



## Occurrence of a new sulphate mineral: $\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$ in the Emet borate deposits, western Anatolia (Turkey)

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Emetite, a new sulphate mineral,  $\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$ , has been identified in two boreholes drilled in the Emet borate district (Miocene; western Anatolia, Turkey). The evaporitic succession in these boreholes is mainly formed of a glauberite-probertite alternation. The new mineral always appears as a diagenetic phase consisting of aggregates of tiny (from few  $\mu\text{m}$  to tens of  $\mu\text{m}$ ) crystals that replace glauberite at the top of glauberite units. The replacement was caused by the interaction of glauberite with K-rich interstitial brines, which are more concentrated than those from which glauberite had precipitated.

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### INTRODUCTION

This paper is a preliminary report on the petrographic and geochemical characteristics of a new sulphate mineral associated with lacustrine glauberite layers. This mineral is present in two boreholes recently drilled in the Emet borate district (Miocene; western Anatolia, Turkey). The evaporitic succession in these boreholes is mainly formed of a glauberite-probertite alternation. We suggest the name “emetite”, after the town of Emet, for the new sulphate mineral, although the fine crystal size hinders the appropriate chemical and crystallographic characterization required to propose it as a new mineral to the International Mineralogical Association.

To our knowledge, emetite is the first identified Ca-Na-K sulphate with the following formula:  $\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$ . Besides its mineralogical significance, the occurrence of this mineral in specific stratigraphic positions in the borehole succession helps in understanding the chemical evolution of the sulphate-borate saline lake.

Emetite was found in core samples from the boreholes Kütahya-Emet n° 2 (UTM: 35S 691346/4350558) and n° 188

(UTM: 35S 691800/4348815) (called “Doğanlar boreholes” in this paper). These boreholes were drilled with continuous rock sampling by the Eti Bor Company (Turkish Government) during 2003 for exploratory purposes in the vicinity of Doğanlar village, located four kilometres to the south-west of Emet. The two boreholes were drilled on the Quaternary alluvium of the Kocaçay River with a distance of 1.8 km between them. [Figure 1](#) shows the borehole sites on a simplified geological map. The main colemanite open pit mines (Espey, Göktepe, Hisarcık and Dereköy) in the area are also indicated.

### GEOLOGICAL SETTING

The borate deposits of western Anatolia (Turkey) were formed during the Miocene in closed lacustrine basins of high salinities (Helvacı and Firman, 1976; Helvacı, 2005). These deposits comprise five separated boratiferous districts: Bigadiç, Sultançayır, Kestelet, Emet and Kirka (Helvacı *et al.*, 1993). All of these were generated during periods of high volcanic and hydrothermal activity (Gemici *et al.*, 2004). Although the min-

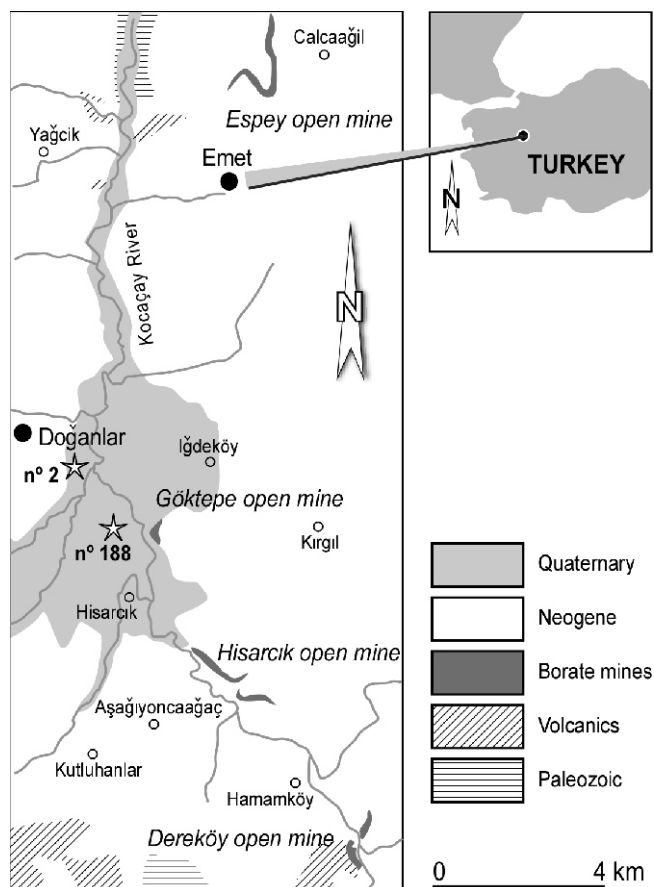


Fig. 1. Geological map of the Emet borate district (after Helvacı, 1986) showing the location of open pit mines and boreholes

eral association of each district shows particular differences, the borates, in association with minor sulphates, are always interbedded with tuffaceous beds (Helvacı and Alonso, 2000).

