

IESCA-2012

POST COLLOQUIUM FIELD TRIP GUIDE-4

**Trip to Kışladağ (Uşak) Gold Mine,
Kırka and Emet Borates Deposits***

by

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ROAD LOG

Thursday, September 6th Departure from İzmir and drive to Kula Volcanics on the way to Uşak.

Kula Volcanics: The Mediterranean region is a complex collage of microplates of different compositions and geological history, which originated in response to late Cretaceous-Cenozoic convergence of Africa-Arabia with Eurasia when numerous continental, microcontinental and ophiolitic terranes amalgamated together. The closure of numerous pre-existing oceanic basins was facilitated by oceanic subduction, continental drift, microplate rotations and migration of subduction arcs. This complicated interaction between orogenic processes and widespread extensional tectonics was especially dramatic in eastern Mediterranean, where Tertiary volcanism of contrasting geochemistry has taken place.



Stop 1: The Kula Volcanics

Objectives

- To view alkali-basalt volcanic cones.
- Observe three different lava flows.
- Study other features of the Kula volcanics.

Thursday, September 6th Drive to Kışladağ Gold Mine :

Located in one of several mid to late Tertiary volcanic complexes in Western Turkey, related to subduction along the Hellenic Trench southwest of Turkey. In the Kışladağ region, the volcanoes erupted onto a basement of metamorphic schist at the northeast margin of the Menderes Massif. Hosted by a number of latitic intrusive bodies. A coarsely porphyritic latite is host to the bulk of the gold mineralization and has undergone extensive and intensive hydrothermal alteration. An early potassic phase of alteration is overprinted by later quartz-tourmaline and advanced argilic alteration. 135 Mt, 1.16g/t Au. The mine began commercial production on July 1, 2006. It is an open pit, heap leach operation with a planned 14 year mine life.

- * Spend most of the day at deposit.
- * Lunch at Deposit. Afternoon drive to Afyon.
- * Dinner and Accommodation: Afyon



Stop 2: Kışladağ Porphyry Gold Mine

Friday, September 7th Kırka Borate Deposit:

The world's largest borax (tincal) ore body. The most important B_2O_3 producer at present in the world, exhibits a symmetrical zonation in a lateral sense; it is comprised of a central body of Na borate (borax), an intermediate zone of Na-Ca borate (ulexite), and an marginal zone of Ca borate (colemanite) This mineral zonation is also developed in a vertical sense, although it is somewhat asymmetrical because of the presence of a discontinuous Mg borate horizon overlying the central body of borax. The genesis of such a mineral zonation in the Tertiary lacustrine borate deposits of the world has been attributed to a number of diagenetic processes.



Stop 3: Kırka Borate Deposit

* Spend most of the day at the mine. Lunch at Deposit.

- a. North of Afyon: The Tertiary Volcanic Rocks
- b. South of Kirka: The pyroclastic rocks in the Kırka Basin
- c. Sarıkaya Locality: The Main Ore Body-The Open-Cast Mine
- d. Sarıkaya Locality: The Upper Part of The Main Ore Body - The Open-Cast Mine
- e. Lepcek Locality: South of the Main Open-Cast Mine : The Old Kirka Mine Works

* Afternoon drive to Emet (Approximately 3 hours drive).

Saturday, September 8th Drive to Emet borate deposit

Emet is located 100 kilometres southwest of Kütahya, which was an important ceramic center in Anatolia in the past. The Emet borate deposits are situated in the middle of the known borate deposits of Western Anatolia. The Emet district includes Palaeozoic metamorphic rocks intruded by granite, and overlying Tertiary sediments associated with volcanic rocks. The deposits are mined by open-pit mining methods in the southern and northern basins.



Stop 4: Emet Borate Deposit

- a. Espey: North of the Emet basin.
The Open-Cast Mine (Former Under -Ground Mine)
Study borates and interbedded sediments with facies changes.
Weathering and alteration of borates and to study alteration textures.
- b. Göktepe: South of Emet Basin
Observation of natural outcropping of borate formation.
Colemanite alteration to calcite on surface outcrops.
- c. Hisarcık: The Main Open-Cast Mine In Southern Basin
Study the borate zone in the main open-cast mine.
Observation of various borate minerals (teruggite and cahnite).
Discuss the nature of colemanite nodules, primary and secondary phases.
- d. Hisarcık: South of Emet Basin
General stratigraphy and location of the borate zone within the sequence.
Related volcanic rocks and interbedded tuffs within the sequence.
- e. Hamamköy: South of Emet Basin, Thermal Springs
- * Evening return to İzmir.

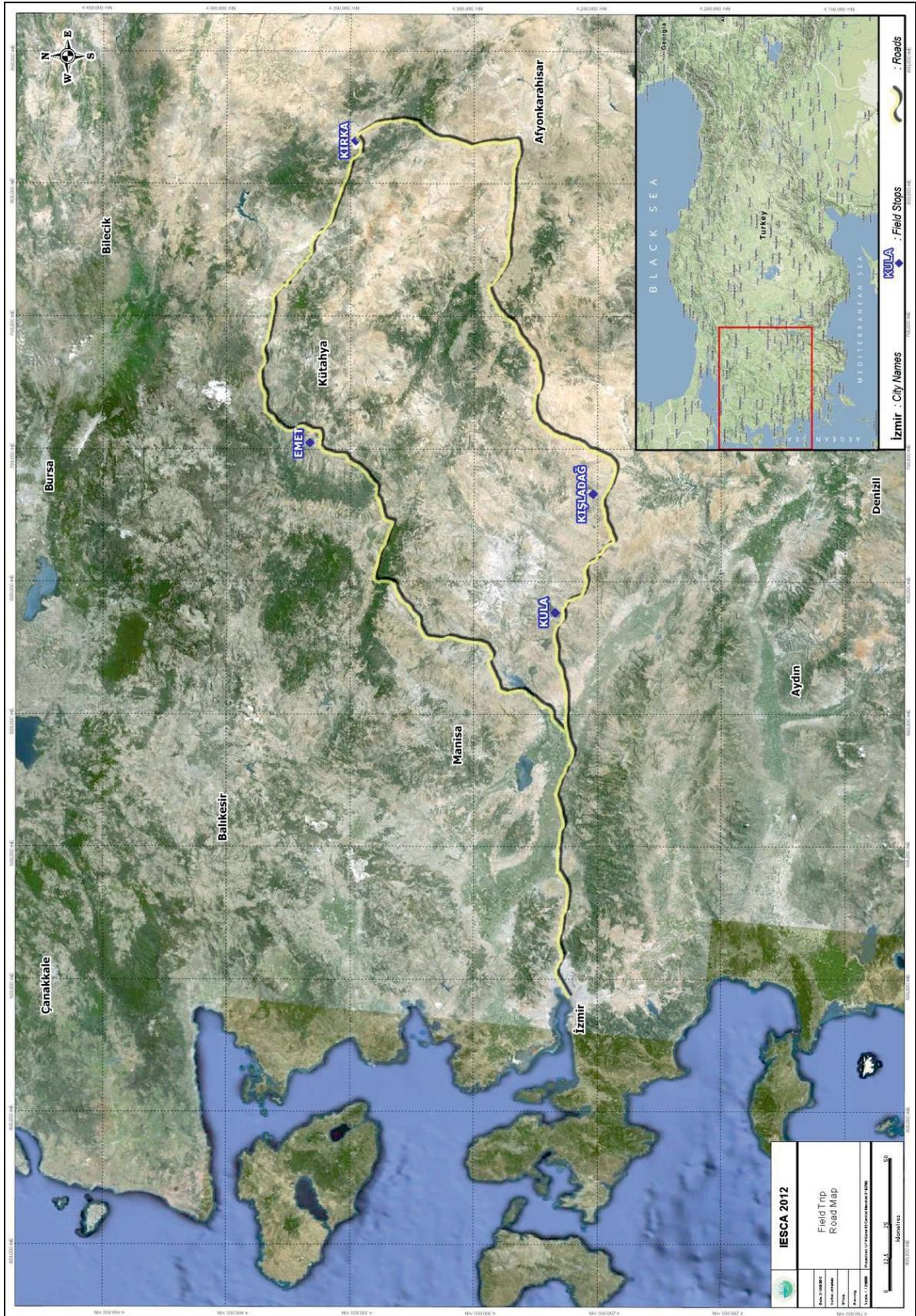


Figure 1. Field-trip log map (The field trip stops and the deposits are shown).

THE KULA VOLCANIC AREA

The General Overview of the Kula Volcanics

The Quaternary alkaline volcanism of Kula is located in a western Anatolian graben system that resulted from an Aegean extensional regime. The Quaternary volcanism of Kula occurred in response to N-S, extension, which resulted in the formation of ~80 monogenetic cinder cones, each with an associated lava flow comprising a total magma volume of ~2.3 km³ (Bunbury et al., 2001). The volcanism of the Kula area is represented by lava flows and monogenetic structures, such as cinder cones, maars. The Kula volcanic province is the best preserved in the field due to their young age, which makes them particularly appropriate for establishing the characteristics of alkalic basic volcanics. They crop out in a small area (~300 km²) adjacent to the western Anatolian active graben system. The volcanic cones are observed in a NW-SE and WNW-ESE direction, which is consistent with the trending of the grabens in western Anatolia. The main period of volcanism is between 1.7 Ma and 1.1 Ma to 0.025 Ma. The Kula volcanism exhibits three volcanic phases, namely from older to younger, Burgaz, Elekçitepe and Divlittepe volcanic rocks. The monogenetic volcanoes of Divlittepe preserve their original shapes (Fig.2).

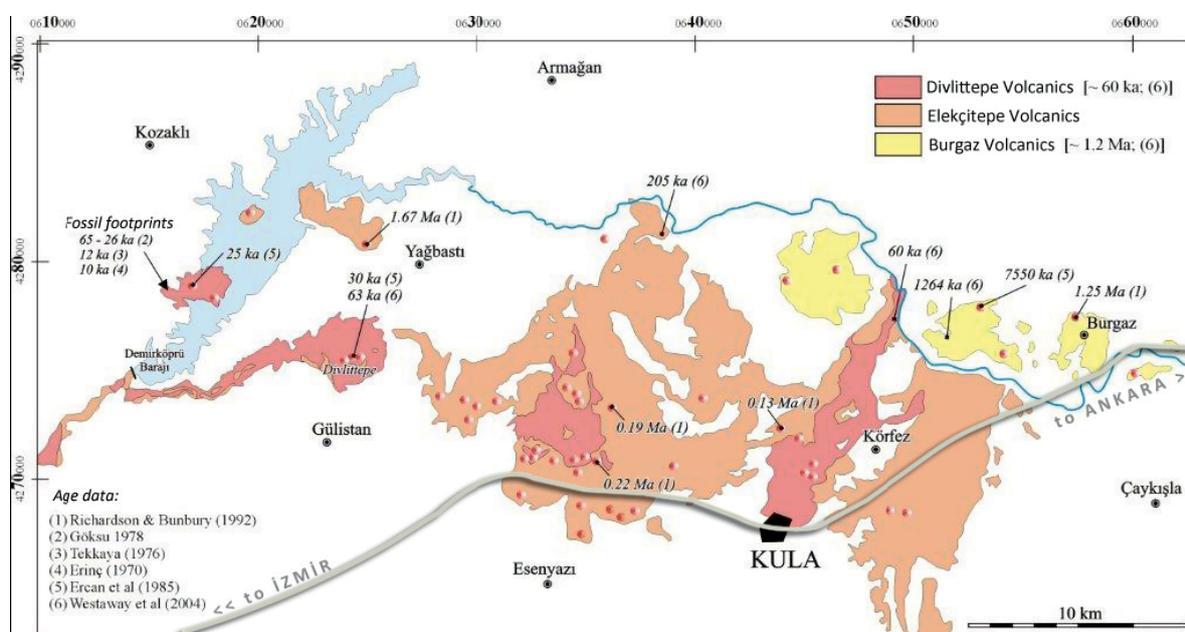


Figure 2. Simplified geological map of Kula area showing distributions of three phases of volcanics (from Alıcı et al., 2002)

The pre-Miocene rocks of the basement are metamorphic rocks comprising the Menderes Massif with a granite gneiss core, surrounded by mica-schists and marble (Ercan et al., 1980). Miocene sedimentary rocks are represented by fluvio lacustrine Kürtköyü and Yeniköy Formations (Ercan et al., 1980). The Kürtköyü Formation consists mainly of conglomerates with ultramaic fragments, and sandstones. The Yeniköy Formation is made up of intercalations of clastic and carbonate originated lacustrine sediments. Middle Miocene rocks comprise the Ahmetler and the Ulubey Formations consist mainly of fluvial and lacustrine sediments (Ercan et al., 1980). The Quaternary-aged units are sedimentary and volcanic rocks.

The typically silica-undersaturated, alkaline lavas of Kula are distinguished in three different sequences, namely Burgaz, Elekçitepe and Divlittepe, with a range of basanite, tephrite and phonotephrite compositions (Alıcı et al., 2002).

Quaternary volcanic rocks in the Kula volcanic field exhibit sodic alkaline features (K_2O/Na_2O ratio ranging between 0.3 and 0.7). They are characterized by low $87Sr/86Sr$ (0.703029-0.703490) and

high $^{143}\text{Nd}/^{144}\text{Nd}$ (0.512773-0.512941) ratios and have OIB- like trace element patterns characterized by enrichment in both LILE and HFSE. But, the enrichment levels of HFSE (Nb and Ta) and some trace element ratios (such as Rb/Nb and K/Nb) in the Kula lavas are higher than typical OIB, indicating the contribution of a lithospheric mantle source (Alici et al., 2002).

Depending on trace element and isotopic compositions, it is clear that the Kula lavas represent a mixture of melts from two distinct mantle sources. These melts have mainly originated from an OIB-like asthenospheric mantle, but melts from a lithospheric source occur as well. The asthenospheric mantle has affinities to a largely isotopically depleted mantle. The lithospheric component exhibits enriched trace element characteristics both in LILE and HFSE. Lithospheric contribution to the asthenosphere-derived melts could be responsible for the enrichment in all incompatible elements relative to the OIB composition.

