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GEOLOGICAL FEATURES OF NEOGENE BASINS HOSTING BORATE DEPOSITS: AN OVERVIEW OF DEPOSITS AND FUTURE FORECAST, TURKEY

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ABSTRACT

The geometry, stratigraphy, tectonics and volcanic components of the borate bearing Neogene basins in western Anatolia offer some important insights into on the relationship between basin evolution, borate formation and mode of extension in western Anatolia. Some of the borate deposits in NE-SW trending basins developed along the İzmir-Balıkesir Transfer Zone (İBTZ) (e.g. Bigadiç, Sultançayır and Kestelek basins), and other deposits in the NE-SW trending basins which occur on the northern side of the Menderes Core Complex (MCC) are the Selendi and Emet basins. The Kırka borate deposit occurs further to the east and is located in a completely different geological setting and volcanostratigraphic succession. Boron is widely distributed; including in soil and water, plants and animals. The element boron does not exist freely by itself in nature, but rather it occurs in combination with oxygen and other elements in salts, commonly known as borates. Approximately 280 boron-bearing minerals have been identified, the most common being sodium, calcium and magnesium salts. Four main continental metallogenic borate provinces are recognized at a global scale. They are located in Anatolia (Turkey), California (USA), Central Andes (South America) and Tibet (Central Asia). The origin of borate deposits is related to Cenozoic volcanism, thermal spring activity, closed basins and arid climate. Borax is the major commercial source of boron, with major supplies coming from Turkey, USA and Argentina. Colemanite is the main calcium borate and large scale production is restricted to Turkey. Datolite and szaibelyite are confined to Russia and Chinese sources. Four Main borax (tincal) deposits are present in Anatolia (Kırka), California (Boron), and two in the Andes (Tincalayu and Loma Blanca). Kırka, Boron and Loma Blanca have similarities with regard to their chemical and mineralogical composition of the borate minerals. Colemanite deposits with/without probertite and hydroboracite are present in west Anatolia, Death Valley, California, and Sijes (Argentina). Quaternary borates are present in salars (Andes) and playa-lakes and salt pans (USA-Tibet). Boron is a rare element in the Earth's crust, but extraordinary concentrations can be found in limited places. The formation of borate deposits can be classified as follows: a skarn group associated with intrusives and consisting of silicates and iron oxides; a magnesium oxide group hosted by marine evaporitic sediments; and a sodium– and calcium–borate hydrates group associated with playa-lake sediments and explosive volcanic activity. Some conditions are essential for the formation of economically viable borate deposits in playa-lake volcano-sedimentary sequences: formation of playa-lake environment; concentration of boron in the playa lake, sourced from andesitic to rhyolitic volcanics, direct ash fall into the basin, or hydrothermal solutions along graben faults; thermal springs near the area of volcanism; arid to semi-arid climatic conditions; and lake water with a pH of between 8.5 and 11. A borate is defined as any compound that contains or supplies boric oxide (B_2O_3). A large number of minerals contain boric oxide, but the three that are most important from a worldwide commercial standpoint are borax, ulexite, and colemanite, which are produced in a limited number of countries. Turkey has the largest borax, ulexite and colemanite reserves in the world and all the world's countries are dependent upon the colemanite and ulexite reserves of Turkey.

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Most of the world's commercial borate deposits are mined by open pit methods. Brines from Searles Lake, and presumably the Chinese sources, are recovered by either controlled evaporation or carbonation. Boric acid is one of the final products produced from most of the processes. Further research on the mineralogy and chemistry of borate minerals and associated minerals will the production and utilization of borate end-products. Many modern industries need industrial borate minerals, and many people use their products. In addition, boron is essential to plant life, and by extension, all life so it's hard to imagine our world without using it. Therefore, borates and their products are critical to the Sustainable Development of the world.

1. Introduction

Borate history is very ancient: derived from the Persian burah (boorak), borax was already known to the Babylonians who brought it from the Himalayas some four thousand years ago for use in the manufacture of rings, amulets, and bracelets. The Egyptians used borax in mummifying, and around 300 AD the Chinese were familiar with borax glazes, as were the Arabs three centuries later. Borax was first brought to Europe in the 13th century, presumably by Marco Polo, and since that time by traders from Tibet and Kashmir.

