 cm thick), banded gypsum (bands are 1 cm to 1 dm thick), banded (pseudomorphic) selenites, nodular gypsum, brecciated gypsum and enterolithic layers.

5.3. Carbonate facies and borate occurrence

In the Çayırhan mine, the abundant clayey-carbonaceous matrix as well as some carbonate laminae accompanying the sodium sulphate facies are mainly composed of magnesite and minor dolomite. In contrast, dolomite with subordinate calcite dominates toward the marginal zones of the Evaporite Member.

In a marginal position (section 5, in Fig. 1), small (up to 2 cm in diameter) nodules composed of a very fine-grained, micritic-like material were found embedded in secondary gypsum rocks (Fig. 11(A)). The same type of nodules was observed locally in the glauberite layers of the Çayırhan mine (Fig. 11(B)), where these nodules replace the glauberite textures (Gündogan, 2000). The microstructure of this mate-
rial, which is very homogeneous, is characterized by prismatic to equant crystals (20–40 μm). XRD analysis enabled us to identify this material as luèneburgite, Mg₃B₂O(PO₄)₃(OH)₄·6H₂O. Other borate minerals in the Beypazari Basin are rare (searlesite has been cited in the trona-bearing Hirka Formation; Helvaci 1998) although some Turkish Neogene basins contain them in association with sulphates. This is the case of the Sultançayır Basin and the Bigadiç Basin (Ortí et al., 1998; Helvaci, 1995; Helvaci and Ortí, 1998).
6. Interpretation of the sulphate facies (bedded lower unit)

6.1. Glauberite and thenardite layers, and glauberite-derived secondary gypsum layers

In the laminated to banded glauberite lithofacies of the Çayırhan mine, the various laminae correspond to environmentally differentiated growth conditions. In the transparent laminae, the clear glauberite seems to reflect a bottom-nucleated precipitate and, at the base of these laminae, some competitive growth (palisade fabric) is developed. This type of glauberite precipitation probably resulted from brine cooling. In the matrix-rich laminae (lamina d, in Fig. 6), the euhedral textures displaying matrix-rich crystalline cores and normal grading correspond to crystals which grew interstitially within the matrix. Given that these crystals have no relics of precursor minerals, this texture can be interpreted as mineralogically primary. A Holocene case of lacustrine precipitation of dirty glauberite with normal grading was illustrated by Mees (1999). This grading is attributed to interstitial nucleation and to crystal growth which occurred close to the sediment-brine interface; this growth resulted from increasing oversaturation. This interpretation can also apply to the normal grading in the matrix-rich glauberite laminae of the Çayırhan mine. The raft-like aggregates present in some of these laminae (Fig. 4(E); lamina b, in Fig. 6) could be tentatively assigned to the settling of floating fragments of glauberite films precipitated in the air—water interface. In the mixed laminae, the upward textural evolution from clear glauberite at the base—a bottom-nucleated palisade fabric changing to a non-competitive blocky fabric—to euhedral, dirty glauberite crystals surrounded by matrix at the top, with associated normal grading, is interpreted as a primary feature (laminae e to i, in Fig. 6). The change in the precipitation conditions could be seasonal. The clear glauberite at the base probably represents deeper water or slower growth precipitates during cool periods, whereas the matrix-rich glauberite at the top would signify interstitial growths close to the lake floor in a shallower setting during warmer periods. In association with the latter periods, carbonate (mainly magnesite) precipitated, oversaturation increased, and normal grading developed. It seems likely that the whole laminae accumulated under subaqueous conditions. In the fan-shaped (curved) aggregates of some of these laminae (Fig. 4(D)), the palisade-like fabric also suggests a primary, competitive growth (lamina i, in Fig. 6). The presence in some laminae of very fine-grained glauberite crystals surrounding (or entrapped in) the larger glauberite crystals, suggests that these fine-grained glauberite inclusions nucleated in the water mass and settled on the floor, where they were entrapped by the bottom-nucleated crystals. In the clastic laminae, where glauberite crystals of most of the former habits are observed, the textural features indicate that these are reworked crystals.

Earlier interpretations mainly considered a (mineralogically) primary origin for glauberite. Nevertheless, any vestige of a possible replacive origin should also be taken into account. Thus, (1) the presence of anhydrite relics in some glauberite crystals (Fig. 5(A)) indicates that a calcium sulphate mineral often preceded the glauberite growth; (2) some geometric aggregates (Fig. 4(E); laminae b and c, in Fig. 6), despite a very local presence, could correspond to