KIŞLADAĞ PORPHYRY GOLD MINE

The General Overview of the Uşak Güre-Basin

The Uşak–Güre area forms an asymmetrical basin shape with a NE–SW-trending axis (overview in Fig. 3) that contains two distinct basins that developed in different geological periods: the Uşak basin in the eastern part of the study area and the Güre basin in the west. In geological section, the Güre basin is a symmetric open synform of 17 km width. In contrast, the Uşak basin is fault bounded along its western side, whereas at its eastern margins the Asartepe Formation lies unconformably on the basement rocks. The age data indicate that the Beydağı volcanism was active up to the Serravallian (late middle Miocene), and migrated from North to south with time. The radiometric age of the Beydağı and Payamtepe volcanic units is crucial, as it marks the timing of the depositional period of the İnay Group within all of the NE–SW-trending basins. Hence, the deposition of the İnay Group commenced at least *c.* 17 Ma ago. The depositional ages of the extremely deformed Hacibekir Group and the undeformed İnay Group are close, such that the maximum time interval between their formation is only 2–3 Ma. This age gap may represent the total uplift time of the basin margin. After the main extension, the development of the final dome geometry of the Menderes Massif Core Complex was initiated by the early Miocene NE-directed shortening, and this resulted in a high degree of folding of the basement and deposition of the early Miocene sediments. These structural elements were further accentuated by Serravallian to Pliocene high-angle faulting. Three distinct extensional tectonic phases and associated fault sets of high-angle normal faults with NE–SW trends faulted the previous NE–SW-trending low-angle normal faults, and determined the configuration of the western boundaries of the Menderes Massif and related volcanic centres. Finally, the NE–SW-trending tectonic elements resulted in the final shape of the Uşak–Güre basin.

The Uşak–Güre basin is a key area among the NE–SW-trending basins as (1) it contains a large amount of volcanic rocks developed in three major volcanic centers located on a NE–SW trend; (2) it is located in the eastern most part of the NE–SW-trending basins associated with exhumation of Menderes Massif (Fig. 3). The first stop comprises make observations on the metamorphic rocks of Menderes Massif, ophiolitic rocks of İzmir Ankara Zone and sedimentary rcks of the early Miocene Hacibekir Group, and structural relations to each other's (Fig. 4).

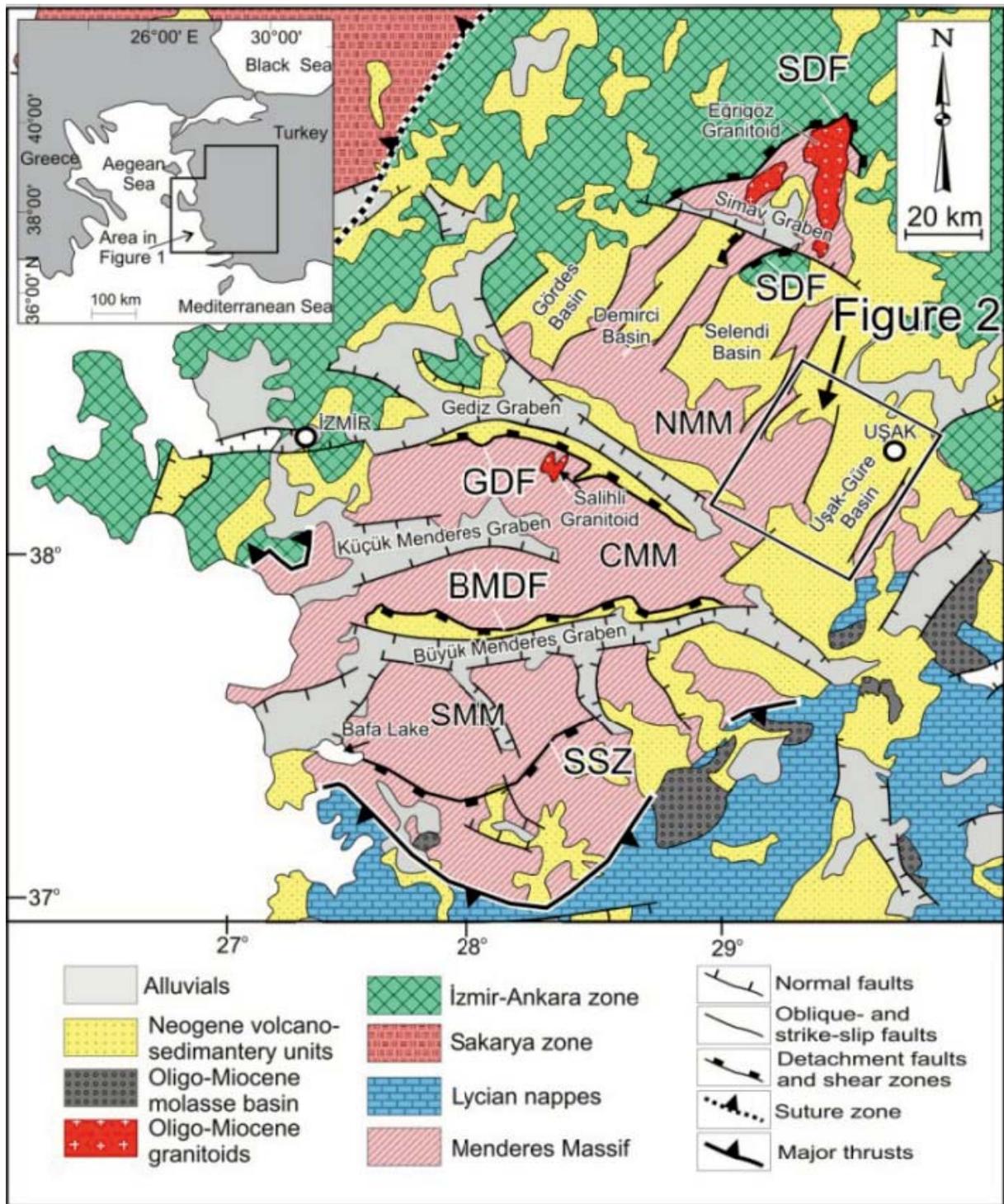


Figure 3 Geological map of western Anatolia showing the major tectonostratigraphic units on which the Neogene and Quaternary sedimentary basins developed. SDF, Simav detachment fault; GDF, Gediz detachment fault; BMDF, Büyük Menderes detachment fault; SSZ, Selimiye shear zone; NMM, Northern Menderes Massif; CMM, Central Menderes Massif; SMM, Southern Menderes Massif (Karaoğlu and Helvacı, 2012)

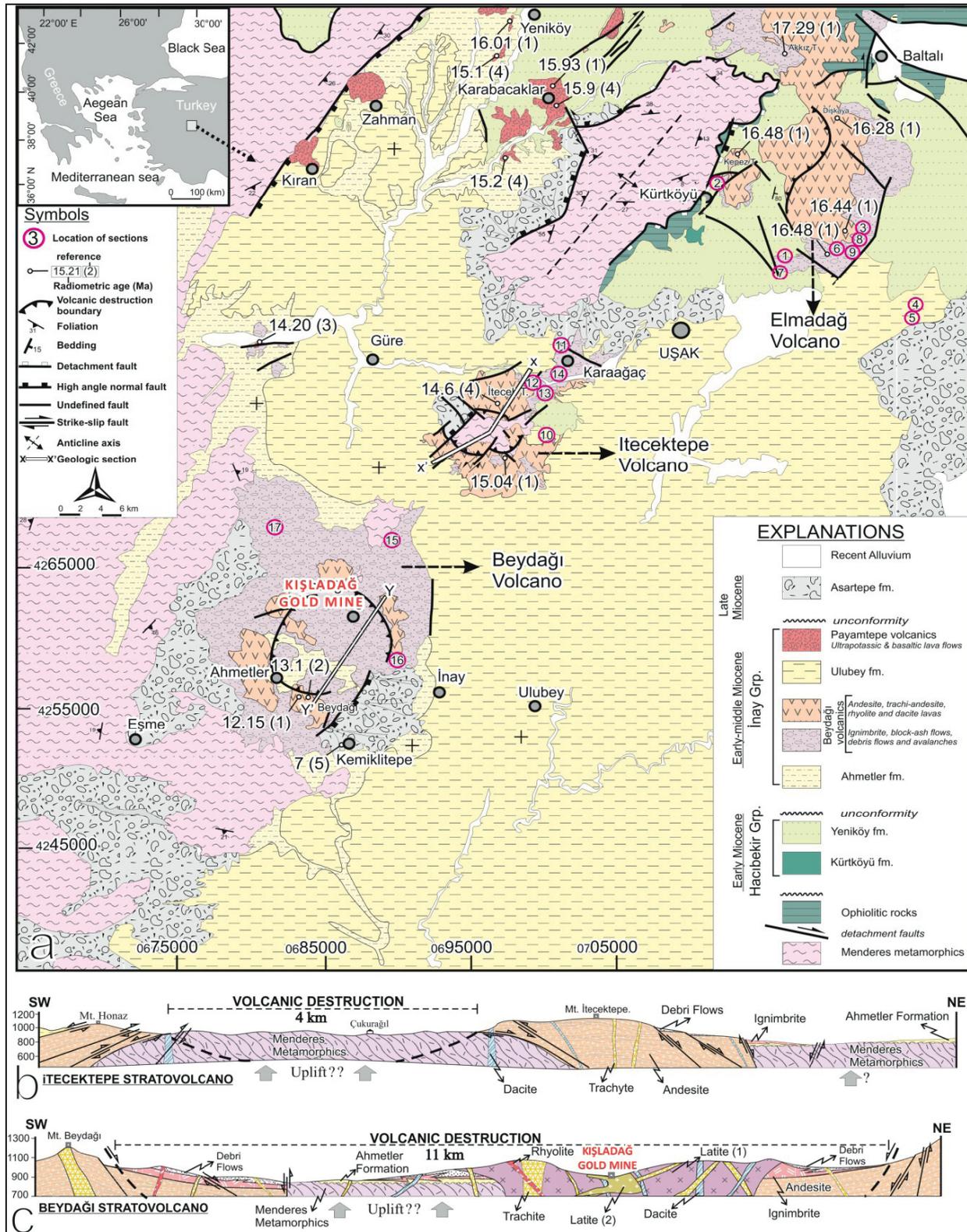


Figure 4. Geological map of the Uşak–Güre basin including radiometric age data from the volcanic rocks and a mammalian age from the Asartepé Formation (from Karaoğlu and Helvacı 2012).

The Beydağı volcanic edifice was constructed by many kinds of lava flows, domes and intrusive bodies prior to its destructive stage, including andesites, latites, trachytes, dacites, rhyodacites and rare basalts. Intrusive bodies show sub-volcanic textures cut by aplites were emplaced throughout the collapse area along with associated mineralization, including the Kışladağ gold deposit in the northern part of the volcanic center (Fig. 4).

Kışladağ Porphyry Gold Mine

Geology & Mineralization

Kışladağ lies within one of several mid- to late-tertiary volcanic complexes in western Turkey, related to subduction along the Hellenic Trench southwest of Turkey. In the Kışladağ region, the volcanoes erupted onto a basement of schist at the northeast margin of the Menderes Massif.

Gold mineralization is hosted by a number of latitic intrusive bodies. The Gökgöz Tepe alteration zone hosting the Kışladağ deposit covers approximately 12 square kilometers. At Gökgöz, a coarsely porphyritic latite is host to the bulk of the gold mineralization and has undergone extensive and intensive hydrothermal alteration. Gold mineralization forms an annular zone around a later weakly mineralized stock of similar composition. Gold is associated with multiple phases of tourmaline-pyrite, pyrite and quartz-pyrite veining and brecciation and is accompanied by small amounts of base metals, principally zinc and molybdenum. Oxidation in the deposit is shallow over the barren intrusive but extends to depths of 40 to 50 meters to the west and east.

Mining & Processing

Initial mining at Kışladağ was carried out by a local contractor using conventional earth-moving equipment. An owner-operated fleet of 150 tonne haul trucks and equivalent loading equipment was brought into operation in Q3 2008. Average ore production is 10,000,000 tonnes per year, with an additional 8,500,000 tonnes of waste moved annually.

A three-stage crushing system using a gyratory crusher and four cone crushers reduces the run-of-mine ore to 80% passing 6.3 mm in size for leaching. Conveyors are used to transfer and distribute the material onto the leach pad in 10 meter lifts for leaching. A conventional carbon adsorption facility (ADR plant) is used to recover the gold from process solutions to a final gold dore product (Fig. 5).

Basic Project Conditions are show in Table 1.

Table 1 Kışladağ Basic Project Conditions (data taken from:
<http://www.eldoradogold.com/s/Kisladag.asp?ReportID=356322>)

ROPERY SIZE	157 km ²
RESERVES (in ounces Au; at December 31, 2010)	
Proven + Probable	10,231,000 @ 0.74 g/t
RESOURCES (in ounces Au; at December 31, 2010)	
Measured + Indicated	12,189,000 @ 0.68 g/t
Inferred	4,384,000 @ 0.43 g/t
PRODUCTION (in ounces Au)	
2006	70,895
2007	135,306
2008	190,334
2009	237,210
2010	274,592
2011	284,648
2012 Forecast	285,000-295,000
CASH OPERATING COST (per ounce Au)	
2006	\$206
2007	\$189
2008	\$254
2009	\$280
2010	\$329
2011	\$374
2012 Forecast	\$385-395



Figure 5. Open pit pre-production mining area

KIRKA BORATE DEPOSIT

Introduction

Borate deposits of sedimentary origin constitute a particular case of lacustrine evaporite formations. In modern non-marine environments, a diversity of boratiferous bodies have small dimensions and a playa-lake setting, in general (Muessig 1966, Alonso 1986, Smith & Medrano 1996). The most important boratiferous deposits, however, formed in deeper lakes during the Tertiary (Kistler & Helvacı 1994, Helvacı & Alonso 2000; Helvacı & Orti, 2004). Three major groups of Tertiary borate formations have been differentiated (Smith & Medrano 1996): (1) Ca- and Na-Ca-borate formations, characterized by colemanite and ulexite facies; (2) Na-borate formations, characterized by the borax (and kernite) facies, and (3) Mg-bearing borate formations.

Studies of the largest Neogene Na-borate lake deposits known at present, including the Kramer deposit in Boron, California, and the Kirka deposit in Turkey, have led workers to their designation as "zoned" in the literature (Bowser & Dickson 1966). This term has a chemical and a mineralogical significance, but also involves a facies symmetry both in a lateral and a vertical sense. Thus, the Neogene zoned borate deposits have been described as having an outer envelope of Ca borates, an intermediate envelope of Na-Ca borates, and a core of Na borates. The origin of such a zonation, however, does not have a simple interpretation: for some authors, e.g., Inan *et al.* (1973) and Palmer & Helvacı (1995) it represents a primary, depositional feature, whereas for others, e.g., Smith & Medrano (1996) it is mainly the result of a number of diagenetic reactions that occurred between a pre-existing borate formation (the core) and external solutions (groundwater) seeping into it. Also the origin, either primary or diagenetic of some borate minerals within the zones has been the subject of debate, as is the case of colemanite in the outermost zones (Helvacı & Orti 1998) and the various Mg-bearing borates developed at the top of some deposits (Crowley 1996).

The Miocene Kırka borate deposit in western Turkey is currently the most active site of borax extraction in the world. The fact that the solubility of borax is more sensitive to thermal variations than is halite confers to this borate mineral great sedimentological significance (Bowser 1965). This deposit has undergone limited burial since its formation. Without doubt, the lacustrine Kırka borates is an excellent zoned deposit that will help (1) to learn more about the sedimentology and diagenesis of borax and borate minerals, in general; (2) to test the genetic discussion of the so-called Neogene zoned borate deposits, and (3) to compare this zoned pattern with the models of the most common evaporites (chlorides, sulfates) (Helvacı & Orti, 2004).