By the 1770s, the French had developed a source of tincal, the old name for crude borax, in Purbet Province, India, and about the same time natural boric acid (sassolite) was discovered in the hot springs in the Maremma region of Tuscany, Italy. The middle of the nineteenth century was a particularly active time for the discovery and commercial development of borate deposits. In particular, Chile started to mine the borate resources of the Salar de Ascotan in 1852 and within a few years their output accounted for a quarter of the world's annual supply of 16.000 tons. In 1856 John Veatch discovered borax in Clear Lake, Lake County, California, which led eventually to the start up of the California Borax Company in 1864 and to beginning of that states dominance of the borate industry. In Turkey modern borate mining began in 1865 when the Compagnie Industrialle des Mazures mined borates from the Aziziye Mine near Susurluk and shipped the ore back to France for processing. Demand encouraged exploitation of large-scale deposits in Turkey and the United States and overwhelmed more modest producers (Travis and Cocks, 1984).

Borates are among the most interesting of the worlds industrial minerals, first for precious metal working and later in ceramics. They form an unusually large grouping of minerals, but the number of commercially important borates is limited, and their chemistry and crystal structure are both unusual and complex. The accounts of the early exploration, mining, and processing of borates are fascinating, because their remote locations often led to unusual difficulties, and hardships in recovering the desired products. This varied from workers wading into Himalayan lakes to harvest the "floor" and then transport the borax in saddlebags on sheep across the Himalayas to the markets, to the "Dante's Inferno" of the Larderello boric acid fumaroles, to the colourful 20-mule teams of the western United States (Kistler and Helvacı, 1994; Helvacı, 2005).

The early history of borate mining in Turkey goes back to Roman times. Substantial amounts of borates have been produced in Turkey since the end of the 1800s. In 1885, a French company was operating the Sultançayırı mine in Balıkesir province. There is a record of production since 1887, which indicates that production has been continuous to the present day except for war periods. Until 1954 all recorded production came from Sultançayır, but since 1950 extensive exploration has resulted in the discovery of several important new Turkish deposits. Bigadiç deposit; Balıkesir province, has operated since 1950, and major production in the M. Kemalpaşa deposit (Kestelek), Bursa province, began in about 1952. In 1956 the Emet borate deposits, Kütahya province, were discovered accidentally by Dr. J.Gawlik whilst carrying out a survey of lignite deposits for MTA. After the discovery, the Emet deposits became the main source of colemanite in the western world. Finally, the most outstanding discovery was the Kırka borate deposit which is mainly a massive borax body, with estimated reserves several times greater than those of Boron, California (İnan, 1972; Baysal, 1972; Arda, 1969; Travis and Cocks, 1984; Dunn, 1986; Kistler and Helvacı, 1994; Helvacı, 2005). Today, however, borate mining is confined to four distinct areas in Turkey: Emet, Kırka, Bigadiç and Kestelek. Turkey is currently the largest producer of borate minerals and has the world's largest reserves. Production more than doubled in 1980 to over one million tonnes (approximately 1.500.000 tonnes) and further increases, particularly of borax from Kırka, are likely to lead to Turkey dominating the world markets. Already Turkey is the major world producer of colemanite, much of which comes from the Emet valley (e.g. 2500 metric tons in 2011). The Eti Maden planned to expand its share in the world boron market from 36% to 39% by 2013, increasing sales to $1 billion by expanding its production facilities and product range.