The Neogene sedimentary record of the Emet Basin has been reported by Helvacı *et al.* (1993) and Helvacı and Alonso (2000). Overlying a Paleozoic metamorphic basement, a lacustrine succession (Fig. 2) is represented by the following units in ascending order:

1. Basal conglomerate and sandstone;
2. Thin-bedded lower limestone, with marl and tuff lenses;
3. Red unit formed of conglomerate, sandstone, clay, marl and limestone, including coal and gypsum bands;
4. Borate-bearing unit of clay, tuff and reworked tuff;
5. Upper limestone, with chert, marl and clay beds.

Basalts overlying the upper limestone unit are the last product of the volcanic activity in the area, dated about 15.4 Ma (Helvacı and Alonso, 2000).

With regards to the mineralogy, remarkable differences exist between the colemanite –  $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot (\text{H}_2\text{O})$  open pit mines, operational for years on the eastern side of the Kocaya River, and the probertite-glauberite alternation recently found in the Doğanlar boreholes. The maximum thickness of the colemanite unit in outcrops is close to 150 m whereas more than

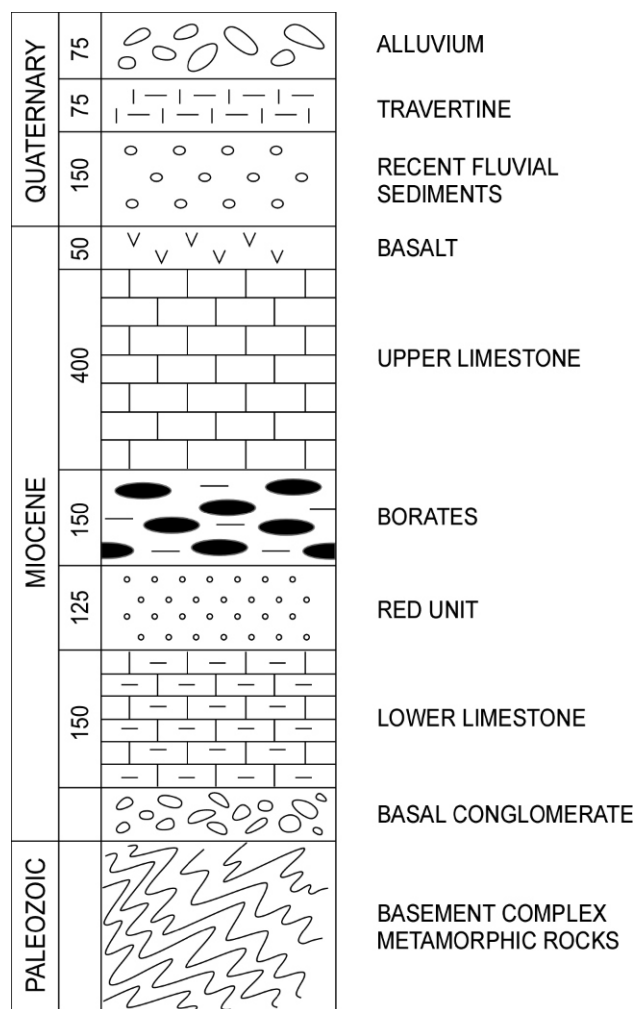


Fig. 2. Generalized stratigraphical column of the Emet borate district (after Helvacı, 1986)

Numbers indicate the maximum thickness (in metres) in outcrops

500 m of the borate-sulphate alternation were intersected in the boreholes studied on the west side of the river.