Geological and Stratigraphical Setting of Kırka Borate Deposit

The volcano-sedimentary, non-marine sequence filling the Kırka Basin in western Turkey (Fig. 6A, 7) is of Miocene age. This sequence, >400 m thick, rests unconformably on a varied substratum composed of Paleozoic metamorphic rocks, a Mesozoic ophiolitic complex, and Eocene limestones. The sequence (Fig. 8B, 9) is comprised of the following rock-units from base to top (Inan 1972, Helvacı 1977, Sunder 1980): (1) volcanic rocks and tuffs (80 m); (2) lower limestone (80 m); (3) lower clay with interbedded marls and tuffs (40 m); (4) borate unit (>70 m); (5) upper claystone, with tuff, marl and coal bands (60 m); (6) upper limestone containing cherty marls (>50 m), and (7) basalt (>30 m).

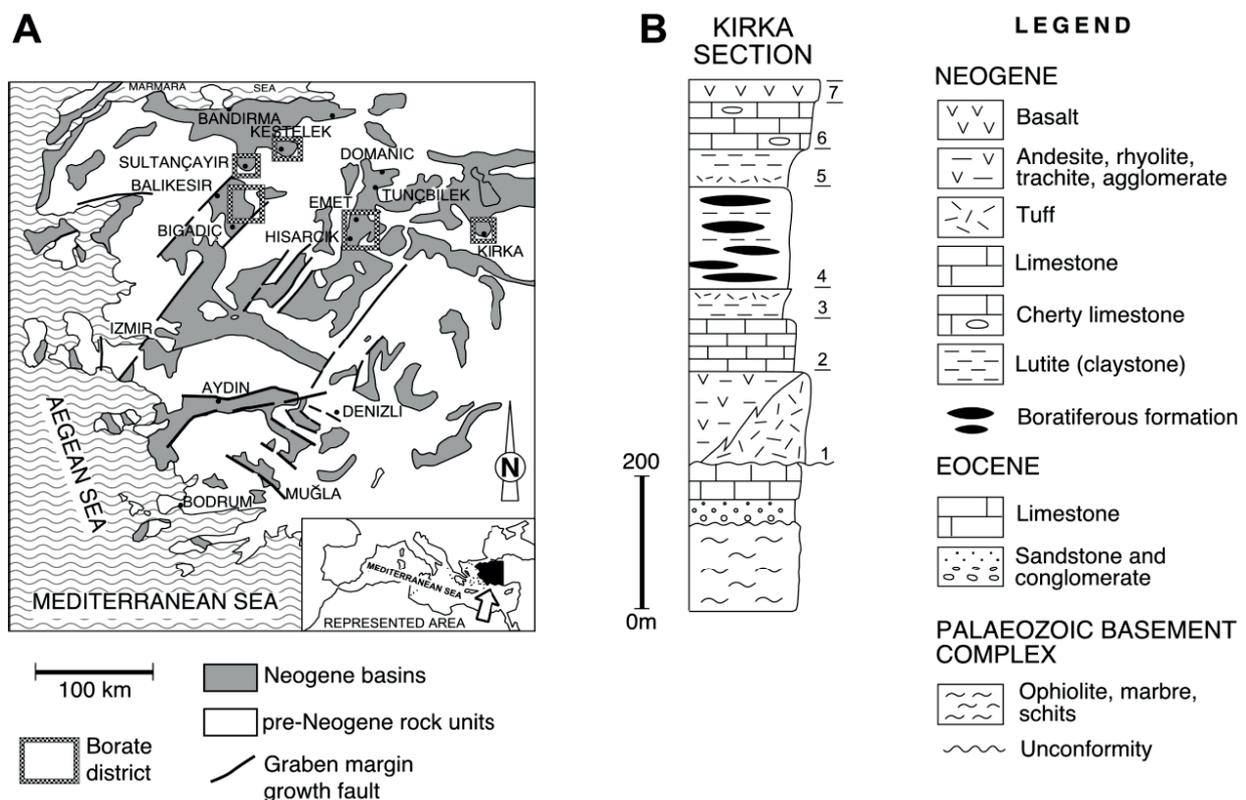


Figure 6. The Kırka borate district in western Turkey. A) Location of the deposit. The position of other borate districts (Kestelek, Bigadiç, Emet and Sultançayır) in this region is indicated. (B) Stratigraphic section of the Kırka borate deposit. Neogene rock units: 1: Tuffs; 2: Lower limestone; 3: Lower clay, marl and tuff; 4: Borate unit; 5: Upper clay, tuff, marl and coal bands; 6: Upper cherty limestone; 7: Basalt (after Helvacı & Orti, 2004).

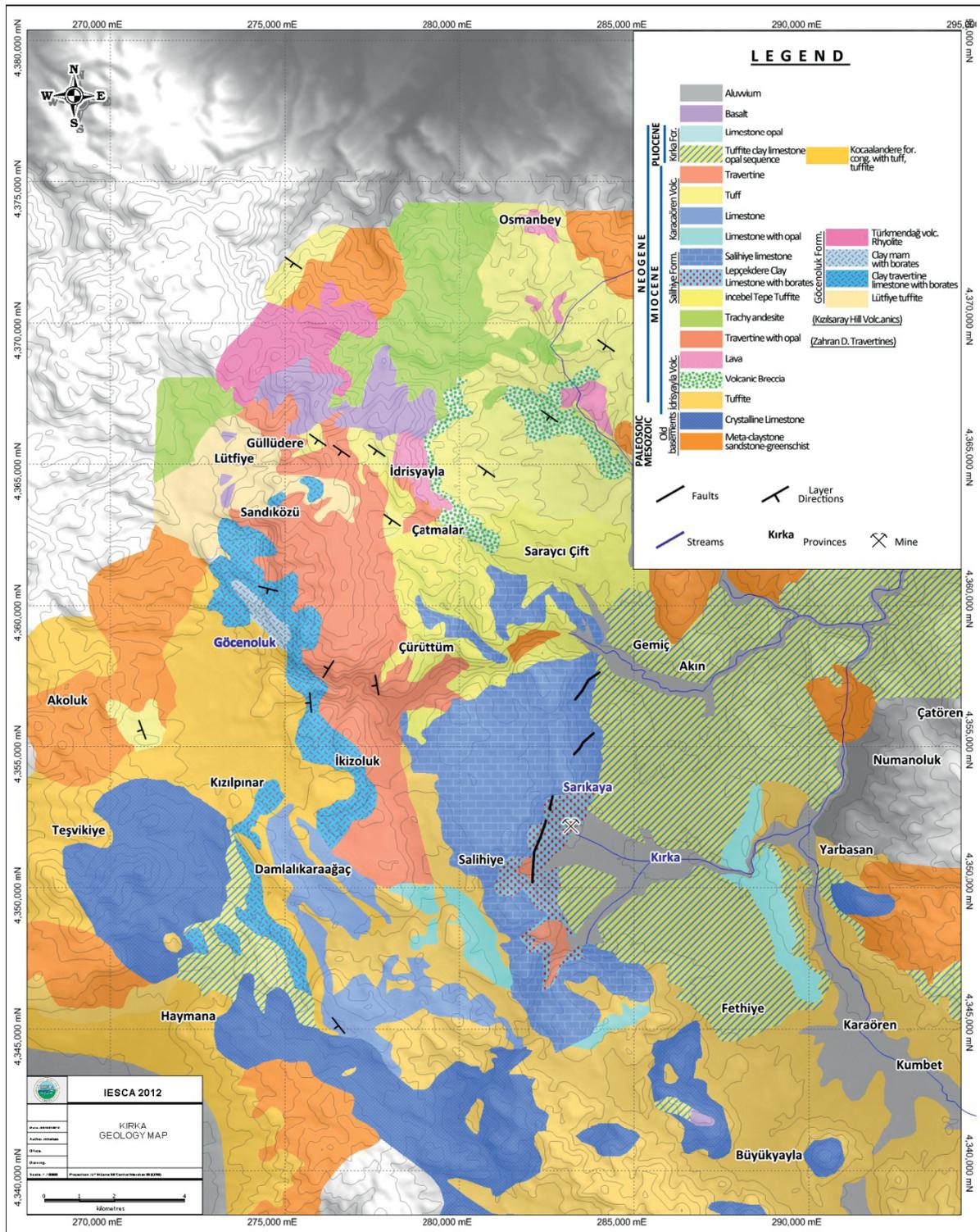


Figure 7. Geological map of Kırka borate district (after Gök et al., 1980).

The borate unit, locally up to 145 m in thickness, was deposited in a lacustrine setting. The borate layers in this unit are interbedded with claystones and tuffs. The main borate minerals are borax, ulexite and colemanite, which are the ore minerals of the commercial-grade bodies (Table 2). Borates of calcium, sodium, magnesium and strontium are formed in subordinate amounts (Inan *et al.* 1973, Helvacı 1978, 1983, Çolak, 1995). The clay layers are made up of smectite-group minerals, mainly hectorite (Çolak 1995) and subordinate illite and chlorite; these layers also contain some volcanic tuffs (commonly altered to zeolites), quartz, biotite, and feldspar (Helvacı 1983, Helvacı *et al.* 1993). Dolomite is the main carbonate mineral accompanying the clay; minor amounts of magnesite, strontianite and calcite are also present (Çolak 1995).

Ca-borates	
Inyoite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$
Meyerhofferite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
Priceite	$\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$
(pandermite)	
Na/Ca-borates	
Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
Probertite	$\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$
Na-borates	
Borax (tincal)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$
Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
Mg-borates	
Inderite	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$
Kurnakovite	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$
Inderborite	$\text{CaMgB}_6\text{O}_{11} \cdot 11\text{H}_2\text{O}$
Hydroboracite	$\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$
Sr-borates	
Tunellite	$\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$

The borax unit in the area of the Kırka district constitutes the only sodium borate orebody in Turkey, with a B_2O_3 content of 20-25%. The Kırka borate deposit, elongate in a N-S direction, is bounded by faults at the eastern and western parts. The western fault is a normal fault that caused a number of slump features. The borax body is enveloped by a thin ulexite-dominant facies followed outward by a colemanite-dominant facies. Stratigraphical, geomorphological and structural estimates in the borate area and throughout the Kırka Basin, suggest that the borate formation underwent only moderate burial after its accumulation (< 300 m), as typical of other borate-bearing Neogene basins in western Turkey (Helvacı & Yagmurlu 1995). The boron in the Kırka deposit is assumed to have been derived from the hydrothermal activity associated with intense contemporaneous calc-alkaline volcanism in the region (İnan *et al.* 1973, Palmer & Helvacı 1995, Floyd *et al.* 1998) and the leaching of country rocks, mainly Paleozoic aluminosilicate rocks and Eocene limestones (Palmer & Helvacı 1997).

Previous investigations

The first descriptions of the lacustrine Kırka borates were done by İnan (1972) and İnan *et al.* (1973). These authors observed in this deposit a symmetrical zoning consisting of the following mineral sequence from base to top: calcite - colemanite - ulexite - borax - ulexite - colemanite - calcite. This zonation was considered to be primary, although the colemanite was interpreted as derived from the alteration of an inyoite precursor.

İnan *et al.* (1973) also considered that the primary precipitates are characterized by subhedral to anhedral habits and fine-grained textures, whereas the secondary precipitates are characterized by (1) an euhedral habit and a large size of the crystals, (2) their particular facies geometries, and (3) their particular relationships with both the stratification and the other borates. In accordance with this classification, İnan *et al.* (1973) interpreted as primary the laminated facies of fine-grained borax

laminae (<1 cm across), the columnar facies of ulexite, and some fine-grained textures of inyoite. They considered to be secondary the coarsely crystalline borax facies, some nodular ulexite facies, and the minor occurrences of meyerhofferite, tunellite and the Mg borates.

Palmer & Helvacı (1995, 1997) carried out isotopic studies on the Kırka borates and concluded that not only ulexite and borax, but also colemanite corresponds to a primary precipitate. Garret (1998) discussed some values of the different impurity contents of the borate minerals at Kırka. Çolak (1995) investigated the claystone beds overlying the borax body and determined the mineralogical and chemical type of smectite-group characterizing the clay minerals and the associated carbonate minerals (dolomite, calcite, magnesite and strontianite). Orti & Helvacı (2000) proposed the subdivision of the depositional sequence of Kırka into two cycles.

According to the published descriptions, mainly those of Inan *et al.* (1973), Helvacı (1977) and Helvacı & Alonso (2000) the geometrical pattern, stratigraphic framework, and distribution of borate facies in the Kırka deposit is shown in Figure 8.

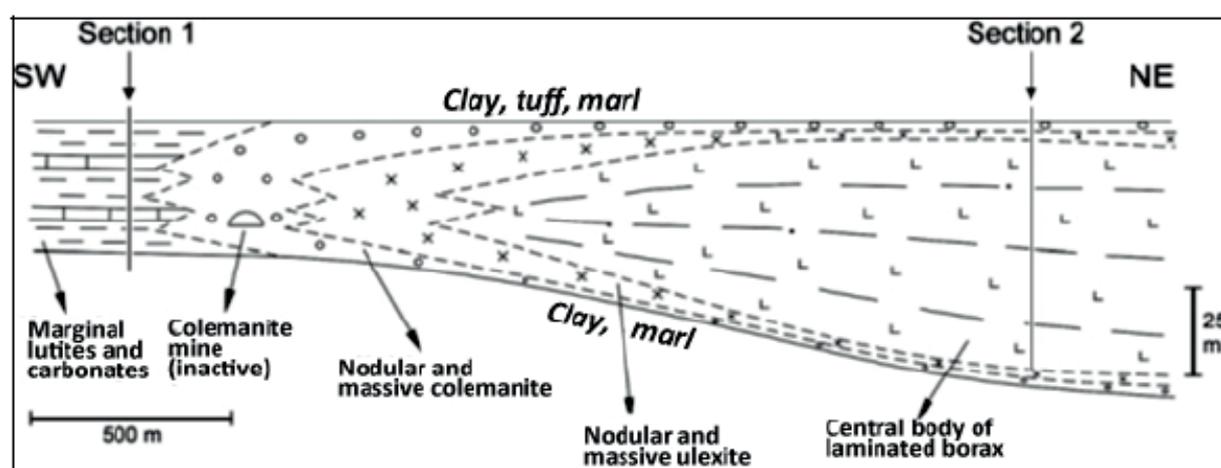


Figure 8. Interpretative scheme of the facies distribution in the Kırka borate unit Section 1 is in the marginal part of the deposit and Section 2 is in the central part of the open-pit mine. Also, the location of an ancient colemanite mine is indicated (after Helvacı & Orti, 2004).