Boron chemistry and reactivity are also fascinating because they form a wide variety of oxygen compounds that occur in an essentially unending variety of simple to exceedingly complex molecules. Determining their crystal structures has given rise to a separate subfield of crystallography. The boron isotopes ^{10}B and ^{11}B, varying widely in nature and their different reactivity during both physical and chemical changes means that they are an important tool in predicting many geologic and other events, again forming a specialized field in geology. Borates are defined by industry as any compound that contains or supplies boric oxide (B_2O_3). A large number of minerals contain boric oxide, but the three that are the most important from a worldwide commercial standpoint are: borax, ulexite and colemanite. These are produced in a limited number of countries dominated by the United States and Turkey, which together furnish about 90% of the world's borate supplies. Production in the United States originated in the Mojave Desert of California; borax and kernite are mined from a large deposit at Boron. Borate containing brines are pumped from Searles Lake, and a limited amount of colemanite is mined from Death Valley. There are over 40 borate deposits located along an 885 km trend in the high Andes near the common borders of Argentina, Bolivia, Chile, and Peru, of which at least 14 are currently in production. Turkish production is controlled by Eti Maden/Etibor, the national mining enterprise, which supplies most of the commercially traded ulexite and colemanite from mines in the Bigadiç and Emet districts, plus borax from the huge deposit at Kırka (Kistler and Helvacı, 1994; Helvacı and Alonso, 2000; Helvacı, 2005).

The most important worldwide borate deposits occur in western Anatolia and have been the topic of several papers which dealt with their genesis (İnan, 1972; Baysal, 1972; Helvacı, 1983; 1984; 1986; Kistler and Helvacı, 1994; Helvacı, 1995; Palmer and Helvacı, 1995; 1997; Helvacı and Orti, 1998; Helvacı and Alonso, 2000; Helvacı, 2004; 2005). They originated in Tertiary continental lacustrine basins during a period characterized by intense magmatic activity affecting western Anatolia. These borate deposits are interbedded with volcanosedimentary rocks (Floyd et al., 1998; Helvacı and Alonso, 2000). The Borate deposits and associated sedimentary rocks were deposited within playa lake environments. These borate deposits show differences between them and the associated sedimentary deposits are mainly represented by claystone, sandstone and limestone.

In this study, new stratigraphic, volcanic and tectonic observations from these basins will be presented in order to outline the main features of the borate bearing basins, and couple them with data from the other basins to produce a tectono-stratigraphic evolutionary model for borate formation within western Anatolia. Recent age data are presented here in order to determine the age of borate formation in western Anatolia. A short review of the borate deposits and future forecasts will also be outlined.

2. Geology

Western Turkey, the easternmost part of the Aegean extensional province, is one of the most famous regions in the world that have been studied in respect of both scientific and economic aspects (Helvacı and Yağmurlu, 1995; Helvacı and Alonso, 2000; Ersoy et al., 2014). The Geological history of western Anatolia is related to Alpine-contractional and subsequent-extensional tectonic activities. The region also contains many industrial raw-material deposits (borates, zeolites, clays, coal etc.) and metallic mines (Au, Ag, Pb, Zn etc.) (Helvacı and Yağmurlu, 1995). These commercial deposits are mainly related to Alpine extensional tectonics that occurred after Oligocene time. This time interval is marked by intense crustal deformation, plutonic-volcanic activity and terrestrial sedimentation; accompanied by formation of metallic deposits and industrial minerals such as gold, silver and borates. The areas located in a region that hosts both gold and boron deposits in the Neogene volcano-sedimentary rock units are the subject of this paper (Helvacı and Alonso, 2000; Yiğit, 2009).

2.1. General Characteristics of the Neogene Basins in Western Anatolia

Western Anatolia has been the focus of many geological studies of the classical extensional tectonics in this region. The NE–SW-trending Neogene volcano-sedimentary basins that characterize western Anatolia, are mainly located on the northern part of the Menderes Massif – a progressively exhumed mid-crustal metamorphic unit that has undergone Neogene extensional tectonics in the area (Yılmaz et al., 2000; Helvacı et al., 2006; Ersoy et al., 2014). The NE–SW-trending basins are Bigadiç, Gördes, Demirci, Selendi, Emet, Güre and Uşak basins. Many studies have been carried out in these basins and different evolutionary models have been proposed by various authors for the stratigraphic and tectonic evolution of these NE–SW-trending volcanosedimentary basins. The NE–SW-trending basins were deformed by NE–SW and NW–SE-trending faulting during the late Miocene, and by E–W-trending normal faulting in the Pliocene–Quaternary. The region has been extended in a N–S-direction since at least the early Miocene, and that this extension occurred episodically in several phases. Recent studies show that there was a close relation in both space and time between the basin formation and the progressive exhumation of the Menderes Massif (Helvacı et al., 2006; Ersoy et al., 2014).