In the open pit mines, colemanite is characterized by a nodular lithofacies forming layers (up to 5–10 m thick) which are cyclically interbedded with thin-bedded carbonates, claystones and tuffs. The associated minor borates are: ulexite –  $\text{CaNaB}_5\text{O}_6(\text{OH})_6 \cdot 5(\text{H}_2\text{O})$ , hydroboracite –  $\text{CaMg}[\text{B}_3\text{O}_4(\text{OH})_3]_2 \cdot 3(\text{H}_2\text{O})$  and tunellite –  $\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3(\text{H}_2\text{O})$  (Helvacı, 1984). According to Helvacı and Ortí (1998), these deposits were formed in settings similar to permanent playas or inland sabkhas where the interstitial growth of colemanite occurred. In contrast, probertite –  $\text{NaCaB}_5\text{O}_7(\text{OH})_4 \cdot 3(\text{H}_2\text{O})$ , a Na/Ca-borate, and glauberite –  $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ , a Na/Ca-sulphate, are the most abundant minerals in the Doğanlar boreholes.

The clastic materials accompanying the evaporites in the two boreholes consist of tuffaceous (pyroclastic) layers mainly composed of rhyolitic cinerites (ash falls), in which quartz and potassium-feldspar crystals can be distinguished, as well as vitreous fragments (mainly shards) of Mg-silicate composition. Helvacı *et al.* (1993) detected clinoptilolite, illite, and smectite

as authigenic silicates in the tuffaceous samples. The dominant clay minerals are smectite and illite with small amounts of kaolinite and chlorite (Çolak *et al.*, 2000). This fine-grained, volcanoclastic material is the host-sediment of the borate and sulphate minerals.

The detailed mineralogical study of these boreholes, the facies description of the various rock-forming minerals in the succession, and the environmental interpretation of the saline lake, are the subject of a different publication (in preparation by the authors). One interesting result of this study has been the identification of a new double salt borate-sulphate mineral, fontarnauite,  $(\text{Na},\text{K})_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot (\text{Sr},\text{Ca})\text{SO}_4 \cdot 3\text{H}_2\text{O}$  (García-Veigas *et al.*, 2010).

A simplified lithological log of borehole 2, the thickest of the two boreholes studied, is shown in Figure 3. The most significant sedimentological feature in this log is the alternation of probertite- and glauberite-dominated units. One unit of halite occurs intercalated within this alternation. Additionally, both the lower- and the uppermost units of the succession are composed predominantly of colemanite. As a whole, this succession can be interpreted as an evaporitic macrocycle (Ca borates  $\rightarrow$  NaCa sulphates and borates  $\rightarrow$  NaCl  $\rightarrow$  NaCa sulphates and borates  $\rightarrow$  Ca borates), which reached its maximum concentration during the accumulation of the halite unit. In this succession, the presence of the new sulphate mineral studied in this paper is limited to the top of some of the glauberite-dominated units (Fig. 3).

#### MINERAL APPEARANCE

The new sulphate,  $\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$ , always appears as a diagenetic mineral replacing millimetre-sized crystals of glauberite. It consists of aggregates of tiny (from few  $\mu\text{m}$  to tens of  $\mu\text{m}$ ), elongated and anhedral crystals, frequently curved, which exhibit second order interference colours. They are arranged in fascicular and radial fabrics and resemble intergrowth textures (Figs. 4–6). The aggregates form round or irregularly-shaped masses, of less than 1 mm in length, that replace the glauberite crystals from their margins, in contact with the matrix, towards the centre (Fig. 4). Commonly, these masses, as well as the host glauberite crystals, are replaced by equant, euhedral crystals of anhydrite from tens of  $\mu\text{m}$  up to 3 mm across (Fig. 5). The intercrystalline matrix consists of fine reworked particles of tuff and clay associated with colloidal arsenopyrite and micrometric clusters of kalistrontite.

In borehole n° 188, emetite also occurs at the top of a glauberite unit, at a depth of 312 m, where the host glauberite crystals are replaced by secondary gypsum (Fig. 6). The new mineral and the anhydrite crystals have also been partly transformed to secondary gypsum, although to a lesser extent in the case of the anhydrite.