![Fig. 5. Glauberite facies. (A) Relics of euhedral anhydrite (a) entrapped in a glauberite crystal. The glauberite has largely replaced the anhydrite prisms. Dark areas correspond to other glauberite crystals in optical extinction. Photomicrograph, crossed nicols. Bar: 0.16 mm. (B) Laminated to banded glauberite lithofacies. Several types of laminae are seen: transparent (t), clastic (c) and matrix-rich (mt) laminae. Polished slab. Scale in centimetres. (C) and (D). Transparent (lower part of the picture) and matrix-rich (upper part) laminae of glauberite. In the transparent lamina, the clear glauberite is mainly formed by sheet-like aggregates (s) characterized by undulose extinction. Note the zoned pattern of euhedral glauberite in the matrix-rich laminae. Photomicrograph, normal light (C), and crossed nicols (D). Bar: 0.32 mm. (E) Mixed lamina of glauberite. The central part of the lamina is composed of transparent (t), clear glauberite, and the top is formed by matrix-rich glauberite (mt). At the base of the picture the matrix-rich top of the underlying lamina can be seen. Photomicrograph, normal light. Bar: 0.64 mm. (F) Detail of a transparent lamina of glauberite (central and upper parts of the picture). A palisade fabric (arrows) is developed at the base of the lamina. Photomicrograph, normal light. Bar: 0.32 mm. (G) Clastic lamina of glauberite. Glauberite crystals are variable in shape and size, and display a mainly subhorizontal orientation. Matrix clasts (in dark) are mixed with the various clastic components of glauberite. Photomicrograph, normal light. Bar: 0.64 mm. (H) Interstitially grown, euhedral thenardite crystal (th) replacing euhedral glauberite (g). Note the zoned growth of thenardite. Matrix is seen in black. Photomicrograph, crossed nicols. Bar: 0.16 mm.](image-url)
pseudomorphs after mirabilite, gypsum or bloedite (?); and (3) the raft-like aggregates of glauberite (Fig. 4(E); lamina b, in Fig. 6) could also represent pseudomorphic geometries of mirabilite rafts, which are very common in modern environments. These observations suggest that glauberite could also have a precursor phase, at least locally, indicating an early diagenetic origin.

Furthermore, the textural relationships between glauberite and thenardite in the laminated to banded glauberite lithofacies are significant (Figs. 6 and 7). Although thenardite commonly replaces glauberite in each lamin, it may be observed that (1) a large number of thenardite crystals grow displacively in the clayey matrix, (2) some thenardite crystals seem to be paragenetic with glauberite, and (3) other thenardite crystals appear to have been incorporated into the clastic laminae. Thus, despite the fact that the thenardite growth postdates the precipitation of glauberite, this growth can be considered as early diagenetic. Presumably, thenardite precipitated from interstitial solutions, displacing, cementing and replacing the porous glauberite texture.

Regarding the depth of the lacustrine environment, the absence of very fine lamination (<1 mm thick) in the laminated to banded glauberite lithofacies together with the presence of a weak tendency to display irregular masses and flattened structures, suggests that the environment was not deep. The massive glauberite lithofacies, in which the coarse crystals have grown displacively within an abundant clayey-carbonaceous matrix, can be assigned to shallower conditions. We interpret these two alternating glauberite lithofacies (Fig. 4(A)) as having been deposited in a shallow, perennial saline lake with water level oscillations.

Even shallower conditions can be assigned to the secondary gypsum lithofacies derived from (precursor) glauberite, which are characterized by fluid-like deformation. These originally glauberitic lithofacies (nodular, nodular banded, banded, enterolithic) and features (irregular masses of macrocrystals and rosette aggregates; Fig. 9(A) and (B)) are mainly found in a marginal position in relation to the sodium sulphate core of the depositional system (i.e. in the Çayarhan mine area). Presumably, these lithofacies developed from brines often oscillating from subaerial to interstitial positions. Similar lithofacies, deformational features and prevalent interstitial growths are common in many of the glauberite units of the Tertiary basins in Spain, where shallow lake to playa-lake conditions have been interpreted (Ortí et al., 1979; Salvany and Ortí, 1994; Ortí and Rosell, 2000; Ortí, 2000).

The thenardite cycles of the Çayarhan mine are depositional features. In the thenardite horizons of these cycles, however, both the coarse crystal size of the various textures and the lack of well defined depositional fabrics suggest a secondary origin for this mineral. The subvertical fabric of the thenardite seems to have a diagenetic nature given that this crystalline arrangement commonly crosscuts several layers, and can easily vary its spatial orientation. The nature of the precursor mineral of this thenardite and the significance of these cycles is discussed in Section 7.

6.2. Secondary gypsum layers derived from (precursor) anhydrite

In general, the secondary gypsum nodules, the nodular-banded lithofacies and the enterolithic layers derived from the hydration of anhydrite in outcrop can be assigned to a playa/sabkha setting (Shearman, 1985; Warren, 1989). In contrast, we interpret the laminated and banded lithofacies derived from the hydration of an anhydritic precursor as being inherited from laminae and bands of subaqueous primary gyp-

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Fig. 6. Petrography of the laminated glauberite lithofacies (laminae a to i) to microscopic scale (thin section BE-6). Several types of glauberite laminae can be distinguished: MT: matrix-rich; TR: transparent; MX: mixed; and CL: clastic. In the petrographic log, the open areas correspond to the sedimentary matrix. To the right side of the log, several features are indicated: (2): the content (between 0 and 100%) in sedimentary matrix (in black); (3): the content (between 0 and 30%) in thenardite crystals accompanying/replacing the glauberite; (4): the glauberite fabrics; and (5): the size of the glauberite crystalline components and the thenardite crystals (the first number refers to the average size; the second number, in brackets, corresponds to the maximum size); the presence of normal grading is indicated by arrows showing the size values at the base and at the top of the laminae.
LEGEND

