Bull. Min. Res. Exp. (2015) 151: 269-283

Bulletin of the
Mineral Research and Exploration

http://bulletin.mta.gov.tr

REVIEW OF THE OCCURRENCE OF TWO NEW MINERALS IN THE EMET BORATE DEPOSIT, TURKEY: EMETITE, $Ca_7Na_3K(SO_4)_9$, and FONTARNAUITE, $Na_2Sr(SO_4)[B_5O_8(OH)](H_2O)_2$

Cahit HELVACI[a]*

[a] *Dokuz Eylül Üniversitesi, Jeoloji Mühendisliği Bölümü Tınaztepe Yerleşkesi, 35160 Buca/İzmir TURKEY*

Keywords:
Neogene borate basins, Emet borate deposit, Mineralogy, Emetite, Fontarnauite, West Anatolia.

ABSTRACT

The Emet borate deposit is situated in the middle of the known borate deposits of western Anatolia. Emet is the world biggest colemanite-probertite deposit which is located in the upper section of the volcano-sedimentary sequence of the Emet basin. Emet borate deposit is unique and has unusual mineral associations. The principal minerals in the Emet borate deposit are colemanite with minor probertite, ulexite and hydroboracite. In addition, rare species such as meyerhofferite, veatchite-A, tunellite, terrugite and cahnite occur sporadically. This is the only deposit known to contain any of the minerals veatchite-A, tunellite, teruggite and cahnite. Arsenic minerals (realgar and orpiment) are very abundant and spatially related to the borates, indicating a common genetic origin. The mineralogical record of Doğanlar boreholes is characterized by the alternation of Na-Ca borate (probertite) and Na-Ca sulphate (glauberite) units including a central halite beds. Colemanite is restricted to the base and top of the sequence in these boreholes and in the whole basin. In this part of the section the major mineral associations probertite-glauberite and halite, with several rare minerals and two new minerals (emetite and fontarnauite) were also discovered in these borehole logs. The Emet borate deposit was formed in two separate parts, possibly part of an interconnected lacustrine playa lake, in areas of volcanic activity, fed partly by thermal springs and partly by surface streams. The early colemanite, meyerhofferite, ulexite and teruggite nodules were formed directly from brines penecontemporaneously within the unconsolidated sediments below the sediment/water interface, and continued to grow as the sediments were compacted. Diagenetic alterations include the partial replacement of colemanite by veatchite-A, cahnite, hydroboracite and calcite. The new mineral, emetite, always appears as a diagenetic phase consisting of aggregates of tiny crystals that replace glauberite at the top of glauberite units. Fontarnauite is most commonly associated with probertite, glauberite and celestine in isolated colorless to light brown prismatic crystals or as clusters of crystals in core samples of these boreholes.

1. Introduction

The Geological evolution of western Anatolia during Neogene time is characterized by basin formation and contemporaneous widespread volcanic activity. The Neogene volcanic activity in western Anatolia was developed contemporaneously with development of NE trending basins, giving rise to formation of thick volcano-sedimentary successions and associated mineral deposits. In this respect, tectonic evolution of the Neogene basins is a fundamental theme in studying the Neogene volcanic evolution as well as the related mineral deposits of the region (Travis and Cocks, 1984; Fytikas et al., 1984; Ercan et al., 1985, 1996; Ersoy and Helvacı, 2007; Ersoy et al., 2011, 2012, 2014; Palmer and

* *Corresponding author: Cahit Helvacı, cahit.helvaci@deu.edu.tr*

Helvacı, 1997; Floyd et al., 1998; Helvacı, 1995; 2005).

The borate deposits of Turkey occur in western Anatolia, south of the Marmara Sea within an area roughly 300 km east-west by 150 km north-south. The main borate districts are Bigadiç, Sultançayırı, Kestelek, Emet, and Kırka (Figure l), and Turkish production supplies most of the commercially traded ulexite and colemanite from mines in the Bigadiç, Kestelek and Emet Districts, plus borax from the deposit at Kırka.

The western Anatolia borate district contains the largest borate reserves in the world (Lyday, 1982; Kistler and Smith, 1983; Helvacı, 1989; Kistler and Helvacı, 1994; Helvacı and Alonso, 2000). All the western Anatolia borate deposits were formed during the Miocene time in closed lacustrine basins with abnormally high salinity and alkalinity (Helvacı, 1986, 1989; Helvacı and Firman, 1976; Helvacı, 2005). The pre-Miocene basement of the basins is represented by the Menderes Massif, which composed of Mesozoic and Paleogene rock units and volcanics. The main borate districts of Turkey are Bigadiç, Kestelek, Sultançayır, Emet and Kırka (Helvacı, 1989, 2005; Kistler and Helvacı, 1994; Helvacı et al., 1993; Helvacı and Alonso, 2000). The important borate minerals from a worldwide commercial standpoint are borax, ulexite and colemanite. Colemanite, a very common calcium borate, is the predominant mineral in all borate districts except for Kırka. A large number of other borate minerals are found in the deposits, including pandermite, inyoite, meyerhofferite, tincalconite, kernite, hydroboracite, inderite, inderborite, kurnakovite, cahnite, terrugite, veatchite-A and tunnelite (İnan et al., 1973; Helvacı, 1977, 1978, 1983; Helvacı and Orti, 1998, 2004; Orti et al., 1998).

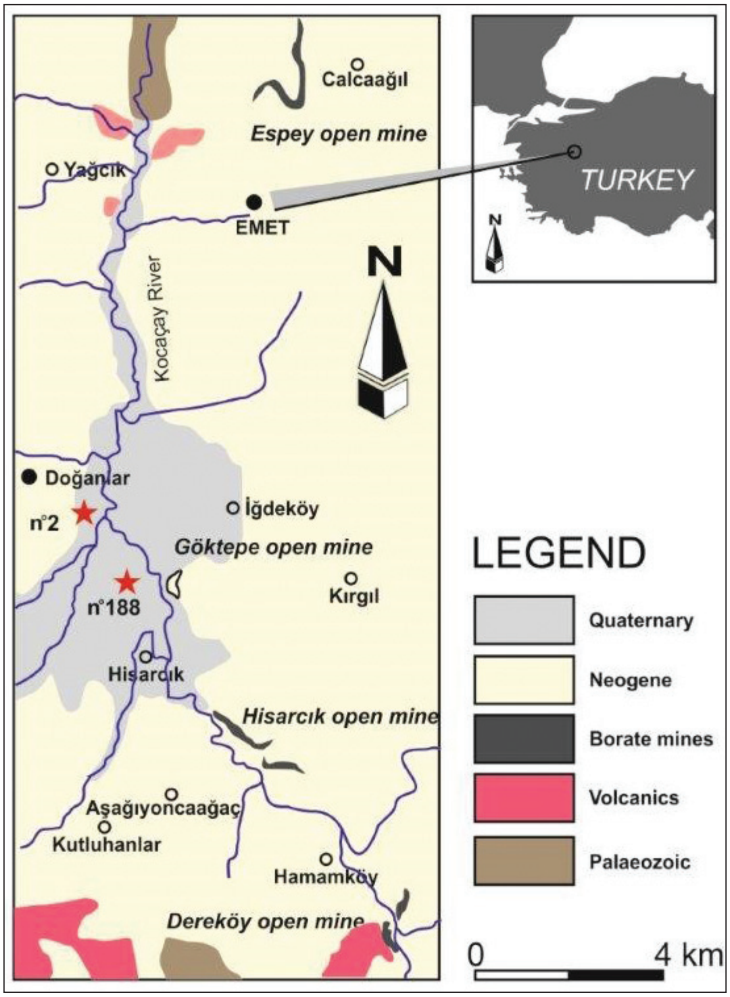

Figure 1- Location of Doğanlar boreholes and geological map of the Emet borate district showing the location of open pit mines and boreholes in western Turkey (after Helvacı, 1986).

The boron in the deposits is assumed to have been derived by leaching of the surrounding rocks by geothermal activity associated with local volcanism (Floyd et al., 1998). The borates then formed when the hydrothermal and spring waters evaporated after flowing into shallow playa lakes (Helvacı, 1995). Boron-rich fluids are presumed to have also circulated along faults into these basins (Helvacı, 1986, 2005).