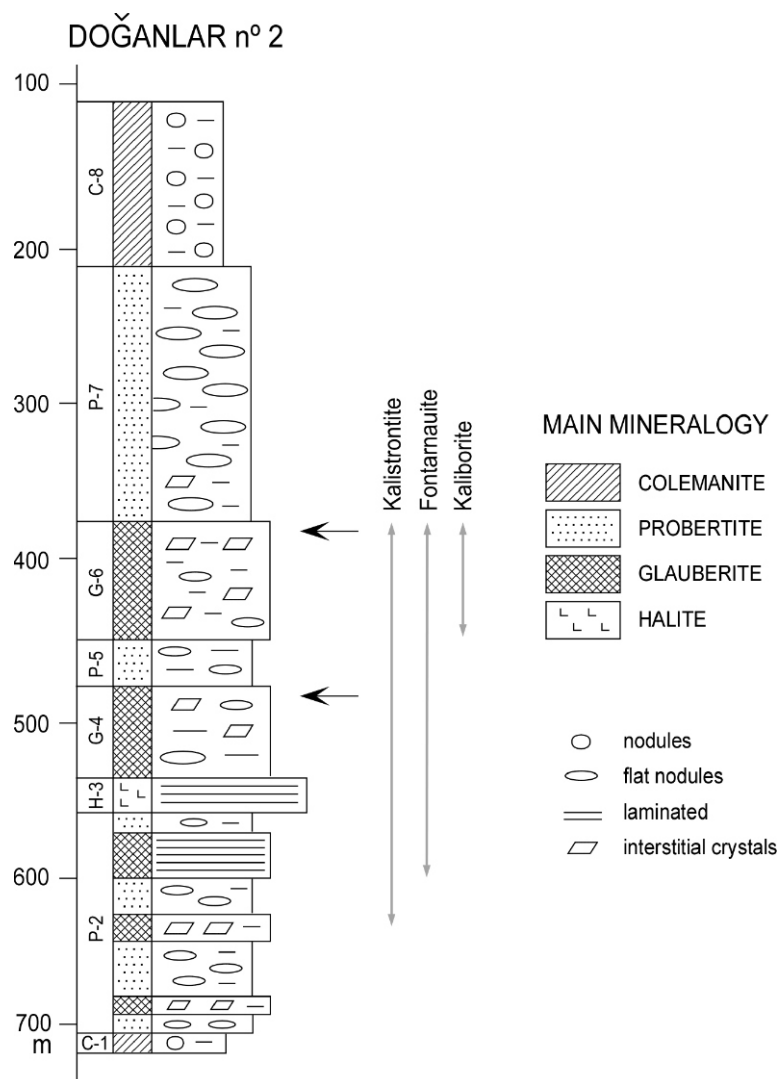
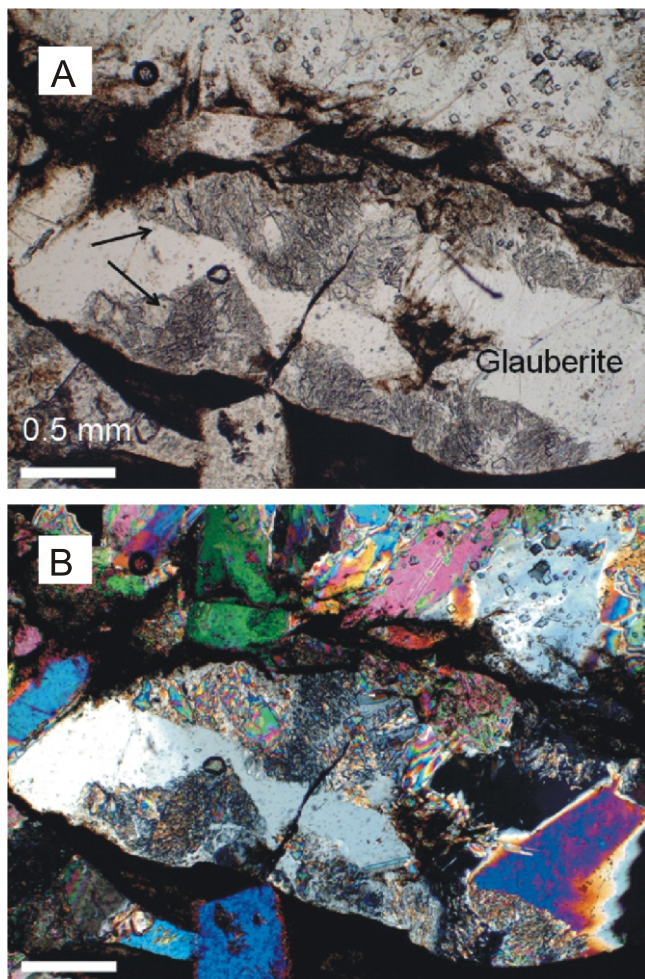