Distribution and relationship of the minerals in the Kırka Deposit

In the Kırka borate deposit the mineral assemblages (with some exceptions) show sequences of precipitation-presumably a function of solubility effects as commonly observed similar to lacustrine evaporite. The most characteristic sequence of mineral formation in the Kırka borate deposit is shown in Fig. 9 a trend from carbonate-borate-carbonate being evident.

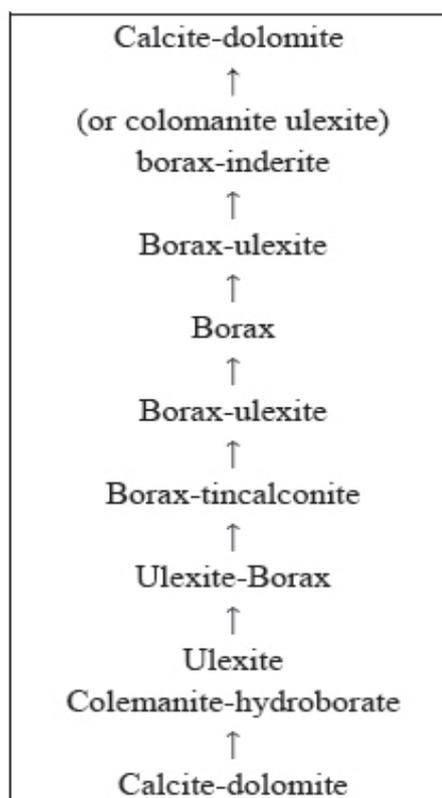


Figure 9. Mineral formation sequence in the Kırka deposits (İnan, 1972;Helvacı,1997)

This trend is considered to represent one cycle of deposition. A further important feature is the coexisting of carbonate in the form of calcite and dolomite with borates at every stage of precipitation, except in the pure monominerallic zones (borax zones) (İnan, 1972; Helvacı, 1997; Helvacı ve Alanso, 2000).

Borax does not, however, coexist with colemanite in any part of this deposit. These minerals are always separated by clay layers, or by ulexite, which form a 'bridge' between borax and colemanite where the precipitation assumed is continuous. This has also been observed by Bowser (1954) in a western U.S.A. deposit.

In the Kırka borate deposit, however existing borax ulexite and colemanite-ulexite pairs are found. Inyoite and meyerhofferite are detected in small quantities from the early stages of mineral precipitation. They are mainly altered. Colemanite is also found as pseudomorphous after ulexite hypothesis that colemanite is a secondary mineral in some parts of the deposit; nevertheless, some colemanite in the Kırka borate deposit does not show secondary features. The answer to this contraditic experimental studies on the system $\text{CaO-Na}_2\text{O-B}_2\text{O}_3\text{-H}_2\text{O}$ at higher temperatures ($>25^\circ\text{C}$) and in the presence of other soluble salts. Colemanite may also be associated with hydroboracite. This mineral pair is restricted to the early stage of crystallization. Inderite is located in the ulexite-borax zone; it forms not continuous layers but lenticular masses. Tunellite is found in many parts of Kırka deposit, especially in the northwest of the area (İnan 1972; Baysal, 1972 and 1973; Helvacı, 1977; 1984, Helvacı and Alanso, 2000). Lateral changes in mineral distribution are also observed in the deposit. At the more important (Helvacı and Orti, 2004).

Mineralogical Description of Borates Minerals in the Kırka Deposit

The principal minerals in the Kırka borate deposit are borax with colemanite and ulexite. In addition, tincalconite and kurnakovite are found. It should be noted that this deposit is the only deposit so far known in Turkey to contain any of the mineral borax, tincalconite, kernite and kurnakovite. (Gawlik, 1955; İnan, 1972; Meixner 1953; Özpeker, 1969; İnan et.al., 1973: Helvacı, 1978 and 1983).

The mineralogy and geochemistry of the deposit make it unique among other Turkish borate beds, which are known to contain Na borate (borax, tincalconite, kernite) Ca borate (colemanite, inyoite, meyerhofferite), Na-Ca borate (ulexite), Mg-Ca borate (hydroboracite) arsenic sulphides (realgar and orpiment), gypsum and celestite (Özpeker, 1969; Inan et al. 1973; Baysal, 1972; Helvacı, 1983). Chemical analyses, xray diffraction, optical studies and differential thermal analyses show that the borate layers contain various hydrated borate minerals, calcite and dolomite, and in clay parting, which have some tuff layers, quartz, biotite and feldspar are found. The clay is made up entirely of simectite-group minerals (Inan et al., 1973; Helvacı et al., 1993).

Borate minerals in Kırka deposit are found to occur as (a) thin layers interbedded with clay, sometimes brecciated; (b) disseminated crystals in the clay matrix; (c) massive borate; and (d) vugh fillings. This behaviour is believed to be either the manifestation of the environment in which the borate minerals were formed or due to post-depositioanl events (Helvacı and Orti, 1998).

Some individual borate minerals from the deposit were chemically analysed and the results obtained are given in Table 4.

Table 3. Chemical analyses of some borate minerals from the Kırka deposit (after Helvacı, 1977).

Oxide %	Tincalconite	Ulexite	Borax and Tincalconite mixture	Ulexite	Tunellite	Kernite	
B ₂ O ₃	45.954	43.392	40.573	41.223	54.878	50.092	50.092
CaO	0.112	13.524	3.598	13.356	0.157	0	0
MgO	0.409	0.793	2.902	0.837	0.528	0.009	0.002
Na ₂ O	21.394	7.98	18.071	8.274	0.136	20.1	20.68
SrO	0.004	1.688	0.238	0.214	27.455	0	0
As ₂ O ₅	0.001	0.001	0.009	0.001	0.017		
SiO ₂	0.064	0.556	2.093	2.414	0.128		
TiO ₂	0	0	0	0.018	0		
K ₂ O	0	0	0.049	0.649	0		
H ₂ O ⁺	31.322	32.169	30.487	31.97	18.464	25.72	24.78
SO ₃	0.544	0.345	0.497	0.577	0.06		
Total Ppm	99.705	100.448	98.517	99.533	101.823		

Borax (Na₂B₄O₇·10H₂O)

Borax is the most abundant mineral found in the deposit and for this reason this deposit is usually called a borax deposit. The highest concentrations of borax are in the central part of the deposit, at the Sarıkaya locality. Fresh, pure borax is colourless and transparent, but in places, where it is fine-grained and interbedded with clay, it is light pink, yellowish orange or grey due to fine inclusion of foreign material. Borax occurs mainly as subhedral and unhedral crystals 1mm-1cm in size (Helvacı and Orti, 1998).

Large masses of subhedral borax crystals are usually found in the cavities created after burial. Borax crystals which cut across the bedding plans have elongated euhedral and subhedral forms and are extremely large, up to 10m in length and 2m in diameter. Borax is also observed as disseminated individual crystals in the clay matrix and as borax-clay beccia. Borax occurs chiefly in almost monominerallic zones interbedded with clay. In many places tincalconite forms a thin film on the exposed part of borax crystals and borate shows a transformation into ulexite at borax-clay interfaces (Inan et al., 1973; Helvacı, 1978, 2005).

Tincalconite Na₂B₄O₇·5H₂O

Tincalconite does not form independent crystals in this deposit but occurs only as an alteration product of borax. The fine microscopic crystals of tincalconite develop very rapidly on borax crystals in contact with a dry atmosphere (Inan et al., 1973; Helvacı, 1978).

Kernite $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$

Kernite has a restricted distribution and is found only at one locality in the underground workings of Kırka deposit. New kernite crystals may be found when the underground workings advance. It is developed in the deeper part of the sodium borate body at Kırka (Helvacı, 1977).

It occurs as colorless, transparent but sometimes white elongated needle-shaped, or group of needle-shaped, crystals which are surrounded by a zone of borax. Individual crystals vary in their length, which is up to 10 cm. Kernite alters by dehydration to white tinalconite which occurs as fine-grained coating on kernite crystals that have been exposed to the atmosphere.

Ulexite $\text{NaCa}_2\text{O}_9 \cdot 3\text{H}_2\text{O}$

Ulexite is the only mineral of the Na, Ca borate series found in this deposit. It occurs throughout, especially in the lower and upper parts enveloping the borax zone, and as a dominant mineral near the edges of the deposit. The ulexite is predominantly massive and fibrous, but there is great variation in texture. In the southern part hard cauliflower-like nodules composed of randomly orientated crystals, 1-5 cm long, from independent layers up to a few metres in thickness. Elsewhere, columnar, cone, rosette and cotton ball textures are observed. Cone and rosette-shaped aggregates of ulexite are found as pseudomorphs after borax on the borax layers at borax-clay interfaces (Helvacı and Orti, 1998). The colour is usually white, and sometimes grey. Ulexite is commonly associated with borax, colemanite and inyoite in borate layers, and with kurnakovite and tunellite in clay layers.

Inyoite $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$

Inyoite occurs predominantly at the southern edge of the deposit, on the top of colemanite layers. It is found as both grown crystal masses and discrete tabular crystals, colourless to white. A few of the crystals are 4-5 cm long, but most are in microscopic scale and altered. Inyoite is found mainly in the Ca borate zone, but some times in the Na, Ca borate zone. It is clearly associated with colemanites, meyerhofferite and ulexite (İnan et al., 1973; Helvacı, 1977).

Meyerhofferite $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$

Meyerhofferite occurs mainly among other Ca borate minerals, and the samples found so far are microscopic crystals as an alteration product of inyoite. It coexists with colemanite and inyoite and sometimes with ulexite (İnan et al., 1973; Helvacı, 1977).

Colemanite $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$

Colemanite is the most abundant mineral of the calcium borate series found in this deposit. It occurs in the lower and uppermost parts of the deposit, where it is found both as individual nodules and geodes a few millimeters to 50 cm in diameter and as continuous layers. It shows elongated and short prismatic forms. The individual crystals which make up the aggregates are colourless, gray to pink. The colemanite geodes studied here have hollow centers with radiating cracks. The hollow parts are sometimes filled with liquid or with second-generation colemanite (Helvacı, 1977).

Hydroboracite $\text{CaMgB}_4\text{O}_{11} \cdot 6\text{H}_2\text{O}$

Hydroboracite is found as small white nodules in clay layers in the central and northern parts of the deposit. It is associated with tunellite, colemanite and ulexite.

Kurnakovite $\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$

Kurnakovite is found in the upper part of the deposit and forms a non continuous layer in the clay just above the main borate body. The kurnakovite layer consists largely of 1 to 20 cm long individual, colourless, grey or sometimes pink elongated, euhedral crystals and crystal aggregates.

Tunellite $\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$

Tunellite occurs in very small amounts, its appearance is limited to the clay layers and it is found as either individual flattened crystals or crystal aggregates. It is colourless and has perfectly developed cleavage, which causes a resemblance to muscovite flakes. It coexists with hydroboracite and ulexite.

Lake Model for the Kırka Borax Sequence

Inan et al. (1973) proposed for the Kırka borate deposit a perennial lake in which the initial zonation of minerals (calcite-inoite-ullexite-borax) occurred on the lake floor under an evaporative control and a lateral gradient of concentration (evaporitic-primary zones). No mention, however, was made to the existence of desiccation phases, or to a temperature control on the borax crystallization. These authors also assumed a contemporaneous, subaqueous (free) precipitation of inoite and ullexite at the margins of the lake, and of borax at the center. This last assumption, however, seems to be inappropriate, given the relatively small size of the lake and the presumed homogeneity of the water mass (Fig. 9). Inan et al. (1973) attributed the most important post-depositional changes in this deposit (the inoite-to-colemanite transformation; the reaction between primary borates and Mg-enriched liquids from the clays to form Mg-bearing borates) to interstitial solutions and circulating groundwater, either in the context of syndepositional conditions, or during early or burial diagenesis (secondary zonation).

Smith & Medrano (1996) agreed that the Kırka deposit accumulated in a perennial, borate-rich lake that periodically (seasonally) precipitated uniformly thick beds of borax. However, these authors considered that the mineral zonation resulted from late reaction diagenesis (secondary zones), as for the rest of the Neogene borate deposits, in general.

In contrast, Helvacı (1977) proposed a playa-lake setting for the Kırka deposit, and Palmer & Helvacı (1995, 1997) considered that the mineral zonation is primary: colemanite, ullexite and borax could have precipitated separately from boratiferous solutions with increasing alkalinity under an evaporative control (evaporitic-primary zones). Çolak (1995) interpreted all the borates interbedded with the claystone bed above the borax as deposited in small pools on a playa-lake environment. Ortí & Helvacı (2000) interpreted as primary the mineral zonation (colemanite- ullexite-borax), and suggested that the borax formed at variable depths in the lake, from relatively deep water to subaerial conditions.

In the interpretation of the borax lake of the Kırka deposit proposed here (Fig.16B), Helvacı and Ortí (2004) also considers an evaporitic-primary origin for the mineral zonation, and combine the presence of a lateral gradient of salinity together with changes in subenvironment from the margins to the lake center (as commonly occurs in other evaporitic lacustrine systems). Massive precipitation of borax was only achieved by intense evaporation acting on a free mass of water during the lake stage, whereas the underground boratiferous brines during both the initial and the final playa-lake stages always remained Ca-rich. During the lake stage, borates of Ca and Na-Ca formed interstitially in an exposed (or very shallow) lake margin, at the same time than free-crystallizing Na borates occurred in the lake center (Helvacı & Ortí, 2004).

Helvacı & Ortí (2004) interpreted that the carbonate is not viewed as the most external zone of the borate deposit, as opposed to Inan et al. (1973). This is because: (1) the carbonate units underlying and overlying the borate unit have great regional extent and are clearly independent of the local borates; (2) the borate unit is mainly enveloped by claystone beds, and it grades laterally to claystone and marls. Thus, the change from a carbonate to a borate sedimentation in the Kırka lacustrine systems is not viewed as a simple change in the chemistry of the same lake. In contrast, it implies the destruction of the carbonate lake in this area and the progressive installation of a local boratiferous lake.