Glauberite textures: crystalline components

- **clear gb**: clear (transparent) glauberite
- **(Eu)** euhedral crystals
- **(Li)** lenticular crystals
- **(Sb)** subhedral crystals
- **(An)** anhedral crystals
- **blocky (anhedral) texture**
- **small rosette aggregate**
- **curved aggregate**
- **rectangular to shaft-like aggregate**
- **fine-grained (< 0.5 mm) glauberite**
- **glauberite crystal with glauberite inclusions**
- **matrix inclusions in the cores of the glauberite crystals**
- **pellet-like tubes of matrix in the glauberite crystals**
- **raft-like polycrystalline plates of glauberite**
- **geometric aggregate of glauberite**
- **sedimentary matrix**

Glauberite fabrics

- **palisade (subvertical)**
- **decussate (unoriented)**
- **parallel to bedding**
- **subhorizontal**
- **clastic**
- **matrix clasts**

Thenardite textures

- **euhedral crystal**
- **lenticular crystal**
- **anhedral plates with undulose extinction**
sum precipitated in shallow-water environments. These lithofacies of primary gypsum were diagenetically transformed into anhydrite during moderate burial.

7. Dissolution structures and nature of the original sodium sulphate mineral

New galleries which have been recently opened in the Cayirhan mine show the presence of two groups of structures with anomalous bedding. The first group is defined by a smooth to sharp angular geometry characterizing the contact between the thenardite cycles and the underlying lutite-glauberite layers acting as a basement; along this contact, the thenardite beds thin out (Fig. 9(E)). The second group corresponds to three types of structures disrupting the bedding in the thenardite cycles: (a) intraclastic breccias (Fig. 9(F)), formed by the accumulation of rectangular clasts (few cm to 1 m long); (b) channel-like structures (Fig. 9(G)), up to >1 m high, made up of transparent, coarse crystalline thenardite. These structures can crosscut one or more thenardite cycles and are covered by the overlying cycles. Some of these structures are symmetrical, whereas others have one side that is almost vertical and the other side that is tilted. Intraclastic breccias are commonly found at the base of these structures, resembling lag deposits where the clasts can display a weakly imbricated fabric; and (c) angular bedding (Fig. 9(H)), in which some thenardite cycles rest obliquely on the cycles underneath. In all types of structures the thenardite texture is coarse crystalline and acts as a cement, having little or no relation with the geometry of the structure. This texture also displays a gradation towards the undisrupted parts of the thenardite layers.

The interpretation of all of these structures can be made on the basis of their geometries. The first group corresponds to smooth irregularities or shoals on the depositional floor, which were unconformably covered by the thenardite cycles in an onlap arrangement. As regards the structures of the second group, the intraclastic breccias correspond to the collapse of the basal glauberite-bearing lutite horizons of the cycles and are interpreted as the insoluble residuum of the dissolution of one or several thenardite cycles.

Fig. 7. Petrography of the laminated glauberite lithofacies to microscopic scale (thin section BE-3). Several types of glauberite laminae can be distinguished, two clastic laminae included. Legend and abbreviations of the lamina types as in Fig. 6.
(Fig. 12). The channel-like structures correspond to local dissolutions and the subsequent fill or cementation of the thenardite cycles. The intraclasts, accumulated at the base of the channel geometries, may reflect some local transport. The angular bedding represents a partial dissolution of the thenardite cycles, with associated thinning out and tilting of the layers. Thus, all the structures of the secondary group can be interpreted as syndepositional dissolution features.

The thenardite texture in the cycles, which is of a secondary nature, can represent either the recrystallization of a primary thenardite texture or the transformation of a precursor mineral. We consider the latter possibility to be more likely given the prevalent mirabilite nature of the sodium sulphate precipitates in modern environments, and the fact that mirabilite is the stable phase in chloride-poor, sodium sulphate-rich solutions (Harvie, 1982). Thus, thick mirabilite layers form in winter or during cool periods in modern environments, as is the case in the northern part of the Great Plains in Canada and the USA, where coarsely crystalline, pure mirabilite is currently precipitating in many saline lakes (Last, 1994). Also, mirabilite layers up to some metres thick are recorded at shallow burial depths in Great Salt Lake, Utah (Spencer et al., 1985). Layers 1 m in thickness of pure mirabilite, with a vitreous, coarse crystalline texture, precipitated during the Holocene in the Laguna Salinas of Perú (Alonso, 1995). Mirabilite layers up to 1 m thick are being harvested yearly in the salt works fed by the brines of Aci Göll, a sodium sulphate lake in central Anatolia (Gündogan et al., 1995).

In contrast, precipitates of thenardite in modern environments are most commonly related to a playa setting, and consist of: (1) efflorescent crusts (Jones, 1965); (2) alteration products of mirabilite layers; (3) irregular crystalline masses in shallow lakes (Gorlovskii, 1978); and (4) discontinuous crusts, as in Saline Valley (Casas, 1987). Last (1994) has pointed out that, in the saline playa lakes of the northern parts of the Great Plains in the USA, thenardite in the surface crusts forms either by mirabilite dehydration or through direct precipitation under high temperatures. On the other hand, any proposal supporting thenardite as the primary precipitate for the cycles in the Çayırhan mine must also account for its pervasive recrystallization. Nevertheless, such a hypothetical thenardite-to-thenardite recrystallization seems to be unlikely in the geological context of the Beypazarı Basin, where the original sedimentary cover on the Evaporite Member was limited to 100–200 m (Yagmurulu and Helvaci, 1994).