Fig. 3. Stratigraphic log of borehole Doğanlar n° 2 showing the distribution of K-bearing minerals in the Miocene borate-sulphate deposit

Arrows indicate the location of the new mineral

Based on optical observation the irregular replacement of glauberite crystals by this sulphate suggests that it is the result of either (1) an alteration or weathering product of glauberite, or (2) a “myrmekite-like” crystallization between the glauberite and this sulphate. As far as the first possibility is concerned, other cases are known in the literature where the glauberite crystals have been irregularly altered to tiny crystals of minerals with chemical compositions very similar to that of glauberite. This is, for instance, the case of the fibrous textures of hydroglauberite described in the glauberite deposits of the Tertiary Tajo (Madrid) Basin in Central Spain (Ortí *et al.*, 1979). However, taking into account the composition of the new mineral, which incorporates K, and the fact that it is not a hydrated phase, an origin derived from weathering seems unlikely. Concerning the second possibility, myrmekitic crystal growths are unknown in sulphates.



**Fig. 4.** Glauberite crystal partially replaced by aggregates of the new sulphate mineral (arrows)

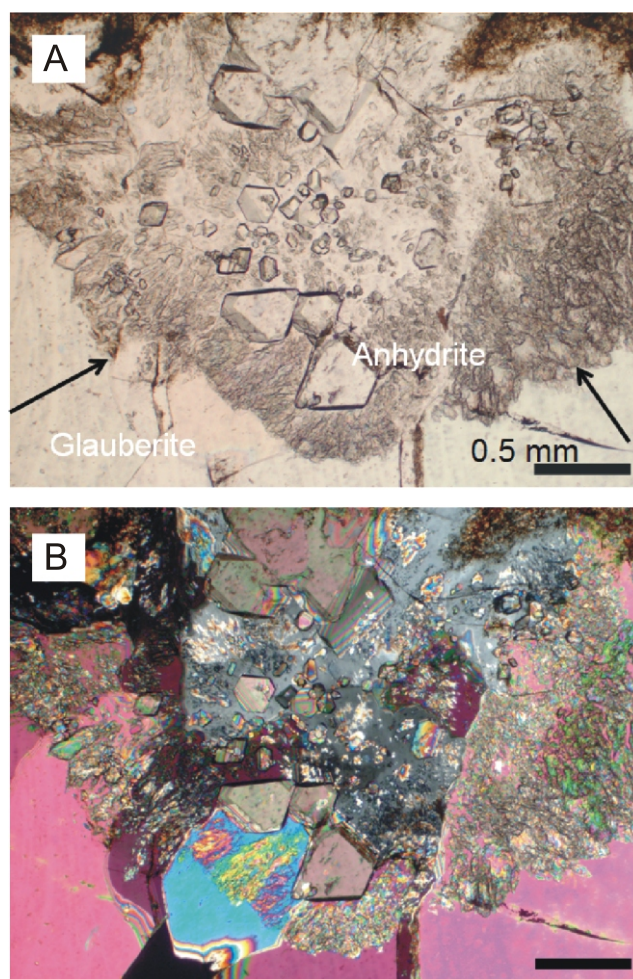
It can be observed that the replacement progresses from the crystal margins in contact with the matrix towards the centre;  
A – plane light, B – crossed polars

#### CHEMICAL AND CRYSTALLOGRAPHIC CHARACTERISTICS

The chemical composition of  $\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$  was determined by electron microprobe (*Cameca SX50*) analysing 28 points of the core sample at 381.5 m of depth in borehole n° 2. The instrumental working conditions were: 20kV of probe energy, 10 nA of intensity current and a defocused probe of 10  $\mu\text{m}$  of diameter.

The average and standard deviation of the points analysed are shown in [Table 1](#). Wollastonite, albite, orthoclase and celestine were used as standards. The analytical accuracy was checked analysing host glauberite crystals.