The stratigraphy, tectonics and volcanic components of the Neogene basins in western Anatolia offer some key insights into the relationship between the basin evolution and mode of extension in this intensely and chaotically deformed and extended area. With the present-day configurations, two main types of Neogene basins are recognized in the western Anatolia: (a) NE–SW and (b) ~E–W trending basins. Stratigraphy and tectonic features of the NE-SW trending basins reveal that their evolution was more complex. The E–W-trending basins are typical grabens which are still being deformed under ~N–S-extension (Ersoy et al., 2014).

The NE–SW-trending basins which occur on the northern side of the Menderes Core Complex (MCC), are the Demirci, Selendi, Uşak-Güre and Emet basins. The basins, formed on the MCC were evolved as successive supra-detachment basins and include two main sedimentary sequences: the early Miocene Hacıbekir Group and the early-middle Miocene İnay Group (Helvacı et al., 2006; Ersoy et al, 2011). There are also NE–SW-trending basins developed along the İzmir-Balıkesir Transfer Zone (İBTZ) (Kestelek, Sultançayır, Bigadiç and Gördes basins). The sedimentary infill of the basins developed on the İBTZ show distinct sequences and is controlled by mainly strike-slip and subsidiary normal faults (Helvacı et al., 2006; Ersoy et al., 2012).

2.2. Basement Units of the Neogene Basins

The Aegean–western Anatolia region is composed of several continental blocks that were originally separated by the northern branch of the Neo-Tethys marked today by the Vardar-İzmir-Ankara Suture (Figure 1; Şengör and Yılmaz, 1981). The Vardar-İzmir-Ankara Suture separated the Sakarya continent to the north and the Anatolide–Tauride block to the south and was formed by late Mesozoic northward subduction and accretion (Figure 1, Şengör and Yılmaz, 1981). The southernmost part of the region is marked by the south Aegean volcanic arc, which is formed from subduction of the African plate along the Hellenic trench (Pe-Piper and Piper, 2007).

The geology of western Anatolia is characterized by Tertiary volcano-sedimentary deposits covering a basement that includes several continental fragments and suture zones. Western Anatolia has a complex history of Late Cenozoic tectonic and magmatic activity. The basement units comprise; (1) the Menderes and Cycladic massifs, (2) the İzmir-Ankara Zone (comprising; (a) the Bornova flysch zone, (b) the Afyon zone, and (c) the Tavşanlı zone), (3) the rocks of the Sakarya Continent to the north, and (4) the Lycian Nappes to the south (Şengör and Yılmaz, 1981; Figure 1).

The region has experienced several tectonic events including subduction, obduction, continental collision and subsequent crustal thickening, extension and crustal thinning, that occurred between several continental blocks and suture zones (Figure 1). These were finally shaped by the Alpine orogeny related to Neo-Tethyan events (Şengör and Yılmaz, 1981). The main continental blocks are, from north to the south, the Sakarya zone of the Rhodope-Pontide Fragment and the Menderes Massif of the Anatolides. These two blocks are separated by the İzmir-Ankara zone that represents closure of a northward subducted Neo-Tethyan oceanic realm. The Menderes Massif is also overlain by the Lycian Nappes to the south. The İzmir-Ankara zone was formed by late Paleocene to early Eocene closure of the northern branch of the Neo-Tethys Ocean between the Sakarya continent and the Anatolide block, with the latter including the Menderes Massif and the Lycian Nappes (Şengör et al. 1984; Şengör and Yılmaz, 1981; Okay et al., 1996). The Menderes Massif is tectonically overlain by several nappes of the İzmir-Ankara Zone to the west and north, and by the Lycian nappes mainly to the south and east. In the west, the nappes are generally composed of graywackes and limestones