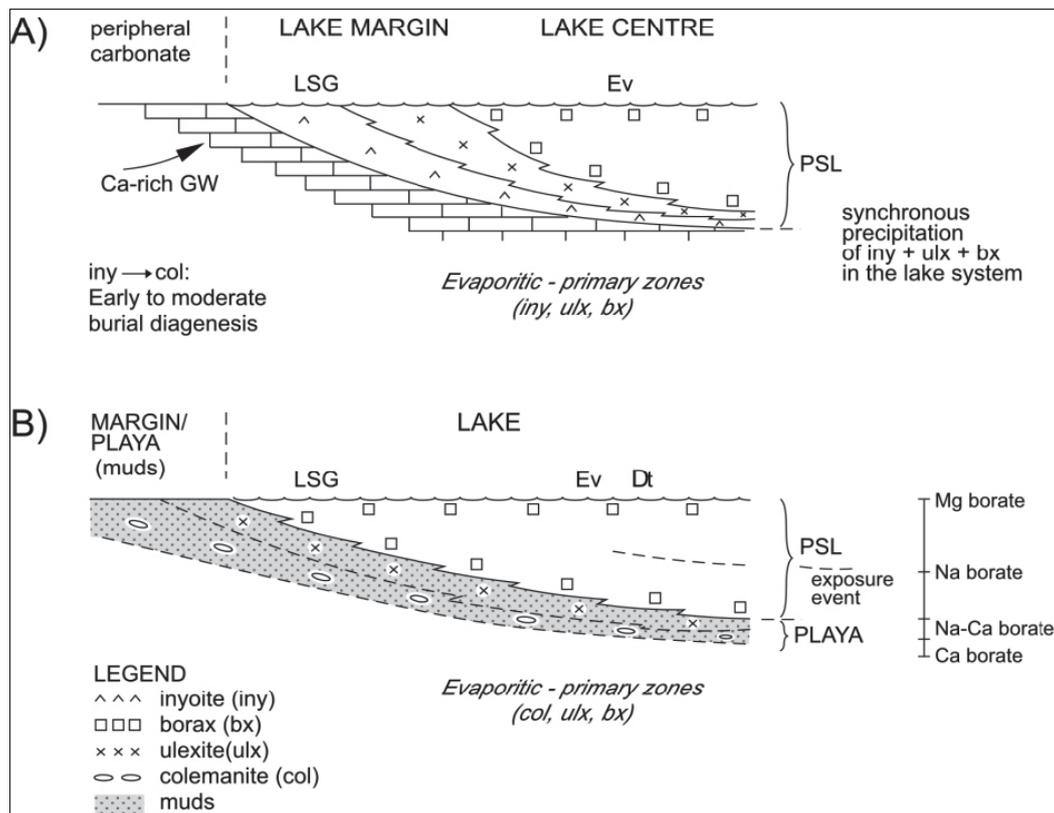


Figure 9. Diagrams summarizing the most relevant features of two interpretations of the zoned Kırka borate deposit (Miocene, Turkey). In the two cases, the diagrams represent the deposition at the end of the borax sedimentation. In diagram A, the formation of Na–Ca- and Ca-borate zones overlying the central body of borax follows the same pattern as in the underlying zones. The same is valid in diagram B, although the Mg-borate layer at the top of the central body (not represented in the diagram) would correspond to a new evaporitic-primary zone in the depositional system. (A) Diagram based on Inan et al. (1973). Subaqueous deposition of borate occurs in the Kramer perennial lake. No events of exposed deposition are recognized in the lake. (B) Diagram based on Orti & Helvacı (2000) and this paper. Subaqueous to exposed deposition of borax occurs in the Kırka lake. Symsedimentary, interstitial crystallization occurs in the external zones (after Helvacı & Orti, 2004).

Presumably, this change was caused by regional tectonism or volcanic activity (or both), together with local faulting, hydrologic changes, and a ready supply of boratiferous solutions in the Kırka area. Other considerations were made by Helvacı & Orti (2004) favor the evaporitic-primary interpretation of the external zones in Kırka instead of the mechanisms involved in the early reaction diagenesis:

(1) Above the borax body, it is difficult to envisage the formation of an envelope of ulexite by mixing solutions (chemical-primary zone) once the borax sedimentation was finished and no more Na-borate brine was being generated. However, the presence of such ulexite layers is common to all Neogene deposits, where they are separated from the borax body by claystone beds, devoid of signs of borax replacement by ulexite.

(2) The repetitions, in some Neogene borate formations, of complex elementary sequences cannot be explained satisfactorily by any variant of the reaction diagenesis. In northwestern Argentina, the Miocene Loma Blanca deposit repeats several times the sequence "inyoite - ulexite - borax" (Alonso et al. 1988) and the thick borate unit of the Monte Amarillo Member in the Miocene Sijes Formation repeats several times the sequence "gypsum (+colemanite) - hydroboracite (+gypsum) - hydroboracite" (Helvacı & Alonso 2000, Ortı & Alonso 2000).

(3) It is possible that the importance of the marginal zones in some Neogene borate deposits could have been underestimated. This seems to be the case of the Ca-borate external zone (colemanite) in Kırka.

(4) The consideration of the Ca-borate external zone as a result of reaction diagenesis instead of an evaporitic-primary zone is largely based on the interpretation that colemanite derives from the transformation of inyoite or from the replacement of ulexite (secondary zone). In contrast, the interpretation of colemanite as a primary borate is based on petrographic and sedimentologic evidence, as mentioned above.

EMET BORATE BASIN

The Emet borate deposits are situated in the middle of the known borate deposits of western Anatolia (Helvacı 1977, 1984, 2005; Helvacı and Alonso, 2000). The Emet district includes Paleozoic metamorphic rocks intruded by granite, and overlying Tertiary sediments associated with volcanic rocks (Holzer 1954; Gawlik 1956; Akkuş 1952) (Figure 10).

The principal minerals in the Emet borate deposits are colemanite and probertite, with minor ulexite, hydroboracite and other trace rare occurrence of borate and sulphate minerals. In addition, meyerhofferite, veatchite-A, tunellite, terrugite, cahnite, fontarnauite, kaliborite, aristarainite, tunellite, glauberite, thenardite, emetite, kalistrontite, arsenopyrite occur sporadically. The deposits are mined by open-pit mining methods in the southern basin (Hisarcik and Dereköy deposits) and in the northern basin (Espey and Killik deposits).

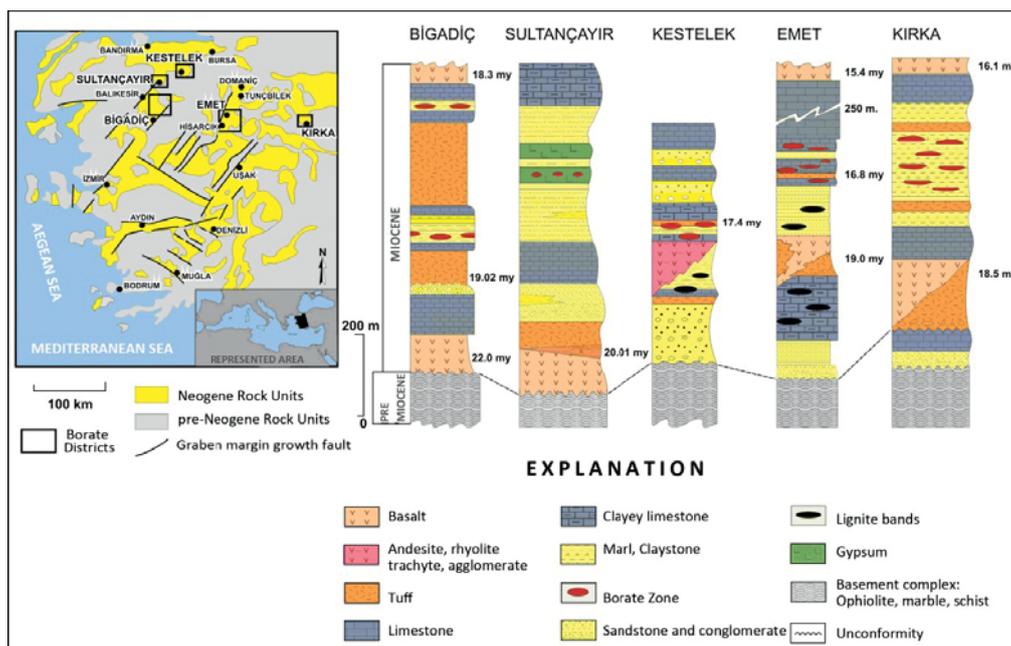


Figure 10. Stratigraphic sections of borate-bearing Tertiary lacustrine basins in western Turkey (Helvacı and Alonso, 2000).

Geological Setting of Emet Borate Basin:

The sedimentary record of the basin has been studied by Helvacı and Firman (1976). Overlying a metamorphic basement of Paleozoic age, a Miocene lacustrine sequence (Fig. 11) is represented, in ascending order by: (1) a basal conglomerate and sandstone unit, (2) a thin-bedded, lower limestone unit with marl and tuff lenses, (3) a red unit of conglomerate, sandstone, clay, marl and limestone, including coal and gypsum beds, (4) a borate-bearing unit of clay, tuff, and reworked tuff, and (5) an upper limestone unit with chert, marl and clay levels. Quaternary sediments consisting of terrace

materials overlay discordantly the Miocene units. The total thickness of the Neogene sequence exceeds 750m. The outcrops of the borate-bearing unit are aligned north-to-south at the east side of the Kocaçay River (Fig. 12).

Intense volcanic activity in the area began in the Early Miocene and continued at least until Late Miocene (Helvacı, 1984; Çolak et al. 2000). Volcanic rocks consist of a series of calc-alkaline flows (Helvacı and Firman, 1976). The earliest lava flows are of the rhyolitic, dacitic and trachytic types. The subsequent lava flows are of the trachyandesitic-andesitic type. The last products of the volcanic activity, of about 15.4 Ma in age, are olivine-rich andesitic basalts, which fingers and overlay the borate unit (Helvacı and Alonso, 2000). Besides the lava flows, abundant pyroclastic tuff layers fill the sedimentary basin making up the host-rock of the borate deposits (Helvacı, 1984).

Hydrothermal springs, which currently are depositing travertine and native sulfur, are active to the west of the Kocaçay River. Also thermal waters are obtained from wells for bath facilities (Hamamköy, Yukarıyoncağağaç, Dereli, Göbel and Emet). The high concentrations of B, As and SO₄, and the elevated salinity of the present-day thermal waters in the Emet area are related to the dissolution of Neogene sediments.

The various outcropping borate deposits in the Emet basin are dominated by thick (up to 5 - 10 m) layers of nodular colemanite with minor amounts of ulexite, hydroboracite and meyerhofferite. These borates are interbedded cyclically with volcanoclastic sediments (tuffs), thin-bedded carbonates, and laminated dark claystones dominated by Mg-smectite. Chlorite and zeolites are abundant within the tuff horizons. Native sulfur, realgar, orpiment and celestine occur in the borate unit. Boron-bearing K-feldspar, clinoptilolite, illite and smectite are the authigenic silicates in the tuffaceous matrix. Volcanoclastic high-sanidine and quartz are also present (Helvacı and Firman, 1976; Helvacı, 1984; Helvacı et al., 1993 and Helvacı and Alonso, 2000). Very limited amounts of gypsum occur in the southern sector of the basin (Helvacı, 1984, 1986). According to the observations done in the Emet district, the abundant nodules of displacive colemanite formed from the interstitial brines of a playa lake system under subsedimentary conditions (Helvacı and Ortı, 1998; Helvacı and Alonso, 2000; García-Veigas et al., 2011)

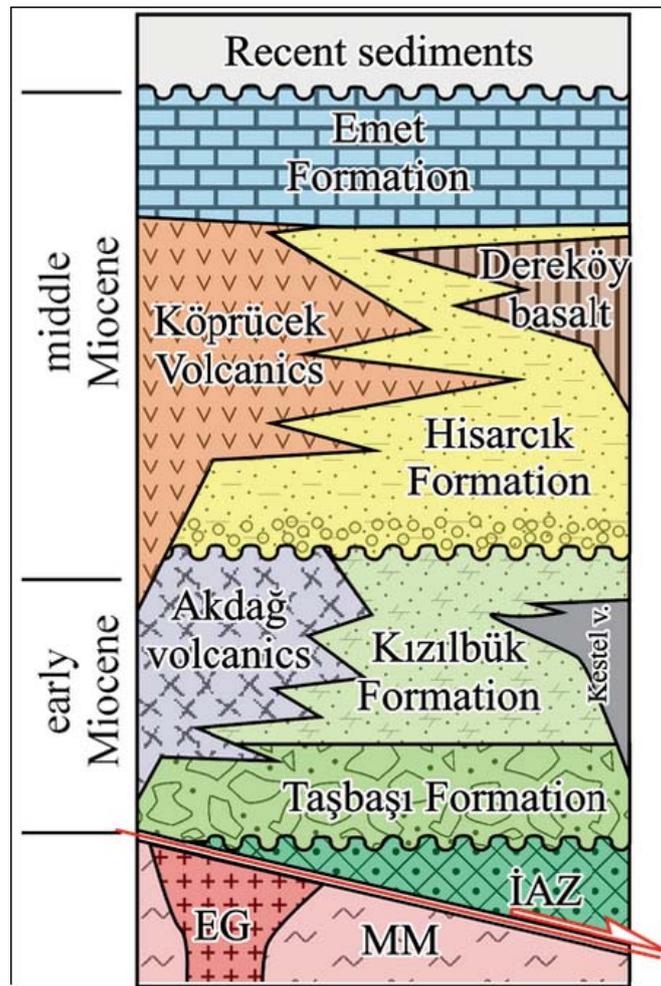


Figure 11. Generalized stratigraphic section of the Emet basin (without scale). MM:Paleozoic Menderes Metamorphic basement; EG: Eğrigöz Granitoid; IAZ: carbonates and ophiolitic rocks of Izmir-Ankara Zone; Taşbaşı Formation: conglomerates; Kızılıbük Formation: clastic unit containing coal; Akdağ, Kestel, Köprücek and Dereköy: volcanic units; Hisarcık Formation: carbonates with clastic, and tuff deposits, containing borates; Emet Formation: upper limestone unit (from García-Veigas at al., 2011; Ersoy et al., 2011).

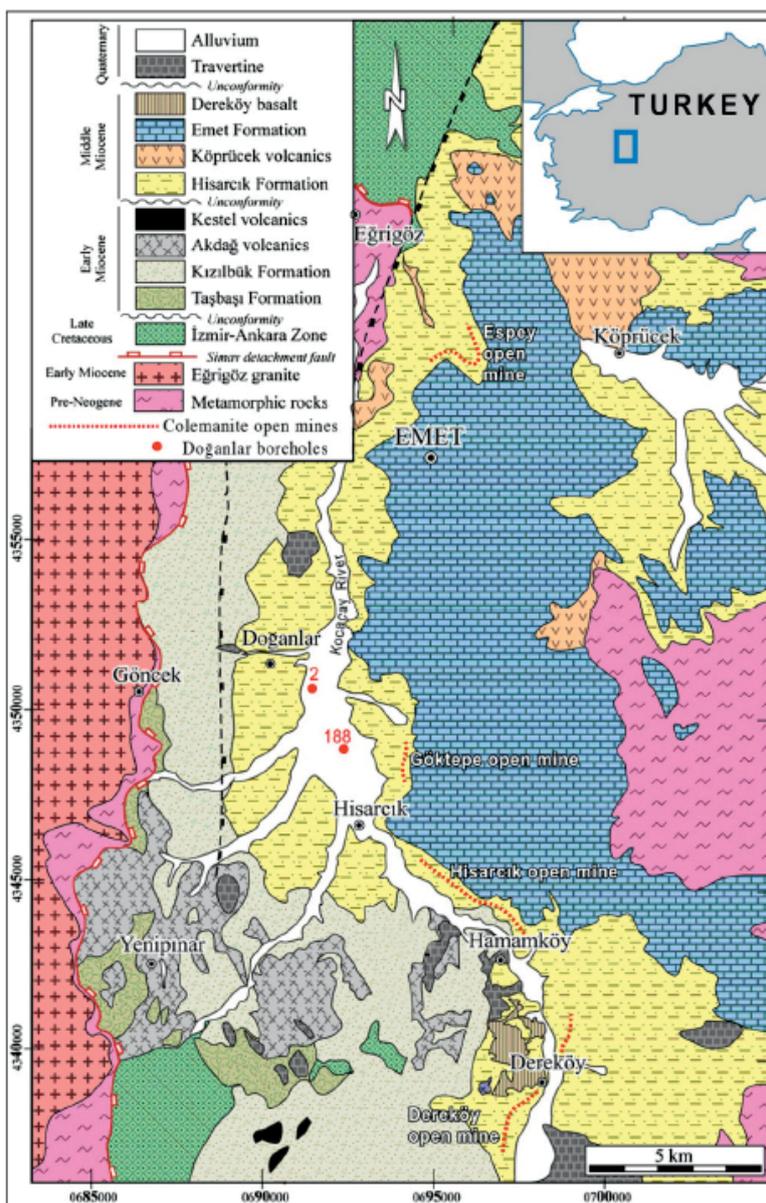


Figure 12. Geological map of the Emet borate district showing the location of the colemanite open pit mines (from Garcia-Veigas et al., 2011 and Ersoy et al., 2011).