Due to the small size of the crystals and the characteristic “myrmekite-like” texture ([Figs. 7 and 8](#)), it was impossible to isolate this phase from the glauberite crystals for X-ray diffraction characterization. [Figure 9](#) shows the XRD pattern of



**Fig. 5.** Round aggregate of the new sulphate mineral (arrows) replacing glauberite crystals

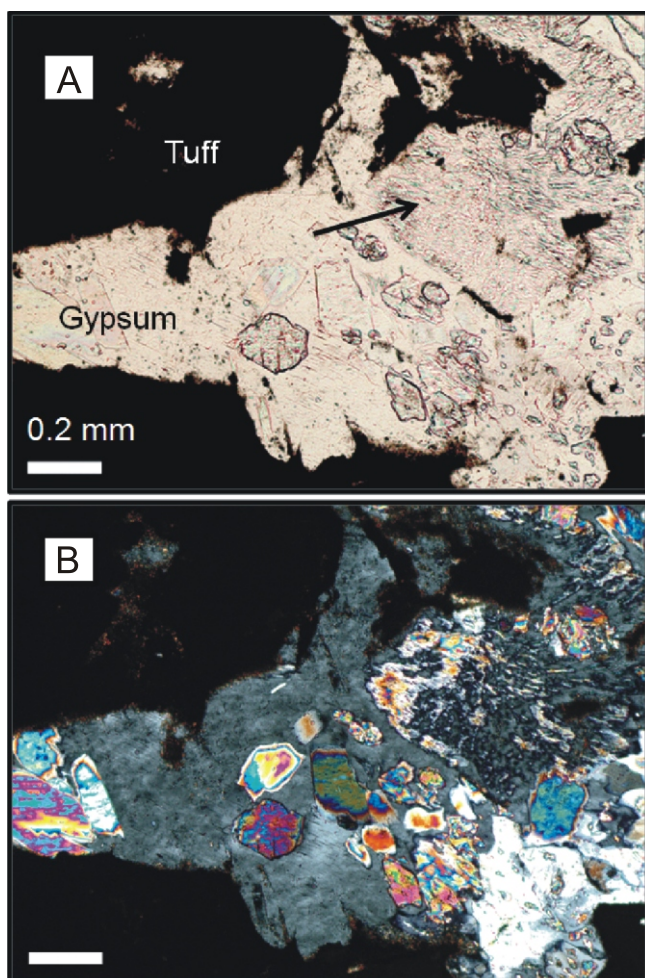
Euhedral anhydrite partially replaces the aggregate and also glauberite;  
A – plane light, B – crossed polars

an impure sample extracted with a micro drill system. If the main peaks corresponding to glauberite and anhydrite are eliminated, we can assign to the new phase the peaks obtained at  $2\theta$ :  $14.5^\circ$ ,  $14.7^\circ$ ,  $25.74^\circ$  and  $29.26^\circ$  ( $d$ : 6.1, 6.0, 3.46 and 3.05 respectively).

#### MINERAL GENESIS

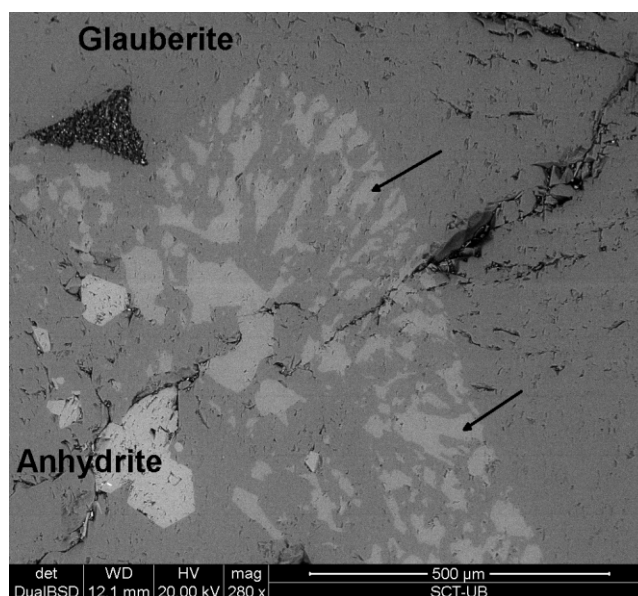
The main mineralogical association (colemanite, proberite and glauberite) suggests that the initial brines correspond to a Ca-Na-SO<sub>4</sub>-B(OH)<sub>3</sub> composition. During initial colemanite precipitation in the Emet Basin, Ca was progressively removed leading to the enrichment of Na, SO<sub>4</sub> and B(OH)<sub>3</sub> in the concentrated brines and resulting in the precipitation of Ca-Na borates (proberite) and sulphates (glauberite).