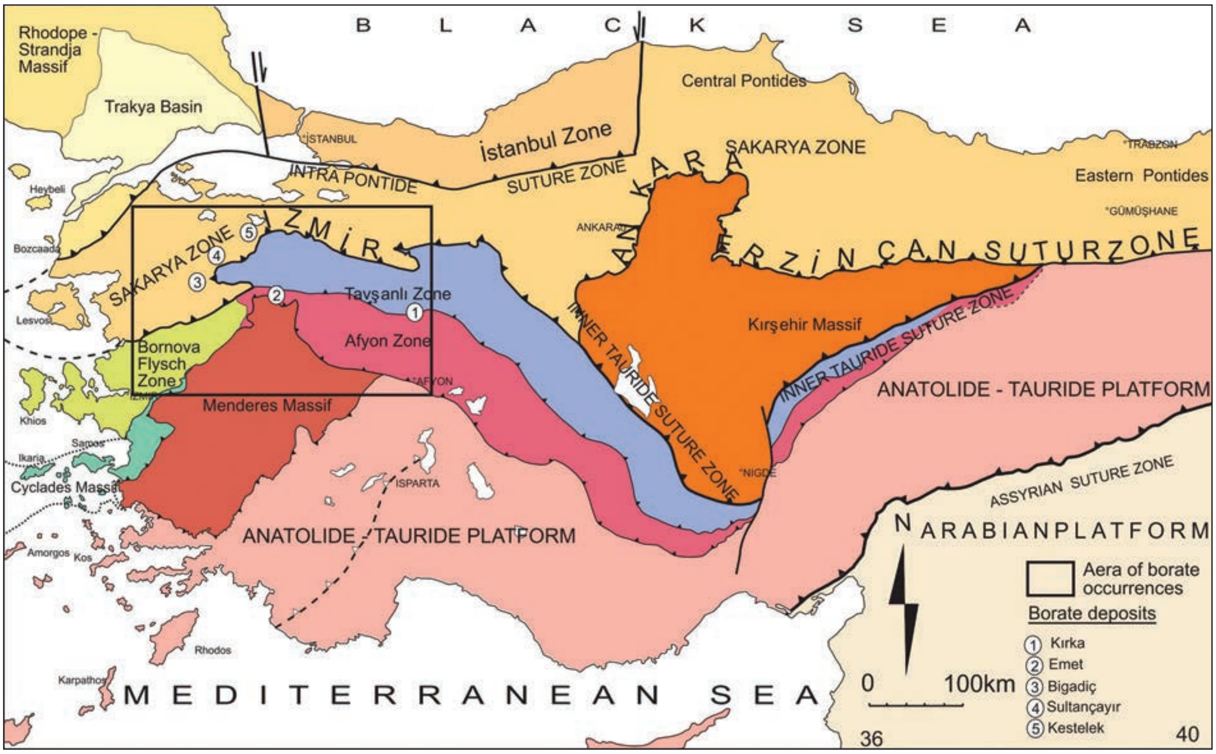

Figure 1- Tectonic map of the northeastern Mediterranean region showing the major sutures and continental blocks. Sutures are denoted by heavy lines, with the polarity of former subduction zones indicated by filled triangles. The Eocene plutonic belts in the Sakarya and Tavşanlı zones are shaded purple. The map was modified by Helvacı et al. (2014) using Şengör (1984), Okay (1989) and Okay et al. (1994, 1996).

with ophiolitic rocks of the Bornova flysch zone, while to the northeast, they are metaclastics, metabasites, and recrystallized limestones of the Afyon zone (Figure 1).

The İzmir-Ankara zone comprises the Bornova Flysch zone, the Afyon zone and the Tavşanlı Zone. The Bornova Flysch Zone comprises chaotically deformed Upper Maastrichtian – Palaeocene greywacke and shale with Mesozoic neritic limestone blocks of several kilometers in diameters (Okay et al., 1996). The Tavşanlı Zone forms a blueschist belt, representing the northward subducted passive continental margin of the Anatolide-Tauride platform (Okay et al., 1996). The Afyon zone comprises shelf-type Devonian to Palaeocene sedimentary sequence metamorphosed to greenschist facies (Okay et al., 1996).