We propose the following depositional/diagenetic succession of events involving the sodium sulphate cycles of the Çayırhan mine: (1) the original phase was mirabilite, which periodically (yearly?) formed at the top of each lutite-(glauberite)-mirabilite cycle; (2) the mirabilite was partly dissolved by dilute waters from subsequent rains or floods and several types of dissolution structures formed; (3) these structures were filled or cemented by new mirabilite generations during the following period of brine concentration; (4) a diagenetic transformation of all mirabilite textures (both primary and cementing) to secondary thenardite occurred during shallow to moderate burial. In this final transformation, it seems very likely that the original mirabilite textures exerted a control over the various thenardite growths as relic structures. For instance, the matrix-free, coarse crystalline texture of the cementing mirabilite (e.g. in the channel-like structures) resulted in thenardite textures with similar characteristics of crystal size and purity. Despite the fact that the mirabilite-to-thenardite transformation theoretically involves a considerable reduction in volume (of about 75%), such a reduction seems to have occurred without a significant disruption of the bedding and the dissolution structures.

8. The massive upper unit

All the gypsum forming this unit in outcrop is secondary. Brecciated gypsum is the prevalent lithofacies along the Çayırhan-Beypazarı monoclinal fold, whereas laminated, banded, and nodular gypsum lithofacies are found in the rest of the basin. Some of the banded lithofacies found in the non-brecciated sections are made up of pseudomorphs after small selenites (Fig. 11(C)), as in Section 7 (Fig. 2(B)).

The gypsum breccias are mainly chaotic accumulations of monomictic, angular clasts and blocks with a fine matrix (Fig. 11(E)), which lie irregularly on the bedded lower unit (Fig. 11(D)). Moreover, laminated gypsum interbedded with brecciated gypsum is com-
mon. In these breccias, erosional boundaries were observed locally as well as some deformation and rare folds with axis attaining 100 m (section 5, in Fig. 3). A number of gypsum breccias appear to have formed in situ, suggesting that the source of the redeposited material was at least partly local. Porosity and/or cementation in the breccia fabric to the macroscopic scale was not observed.
The petrographic study of these breccias (Table 2) shows the presence in the matrix of small pseudomorphs after discrete anhydrite laths (Fig. 11(F)) and gypsum crystals. This indicates that the secondary gypsum currently forming this matrix is derived from both anhydrite and primary gypsum. The latter presumably was transformed into anhydrite during moderate burial. This study also indicates that a number of the pseudomorphs in the matrix are oriented in the same direction indicating that the matrix was not completely lithified at the time of brecciation.

Two main genetic mechanisms can be considered for these gypsum breccias: (1) resedimentation due to gravitational instability with associated slumping and syndepositional brecciation; and (2) dissolution and collapse during early or late diagenesis. A collapse-breccia origin seems to be unlikely given the absence of (a) palaeokarst features (endokarstic or exokarstic) or morphologies, both to the macroscale and the microscale, and (b) sodium sulphate-bearing minerals in the clasts and matrix. Moreover, no regional indices exist suggesting the presence of residual salt bodies in the subsurface, such as sodium chloride springs or evaporative salinas. By contrast, an origin due to syndepositional, gravitational instability and associated brecciation of the calcium sulphate deposits could be proposed on the basis of (1) the scope of the brecciation process; (2) the local presence of medium-scale folds, which can be attributed to slumping; (3) the sharp nature of the boundary separating the lower and the upper units in some localities; (4) the lateral gradation from almost undisturbed gypsum layers interbedded with little brecciated layers, to progressively brecciated strata and massive gypsum breccias observed in some localities; and (5) the restriction of these breccias to the northern part of the basin (i.e. to the south of the Çayırhan-Beypazarı monoclinal fold), which agrees with an original distribution of debris flow deposits in the deeper part of the basin under a structural control. In fact, active tectonism seems to have influenced the sedimentation in this basin, in particular the ENE to SSW trending growth faults and associated monoclinal structures (Demirci, 2000).

We interpret the successive evolution of the massive upper unit as follows: (1) sedimentation of laminated to banded (selenitic) gypsum in shallow lacustrine settings, with syndepositional conversion of a part of the gypsum into anhydrite during playa episodes; (2) syndepositional formation of gypsum/anhydrite mass and debris flow deposits in particular areas of the basin under a structural control. In this process, resedimentation of gypsum/anhydrite as well as in situ brecciation of the calcium sulphate layers occurred; (3) conversion of the primary gypsum into anhydrite during moderate burial; and (4) conversion of the anhydrite into secondary gypsum during the exhumation. Presumably, the gypsum-to-anhydrite conversion during moderate burial occurred under a relatively high geothermal gradient due to the intense Neogene volcanism in the Beypazarı Basin. A similar problem has been reported in the Sultançayıir Basin (western Anatolia), where a large secondary gypsum unit of upper Miocene age accumulated fault-controlled gypsum breccias (Ortı et al., 1998).