Unpublished results (García-Veigas *et al.*, 2010) on the fluid inclusion composition of chevron halite crystals (H-3 unit; [Fig. 3](#)), analysed by the *Cryo-SEM-EDS* technique (de-



**Fig. 6.** Secondary gypsum having replaced glauberite crystals and partially replacing an aggregate of the new sulphate mineral (arrow)

Anhydrite crystals have also been partially replaced but to a lesser extent; A – plane light, B – crossed polars



**Fig. 7.** Backscatter SEM image of glauberite sample at 381.5 m depth from borehole Doğanlar n° 2

Arrows indicate the “myrmekite-like” texture of the new mineral replacing glauberite and the relation with euhedral anhydrite crystals

scribed in García-Veigas *et al.*, 2009), indicate that the concentrated brines correspond to a Na-K-SO<sub>4</sub>-Cl system with highly depleted Ca and Mg during halite deposition.

The evolution path from the initial Ca-Na-SO<sub>4</sub>-B(OH)<sub>3</sub> to the final Na-K-SO<sub>4</sub>-Cl system does not correspond to any of the major types of nonmarine brines described by Hardie and Eugster (1970) given that B(OH)<sub>3</sub> is not considered in the initial solutions of these authors. However, this component, that is present in significant proportion in the initial solutions under study, combines with Ca and Na thus determining the brine evolution path. The lack of K-bearing minerals as subaqueous cumulated phases suggests that the concentration of this electrolyte was initially low and became progressively more con-

Table 1

EPMA analysis [% wt.] of  $\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$  in sample at 381.5 m depth in borehole Doğanlar n° 2, Emet, Turkey

Experimental	Na	K	Ca	S	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	SO <sub>3</sub>	Total
Average	5.42	3.16	22.25	23.86	7.26	3.79	31.15	59.41	101.61
Std. Dev.	0.45	0.29	1.63	1.72					
Empirical formula:								$\text{Ca}_{6.9}\text{Na}_{2.9}\text{K}(\text{SO}_4)_{9.2}$	
Ideal	Na	K	Ca	S	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	SO <sub>3</sub>	Total
	5.50	3.12	22.39	23.11	7.37	3.74	31.34	57.54	100
Ideal formula:								$\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$	

EPMA – Electron Probe Micro-Analysis, Std. Dev. – standard deviation

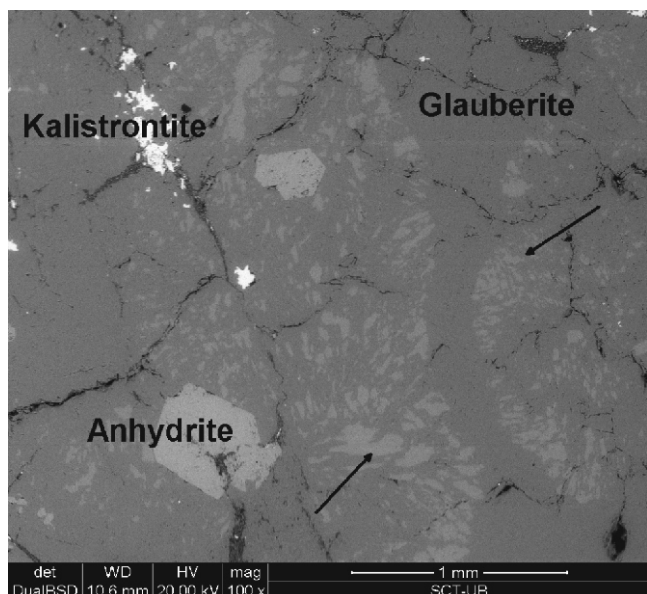


Fig. 8. Backscatter SEM image of glauberite sample at 381.5 m depth from borehole Doğanlar n° 2

Arrows indicate the new mineral replacing glauberite and the relation with the tuffaceous matrix containing kalistrontite crystals