2.3. Neogene Basins and Volcanism in Western Anatolia

Exhumation of the Menderes Massif resulted in the formation of several NE–SW-trending basins on its northern flank (the Demirci, Selendi, Güre and Emet basins), and was accompanied by strike-slip faulting and related basin formation along the İzmir-Balıkesir Transfer Zone in the west (Gördes basin; Bozkurt, 2003; Helvacı et al., 2006; Ersoy et al., 2011). The Miocene volcanic rocks occur in NE–SW-trending supra-detachment basins developed on the metamorphic rocks of the Menderes Massif (Yılmaz, 1990; Yılmaz et al., 2000; Helvacı et al., 2009; Karaoğlu et al., 2010; Ersoy et al. 2010, 2011; Ersoy et al., 2012).

The Geological evolution of western Anatolia during Neogene time is characterized by basin formation and contemporaneous wide-spread volcanic activity. The basins in the region were developed mainly in two directions: NE- and E–W-trends (Figure 2). The main NE-trending basins in the region are Bigadiç, Gördes, Demirci, Selendi and Uşak-Güre basins, while the E–W-trending basins are characterized by actively deforming grabens such as the Simav, Gediz, Büyük Menderes and Küçük Menderes grabens. The E–W-trending basins are younger in age and cut the NE-trending basins (Figure 2).

Several models have been proposed concerning the development of these basins in western Anatolia.