The borate deposits of Turkey were formed in the lacustrine sediments of Neogene age during periods of volcanic activity. Although the sediments deposited in the borate lakes show some differences, they are generally represented by tuffaceous rocks, claystones, limestones and Ca, Na, Mg, Sr-borates. Sandstone and conglomerates occur near the base of each basin (Gawlik, 1956; Özpeker, 1969; İnan et al., 1973; Helvacı and Firman, 1976; Helvacı, 1977). Sediments in the borate lakes often show clear evidence of volcanic cyclicity. Borate minerals were deposited in a separate or possibly interconnected lake basins under arid or semi-arid climatic conditions. Pyroclastic and volcanic rocks of rhyolitic, dacitic, trachytic, andesitic and basaltic composition are intercalated with these lacustrine sediments. The existence of volcanic rocks in every borate district suggests that volcanic activity may have been necessary for the formation of borates. Much of the sediments in the borate basin seems to have been derived from volcanic terrain. Generally, the borates are enveloped between tuff and clay-rich horizons. The lithologies of the borate deposits show some differences from one to another, and they are generally interbedded with conglomerate, sandstone, tuff, claystone, marl, and limestones, and are usually enveloped by, or grade into, limestones or claystones (İnan et al., 1973; Helvacı, 1977, 1986, 2005; Sunder, 1980; Helvacı et al., 2012); and sediments often exhibit both lateral and vertical facies changes. Volcanic rocks in the vicinity of the playa lakes in which the borate deposits were formed are extensive (Floyd et al., 1998). Intense calc-alkaline volcanic activity took place simultaneously with the borate sedimentation. The volcanic rocks are generally represented by a calc-alkaline series of flows ranging from acidic to basic and by associated pyroclastic rock (Ersoy et al., 2011, 2012).

All of these sediments were generated during periods of high volcanic and hydrothermal activity. Although the mineral 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 Emet borate deposits are situated in the middle of the known borate deposits of western Anatolia (Helvacı 1977, 1984, 1986, 2005). The Emet district includes Palaeozoic metamorphic rocks intruded by granite, and overlying Tertiary sediments associated with volcanic rocks (Holzer 1954; Gawlik 1956; Akkuş 1962). The principal minerals in the Emet borate deposits are colemanite with minor ulexite and hydroboracite. The deposits are mined by open-pit mining methods in the southern basin (Hisarcik and Derekoy deposits) and underground and recently open-pit mining methods in the northern basin (Espey and Killik deposits). Investigations have been carried out on various sections of the basin and samples have been collected from the open-pit, underground workings and the drill cores.

Earlier published papers by Helvacı and Firman (1976) and Helvacı (1984, 1986) indicated that the deepest part of the N-S trending Emet basin is around the Doğanlar-İğdeköy locality, where there were only weathered outcrops on both side of the Emet (Kocaçay) River. In this locality whole sequence was covered with recent Quaternary and alluvial sediments, and deep drillings were suggested to the Eti Maden Company. Concequently, in the years of 1986 and 2003 deep drilling project took place in the Doğanlar-İğdeköy locality. A number of deep boreholes intersected the thickest part of the borate zone in this area, with deepest one at about 700 meters below the surface (Figures 1, 2 and 3).

This paper is a preliminary report on the petrographic and geochemical characteristics of a new sulphate and a borate-sulphate minerals associated with lacustrine probertite-glauberite layers in these Doğanlar boreholes. These minerals are present in two boreholes recently drilled in the Emet borate district (Miocene; western Anatolia, Turkey). These boreholes were drilled with continuous rock sampling by the Eti Maden Company (Turkish Government) during 2003 for exploratory purposes in the vicinity of Doğanlar village, located seven 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 and Hisarcık) in the area are also indicated (Figures 1 and 3). The evaporitic succession in these boreholes is mainly formed of a glauberite-

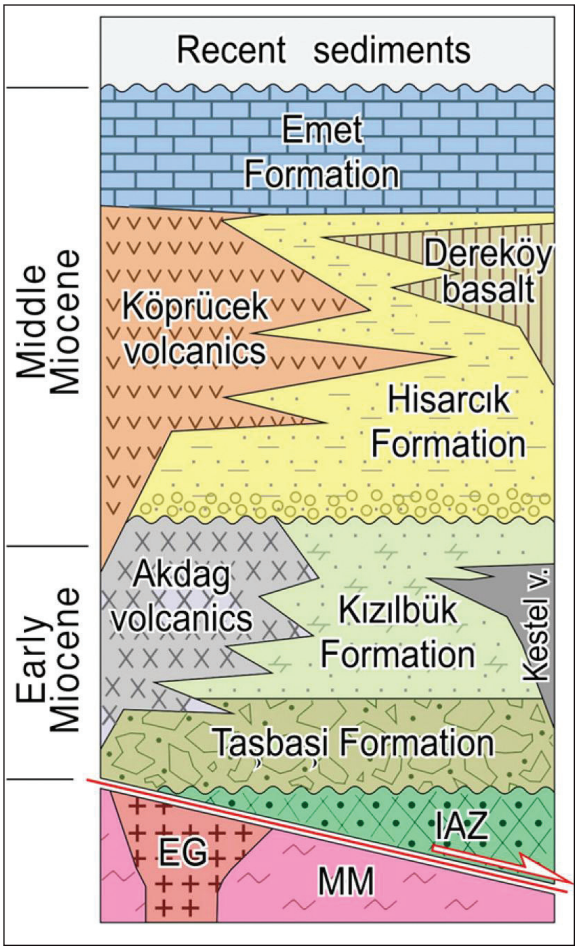

Figure 2- Generalized stratigraphic section of the Emet basin (without scale). MM: Paleozoic Menderes Metamorphic basement; EG: Eğrigöz Granitoid; IAZ: carbonates and ophiolitic rocks of Izmir-Ankara Zone; Taşbaşı formation: conglomerates; Kızılbük formation: clastic unit containing coal; Akdag, Kestel, Köprücek and Dereköy: volcanic units; Hisarcık formation: carbonates with clastic, and tuff deposits, containing borates; Emet formation: upper limestone unit (modified after Helvacı, 1984).

probertite alternation. In this part of the section the major mineral associations probertite-glauberite and halite, with several rare minerals and two new minerals (emetite and fontarnauite) were also discovered in these boreholes. They were already published elsewhere (Garcia-Vegias et al., 2010*a*, 2010*b*, 2011; Cooper et al., in press).

Emetite was found in core samples from the boreholes Kütahya-Emet no: 2 (UTM: 35S 691346 / 4350558) and no: 188 (UTM: 35S 691800 / 4348815) (called "Doğanlar boreholes") (Figure 4). We suggest the name "emetite" for the new sulphate mineral after the town of Emet. It is also noted that the fine crystal size of this new mineral hinders the appropriate chemical and crystallographic characterization required to propose it as a new mineral to the International Mineralogical Association (Garcia-Veigas et al., 2010*a*). This mineral still needs to be worked on in order to get all the data to be approved by IMM.

Fontarnauite is a new mineral found in core samples of the Doğanlar boreholes no: 2 and no: 188 drilled in the vicinity of the Doğanlar village, located seven kilometres to the southwest of the Emet town (western Anatolia, Turkey) (Figure. 1 and 4). Fontarnauite is a double salt (borate-sulphate) of sodium and strontium with minor contents of potassium and calcium. The proposed name is for deceased Dr. Ramon Fontarnau (1944-2007), Director of the Material Characterization Section of the Scientific-Technical Survey at the University of Barcelona for his effort to promote the development of scientific facilities focused on mineral characterization (Garcia-Veigas et al., 2010*b*; Cooper et al., in press).

This paper presents the short story of the two new minerals, emetite and fontarnauite (borate and borate-sulphate minerals), recently discovered in the Emet borate deposits, and attempts to define both the relationships between mineral associations, and the nature of their occurrences. The full papers of these minerals were treated elsewhere.

2. Geological Setting of Emet Basin

Emet basin (Akdeniz and Konak, 1979; Helvacı, 1984, 1986; Figure 3), is located between the Eğrigöz granitoid intruded into the Menderes Massif metamorphic rocks to the west, and the Afyon zone metamorphic rocks to the east (Figures 1, 2 and 3). The Neogene sequence rests unconformably on Paleozoic metamorphic rocks that consist of marble, mica-schist, calc schist and chlorite schist.