Mineralogical Description of the Borate Minerals in Emet Borate Basin

Mineralogical studies have shown that the borate deposits in the Emet district are far more complex than was first thought (Özpeker 1969). Meyerhofferite, hydroboracite, veatchite-A, tunellite and cahnite have been found during the recent investigation (Helvacı, 1974, 1977 and 1984; Helvacı and Firman 1976; Kumbasar, 1979; Helvacı and Orti, 1998; García-Veigas et al., 2011), in addition to the minerals previously recorded (Özpeker 1969).

Table 4. Borate and non-borate minerals occurring in the Emet deposits (after Helvacı, (1984) and Garcia-Vegias et al., 2011).

Mineral Name	Oxide Formula	Deposit
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	All deposit
Probertite	$\text{NaCaB}_5\text{O}_7(\text{OH})_4 \cdot 3(\text{H}_2\text{O})$	Doğanlar
Meyerhofferite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$	Killik, Espey
Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$	Killik, Espey
Veatchite-A	$\text{Sr}_2\text{B}_{11}\text{O}_{16}(\text{OH})_5 \cdot \text{H}_2\text{O}$	Killik, Espey
Tunellite	$\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	Killik, Espey
Hydroboracite	$\text{CaMg}(\text{B}_3\text{O}_4(\text{OH})_2)_2 \cdot 3(\text{H}_2\text{O})$	Killik, Espey, Hisarcık, Doğanlar
Terrugite	$\text{Ca}_4\text{MgAs}_2\text{B}_{12}\text{O}_{22}(\text{OH})_{12} \cdot 14\text{H}_2\text{O}$	Hisarcık
Cahnite	$\text{Ca}_2\text{B}(\text{OH})_4\text{AsO}_4$	Killik, Espey, Hisarcık
Fontarnauite	$(\text{Na},\text{K})_2(\text{Sr},\text{Ca})\text{SO}_4[\text{B}_4\text{O}_6(\text{OH})_2] \cdot 3\text{H}_2\text{O}$	Doğanlar
Kaliborite	$\text{KMg}_2\text{H}(\text{B}_6\text{O}_3(\text{OH})_5)_2 \cdot 4(\text{H}_2\text{O})$	Doğanlar
Aristarainite	$\text{NaMgB}_{12}\text{O}_{16}(\text{OH})_8 \cdot 4(\text{H}_2\text{O})$	Doğanlar
Tunellite	$\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$	Doğanlar
Anhydrite	CaSO_4	Doğanlar
Glauberite	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$	Doğanlar
Thenardite	$\text{Na}_2(\text{SO}_4)$	Doğanlar
Emetite	$\text{Ca}_7\text{Na}_3\text{K}(\text{SO}_4)_9$	Doğanlar
Kalistrontite	$\text{K}_2\text{Sr}(\text{SO}_4)_2$	Doğanlar
Arsenopyrite	FeAsS	Doğanlar
Celestite	SrSO_4	Hisarcık, Espey, Doğanlar
Realgar	AsS	Hisarcık, Espey, Doğanlar
Orpiment	As_2S_3	Hisarcık, Espey, Doğanlar
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Göktepe, Espey, Doğanlar
Sulphur	S	Hisarcık, Espey
Calcite	CaCO_3	All deposit
Montmorillonite	$(\text{Mg},\text{Al})_2\text{SiO}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	All deposit
Illite	$(\text{K},\text{H}_3\text{O})\text{Al}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	All deposit
Chlorite	$(\text{SiAl})_8(\text{Mg},\text{Fe})_6\text{O}_{20}(\text{OH})_4$	All deposit

Recent studies on dip drilling in the Hisarcık area show that several new minerals occur in the deposits such as montmorillonite, illite and chlorite are the only clay minerals identified, but montmorillonite is the dominant mineral in all of the samples studied and occurs as Al-montmorillonite, Mg- montmorillonite or Al-Mg-Fe montmorillonite (García-Veigas et al., 2011). Illite is only a minor component and distributed randomly. Chlorite has a continuous distribution within the deposit and is relatively abundant near or within the horizon of tuffs. Native sulphur, realgar, orpiment and celestite occur in the borate zone throughout the area. Gypsum associated with borate minerals have been observed in the Hisarcık deposits. Calcite also occurs frequently in surface outcrops and adjacent to faults as a result of modern weathering (Helvacı, 1984). Table 5 lists the borate and non-borate minerals so far recorded in the deposits.

The sequence of minerals in the southern area are different from those in the northern area, as shown in Fig.13. Nevertheless both areas show a similar trend, which is considered to represent deposition from carbonate to borate and back to carbonate.

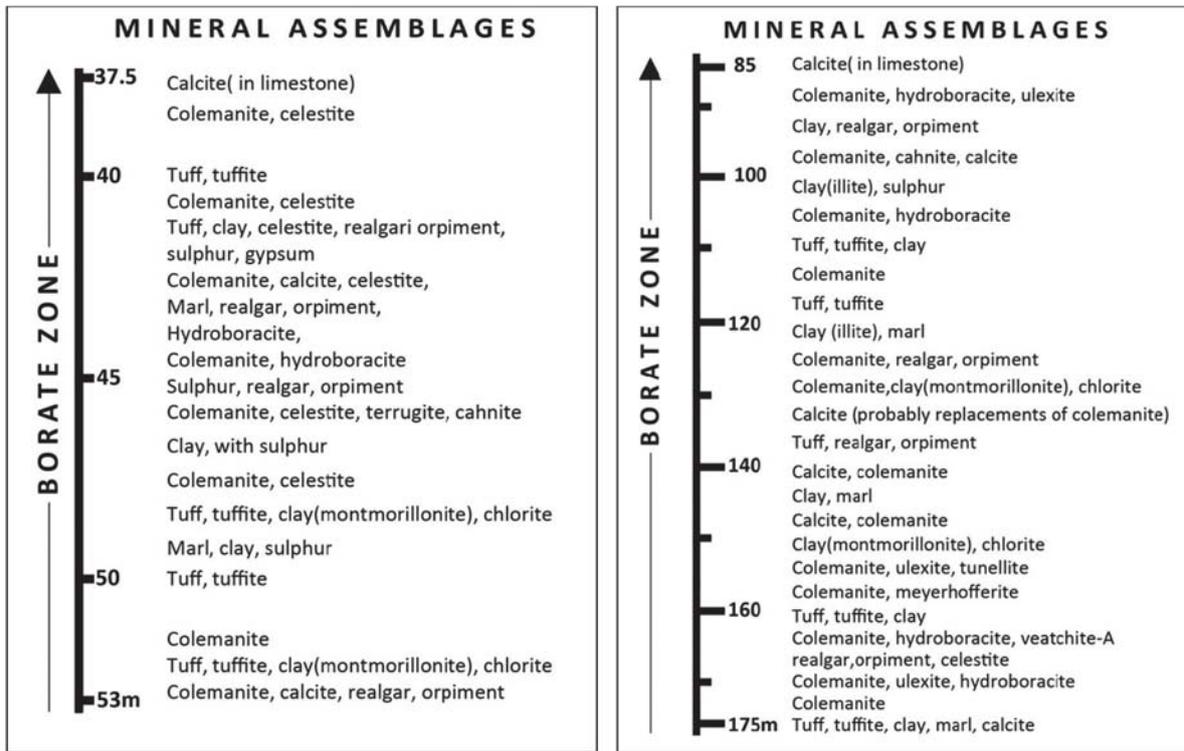
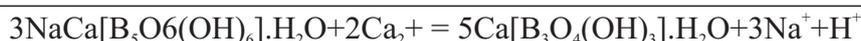


Figure 13. A: Mineral assemblages variation with depth in the southern area (Hisarcık and Dereköy deposits).
B: Mineral assemblages variation with depth in the northern area (Espesey and Killik deposits) (after Helvacı, 1984).

Colemanite $\text{Ca}_2\text{B}_6\text{OH}\cdot 5\text{H}_2\text{O}$ is by far the commonest mineral in both areas—for this reason the Emet borate deposits are usually referred to commercially as colemanite deposits (Gawlik, 1956; Özpeker, 1969). It occurs in many different forms, that range from minute stellate clusters of crystals in clay to ovoid nodules up to 0.5m in diameter. Among the commoner habits are nodular forms with radiating structures; massive granular colemanite; disseminated crystals, often stellate, in a clay matrix; fibrous layers surrounding nodules; thin layers interbedded with clay, sometimes brecciated; and vugh fillings (Helvacı and Firman, 1976).

Nodules are by far the commonest form of colemanite, but these nodules exhibit a large variety of shapes and sizes. There is a tendency for the smaller nodules to be spherical and the larger ones to be ovoid. Some irrespective of size, contain vughs; others have a core of granular colemanite. Many of the larger nodules are composed of aggregates of smaller spherical nodules composed of radiating crystals. In some of the medium-size nodules, the crystals are curved, as if they grew while the sediment was being compacted. Closer inspection reveals that these nodules grew in successive stages, each layer being separated by a thin discontinuous veneer of clay. Later generations of colemanite crystals radiate from separate centers of nucleation on the original nodule. Often it is difficult to identify all stages of nodule growth, but from the presence of included clay it is clear that these nodules formed within the clays and tuffs below the sediment-water interface and probably continued to grow as the sediment were compacted (Helvacı, 1977, 1984, 1986; Helvacı and Firman, 1976; Helvacı and Orti, 1998).

The genesis of colemanite by the alteration of ulexite, does not appear to be applicable to the Emet Valley colemanite for the following reasons: ulexite is rare even in the northern area; nowhere have cores of colemanite been found in indurated masses of 'cottonball' ulexite as at Kramer California (Bowser, 1965; Bowser and Dickson, 1966); interbedded clays at Emet are notably deficient in Na^+ (Helvacı, 1984), not enriched as theoretically they should have been if the following chemical reaction (Özpeker, 1969), took place by base Exchange between ulexite and clays



suggesting that alteration of ulexite leads to the formation of the mineral pair colemanite + borax are inapplicable to the Emet area where neither borax nor any other Na-bearing mineral, other than ulexite and probertite, occurs, and colemanite and ulexite always occur as separate nodules (Helvacı, 1977, 1984; Helvacı and Orti, 1998; Palmer and Helvacı, 1995, 1997).

Alternative suggesting for the genesis of colemanite are equally difficult to substantiate. Metasomatic replacement of limestone (Gale, 1913), is improbable, since the colemanite beds do not pass laterally into limestone nodules, and no partially altered limestones have been found. Petrographic evidence from elsewhere, e.g. Death Valley, California (Rogers, 1919), and Bigadiç area, Turkey (Meixner, 1952, 1953 and 1956), suggest that the higher hydrate inyoite ($\text{Ca}[\text{B}_3\text{O}_3(\text{OH})_5]\cdot 4\text{H}_2\text{O}$) was the first-formed Ca borate mineral $[(\text{OH})_5]^{-2}$, which on burial and diagenesis was dehydrated to inyoite and meyerhofferite or, more commonly, to colemanite, whereas colemanite has different polyanion $[\text{B}_3\text{O}_4(\text{OH})_3]^{-2}$. In order to formation of colemanite by dehydration of either inyoite or meyerhofferite on burial and diagenesis, polyanions of these minerals have to be broken down and to form colemanite polyanions. But, temperature conditions and pressure never reached so high to provide these conditions. That is why it does not seem possible to form colemanite by solid-solid mineral transformations. The presence of drusy cavities; often containing water, and of are septarian cracks, filled with a clear colemanite, suggest that reduction in volume has occurred in some nodules. However, no inyoite has been found in the Emet district, and no pseudomorphs of colemanite after inyoite have been recorded (Gawlik, 1956; Helvacı, 1974, 1977, 1984 and 1986; Helvacı and Firman, 1976; Özpeker, 1969; Yalçın and Gündoğdu, 1977; Helvacı and Orti, 1998, Palmer and Helvacı, 1997); shrinkage cracks and drusy cavities need not be due to dehydration of inyoite. Whether inyoite was ever formed at Emet remains an open question.

Inyoite is the only Ca borate mineral found in modern deposits, (Muessig 1966; Helvacı and Alonso, 1990) experimental work by İnan et al. (1973) showed that pressure is required to form colemanite. In their experiments, at 1 atm and below 38°C, inyoite was the stable Ca borate mineral in contact with calcium borate solutions; and above 38°C it transformed to meyerhofferite and not to colemanite. At 500 atm and 38°C, inyoite was replaced by colemanite + H₂O. Although they did not establish the threshold conditions for this reaction, their work implies that colemanite will not form at the pressures found in shallow lakes or unconsolidated lacustrine muds. Thus many strands of evidence, from field work, petrology experiments indicate that colemanite forms by diagenetic replacement of inyoite on burial, or directly from calcium borate solutions above 38°C under comparatively high pressures during post-depositional mineralization (İnan, et al., 1973). If inyoite has been replaced by colemanite at Emet, the replacement has been remarkably complete, since in spite of the most diligent search no relics or pseudomorphs of inyoite have been found (Helvacı, 1977, 1984; Helvacı and Firman, 1976; Yalçın and Gündoğdu, 1987). Could it be that notwithstanding the experimental evidence colemanite did form as a primary mineral in the physico-chemical conditions not yet defined or experimentally investigated? As Christ (1972) stated, the hydrated calcium borates form a more complex series than do the sodium borates, and experimental physico-chemical data should prove correspondingly more revealing for an understanding of the behaviour of hydrated minerals in general. Such an experimental study would be difficult. Unlike the sodium borates, the calcium borates are relatively insoluble in water, and for this and possibly other reasons, the crystalline solids and aqueous solution are not readily brought into equilibrium. The Emet borate zones are characterized by relatively high arsenic and strontium contents, and the effects of these elements on the crystallization of the calcium borates is unknown. Similarly, the effects of low partial pressures of H₂O have yet to be investigated.