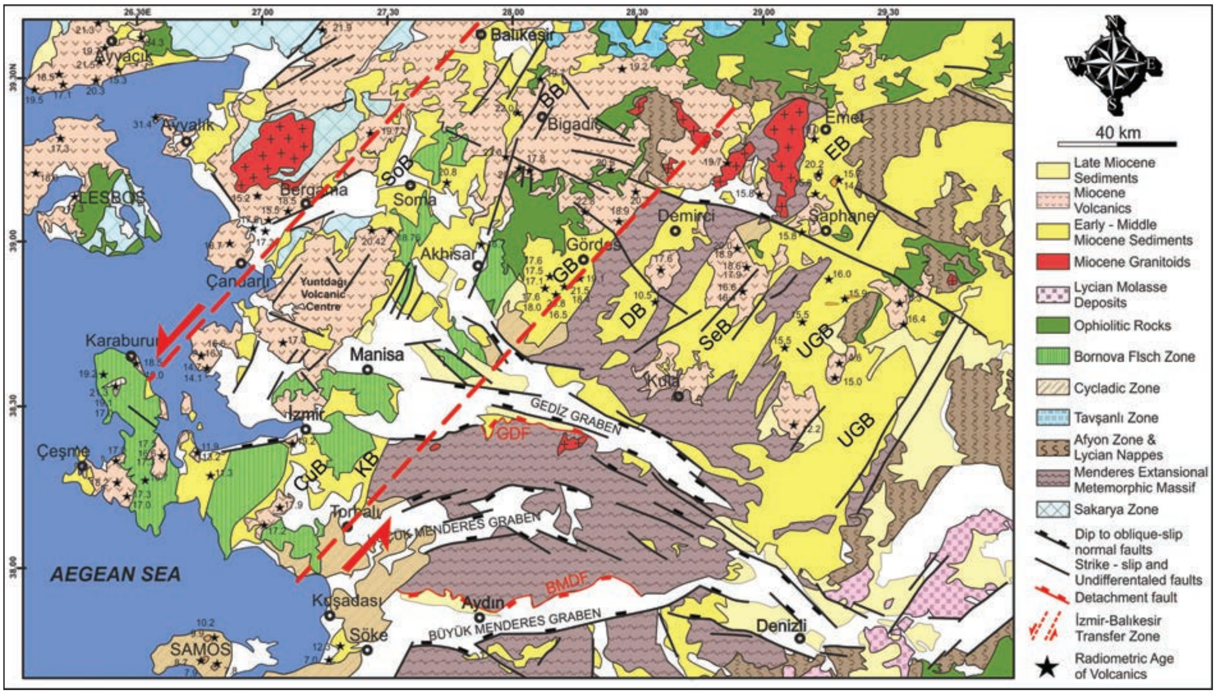

Figure 2- Geological map of the western Anatolia showing the distribution of the Neogene basins, radiometric ages of the volcanic intercalations in the Neogene sediments and major structures (modified from 1/500,000 scaled geological map of Turkey (MTA); and studies cited in the text). Abbreviations for granitoids: EyG: Eybek, KzG: Kozak, AG: Alaçamdağ, Kog, Koyunoba, EG: Eğrigöz, BG: Baklan, TG: Turgutlu and SG: Salihli granitoids. Abbreviations for basins: KB: Kocaçay Basin, BB: Bigadiç Basin; CuB: Cumaovası Basin; SoB: Soma Basin, GB: Gördes Basin, DB: Demirci Basin, SeB: Selendi Basin, UGB: Uşak–Güre Basin, EB: Emet Basin. Abbreviations for detachments: GDF: Gediz (Alaşehir) Detachment Fault, SDF: Simav Detachment Fault, BMDF: Büyük Menderes Detachment Fault (after Ersoy et al., 2014).

These are the cross-graben model, the orogenic collapse model, the two-stage episodic extension model, and the pulsed extension model (Şengör, 1987; Seyitoğlu and Scott, 1996; Purvis and Robertson, 2004). The NE-SW trending basins host the world class huge borate deposits, which are the main subject of this paper. The western Anatolian extensional basins are also rich in terms of geothermal energy resources due to their extensional tectonic setting and high heat flow (Çemen et al., 2014).

In western Anatolia, volcanic rocks from the latest Oligocene to Quaternary can be divided into two groups based on their chemical composition with temporal and spatial distribution (Yılmaz, 1990; Güleç, 1991; Seyitoğlu and Scott 1992; Ercan et. al. 1996; Seyitoğlu et al. 1997; Yılmaz et al. 2000; Aldanmaz et al. 2000). The magmatic rocks of the Late Oligocene - Early Miocene time are mainly rhyolite to basaltic andesite in composition and exhibit calc-alkaline and shoshonitic affinity. These rocks are enriched in HREE with respect to LILE and LREE, and have higher $^{87}Sr/^{86}Sr$ and lower $^{143}Nd/^{144}Nd$ isotopic composition (e.g., Bingöl et al., 1982; Güleç 1991; Aldanmaz et al. 2000). There is a time break in volcanic activity from the end of the Middle Miocene to beginning of the Late Miocene in western Anatolia (Yılmaz,1990). The volcanic rocks of mainly Late Miocene – Early Pliocene and are more basic in composition and exhibit an alkaline character. These rocks are depleted in HREE and enriched in LILE, HFSE, MREE and LREE. The volcanic rocks of the Late Miocene – Early Pliocene exhibit lower $^{87}Sr/^{86}Sr$ and higher $^{143}Nd/^{144}Nd$ isotopic ratios (Güleç,1991; Aldanmaz et al., 2000). In addition, the alkaline basaltic volcanism in the Miocene-Pliocene changed from a potassic to a sodic character (Kula volcanics: Güleç, 1991; Alıcı et al., 2002; table 2 and figure 8).

The geologic evidence indicates that the evolution of the magmatic activity in the region was related to post-collisional extensional tectonics and that the Miocene volcanic rocks in the NE–SW trending basins were emplaced during early-middle Miocene episodic exhumation of the Menderes Massif as a core complex. The Menderes Massif was asymmetrically uplifted and collapsed, starting from the north and continuing to the south during the early to middle Miocene. The high-K calc-alkaline, shoshonitic, and ultrapotassic volcanic rock groups were produced during this interval in the region. Geochemical data show that the origin of the high-K calc-alkaline volcanics include crustal contributions to the mantle-derived magmas. While rhyolites dominated during the early Miocene, more primitive andesites are seen during the middle Miocene. At the same time, rapid increase in the amount of the ultrapotassic and shoshonitic volcanic rocks is compatible with lithospheric thinning (Ersoy et al., 2012).