The borate deposits of Turkey were formed in lacustrine environments during periods of volcanic activity. The borates of the Emet area are part of the Tertiary lacustrine sediments which rest unconformablv on Palaeozoic metamorphic rocks, consisting of marble, micaschist, calc-schist and chlorite-schist (Figure 3). The sediments of the Emet district consist of predominantly lacustrine sequence. The stratigraphy of Emet basin comprises two Neogene volcanosedimentary units separated by a

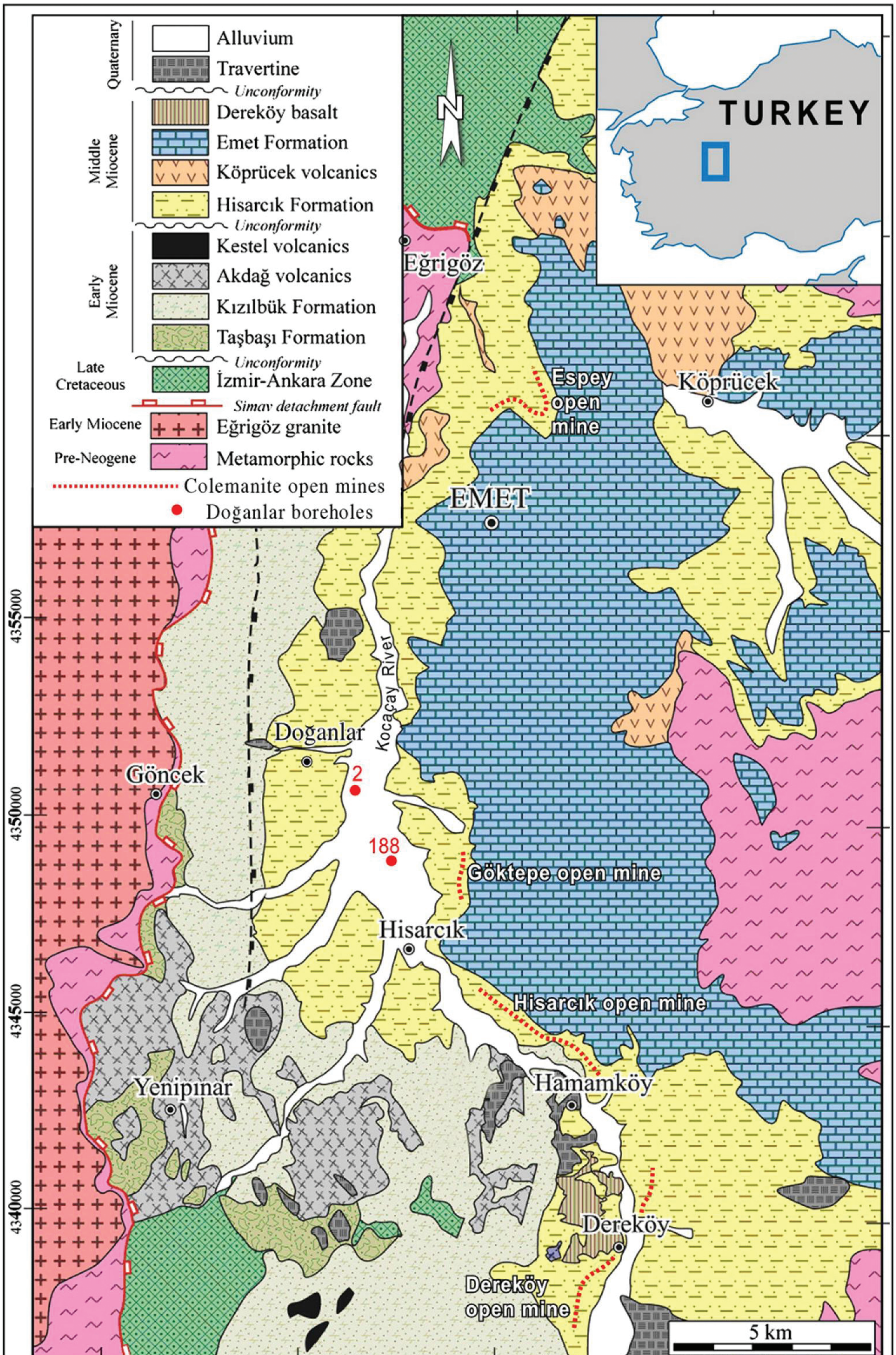

Figure 3- Geological map of the Emet borate district (modified after Helvacı, 1984) showing the location of the colemanite open pit mines and the studied boreholes.

regional unconformity (Figures 2 and 3). These units can be correlated with similar rocks from other basins on the basis of their age, lithology and deformational features, and they are named as the Hacıbekir and İnay groups. In the Emet basin, the İnay Group hosts the world's biggest colemanite and probertite borate deposits (Gawlik, 1956; Helvacı, 1984, 1986; Helvacı and Orti, 1998; Helvacı and Alonso, 2000; Garcia et al., 2011).

The Hacıbekir Group consists of the Taşbaşı and Kızılbük formations and the Akdağ and Kestel volcanics (Figures 2 and 3). The Taşbaşı formation crops out to the western and southwestern parts of the Emet basin, and is made up of reddish-brown colored conglomerates with grayish sandstone intercalations deposited in alluvial fan facies. The Taşbaşı formation is locally interfingered with rhyolitic pyroclastic rocks of the Akdağ volcanics, and is conformably overlain by the Kızılbük formation.

The age of the unit is early Miocene on the basis of radiometric age data from the volcanic rock intercalations. The Kızılbük formation crops out in a large area to the western and southwestern parts of the Emet basin, and is composed of coal-bearing yellowish sandstone–siltstone–mudstone alternations and laminated limestone of fluvio-lacustrine origin. The Kızılbük formation is interfingered with pyroclastic rocks of the Akdağ volcanics, which are composed of rhyolitic lava flows, domes, pyroclastics and epiclastics. The Akdağ volcanics have yielded 20.3±0.6 (Seyitoğlu et al., 1997) and 19.0±0.2 Ma (Helvacı and Alonso, 2000) K–Ar ages (Table 1). The Kestel volcanics emplaced in a NE–SW-direction to the southwest of the basin, and are composed of syn-sedimentary mafic lava flows. These volumetrically small volcanic rocks conformably overlie the Kızılbük Formation. The age of the Kestel volcanics is stratigraphically accepted to be early Miocene.

The İnay Group in Emet basin is made up of the Hisarcık and Emet formations that interfinger with the Köprücek volcanics and th Dereköy basalt (Figure 3). The Hisarcık formation (Akdeniz and Konak, 1979) crops out in a large area in the Emet basin and is composed of conglomerates, pebblestones and sandstone intercalations. The age of the Hisarcık formation is accepted to be middle Miocene on the basis of volcanic intercalations in the İnay Group. Towards the center of the basin, the Hisarcık formation passes laterally into the Emet formation that is composed of sandstone – claystone – mudstone - limestone alternations of fluvio-lacustrine origin. The fine-grained parts of the unit, especially the mudstone – claystone levels contain large borate deposits which are mined for colemanite and probertite (Helvacı and Alonso, 2000; Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy et al., 2012).