Mechanical resedimentation of gypsum/anhydrite was first pointed out in the Messinian deposits of Sicily by Schreiber et al. (1976). In the Middle Badenian (Middle Miocene) evaporites of the Carpathian Foredeep, the presence of interbedded laminated anhydrite and anhydrite breccias has been attributed by Pertz (2000) to redeposition in the central parts of the basin. Moreover, several features suggest that a short distance for transport and in situ reworking and breaking were common. The resedimentation process was probably triggered by earthquakes generating

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Fig. 8. Thenardite facies in the galleries of the Çayırhan mine (A–D), mirabilite texture (E), and secondary gypsum textures (F and G). (A) Thenardite layers. Hammer for scale. (B) Detail of the coarse-grained thenardite texture composing the thenardite layers. White bands in the central part of the picture correspond to secondary mirabilite. Lens cap: 6 cm. (C) Thenardite texture displaying a crude, subvertical fabric. The thenardite cycles are formed by basal lutite (l) horizon, intermediate glauberite (g) horizon, and thenardite (th) horizon at the top. (D) Pure, very coarse crystalline thenardite. Subvertical surfaces can correspond to cleavage planes. (E) Close-up view of a weathering film developed on a thenardite sample. The film is composed of planar to corrugate mirabilite laminae. (F) Alabastrine textures of secondary gypsum derived from (precursor) glauberite. The texture in the central part of the picture is of the reticulated type. Photomicrograph, crossed nicols. Bar: 0.32 mm. (B) Detail of a reticulated alabastrine texture. Each lamina of the texture is composed of prismatic to equant polygonal microcrystals, whose optical extinctions can be parallel or variable. Photomicrograph, crossed nicols. Bar: 0.32 mm.
mass flow and eventually turbidites (Peryt, 2000; Peryt and Kasprzyk, 1992). In the Middle Miocene Belayim Formation of the Red Sea, Rouchy et al. (1995) ascribed the resedimentation of unconsolidated anhydrite deposits in the deeper parts of the basin to seismic activity.

9. Isotopic composition and origin of the sulphate

The oxygen and sulphur isotopic compositions ($\delta^{18}O_{SMOW}$ and $\delta^{34}S_{CDT}$, expressed in $\%_o$) of 10 sulphate samples corresponding to secondary gypsum, glauberite and thenardite were analysed. In six of these samples the strontrium ratios ($^{87}Sr/^{86}Sr$) were also investigated (Table 3). In the bedded lower unit, the $\delta^{34}S$ values of glauberite and thenardite, which are very homogeneous, range between 20.0 and 20.6 $\%_o$, whereas those of secondary gypsum derived from a glauberite precursor, which are also very homogeneous, vary between 21.3 and 21.9 $\%_o$ (Fig. 13). In the massive upper unit, one sample of secondary gypsum derived from anhydrite has a value of 21.8 $\%_o$. At the top of the basal Gypsiferous Claystone Member, one
sample corresponding to a macroscopic rosette has a lower value (19.3 \(^\circ\)). The \(\delta^{18}O\) values of these 10 samples are also well differentiated. In the bedded lower unit they range between 17.1 and 18.8 \(^\circ\) for the glauberite-thenardite samples, and between 19.9 and 20.7 \(^\circ\) for the secondary gypsum samples derived from glauberite in the massive upper unit, the value of the secondary gypsum after anhydrite is 18.7 \(^\circ\); and in the Gypsiferous Claystone Member, the macroscopic rosette has a value of 16.1 \(^\circ\). In the Çayırhan
mine, the higher values found for δ^{18}O and δ^{34}S in the three secondary gypsum samples compared with the precursor glauberite samples seem to be related to the fractionation involved in the glauberite dissolution followed by the gypsum reprecipitation (Fig. 13).

The δ^{34}S values of these sulphates, which range between 19 and 22‰, would suggest a marine or marine-derived origin for the sulphate anion (Claypool et al., 1980). Nevertheless, their δ^{18}O values are all higher, between 16 and 21‰, than those known for the Miocene sulphates of marine origin (12–15‰; Claypool et al., 1980). In fact, there is no marine record of the sedimentary fill in the Neogene Beypazari Basin, and there are no ancient evaporite formations below or around this basin which can act as a possible source of marine-derived sulphate anion to be supplied via chemical recycling (Utrilla et al., 1992; Playà et al., 2000). In Anatolia, a marine influence during the Tertiary is only cited in the easternmost Neogene basins, but not in the central and western basins (Görur et al., 1995). More clearly, the six values of the ^{87}Sr/^{86}Sr ratios, which range between 0.707565 and 0.707760, confirm the non-marine origin for the strontium of these sulphates (the values of these ratios for upper Miocene marine samples are higher than 0.7089; Burke et al., 1982; Müller and Mueller, 1991).

Despite the fact that the isotopic compositions (δ^{18}O, δ^{34}S, ^{87}Sr/^{86}Sr) of the volcanic rocks and hydrothermal fluids in the area of the Beypazari Basin and central Anatolia, in general, are currently unavailable, we consider these rocks and fluids as a valid source for the sulphate anion in the Evaporite Member of the Kirmir Formation given the intense volcanism and related hydrothermal activity during the Miocene in this region (Yilmaz et al., 2000). In fact, positive δ^{34}S values up to 25‰ were considered by Holser and Kaplan (1966) as common in volcanic rocks.