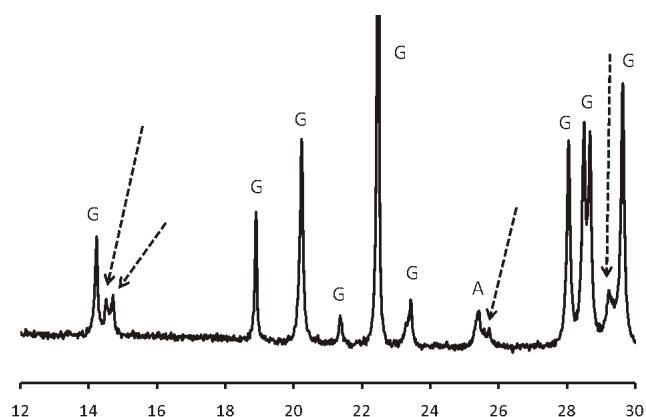


Fig. 9. XRD diagram of powder extracted with a micro drill system in a sample at 381.5 m from borehole Doğanlar n° 2

Arrows indicate the peaks not assigned to glauberite (G) or anhydrite (A) and attributed to the new mineral

concentrated in the evolved brines, reaching the maximum concentration close to halite precipitation. The low Mg contents in halite fluid inclusions are consistent with the absence of Mg-bearing borates (hydroboracite) in the mineralogical record pointing to very low Mg concentrations in the inflow waters, or to the early consumption of Mg, either during dolomite precipitation or by reaction with clay minerals.

The precise conditions for precipitation of emetite in the crystallization sequence of the Ca-Na-K-Cl-SO<sub>4</sub>-B(OH)<sub>3</sub>-H<sub>2</sub>O system cannot be determined by us due to the lack of experimental or modelled solubility data. At low concentrations, boron exists in aqueous solution as boric acid and as the ion

orthoborate; however, in highly concentrated brines a variety of polyborate species have been hypothesized to exist in solution, thus increasing the difficulty of predicting the mineral equilibria of the borates (Felmy and Weare, 1986). The petrographic study allows us to propose a hypothesis about the characteristics and evolution of the interstitial brines from which this new sulphate mineral precipitated.

The association of this mineral with glauberite units suggests high contents of Na and SO<sub>4</sub> in the interstitial brines. Moreover, the K content in the emetite composition, as well as the presence of other K-bearing minerals, either in close association with it, in the case of kalistrontite, or in other units of the succession, in the case of fontarnauite and kaliborite – KMg<sub>2</sub>H[B<sub>6</sub>O<sub>8</sub>(OH)<sub>5</sub>]<sub>2</sub> · 4H<sub>2</sub>O, reinforce the assumption of the K-rich character of the interstitial brines at the moment of the emetite precipitation. Given that this precipitation occurred just at the top of the glauberite units, it can be assumed that the interstitial brines in this uppermost part of the glauberite units were more evolved than those from which glauberite crystallized. At this stage of brine evolution, however, the appropriate conditions for halite formation were generally not reached.

The presence of euhedral anhydrite crystals replacing both the emetite and the host glauberite crystals suggests a final dilution of the interstitial brines. Given that the glauberite units are overlain by probertite units – i.e., by a mineral of lower solubility than glauberite – the dilution would be related to the sedimentation of the latter unit (probertite precipitation implies brine dilution with respect to glauberite). Thus, it seems likely that, at the beginning of formation of the probertite units, the percolation of Ca-rich interstitial solutions caused the partial replacement of the underlying glauberite and emetite by anhydrite.

According to the mineral association, petrographic characteristics and the inferred composition of the brines, emetite could be formed in other evaporitic deposits containing glauberite in which the evolved brines were enriched in potassium sulphate. However, the principal nonmarine brines found in recent evaporitic lakes are enriched in Mg compared to K (Hardie and Eugster, 1970; Warren, 2010) suggesting that the formation of emetite requires a volcanoclastic setting where K is leached from the volcanic sediments and concentrated in alkaline-lakes with or without associated borates.

## CONCLUSIONS

The chemical characterization of the mineral phases in the Doğanlar boreholes has led to the identification of a new K-bearing sulphate mineral, Ca<sub>7</sub>Na<sub>3</sub>K(SO<sub>4</sub>)<sub>9</sub>, named here as “emetite”. This mineral always appears forming aggregates that partially replace the glauberite crystals at the top of the glauberite units. The replacement was caused by the interaction of the glauberite crystals with K-rich interstitial brines more concentrated than those from which glauberite had precipitated. The evolution of the brines that produced the crystallization of this new K-bearing sulphate did not reach, in general, the stage of halite precipitation.

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