In the Emet basin, the Köprücek volcanics (16.8±0.2 Ma K–Ar age; Helvacı and Alonso, 2000) crop out to the northern part of the Emet basin. The unit is composed of andesitic to rhyolitic lava flows, dykes and associated pyroclastics which interfinger with the Hisarcık formation. The thickness of the pyroclastic intercalations in the Hisarcık formation increases towards the north of the basin, which suggests that the Köprücek volcanics originated from this area. The Köprücek volcanics are overlain by the

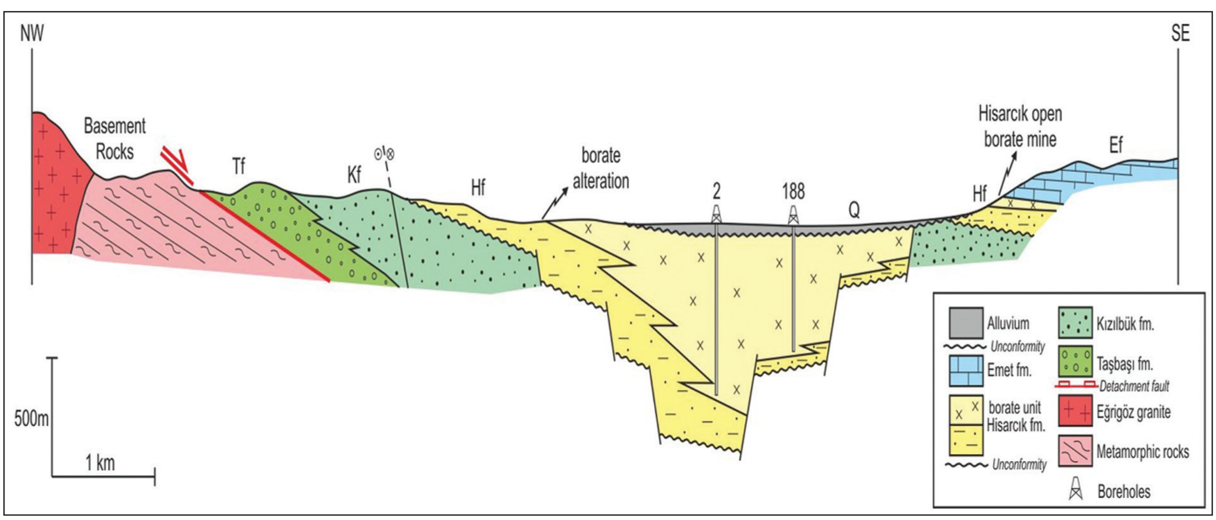

Figure 4- Cross section along the Doğanlar locality and Hisarcık opencast mine showing the deep boreholes numbers 2 and 188.

Table 1- Borates, sulphates and sulphides recognised in the Emet basin and their chemical formulas.

Borates	Ca	Colemanite	$CaB_3O_4(OH)_3\ H_2O$
		Meyerhofferite	$Ca(B_3O_3(OH)_5).H_20$
	Ca-Na	Probertite	$NaCaB_5O_7(OH)_4\ 3(H_2O)$
		Ulexite	$NaCaB_5O_6(OH)_6\ 5(H_2O)$
	K	Fontarnauite	$(Na,K)_2(Sr,Ca)SO_4[B_4O_6(OH)_2]\ 3H_2O$
		Kaliborite	$KMg_2H(B_6O_8(OH)_5)_2\ 4(H_2O)$
	Mg-Na	Aristarainite	$NaMgB_{12}O_{16}(OH)_8\ 4(H_2O)$
		Rivadavite	$Na_6Mg(B_6O_7(OH)_6)_4.10H_2O$
		Hydroboracite	$CaMg(B_3O_4(OH)_3)_2\ 3(H_2O)$
	Sr	Tunellite	$SrB_6O_9(OH_2)\ 3H_2O$
		Veatchite-A	$Sr_2(B_{11}O_{16}(OH)_5).H_2O$
	As	Cahnite	$Ca_2B(AsO_4)(OH)_4$
		Teruggite	$Ca_4MgAs_2B_{12}O_{22}(OH)_{12}.12H_2O$
Sulphates	Ca	Anhydrite	$CaSO_4$
		Gypsum	$CaSO_4\ 2H_2O$
	Ca-Na	Glauberite	$Na_2Ca(SO_4)_2$
	Na	Thenardite	$Na_2(SO_4)$
	K	Emetite	$Ca_7Na_3K(SO_4)_9$
	Sr	Celestine	$SrSO_4$
		Kalistrontite	$K_2Sr(SO_4)_2$
Sulphides	As	Arsenopyrite	FeAsS
		Orpiment	As_2S_3
		Realgar	As_4S_4

limestones of the Emet formation. The pyroclastic intercalations yield 16.8±0.2 Ma K–Ar age (Helvacı and Alonso, 2000; table 1). In the southern part of the basin, the Hisarcık formation is also conformably overlain by basaltic lava flows of the Dereköy basalt. Along the basal contact of the Dereköy basalt several pepperitic textures are developed, indicating a syn-sedimentary emplacement of the lavas. The Dereköy basalt has been dated as 15.4±0.2 and 14.9±0.3 Ma (K–Ar ages; Seyitoğlu et al., 1997; Helvacı and Alonso, 2000).

The volcanic activity in the Emet basin is thought to be the source of the borate deposition. Thermal springs associated with local volcanic activity are thought to be the possible source of the borates (Helvacı, 1977; Helvacı, 1984; Helvacı and Alonso, 2000). The older acidic lavas contain higher B levels than the more recent intermediate alkaline lavas. The Early Miocene acidic volcanism at Emet basin has high levels of elements associated with mineralization, as well as having a close spatial and temporal relationship with the borates and it is therefore considered a likely source. Possible mechanisms by which volcanism might supply B, S, Sr, As and Li to the basin sediments include the leaching of volcanic rocks by hydrothermal waters, the direct deposition of ash into the lake sediments, or the degassing of magmas (Helvacı, 2015, in this volume).

3. Mineralogy of Emet Deposit

Mineralogical studies have shown that the borate deposits in the Emet district are far more complex than previously thougt in addition to the minerals previously recorded (Özpeker 1969). The Emet basin is one of the Neogene basins in western Turkey containing significant amounts of rare borate minerals. The borates are interlayered with tuff, clay and marl with limestone occurring above and below the borate lenses. Sedimentary and early diagenetic processes controlled the crystal growth both subaqueously and interstitially. The principal borate minerals are colemanite and probertite (Table 1; figures 5 and 6), with minor ulexite, hydroboracite and meyerhofferite. The Emet borate deposits contain many of the rare borate minerals such as veatchite-A, tunellite, teruggite, and cahnite (Helvacı and Firman, 1976; Helvacı, 1977, 1984, 1986; Helvacı and Orti, 1998; Garcia-Veigas et al., 2011). Montmorillonite, illite and chlorite are clay minerals that have been identified, and zeolites are abundant along the tuff horizons (Helvacı et al.,1993; Çolak et al., 2000).

The petrologic study of core samples from two exploratory wells in the Doğanlar sector, reveals a complex mineral association in which probertite, glauberite and halite constitute the major primary phases precipitated in a saline lake within a volcano-sedimentary context (Garcia-Veigas et al., 2011). Other sulphates (anhydrite, gypsum, thenardite, celestite and kalistrontite), borates (colemanite, ulexite, hydroboracite, tunellite, kaliborite and aristarainite) and sulphides (emetite, arsenopyrite, realgar and orpiment) are attributed to early diagenesis. The Doğanlar deposit is the most important deposit of probertite known up to now (Garcia-Veigas et al., 2011). Emetite paper is already published in an international journal (Garcia-Veigas et al., 2010*a*). A new sulphate-borate mineral (fontarnauite) has been found in the deposit (Garcia-Veigas et al., 2010*b*) (Table 2) and the paper concerning this mineral is in press in the Canadian Mineralogist (Cooper et al., in press).

The mineralogical record of Doğanlar boreholes is characterized by the alternation of Na-Ca borate (probertite) and Na-Ca sulphate (glauberite) units including a central halite beds. Colemanite is restricted to the base and top of the sequence. Kalistrontite is abundant in the sequence indicating a significant concentration of Sr in brines. Fontarnauite appears as an early diagenetic phase, replacing both probertite and glauberite, as a consequence of an anomalous chemical composition achieved by the residual brines duringevaporation in a saline lake environment with volcaniclastic contribution. Other minor minerals found in the boreholes include: borates (aristarainite, colemanite, hydroboracite, kaliborite tunellite and ulexite), sulphates (anhydrite, celestine, gypsum, kalistrontite and thenardite), and sulphides (emetite, arsenopyrite, orpiment and realgar) (Helvacı, 1984; Garcia-Veigas et al., 2011) (Figures 5 and 6; table 1).