![Fig. 12. Scheme (based on a photographic composition) of a gallery portion (of about 6 m in length) in the Çayirhan mine showing the dissolution structures affecting the thenardite cycles and the distribution of the thenardite textures. The lutite horizons of the cycles seen in this figure are arbitrarily numbered 1–5.](image-url)
central Anatolia, hydrothermal activity is at present an important source of solutes for the modern evaporitic lakes. Thus, sulphate-rich brines are found in the Bolluk Lake—a small saline lake close to the large Tuz Gölü lake—which are genetically related to the active hydrothermal system of andesitic volcanism. This system contributes sulphate anions to the groundwater feeding the lake (Gündogan and Helvaci, 1996):

\[
\text{SO}_4^2-/\text{Cl}^- \text{ ratio are 3.0 in the groundwater and 1.04 in the Bolluk Lake, whereas in the adjacent salty Tuz Gölü lake it is only 0.04. Similar sulphate supplies could have remarkably increased the sulphate content in the Kirmir Formation during the Miocene.}
\]

### 10. Discussion

#### 10.1. Processes of lacustrine precipitation of glauberite

Some of the best documented cases of glauberite precipitation in modern and Holocene lacustrine environments are shown as follows.

1. **Precipitation in the vadose-capillary and phreatic zones.** In the endorheic drainage system of the Karinga Creek (Northern Territory, Australia), glauberite currently forms at the top of the phreatic zone and in the lower part of the vadose zone (Arakel and Cohen, 1991). In the phreatic zone, primary crystals of glauberite grow displacively in the soft sediment forming small nodules and discontinuous, lenticular layers. In the vadose-capillary zone, early diagenetic crystals of glauberite partly replace the gypsum and poikilitically/displacively cement the sedimentary matrix.

2. **Precipitation in playa-lakes and salars.** In Saline Valley (California), the glauberite also occupies an interstitial position and forms isolated crystals and crystalline crusts. Hardie (1968) interpreted

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**Table 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{18}$O</th>
<th>$\delta^{34}$S</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>Mineralogy</th>
<th>Unit</th>
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<td>BZ-4</td>
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<td>–</td>
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<tr>
<td>BE-2</td>
<td>18.8</td>
<td>20.4</td>
<td>0.707565</td>
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</tr>
<tr>
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<td>bed. low. unit</td>
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<tr>
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<td>0.707725</td>
<td>glauberite</td>
<td>bed. low. unit</td>
</tr>
<tr>
<td>BE-9</td>
<td>17.1</td>
<td>20.6</td>
<td>–</td>
<td>glauberite</td>
<td>bed. low. unit</td>
</tr>
<tr>
<td>BE-61</td>
<td>19.9</td>
<td>21.4</td>
<td>–</td>
<td>thenardite</td>
<td>bed. low. unit</td>
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<tr>
<td>BE-62</td>
<td>20.7</td>
<td>21.3</td>
<td>–</td>
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<td>bed. low. unit</td>
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<tr>
<td>BE-81</td>
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<td>21.9</td>
<td>0.707694</td>
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<tr>
<td>BE-71</td>
<td>16.1</td>
<td>19.3</td>
<td>0.707715</td>
<td>sec. gyp. after glaub. rosette</td>
<td>G.C.M.(^a)</td>
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<tr>
<td>SNK-2</td>
<td>18.7</td>
<td>21.8</td>
<td>0.707722</td>
<td>sec. gyp. after anhydrite</td>
<td>mass. up. un.</td>
</tr>
</tbody>
</table>

\(^a\) G.C.M.: Gypsiferous Claystone Member.
this glauberite as an authigenic precipitate within the soft sediment due to the reaction of interstitial brines rich in SO$_4^{2-}$ and Na$^+$ with preexisting, early diagenetic gypsum crystals. The reaction is as follows:

$$2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) + 2\text{Na}^+(aq)$$

$$\leftrightarrow \text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4(\text{s})(s) + \text{Ca}^{2+}(aq) + 4\text{H}_2\text{O}(aq)$$

Hardie (1968) also attributed part of this glauberite to the mixing of the sodium sulphate-rich brines of the playa with calcium sulphate-rich groundwater solutions. López et al. (1999) have documented the subaqueous precipitation of small amounts of glauberite in a shallow pond of a salar in the Andean region in Chile.

3. Precipitation in playas and saline lakes of central Asia. The numerous glauberite deposits in Holocene and modern playas and shallow saline lakes of this large region have been reviewed by Kurilenko et al. (1988); Grokhovskii (1978). In these playas, the formation of glauberite has been ascribed to complex diagenetic processes involving the systematic replacement by glauberite of various paragenesis composed of mirabilite, bloedite, thenardite and halite, when affected by Ca-rich groundwater solutions (Grokhovskii, 1978). In this setting, glauberite represents a syngenetic, interstitial precipitate which occurs at the end of the evaporitic evolution of the playas and is commonly located at the base of the halite or thenardite layers. Grokhovskii (1978) also attributed some primary glauberite, in certain playas, to the mixing of sodium sulphate brines with calcium-rich groundwater solutions of several anionic (bicarbonate, sulphate, chloride) compositions.

4. Precipitation in perennial lakes of variable depth. A case of halite-glauberite formation has been studied by Mees (1999) in the Holocene palaeolacustrine system of the Taoudenni-Agorgott Basin (Mali). This author interpreted this glauberite as a primary, subaqueous precipitate in a perennial lake. Some glauberite laminae present both normal and reverse grading of a chemical origin. Moreover, some laminae with normal grading are composed of crystals rich in solid inclusions, which grew in an interstitial position. Details of the glauberite microcycle of shallow water origin described by Mees (1999) are shown in Fig. 14.