Experiments by Helvacı (1977 and 1986) have shown that colemanite and calcite form when the evaporation products of 1:1 and 1:2 mixtures of colemanite and calcite dissolved in HCl are exposed to the atmosphere for several months (at least 5 or 6 months). These reaction takes place at atmospheric pressures may not be necessary for the solution and reprecipitation of colemanite in natural conditions. Similar experiments with ulexite and calcite results in calcite reprecipitation, probably due to deficiency of Ca^{++} in the solutions.

In the borate zone, rhythmic deposition of colemanite, clay, tuff and limestone beds (Helvacı 1977) indicates that when the brines were oversaturated with B and Ca, colemanite was deposited and during the period when B concentration decreased calcite precipitated. Clays and tuffs were continuously deposited. In the thin section of the colemanite nodules, clay and tuff inclusions in the early formed colemanite have been commonly observed and it is difficult to believe that these textures would have been preserved had the replaced inyoite or ulexite (Helvacı, 1986; Helvacı and Orti, 1998; Palmer and Helvacı, 1995, 1997).

Meyerhofferite $\text{Ca}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$

Meyerhofferite $\text{Ca}_2\text{B}_6\text{O}_{11}\cdot 7\text{H}_2\text{O}$ occurs as nodules of coarsely crystalline radiating crystals intergrown with the clay at the margins. Small vughs in the centre of the nodules contain delicate acicular crystals, which are also meyerhofferite, and no alteration to or from any other mineral has been observed (Helvacı, 1977; Helvacı and Firman 1976). İnan, et al. 1973 demonstrated that, at temperatures in excess of 38°C and the atmospheric pressures, meyerhofferite forms from calcium borate solutions. The rarity of meyerhofferite may thus be due to the rarity of ground or surface waters above 38°C .

Ulexite $\text{NaCa}_5\text{O}_9\cdot 8\text{H}_2\text{O}$

Ulexite $\text{NaCa}_5\text{O}_9\cdot 8\text{H}_2\text{O}$, like meyerhofferite, is mainly restricted to the northern basin. It occurs at three levels, always as cauliflower-like nodules; veins and encrustations on other minerals are unknown in the Emet district. The purest forms of ulexite are white, but many are grey, owing to growth of the nodule in the clay. Thus, like colemanite and meyerhofferite, ulexite nodules appear to have developed within and not on the sediments (Helvacı, 1977; Helvacı and Firman 1976).

Veatchite-A ($\text{Sr}_2\text{B}_{11}\text{O}_{16}(\text{OH})_5\cdot \text{H}_2\text{O}$)

Veatchite-A ($\text{Sr}_2\text{B}_{11}\text{O}_{16}(\text{OH})_5\cdot \text{H}_2\text{O}$) is very rare, occurring sporadically at one horizon in the northern basin. It appears as very pure white mineral often with clay inclusions, in small (up to 2 cm in diameter) or large (up to 6 cm in diameter) nodules made up of little needle-shaped crystals. Sometimes very small nodules are associated together and show mammillary appearance (Helvacı, 1977 and 1984).

Veatchite-A was first recorded from the Emet borate deposits by Helvacı (1974). Helvacı and Firman (1976) reported the same mineral as veatchite (*sensu lato*) due to the absence of suitable crystals which are straight enough to make a positive determination of the structure. Finally, Kumbasar (1979) was able to determine the crystal structure of this mineral from the Emet deposits. It was named veatchite-A, in order to correspond to the recommended nomenclature system of polytypes, as new modifications of veatchite (Briatsch 1959; Kumbasar (1979).

This mineral is usually associated with colemanite. In thin sections it shows very fine, small crystals, which sometimes grow in or on top of colemanite nodule. Field and textural evidence shows that this mineral replaces colemanite and is not associated with the tunellite (Helvacı, 1977 and 1984).

Tunellite ($\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$)

Tunellite ($\text{SrB}_6\text{O}_9(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), like veatchite-A, has a restricted distribution and has been found only in the lower part of the borate zone in the northern basin (Helvacı, 1977; Helvacı and Firman 1976).

Tunellite commonly occurs either as individual flattened crystals, 1-5cm in length, or as thin, tabular crystals which have nucleated on, but not replaced ulexite. Pure, flattened tunellite crystals are colorless, transparent and have perfectly developed cleavages parallel to flattened surface, which resemble muscovite flakes. Alternatively, tunellite occurs as small white nodules with radiating structures, which have apparently grown in the interbedded clays (Helvacı, 1984).

In the Emet deposits, it is associated with ulexite and colemanite. Tunellite appears to have formed later than ulexite and colemanite, but not as a replacement. This mineral was first described from Kırka deposit by Baysal (1972), but not hitherto been identified in any other Turkish borate deposits (Helvacı, 1977 and 1978).

Teruggite ($\text{Ca}_4\text{MgAsB}_{12}(\text{OH})_{12} \cdot 14\text{H}_2\text{O}$)

Teruggite ($\text{Ca}_4\text{MgAsB}_{12}(\text{OH})_{12} \cdot 14\text{H}_2\text{O}$) is rare, occurring sporadically at one horizon in the southern basin as very pure white, powdery potato-shaped nodules containing countless minute, white euhedral crystals. The nodules of teruggite range from 2 to 10 cm in diameter.

Occasionally, these powdery potato-shaped teruggite nodule contain very small spherulites of cahnite. This is the first record of this type of teruggite and cahnite occurrence from borate deposits (Helvacı, 1977; Helvacı, 1984). The crystal structure of teruggite from the Emet deposits was described by Negro et al. (1973).

The sporadic occurrence of teruggite and cahnite, compared with the almost universal distribution of arsenic sulphides in the Emet deposits, suggest that they developed in areas in which the brines were S-deficient (probably H_2S) which would have otherwise precipitated the arsenic as realgar instead of arsenic bearing borates (Helvacı, 1984). Teruggite is associated with cahnite and colemanite.

In thin section, the crystal of teruggite are colorless, prismatic and are strongly elongated along the c axis. These crystals usually are very small. Occasionally spherulites of cahnite occur in teruggite masses and fibrous lites crystals of cahnite show a radial texture (Helvacı, 1984).

Cahnite ($\text{Ca}_2\text{B}(\text{OH})_4\text{AsO}_4$)

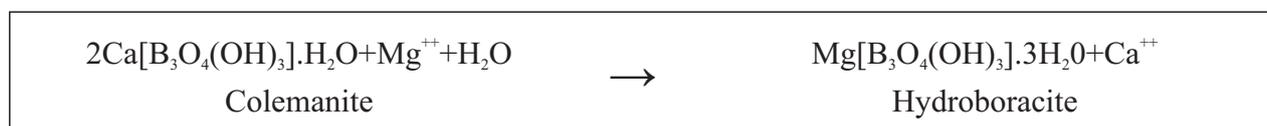
Cahnite ($\text{Ca}_2\text{B}(\text{OH})_4\text{AsO}_4$), a very rare borate mineral, was first recorded from Franklin, New Jersey, by Palache et al. (1927), appearing in the cavities of axinite veinlets. Later discoveries of this mineral are associated with skarn zones, as reported from the Klodborg mine, Arendal, Norway by Bugge (1951) and from Eastern Siberia, U.S.S.R. by Malinkio (1956). Cahnite was also recorded by Embrey (1960), from a cavity in dark grey, leucitic lava at Capa di Bove, Rome Italy, where it is found on calcite associated with philipsite and chabazite.

Until the work carried out in the Emet borate deposit by Helvacı (1977; Helvacı, 1984), cahnite had not been identified from borate deposits. In the Emet deposits, cahnite occurs as very small spherulites in powdery potato-shaped teruggite nodules in the southern area and as a coating on euhedral colemanite crystals in the vugs in colemanite nodules in the northern area. Cahnite is rare, occurring sporadically only at one horizon. It is associated with colemanite and calcite in the northern area, whereas it is associated with teruggite and colemanite in the southern basin (Helvacı, 1977, 1978 and 1984). The spherulites of cahnite are generally very small, rarely exceeding 2 mm in diameter and occurring usually singly, but occasionally 2 or 3 coalesce together. Cahnite is white and light brown in colour with a notable glassy lustre.

This section show that the cahnite spherulites contain needle-shaped and fibrous crystals which often display a radial texture (Helvacı, 1984).

Hydroboracite $\text{CaMgB}_6\text{O}_{11}\cdot 6\text{H}_2\text{O}$

Hydroboracite $\text{CaMgB}_6\text{O}_{11}\cdot 6\text{H}_2\text{O}$ is commonly intimately intergrown with colemanite and is sometimes cut by later colemanite veins. The transformation of colemanite to hydroboracite involves only the substitution of Mg^{++} for Ca^{++} and additoin of H_2O :



This reaction might well proceed by base exchange with Mg-rich tuffs and clays during early diagenesis. The presence of carbonic acid during this processes would account for the colemanite (Helvacı, 1977, Helvacı and Firman 1976). Calcite also occurs, however, in surface outcrops and adjacent to faults as a results of modern weathering. Much of the calcite may therefore be of very recent origin.

Of the minerals in vughs and veins, colemanite is almost ubiquitous; but realgar, frequently, celestite and cahnite, more rarely, are found encrusting in vughs of colemanite crystals.

Native sulphur and realgar are almost ubiquitous in clays and borates, and appear to have formed at all stages during deposition and diagenesis.

Chemical analyses of borate minerals from the Emet deposits are given table 7, 8 and 9.

Table 5. Chemical analyses of rare borate minerals and colemanite from the Emet deposits (after Helvacı, 1977 and 1984).

Oxide (%)	Veatchite-A		Tunellite	Terrugite			Cahnite	Colemanite (1013)
	1	2	3	4	5	6	7	8
B_2O_3	57.2	57.62	52.07	34.1	34.14	33.2	23.36	51.56
CaO	0.63	0.32	0.93	17.4	17.43	16.8	32.48	25.73
MgO	1.27	0.69	1.12	3.2	3.6	4.17	1.8	1.02
Na_2O	0.16	0.02	0.06	0.23	0.26	0	0	0
SrO	27.8	29.78	27.09	0.12	0.18	0.02	0.65	0.97
As_2O_5	0.57	0.05	0.09	18.7	18.69	18.2	31.38	0.01
SiO_2	1.38	0.45	1.37	0.5	1.25	0.05	2.02	0.04
TiO_2	0	0	0.01	0	0	0	0.05	0
K_2O	0.01	0	0	0	0	0	0.75	0
H_2O^+	9.95	9.75	17.54	25.4	24.3	27.3	9.14	20.69
SO_3	0.1	0.02	0.09	0.1	0.27	0.02	0	0.06
Total Ppm	99	98.7	100.37	99.8	100.1	99.7	101.63	100.06
Al	734	225	876	146	362	3*	3.313	64
Fe	701	142	369	845	518	63	3.368	74
Mn	42	3*	29	40	67	25	118	26
P	32*	14*	53*	34*	38*	27*	200	43*
Cl	90*	61*	137*	155*	235	157	131*	151*
Br	0*	9	1*	0*	0*	0*	0*	1*
Be	0*	305	4.701	0*	0*	0*	0*	363

* indicates values below the detection limits as ppm: Al: 82. Fe: 29. Mn: 16. P: 75. Cl: 185. Br: 9. Be: 296.

Table 6. Chemical analyses of colemanite samples from the Emet borate deposits (after Helvacı, 1977, 1986).

Colemanite		Colemanite from southern area					Colemanite from northern area				
Oxide %	1013	1	2	3	4	5	6	7	8	9	10
B ₂ O ₃	51.56	49.1	44.7	50.2	51.1	50.99	47.6	51.3	48.5	52.07	50.5
CaO	25.73	25.2	18.2	22.4	25.4	25.37	24.8	29.5	24.6	25.54	25.4
MgO	1.02	0.64	3.12	3.29	0.57	1.1	0.75	0.32	0.4	1.04	1.15
Na ₂ O	0	0.26	0.26	0.35	0.27	0	0.19	0.25	0.32	0	0
SrO	0.97	1.35	1	0.88	0.78	1.34	1.69	0.31	1.82	0.97	0.33
As ₂ O ₅	0.01	0.16	1.49	0.32	0.04	0	0.06	0.04	0.04	0	0.02
SiO ₂	0.04	0.65	4.55	1.33	0.48	0.06	1.7	0.09	0.26	0.04	0.11
TiO ₂	0	0	0	0	0	0	0.02	0	0	0	0
K ₂ O	0	0	0.01	0	0	0	0.3	0	0	0	0
H ₂ O ⁺	20.69	20.4	19.4	20.1	20.7	21.29	19.5	20.5	20.5	20.73	21.4
CO ₂	0	1.55	6	0	0	0	3.08	0	0	0	0
SO ₃	0.06	0.2	1.13	0.04	0.22	0.03	0.25	0.33	2.51	0.06	0.13
Total ppm	100.06	99.6	99.9	99.3	99.4	100.2	100	99.1	98.9	100.5	99.1
Al	64	338	610	453	133	0*	2348	120	338	0*	21*
Fe	74	608	0*	315	301	63	1830	1025	9044	60	250
Mn	26	3*	49	44	7*	4*	16*	33	10*	2*	5*
P	43*	60*	801	29	89	38*	93	62*	27*	57*	59*
Cl	151*	151*	108*	156*	107*	76*	978	104*	122*	77*	64*
Br	1*	0*	0*	0*	0*	1*	0*	0*	2*	1*	1*
Ba	363	0*	0*	0*	32*	444	176*	39*	71*	336	308

Table 7. Chemical analyses of meyerhofferite, ulexite and hydroboracite from the Emet borate deposits (after Helvacı, 1977, 1986).