4. Occurrence of Emetite (a new sulphate mineral): $Ca_7Na_3K(SO_4)_9$ in the Emet Borate Deposit

Emetite, a new sulphate mineral, $Ca_7Na_3K(SO_4)_9$, has been identified in two boreholes drilled in the Emet borate district. The evaporitic succession in these boreholes is mainly formed of a glauberite-probertite alternation. The chemical characterization of the mineral phases in the Doğanlar boreholes has led to the identification of a new K-bearing sulphate mineral, $Ca_7Na_3K(SO_4)_9$ named here as "emetite". The new mineral always appears as a diagenetic phase consisting of aggregates of tiny crystals that replace glauberite at the top of glauberite units. The replacement was caused by the interaction of glauberite with K-rich in terstitial brines, which are more concentrated than those from which glauberite had precipitated (Garcia-Veigas et al., 2010*a*).

This paper is to report on the petrographic and geochemical characteristics of a new sulphate mineral associated with lacustrine glauberite layers. The evaporitic succession in these boreholes is mainly formed of a glauberite-probertite alternation. Emetite was found in core samples from the boreholes Kütahya-Emet no: 2 (UTM: 35S 691346/4350558) and no: 188 (UTM: 35S 691800/4348815) (Doğanlar boreholes). This mineral is present in two boreholes recently drilled in the Emet borate district (Miocene; western Anatolia, Turkey). The name "emetite", after the town of Emet, is suggested for the new sulphate mineral (Garcia-Viagas et al., 2010*a*).

The new sulphate, $Ca_7Na_3K(SO_4)_9$, always appears as a diagenetic mineral replacing millimetre-sized crystals of glauberite. It consists of aggregates of tiny, elongated and anhedral crystals, frequently curved, which exhibit second order interference colours. They are arranged in fascicular and radial fabrics and resemble intergrowth textures (Figures 7 and 8) (Garcia-Veigas et al., 2010*a*). 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 (Figure 7). Commonly, these masses, as well as the host glauberite crystals, are replaced by equant, euhedral crystals of anhydrite from tens of mm up to 3 mm across (Figure 8). In borehole no: 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 (Figure 6). The new mineral and the anhydrite

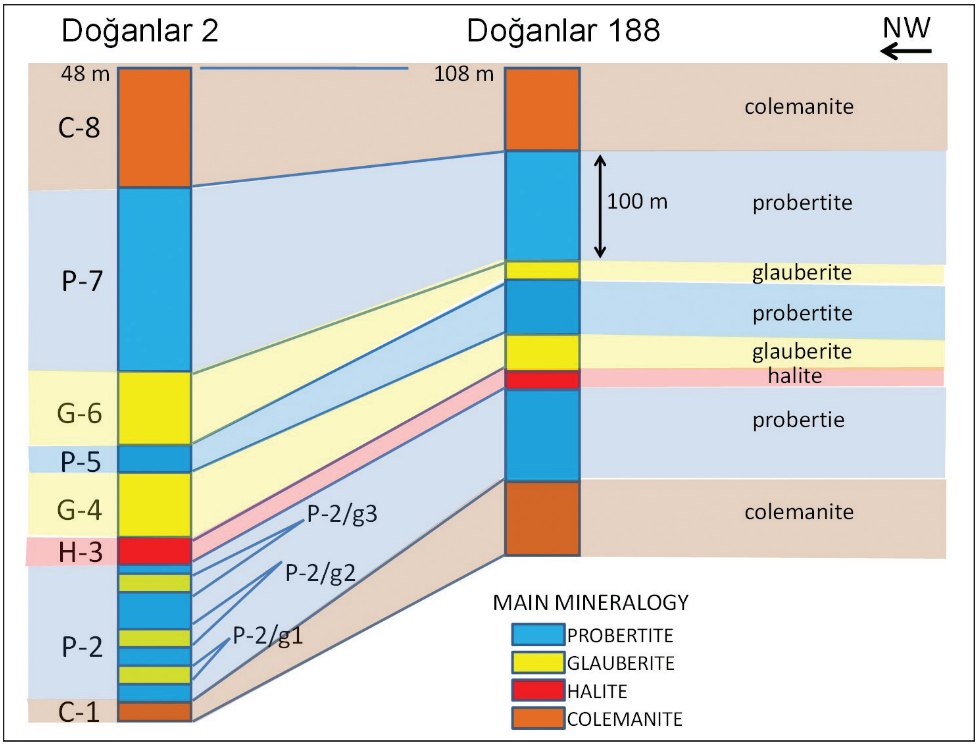

Figure 5- Lithological log correlation of the Doğanlar boreholes based on mineral associations. C-1: Basal Colemanite Unit, P-2: Lower Probertite Unit, P-2/g1: Lower-Anhydrite Subunit, P-2/g2: Intermediate Glauberite-Kalistrontite Subunit, P-2/g3: Upper Glauberite-Fontarnauite Subunit, H-3: Halite Unit, G-4: First Glauberite Unit, P-5: Intermediate Probertite Unit, G-6: Second Glauberite Unit, P-7: Upper Probertite Unit, C-8: Upper Colemanite Unit (Garcia-Veigas et al., 2011).

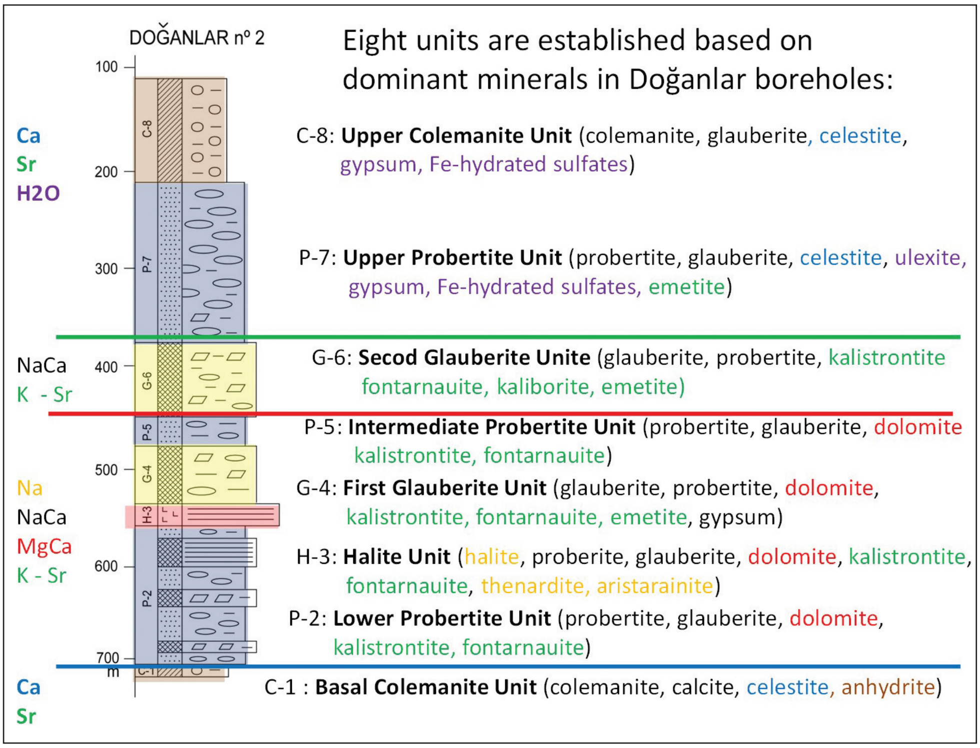

Figure 6- Schematic distribution of the evaporitic minerals with depth (borehole Doğanlar no. 2). Units as in figure 5 (Garcia-Veigas et al., 2011).

Table 2- Documents of new mineral Fontarnauite published in Mineralogical Magazine October 2014.