To sum up this brief review of occurrences, a number of mechanisms can account for the glauberite precipitation in lacustrine settings: (a) synsedimentary replacement of gypsum by glauberite (Hardie, 1968, 1984; Eugster and Hardie, 1978; Smoot and Lowenstein, 1991; Arakel and Cohen, 1991; Lowenstein et al., 1999); (b) synsedimentary, interstitial replacement
of other sulphates and/or halite by glauberite (Grokhovskii, 1978); (c) primary, interstitial precipitation by brine mixing (Hardie, 1968; Eugster and Hardie, 1978; Grokhovskii, 1978); (d) primary nucleation and growth from a brine of the appropriate composition in the water mass (Mees, 1999), in a subaqueous interstitial position close to the lake floor (Mees, 1999), and in the phreatic zone (Arakel and Cohen, 1991). It should be pointed out that, in modern lacustrine environments, a primary, ‘free’ precipitation of glauberite in a water mass (i.e. direct nucleation and growth on the lake floor as a competitive growth) has not been well documented to date.

10.2. Depositional model of the sodium sulphates in the Kirmir Formation

In the Evaporite Member of the Kirmir Formation, some of the aforementioned mechanisms are thought to have contributed to the extensive glauberite precipitation: (I) Primary, ‘free’ precipitation. In the Çayırhan mine, some glauberite precipitation on the depositional floor forming transparent (competitive, ‘clear glauberite’) laminae seems to have occurred sporadically. These laminae could have resulted from the cooling of solutions saturated in sodium sulphate. (II) Primary, subaqueous, interstitial precipitation. In the Çayırhan mine, the precipitation of glauberite forming matrix-rich laminae composed of crystals displaying matrix-rich cores (i.e. without a gypsum/anhydrite precursor) seems to have occurred in an interstitial position. Furthermore, in these laminae, the upward change from clear to matrix-rich glauberite (Fig. 6) suggests that the transition from a ‘free’ to an interstitial precipitation is a primary feature. (III) Subaqueous to subaerial, primary to replacive precipitation. Throughout a wide area surrounding the Çayırhan mine, a unique growth mode explaining the characteristics of the glauberite (the particular lithofacies; the deformational structures affecting these lithofacies; the common presence of anhydrite relics in the glauberite crystals; the absence of pseudomorphs after primary gypsum) cannot be proposed. Presumably, a very shallow environment with an

<table>
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<tr>
<th>Sedimentary intervals</th>
<th>Features of the glauberite crystals</th>
<th>Place and mode of glauberite precipitation</th>
<th>Crystal size (mm)</th>
<th>Salinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay layer (little glauberite)</td>
<td>- solid inclusions - random orientation</td>
<td>Intra-sediment growth</td>
<td>2-10</td>
<td>Dilution (important supply of water and clay)</td>
</tr>
<tr>
<td>Glauberite layer (without clay)</td>
<td>- no solid inclusions - random orientation</td>
<td>Settling of crystals that nucleated and developed along the lake surface</td>
<td>5</td>
<td>Oversaturation decrease (no supply of water and clay)</td>
</tr>
<tr>
<td>Banded glauberite-bearing layer (high clay content)</td>
<td>- solid inclusions - random orientation - syntaxial overgrowth</td>
<td>Interstitial growth close to the sediment-water interface</td>
<td>1-3 cm</td>
<td>Progressive concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Increasing oversaturation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(limited supply of water and clay)</td>
</tr>
</tbody>
</table>

Fig. 14. Representative microcycle of laminated glauberite with graded bedding in the lake palaeosystem of the Taoudenni-Agorgott basin (Mali). This figure is based on the descriptions by Mees (1999).
oscillating water table, from subaerial to underground positions, could account for both an interaction between variable growth mechanisms (primary precipitation of glauberite vs. replacement of a calcium sulphate precursor) and a variability of the nucleation sites (on a depositional floor vs. in an interstitial position). (IV) Primary, interstitial precipitation by brine mixing. This mechanism, which results from the mixing of dense lake brines with calcium-rich underground solutions seeping into the lake floor, could also have contributed to the interstitial growth of glauberite. Probably, some of the sodium sulphate-rich lake brines that descended onto the lake floor derived from the periodic (annual?) dissolution of ephemeral mirabilite precipitates. Such a multiepisoodic growth/overgrowth of glauberite could result in the progressive deformation of the nodular and banded lithofacies.

The interpretation of the sodium sulphate lake of the Kirmir Formation is shown in Fig. 15(A). In the deeper parts of this system, the (so-called) thenardite cycles were deposited in a pond occupying only a small area with respect to the whole system. The glauberite beds underlying the thenardite cycles

![Sodium Sulphate Lake Model](image1)

![Mirabilite-to-Thenardite Conversion](image2)

Fig. 15. (A) Interpretation of the lacustrine evaporative system precipitating sodium sulphates in the bedded lower unit (Evaporite Member of the Kirmir Formation). (B) Interpretation of the genesis of mirabilite and its synsedimentary dissolution and final conversion to thenardite during (moderate) burial. Scheme out of scale.
(Fig. 2(C)) reflect the initial formation of a shallow perennial water body in which some clear galuberite formed as a free precipitate on the lake floor. The thenardite cycles reflect the moment in which the pond was deep enough to preserve the mirabilite from the next dissolution period. Subsequently, only a sporadic and partial dissolution of the mirabilite layers occurred (Fig. 15(B)). The dissolution structures cutting through these layers suggest a shallow (up to few metres deep?) lake. The common presence of thenardite crystals within the various glauberite lithofacies indicates that, immediately after the glauberite formation, thenardite precipitated interstitially from the sodium sulphate-rich pore brines cementing and partly replacing the glauberite fabric also. In fact, isolated, primary crystals of thenardite associated with mirabilite are currently precipitating in the mirabilite production pools of the Bolluk Lake (central Anatolia) when the temperature exceeds 32°C and the salinity is higher than 50 g/100 ml (Gündogan and Helvaci, 1996).