Oxide %	Meyerhofferite			Ulexite		Hydroboracite			
	1	2	3	4	5	6	7	8	9
Be ₂ O ₃	45.69	45.95	44.03	42.61	43.65	42.12	50.16	50.09	49.52
CaO	24.96	23.24	23.35	16.66	13.52	13.66	13.88	12.66	13.44
MgO	0.77	0.95	2.5	0.85	0.9	0.85	11.25	10.63	10.64
Na ₂ O	0.16	0.22	0.26	7.94	7.67	7.57	0.21	0	0
SrO	0.03	0.25	0.51	0.33	0.26	0.11	0.01	0.01	0.01
As ₂ O ₅	0.22	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0
SiO ₂	1.06	1.63	1.88	0.31	1.75	0.31	0.67	0.03	0.06
TiO ₂	0	0.01	0.01		0	0.02	0	0	0
K ₂ O	0.1	0.28	0.36	0.03	0.03	0.03	0.05	0	0
H ₂ O ⁺	26.39	25.58	26.08	33.67	31.62	35.34	23.89	25.54	25.66
CO ₂	0	0	0	0	0	0	0	1.42	0.25
SO ₃	0.53	0.2	0.07	0.32	0.48	0.14	0.29	0.07	0.13
Total ppm	99.91	98.33	99.07	99.74	100.25	100.14	99.91	100.46	99.8
Al	651	1214	1447	256	1894	256	485	2*	14*
Fe	399	1101	1046	316	2307	316	435	77	100
Mn	22	23	29	7*	41	7*	95	41	31
P	88	43*	68*	10*	47*	10*	22*	30*	6*
Cl	151*	163*	72*	174*	161*	91*	160*	68*	68*
Br	0*	2*	0*	0*	1*	0*	0*	0*	0*
Ba	0*	90*	338*	190*	139*	361*	126*	306*	58*

Chemical zones in the saline lake sequence of Emet Borate Deposits

The complex mineral association recorded in the studied boreholes points to a scenario where sedimentary and early diagenetic processes took place in a saline lacustrine environment influenced by volcanoclastic deposits, hydrothermal reactions, and intense biological activity.

According to the chemical composition and distribution of the major borates and sulfates, the evaporite sequence records a significant change of the parent-waters from (1) initial Ca-rich solutions producing colemanite, to (2) Ca-Na brines represented by probertite and glauberite units, and finally to (3) Na-brines from which halite and thenardite precipitated. Although no K-bearing minerals (kaliborite, kalistrontite, fontarnauite and emetite) precipitated as isolated beds, their formation during early diagenesis in the central units of the sequence suggests a progressive enrichment of K in the more concentrated Na-brines. According to the main mineral association of each unit, after halite deposition the saline brines returned to a Na-Ca composition characterized by the precipitation of probertite and glauberite, and finalized with colemanite and anhydrite crystallization from the end Ca-brines (García-Veigas et al., 2011).

Hydrochemical model in Emet Borate Deposits

The integration of petrographic and chemical data allows us to propose a hydrochemical model for evaporite deposition of the borates, sulfates, and salt under study, in which both primary precipitation and early diagenetic processes occurred. A simplified drawing of the model is shown in Fig.14. The model envisages a saline lake surrounded by an extensive, slightly sloped, saline tuff-flat. The water column of the lake ranges from shallow to moderately deeper (saline lake stage) to

very shallow (saltpond stage). The size of the lake should have been small (kilometerorder) according to the limited extension of the glauberite-probertite deposits respect to the colemanite deposits outcropping in the area (tens of kilometers-order; Fig. 14) (García-Veigas at al., 2011).

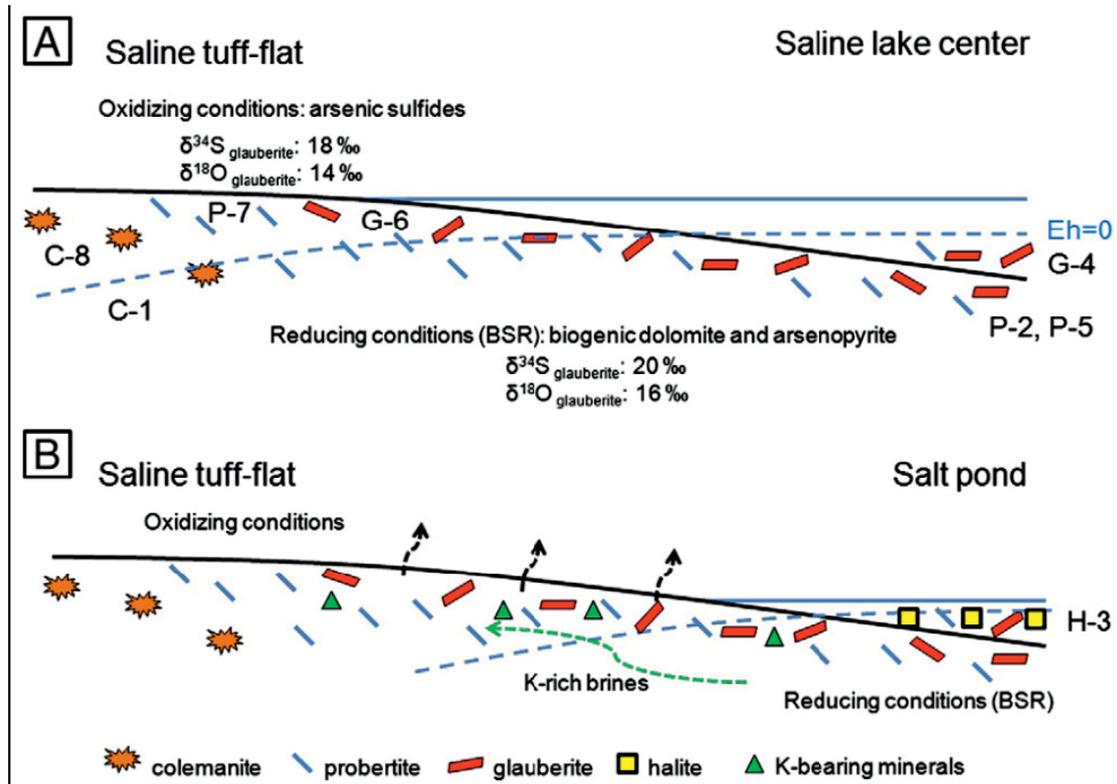


Figure 14. Hydrochemical and mineralogical model of evaporitic precipitation in the Doğanlar saline lake. A: Common situation for predominant precipitation of the various borates and sulfates, B: Halite precipitation stage (after García-Veigas at al., 2011).

Saline lake stage:

During the saline lake stage, the bottom waters and the underground brines in the surrounding tuff-flat remain under reducing conditions. The mineral precipitation in this tuff-flat reflects a lateral salinity gradient of inflows towards the center of the lake. Colemanite precipitates extensively below the surface in the outermost zone of the tuff-flat. Ca consumption during colemanite formation causes enrichment in Na, allowing the precipitation of probertite and glauberite in both the nearshore area (interstitially) and the lake bottom (subaqueously). Anoxic conditions favor, in both environments, the microbial sulfate reduction of the glauberite and the dissolved sulfate producing sulfide and bicarbonate. Sulfide reacts with iron and arsenic in volcanoclastic sediments yielding colloidal arsenopyrite precipitation, while the increase of carbonate alkalinity leads to the precipitation of dolomite induced by microorganisms. The BSR modifies the isotopic composition of the remaining sulfate enriching the precipitated glauberite in heavy isotopes (García-Veigas at al., 2011).

Salt pond stage:

At moments of severe restriction, the lake remains very shallow (salt-pond stage) and the groundwater level drops in the surrounding tuff-flat. Although the bottom lake-water remains under reducing conditions, the fall of the water table generates oxidizing conditions in the groundwater of the tuff-flat. Increasing salinity related to this restriction results in the direct precipitation of probertite, glauberite, and halite in the pond, in which biogenic dolomite and arsenopyrite still form. The change to oxidizing conditions in the underground brine, below the surface of the tuff-flat, prevents the bacterial reduction of dissolved sulfate. Thus, interstitial glauberite precipitates with the original isotopic signal. These conditions avoid the generation of bacterially-induced dolomite and

colloidal arsenopyrite, and favor the biogenic precipitation of arsenic sulfides (García-Veigas et al., 2011).

Depositional and Post-depositional History of Emet Borate Deposits

It is certain that percentage of mineral which constituted more than 95 % of the original deposit was a Ca borate in the Emet deposits. Arsenic sulphides and native sulphur, although present in minor quantities, are as widely distributed as the Ca borates, and hence it may be assumed that the initial brines at all times contained an abundance of calcium and boron with minor amounts of arsenic and sulphur. Strontium and sodium may also have been present in the initial brines, or alternatively, may have been added to the mineralizing solutions periodically.

Geochemical investigations suggest that the most likely sources of B, As and S were from the weathering products of Tertiary volcanic rocks transported into the borate basins by streams; or from volcanic ash deposited directly in to the borate basins; or from hydrothermal systems, similar to the playa-lake depositional model summarized by Helvacı (2005) (Fig. 15). Streams may also have carried some Na^+ , Ca^{++} and other elements in solution into the basins as the result of weathering of rocks exposed in the catchment area, but the major source of Ca^{++} and Sr^{++} , by the analogy with present-day hydrology, is considered to be due to leaching of underlying Tertiary limestone by thermal spring (Helvacı, 1977, 1984 and 1986).

The composition of the brines changed with each influx of water-borne sediment, with the addition material from hydrothermal systems related to the volcanic activity, and as a result of crystallization. Some general tendencies have been established, but owing to the rarity of borate minerals other than colemanite it is not known if these trends are universally valid.

Both lateral and vertical changes from calcite marls to colemanite-bearing clays have been observed; a gross zoning, both laterally and vertically, from calcite to colemanite and back to calcite, seems to be general in both areas. In the southern area, the sporadic occurrence of gypsum suggest that where sulphates are present the sequence is calcite-gypsum-colemanite. In the northern basin the early colemanite phase and ulexite crystallize before tunellite, implying that Sr borates will not crystallize from solution until Ca borates and Na-Ca borates have been precipitated (Helvacı and Firman, 1976). The retention of Sr^{++} in the interstratal brines accounts for both the diagenetic replacement of colemanite by veatchite-A in the northern basin and the late post-depositional crystallization of celestite (SrSO_4) in the northern and southern basins. Sr borates and arsenic-bearing borates have not been found together in the same bed. It is not known whether this is genuine incompatibility, or merely a reflection of the scarcity of terrugite and cahnite (Helvacı, 1984).

The history of Emet deposits may therefore be tentatively summarized by Helvacı (1977, 1984) and Helvacı and Firman (1976) as noted below.

(1) Playa lakes were established in seismically active areas fed by hydrothermal systems and surface streams.

(2) In these lakes, clay and volcanic ash were deposited and Ca borate nodules developed within the unconsolidated sediments during periods of evaporation. In the northern basin, ulexite and tunellite were also periodically formed and the arsenic-bearing borate (terrugite) was precipitated occasionally in the southern basin. Small amounts of sulphur and realgar were also formed within the sediments contemporaneously with the borates.

(3) After burial Ca borate nodules continued to grow. Colemanite was reprecipitated in vughs together with realgar and, more rarely, celestine and cahnite.

- (4) Chemical reaction between Mg-rich calcs and colemanite led to the formation of hydroboracite.
 - (5) Reaction between Sr-rich interstratal brines and colemanite led to its partial replacement by a veatchite-A mineral.
 - (6) Solution and reprecipitation of colemanite took place in veins and around colemanite nodules.
 - (7) Uplift and erosion led to the weathering of colemanite and its replacement by calcite in surface outcrops and adjacent to faults. Realgar was altered to orpiment on exposure to air.
- In many areas the colemanite appears to be unaltered apart from recrystallization, so the post-depositional changes (4)-(5) above apply only restricted parts of the deposits. Realgar and sulphur appear to have been deposited both during and after the formation of the Ca borates.

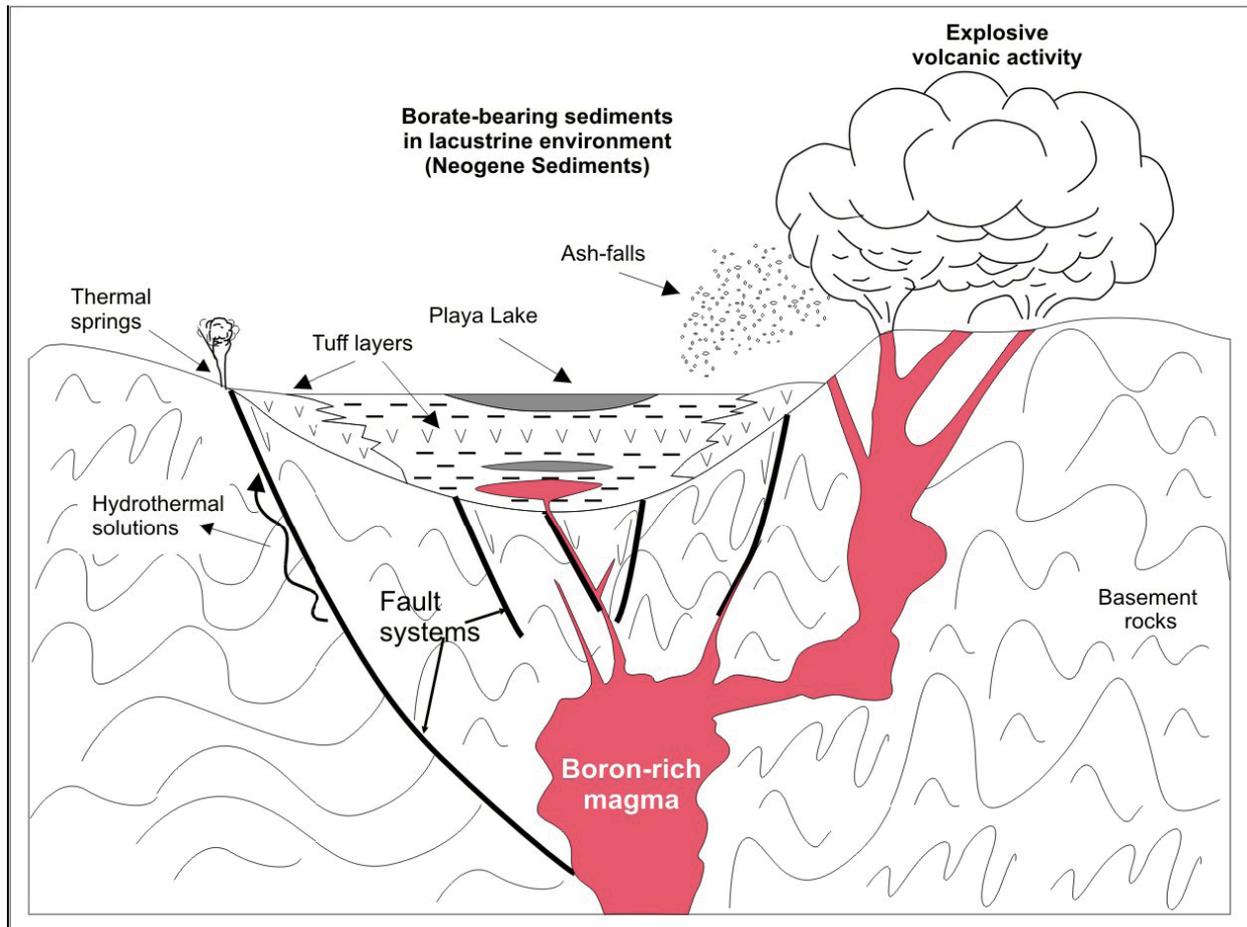


Figure 15. Generalized playa-lake depositional model, showing the formation of borate deposits in the Neogene basins of western Anatolia, Turkey (after Helvacı, 2005).

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