NEW MINERAL PROPOSALS APPROVED IN SEPTEMBER 2014 IMA No. 2009-096a	
Fontarnauite	
Kütahya-Emet 2 and 188 boreholes, near the village of Doğanlar, Kütahya Province, Western Anatolia, Turkey Mark A. Cooper, Frank C. Hawthorne, Javier Garcı´a-Veigas, Xavier Alcobe´, Cahit Helvaci, Edward S. Grew* and Neil A. Ball *E-posta: esgrew@maine.edu	
Chemical Properties of Fontarnauite	
Formula: $(Na,K)_2(Sr,Ca)\ (SO_4)[B_5O_8(OH)]\cdot 2H_2O$	
Crystallography of Fontarnauite	
Crystal System:	Monoclinic: P21/c; structure determined (New structure type)
Class (H-M):	2/*m* – Prismatic
Space Group:	*P*21/*b*
Space Group Setting:	*P*21/*c*
Cell Parameters:	a = 6.458(2) Å b = 22.299(7) Å c = 8.571(2) Å β = 103.05(1)°
Ratio:	a:b:c = 0.29 : 1 : 0.384
Unit Cell Volume:	V 1,202.41 Å? (Birim Hücreden hesaplanmıştır)
X-Işınları Powder Diffraction Data:	**d-spacing** **Intensity** 11.15 -100 3.395 -8 3.339 -20 3.199 -30 3.046 -10 3.025 -7 2.750 -10 2.400 -8
Type material is deposited in the collections of the Royal Ontario Museum, 100 Queens Park, Toronto, Ontario M5S 2C6, Canada, accession number M56745	
How to cite: Cooper, M.A., Hawthorne, F.C., Garcı´a-Veigas, J., Alcobe´, X., Helvaci, C., Grew, E.S. and Ball, N.A. (2014) Fontarnauite, IMA 2009-096a. CNMNC Newsletter No. 22, October 2014, page 1244; Mineralogical Magazine, 78, 1241-1248.	

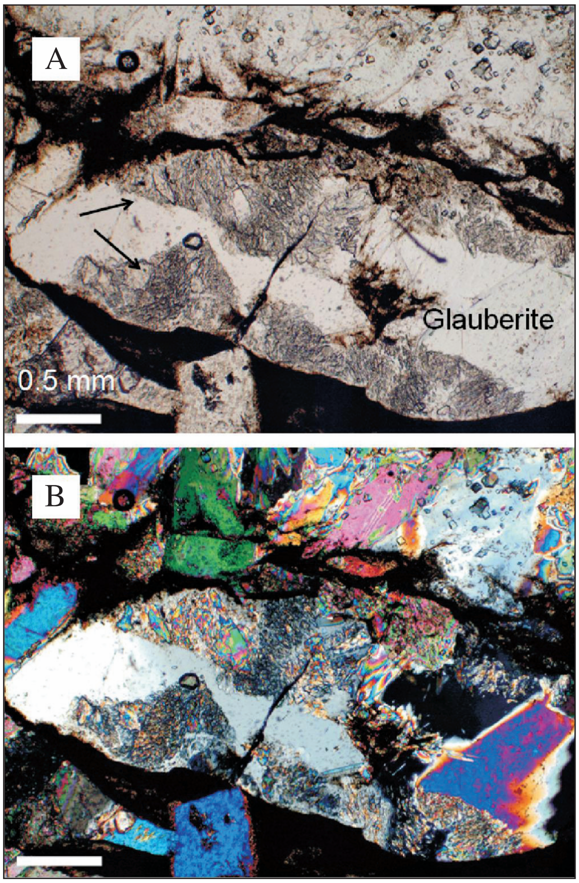

Figure 7- Glauberite crystal partially replaced by aggregates of the new sulphate mineral emetite (arrows) (A: parallel nicols, B: crossed nicols) (Garcia-Veigas et al., 2010*a*).

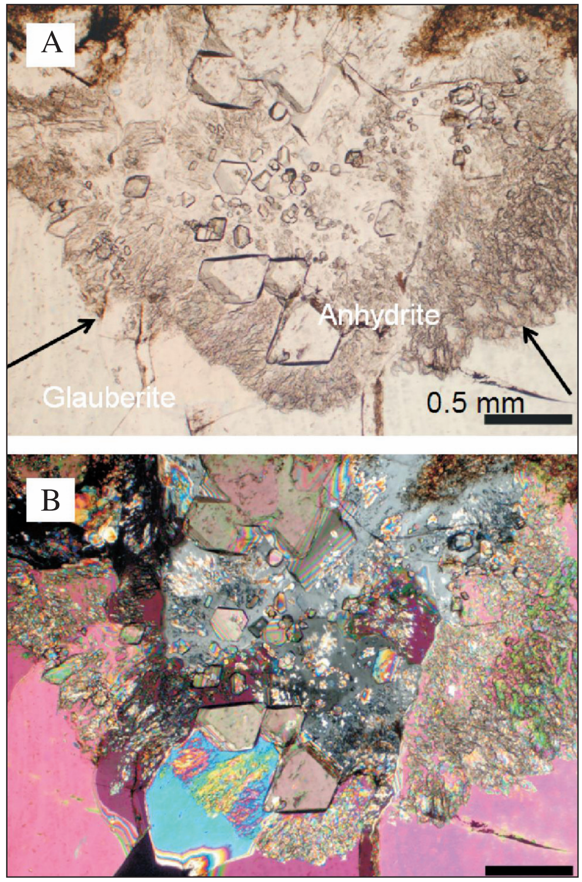

Figure 8- Round aggregate of the new sulphate mineral emetite (arrows) replacing glauberite crystals (A: parallel nicols, B: crossed nicols) (Garcia-Veigas et al., 2010*a*).

crystals have also been partly transformed to secondary gypsum, although to a lesser extent in the case of the anhydrite (Garcia-Veigas et al., 2010*a*).

5. Occurrence of fontarnauite (a new sulphate-borate mineral): $Na_2Sr(SO_4)[B_5O_8(OH)](H_2O)_2$ in the Emet borate deposit

Fontarnauite was recovered from the Kütahya-Emet 2 and 188 (Doğanlar boreholes) boreholes drilled in the Emet basin near the village of Doğanlar (García-Veigas et al. 2010*b*, 2011; Helvacı 1986, Helvacı and Orti 1998). The exploration holes were drilled during 2003 in the area to the north of the Hisarcık open cut mine in Quaternary alluvium of the Kocaçay River (Figure 4). The distance between the two boreholes is about 1.8 km. Borehole 2 is 716 m in depth; fontarnauite was observed between 530 and 581.5 m depth; borehole 188 (516 m in depth) yielded fontarnauite between 249 and 351.9 m (Garcia-Veigas et al., 2011).

Fontarnauite is most commonly associated with probertite, glauberite and celestine (Figures 9, 10 and 11). In addition, García-Veigas et al. (2010*b*) reported fontarnauite with (1) halite, (2) kaliborite replacing probertite, and (3) kalistrontite, which replaced fontarnauite in pseudomorphs after glauberite. Other minerals occurring in the boreholes, most abundantly colemanite, ulexite, dolomite, arsenopyrite, realgar and orpiment, have not been found with fontarnauite (Garcia-Veigas et al., 2011).

Fontarnauite, $Na_2Sr(SO_4)[B_5O_8(OH)](H_2O)_2$, was discovered in 2009 in cores recovered from the borate-bearing Miocene Emet basin (García-Veigas et al. 2010*b*, 2011). The mineral and its name have been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature (IMA no. 2009-64a). The holotype is

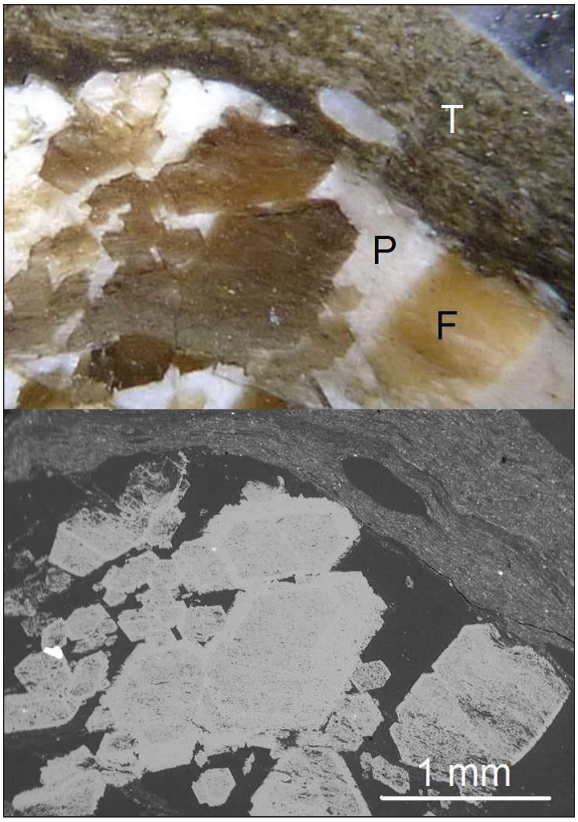

Figure 9- Optical (upper) and BSE-SEM (lower) images of a cluster of fontarnauite crystals. (F: fontarnauite, P: probertite,T: tuff). (García-Veigas et al., 2010*b*).