Around this mirabilite pond, a glauberite-precipitating shallow lake covered a very broad area where nodular banded glauberite lithofacies and various interstitially grown features (rosettes, isolated nodules) developed. These lithofacies and features formed under subaqueous to exposed conditions. Calcium sulphate-rich solutions probably seeped into this large subenvironment from the marginal areas of the system. Although the presence of gypsum pseudomorphs was not confirmed, the common presence of anhydrite relics in the glauberite crystals suggests that some gypsum/anhydrite existed as a precursor phase of glauberite. In the outermost zones of this evaporative system a saline mudflat developed. In the latter, the glauberite layers thin out and glauberite rosettes and veins are recorded, reflecting a subaerial setting. Adjacent to this system, only gypsum, anhydrite and gypsiferous sandstones are found.

10.3. Evolution of the salinity in the Kirmir Formation

The salinity evolution in the evaporative systems of the Kirmir Formation can be evaluated on the basis of the following observations: (1) only gypsum is present in the lower and central parts of the basal Gypsiferous Claystone Member; (2) glauberite rosettes and veins filling desiccation cracks occur toward the top of this member; (3) the precipitation of sodium-bearing sulphates is recorded in the lower part of the Evaporite Member (the bedded lower unit); (4) only calcium sulphates are identified in the upper part of this member (the massive upper unit); and (5) no evaporites are found in the Claystone Member at the top. According to these observations, the Kirmir Formation reflects an evaporite cycle beginning with calcium sulphate at the base, evolving to sodium sulphate in the central part, and returning to calcium sulphate at the top (Fig. 16). Brines in this cycle are of
the Ca-Na-(Mg)-SO₄-(Cl) type (Hardie, 1968). The initial saline mudflat is represented by the gypsum/glauberite precipitates of the Gypsiferous Claystone Member. The presence of glauberite and thenardite layers at the base of the Evaporite Member reflects the formation of an ephemeral to perennial, shallow water body. The salinity of the sodium sulphate-precipitating brines seem to have been low in chloride given that no evidence of halite was found. Moreover, the faecal pellets associated with the glauberite precipitation (Fig. 4(G)) suggest that animal activity cannot be ruled out. The magnesium content of these brines does not seem to have been very high after the magnesite precipitation.

In the thick massive upper unit, the absence of sodium-bearing sulphate precipitation seems to be the result of either impoverishment/depletion of sodium in the mother brines or some dilution of the evaporitic basin. The thick gypsum breccias resulted from re-sedimentation linked to active tectonics and associated rapid subsidence in specific zones of the basin. Thus, the depocenter of the bedded lower unit (section 7, in Fig. 1) shifted to a new position in the upper unit (section 4, in Figs. 1 and 3(A)). Keeping with this new structural context, renewed hydrologic conditions would have prevented further precipitation of sodium sulphates. A general dilution occurred in the basin during the accumulation of the top Claystone Member (Fig. 16).

11. Conclusions

1. The Evaporite Member of the Kirmir Formation is made up of a bedded lower unit dominated by glauberite layers, with associated thenardite cycles locally, and a massive upper unit characterized by gypsum breccias.
2. In the sodium sulphate depocenter (bedded lower unit), the various glauberite textures suggest that this mineral is mainly primary and commonly formed as interstitial crystals within the clayey-magnesitic matrix. In some cases, however, the glauberite nucleated very close to the sediment-brine interface, and less frequently formed as free, bottom-nucleated crystals. Early diagenetic thenardite crystals grew in association with these glauberite textures.
3. The thenardite cycles are affected by several types of syndepositional dissolution structures. These structures, together with the textures of the thenardite, suggest that mirabilite was the precursor phase in the cycles, the thenardite being a replacive mineral that developed during shallow to moderate burial diagenesis.
4. The thenardite cycles formed in a pond located in a broad, shallow glauberitic system. The pond was sufficiently deep to preserve mirabilite from periodic dissolution. The chloride content of the sodium sulphate-precipitating brines was always low.
5. Moving away from this pond, the glauberite layers passed into lithofacies characteristic of shallow water to subaerial environments.
6. The thick gypsum breccias (massive upper unit) accumulated under tectonic control. Both primary gypsum and early diagenetic anhydrite were re-sedimented by gravitative debris flows and were also affected by in situ brecciation. The gypsum transformed into anhydrite during shallow to moderate burial.
7. During the exhumation phase, both the glauberite layers and the anhydrite layers were transformed into secondary gypsum by meteoric waters.
8. In the Kirmir Formation, a broad cycle of calcium sulphate (Gypsiferous Claystone Member)—sodium sulphate (bedded lower unit)—calcium sulphate (massive upper unit) developed.
9. In the Kirmir Formation, a non-marine origin (presumably linked to volcanic rocks and associated hydrothermal fluids) is interpreted for the sulphate anion, despite the marine-derived supply suggested by the δ³⁴S values.

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