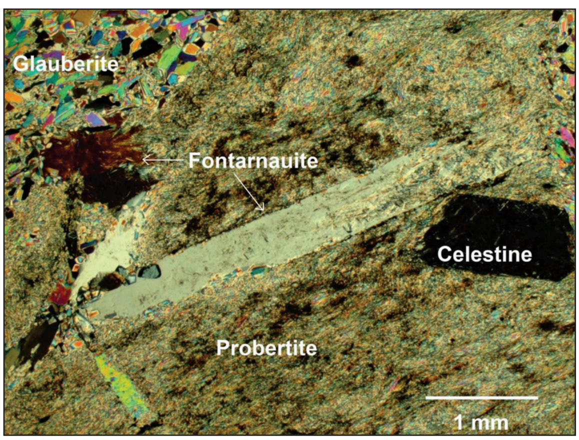

Figure 10- Prismatic fontarnauite crystals in thin section with crossed polars. Photomicrograph of prismatic fontarnauite crystals elongate along [100] (crossed polars) (García-Veigas et al., 2010*b*).

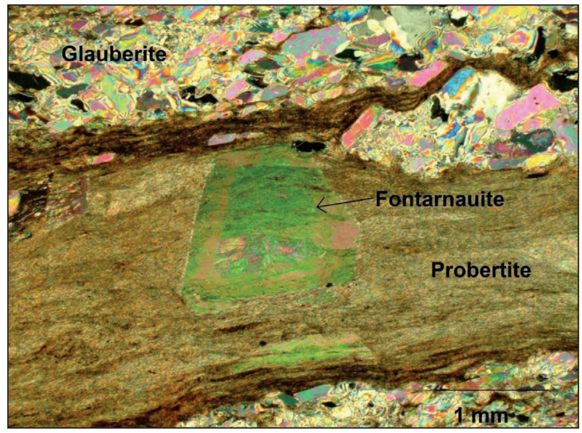

Figure 11- Photomicrograph of fontarnauite crystals with hexagonal outline formed from the {010} side pinacoid and the {011} prism (crossed polars) (after Cooper et al., in press).

deposited in the mineralogy collection of the Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6, Canada, accession number M56745 (Cooper et al., in pres) (Table 2).

Fontarnauite is most commonly associated with probertite, glauberite and celestine in isolated colorless to light brown prismatic crystals or as clusters of crystals less than 5 mm long (Figure 10). More often it displays pseudohexagonal sections less than 1 mm in diameter. Under microscope it shows a perfect cleavage parallel to (010) (Figure 11). It has a pearly, transparent to translucent lustre, a brittle tenacity and a white streak (Cooper et al., in press).

Fontarnauite is interpreted to be an early diagenetic phase, replacing both probertite (Figures 9, 10 and 11) and glauberite, as a consequence of the K-SO_4-enriched composition in residual brines during the evaporation in a saline lake environment to which volcaniclastic material had been added (Helvacı and Alonso, 2000; Orti et al., 1998; Garcia-Veigas et al., 2010*b*; Cooper et al., in press).

6. Conclusions

The Emet borates were formed in playa lakes, fed partly by thermal springs and partly by streams draining the catchment areas, and it may be assumed that the initial brines at all times contained an abundance of calcium and boron with minor amounts of arsenic, sulphur, strontium, magnesium and sodium. Early precipitated minerals seem to have formed within the clastic sediments. Brines were evidently rich in Ca and B in both the northern and southern parts of the basin throughout the sequence. Both lateral and vertical changes from calcite-marls to colemanite bearing clays have been observed and a gross zoning both laterally and vertically from calcite to colemanite and back to calcite seems to be general in both areas. Ca borates, ulexite and teruggite crystallized within the sediments and did not precipitate from open water. Co-precipitation of ulexite and later diagenetic formation of tunellite occurs only rarely in the northern basin. Field and textural evidence clearly indicates the sequence Ca borate + Ca-Na borate + Sr borate.

In the southern area the sporadic occurrence of gypsum suggests that where sulphates are present the sequence is calcite + gypsum + colemanite.

Two new minerals, emetite and fontarnauite, have been discovered in the Doğanlar boreholes located in the central part of the Emet borate basin. The chemical characterization of the mineral phases in the Doğanlar boreholes has led to the identification of a new K-bearing sulphate mineral, $Ca_7Na_3K(SO_4)_9$, named as “emetite”. This mineral always appears forming aggregates that partially replace the glauberite crystals at the top of the glauberite units. Fontarnauite is most commonly associated with probertite, glauberite and celestine. Fontarnauite is interpreted to be an early diagenetic phase, replacing both probertite and glauberite in the volcanostratigraphic sequence of the Emet basin.

Acknowledgments

I am especially grateful to Eti Maden Company and MTA and their managers for their generosity during fieldwork. This study has been supported by the Dokuz Eylül University and The Scientific and Technical Research Council of Turkey. Mustafa Helvacı is gratefully acknowledged for his typing and drafting assistances which improved the manuscript. I would like to thank the reviews of P. A. Schroeder and İbrahim Uysal for their constructive comments and suggestions, which have considerably improved the final version of the manuscript.

Received: 03.04.2015
Accepted: 18.06.2015
Published: December 2015

References

Akdeniz, N., Konak, N. 1979. Simav–Emet–Dursunbey–Demirci yörelerinin jeolojisi [Geology of the Simav–Emet–Dursunbey–Demirci areas]. *Maden Tetkik ve Arama Genel Müdürlüğü Rapor* No: 6547, Ankara (unpublished).

Akkuş, M.F. 1962. Geology of the Kütahya-Gediz area. *Journal of Mineral Research and Exploration Institute of Turkey*, 58: 21-30

Cooper, M.A., Hawthorne, F.C., Garcia-Veigas, J., Alcobé, X., Helvacı, C., Grew, E. S., Ball, N. A. 2014. Fontarnauite, $(Na,K)_2$ (Sr,Ca) (SO_4) $[B_5O_8$ (OH)] $(H_2O)_2$, a new sulfate-borate from Doğanlar (Emet), Kütahya Province, Western Anatolia, Turkey. *Candian Mineralogist* (baskıda).

Çolak, M., Helvacı, C., Maggeti, M. 2000. Saponite from the Emet colemanite mines, Küthahya, Turkey. *Clays and Clay Miner*., 48: 409–423.

Ercan, T., Satır, M., Kreuzer, H., Türkecan, A., Günay, E., Çevikbaş, A., Ateş, M., Can, B. 1985. Batı Anadolu Senozoyik volkanitlerine ait yeni kimyasal, izotopik ve radyometrik verilerin yorumu (Interpretation of new chemical, isotopic and radiometric data on Cenozoic volcanics of western Anatolia). *Bullettin of Geological Society of Turkey,* 28, 121-136.

Ercan, E., Satır, M., Sevin, D., Türkecan, A. 1996. Batı Anadolu’daki Tersiyer ve Kuvaterner yaşlı volkanik kayaçlarda yeni yapılan radyometrik yaş ölçümlerinin yorumu [Some new radiometric ages Tertiary and Quaternary volcanic rocks from West Anatolia]. *Mineral Research Exploration Bulletin* (Turkey) 119, 103–112.

Ersoy, Y., Helvacı, C. 2007. Stratigraphy and geochemical features of the Early Miocene bimodal (ultrapotassic and calc-alkaline) volcanic activity within the NE-trending Selendi basin, western Anatolia, Turkey. *Turkish Journal of Earth Science*, 16, 117 - 139.

Ersoy, E.Y., Helvacı, C., Palmer, M.R. 2011. Stratigraphic, structural and geochemical features of the NE–SW-trending Neogene volcano-sedimentary basins in western Anatolia: implications for associations of supradetachment and transtensional strike-slip basin formation in extensional tectonic setting. J. *Asian Earth Sci*. 41, 159–183.

Ersoy, E. Y., Helvacı, C., Palmer, M. R. 2012. Petrogenesis of the Neogene volcanic units in the NE–SW-trending basins in western Anatolia, Turkey. *Contrib Mineral Petrol* (2012) 163:379–401.

Ersoy E.Y., Çemen, İ., Helvacı, C., Billor, Z. 2014. Tectono-stratigraphy of the Neogene basins inWestern Turkey: Implications for tectonic evolution of the Aegean Extended Region. *Tectonophysics* 635 (2014) 33–58.

Floyd, P.A, Helvacı, C, Mittwede S.K. 1998. Geochemical discrimination of volcanic rocks, associated with borate deposits: an exploration tool. *Journal of Geochemical Exploration* 60: 185-205.

Fytikas M, Innocenti F, Manetti P, Mazzuoli R, Peccerillo A, Villari L. 1984. Tertiary to Quaternary evolution of volcanism in the Aegean region. In The Geological Evolution of the Eastern Mediterranean, Dixon JE, Robertson AHF (eds). Special Publications 17. *Geological Society*: London; 687–699.

García-Veigas, J., Ortí, F., Rosell, L., Gündoğan, I., Helvacı, C. 2010*a*. Occurrence of a new sulphate mineral Ca_7Na_3 $K(SO_4)_9$ in the Emet borate deposits, western Anatolia (Turkey). *Geological Quarterly* 54, 431-438.

Garcia-Veigas, J., Rosell, L., Alcob, X.,Subias, I., Orti, F., Gündoğan, İ. and Helvacı, C. 2010*b*. Fontarnauite, a new sulphate-borate mineral from the Emet bo rate district (Tur key). Macla, 13: 97–98.

García-Veigas, J. , Rosell, L., Ortí , F., Gündoğan, İ., Helvacı, C. 2011. Mineralogy, diagenesis and hydrochemical evolution in a probertite–glauberite–halite saline lake (Miocene, Emet Basin, Turkey). *Chemical Geology* 280, 352–364.

Gawlik, J. 1956. Borate deposits of the Emet Neogene basin. *Mineral Research and Exploration Institute of Turkey* Report No. 2479, Ankara (Turkish and German Text) (unpublished).

Helvacı, C. 1977. Geolgy, mineralogy and geochemistry of the borate deposits and associated rocks and the Emet Valley, Turkey. PhD Thesis, University of Nottingham, England (unpublished).

Helvacı, C. 1978. A review of the mineralogy of the Turkish borate deposits. *Mercian Geology* 6: 257-270.

Helvacı, C. 1983. Mineralogy of the Turkish borate deposits. *Geological Engineering* 17, 37-54.

Helvacı, C. 1984. Occurence of rare borate-minerals: veatchite-A, tunellite, teruggite and cahnite in the Emet borate deposits, Turkey. *Mineralium Deposita* 19: 217-226.

Helvacı, C. 1986. Geochemistry and origin of the Emet borate deposits, western Turkey. Faculty of Engineering Bulletin, Cumhuriyet University, Series A. *Earth Sciences* 3: 49-73.

Helvacı, C. 1989. A mineralogical approach to the mining, storing and marketing problems of the Turkish borate production. *Geological Engineering* 34-35, 5-17.

Helvacı, C. 1995. Stratigraphy, mineralogy, and genesis of the Bigadiç borate deposits, western Turkey. *Economic Geolgy* 90: 1237-1260.

Helvacı, C. 2005. Borates. In : Selley R.C., Cocks, L.R.M and Plimer, I.R. (editors) Encyclopedia of Geology. *Elsevier*, December 2004, vol.3, p. 510-522.

Helvacı, C. 2015. Geological faetures of Neogene basins hosting borate deposits: An overview of deposits and future forecast, Turkey. *Bulletin of the Mineral Research and Exploration* (in press).

Helvacı, C., Firman, R.J. 1976. Geological setting and mineralogy of Emet borate deposit, Turkey. Transactions/section B, *Institute of Mining and Meatllurgy* 85: 142-152.

Helvacı, C., Stamatakis, M.G., Zagouroglou, C., Kanaris, J. 1993. Borate minerals and related authigenic silicates in northeastern Mediterraean Late Miocene continental basins. *Exploration Mining Geology* 2: 171-178.

Helvacı, C., Orti, F. 1998. Sedimentology and diagenesis of Miocene colemanite-ulexite deposits (Western Anatolia, Turkey), *Journal of Sedimentary Research* 68: 1021- 1033.

Helvacı, C., Alonso, R.N. 2000. Borate deposits of Turkey and Argentina : a summary and geological comparison. *Turkish Journal of earth Sciences* (Turkish J. Earth Sci.) vol. 24: 1-27.

Helvacı, C., Ortí, F. 2004. Zoning in the Kırka borate deposit, western Turkey: primary evaporitic fractionation or diagenetic modifications?. *Canadian Mineralogists* 42, 1179-1204.

Helvacı, C., Ersoy, E.Y. 2006. The facies characteristics and geochemical featuresof the volcanic rocks of the Selendi and Simav area, and their relations with the basin sedimentary rocks, western Anatolia. DEÜ. Bilimsel Araştırma Projesi No: 03.KB.FEN.058. January 2006, İzmir, 116 s.

Helvacı, C., Ersoy, Y., Erkül, F., Sözbilir, H., Bozkurt, E. 2006. Selendi Havzasının stratigrafik, petrografik, jeokimyasal ve tektonik veriler ışığında volkonosedimanter evrimi ve ekonomik potansiyeli. Türkiye Bilimsel ve Teknik Araştırma Kurumu Proje No: ÇAYDAĞ/103Y124, Aralık 2006, 134 s.

Helvacı, C., Orti, F., Garcia-Veigas, J., Rosell, L., Gündoğan, İ., Yücel-Öztürk, Y. 2012. NEOGENE BORATE DEPOSITS: Mineralogy, Petrology and Sedimentology; A workshop with special emphasis on the Anatolian deposits. International Earth Sciences Colloquium on the Agean Region, IESCA 2012, İzmir, Turkey, 64p.

Holzer, H. 1954. Geological report of the Beyce-54/4 and Simav-71/2 area. *Mineral Research and Exploration Institute of Turkey* Report. no. 2366, Ankara (unpublished).

İnan, K., Dunham, A.C., Esson, J. 1973. Mineralogy, chemistry and origin of Kırka borate deposit, Eskişehir Province, Turkey. Transactions/section B, *Institution of Mining and Metallurgy* 82: 114-123.

Kistler, R.B., Smith, W.C. 1983. Boron and borates. In: LEFONDS,S.J. (ed), Industrial Mineral and Rocks. 5th Edition, *Society of Mining Engineers of AIME*, 533-560.

Kistler, R.B., Helvacı, C. 1994. Boron and borates. In: CARR, D.D. (ed) Industrial Minerals and Rocks. 6th Edition, Society for Mining, Metallurgy and Exploration Inc., Littleton, Colorado, 171-186.

Lyday, P.A. 1982. Boron: Minerals Yearbook 1980, U.S. Bureau of Mines, 1: p 3

Orti, F., Helvacı, C., Rosell, L., Gündoğan, İ. 1998. Sulphate-borate relations in an evaporitic lacustrine environmet: the Sultançayır Gypsum (Miocene, Western Anatolia). *Sedimentolgy* 45: 697-710.

Özpeker, İ. 1969. Western Anatolian Borate Deposits and Their Genetic Studies. PhD Dissertation, İstanbul Technical University (in Turkish, unpublished).

Palmer, M. R., Helvacı, C. 1997. The boron istope geochemistry of the Neogene borate deposits of western Turkey. *Geochemica et Cosmochimica Acta* 61: 3161-3169.

Seyitoğlu, G., Anderson, D., Nowell, G., Scott, B.C. 1997. The evolution from Miocene potassic to Quaternary sodic magmatism in western Turkey: implications for enrichment processes in the lithospheric mantle. *Journal of Volcanology and Geothermal Research,* 76, 127-147.

Sunder, M.S. 1980. Geochemistry of the Sarıkaya borate deposits (Kırka-Eskişehir). *Bulletin of the Geological Society of Turkey* 2: 19-34.

Travis, N.J., Cocks, E.J. 1984. The Tincal Trail. A history of borax. Harrap, London, 311.