In the NE-trending basins, the late Cenozoic volcanic activity is represented mainly by Early-Middle Miocene calc-alkaline moderate to felsic volcanic rocks and Plio-Quaternary alkaline volcanism. In addition to these, in the Bigadiç Basin, Early Miocene alkali basaltic volcanism has been documented (Helvacı and Erkül, 2002; Helvacı et al., 2003; Erkül et al., 2005*b*). To the east, the data show that the alkaline volcanism had already begun in the Early Miocene in the NE-trending basins, and alkaline lamproitic volcanic rocks were also introduced (Ersoy and Helvacı, 2007).

Volcanic intercalations in the NE–SW-trending Neogene volcano-sedimentary basins can be grouped as: early Miocene high-K calc-alkaline andesite, dacite and rhyolite; early-Miocene mafic volcanics; middle Miocene high-K calcalkaline andesite and dacite; middle Miocene mafic volcanics; Late Miocene mafic lavas; and Quaternary alkali basaltic volcanism.

Early-Miocene mafic volcanic units in Bigadiç basin comprise the Gölcük basalt (calc-alkaline shoshonite), which differs from the other early-Miocene mafic samples of the Selendi and Emet basins that have higher K contents (shoshonitic to ultrapotassic Kuzayır lamproite and Kestel volcanics). The early Miocene volcanism in all the NE–SW-trending basins is characterized by a bimodal volcanic association, dominated by calc-alkaline dacitic–rhyolitic members. During the early Miocene, wide-spread dacitic-rhyolitic volcanism occurred in the region (Helvacı and Erkül, 2002; Erkül et al., 2005*b*; Ersoy and Helvacı, 2007).

The middle Miocene volcanism in the region is characterized by a second-stage bimodal volcanic association, including a group of high-K calc-alkaline to andesites and dacites, and a group of shoshonitic to ultrapotassic mafic products such as lamproites, ultrapotassic shoshonites and ultrapotassic latites. These volcanic rocks interfinger with the Middle Miocene İnay Group in the Demirci, Selendi, Güre and Emet basins (Ersoy and Helvacı, 2007).

During the late Miocene a volcanic rocks group (comprising mildly alkaline basalts, K-trachybasalt and shoshonites) were produced which are characterized by the absence of the felsic magmas, and occur only in the Demirci and Selendi basin. Finally, the Quaternary is represented by the strongly alkali group of basaltic (tephrite, basanite, phonotephrite) volcanic activity emplaced on the northern flank of the Gediz graben (Kula volcanics). Overall, it is apparent that the volcanic rocks in the different basins can be correlated into distinct groups on the basis of their geochemical properties and ages of eruption (Ersoy et al., 2014).

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 several mineral deposits. In this respect, tectonic evolution of the Neogene basins, especially of the NE-trending ones, is a fundamental theme in studying the Neogene volcanic evolution as well as the related mineral deposits of the region. The stratigraphy of the basin fills and volcanic units are summarized in figure 3. Tectonic evolution of the NE-trending basins seems to be related to exhumation of the Menderes Massif. This episode took place in the region during the early Miocene. E–W trending grabens began to develop later. Both stages were accompanied by volcanic activity. Therefore, it is clear that tectonic shaping of the basins played a key role in the volcanic evolution and deposition of the borate and other related mineral deposits of the region.

The Miocene borate deposits of western Turkey are associated with extensive medium- to high-K calc-alkali ignimbritic volcanism and a differentiated comagmatic alkaline trachybasalt–trachydacite lava suite. Ignimbritic air-fall and reworked pumiceous clastic materials are intimately associated with the lake sediments that host the borate deposits. Local ignimbritic volcanism is considered to be the primary source of the B for the Kırka and other borate deposits. The geochemical composition of the ignimbrites associated with the borates exhibit a

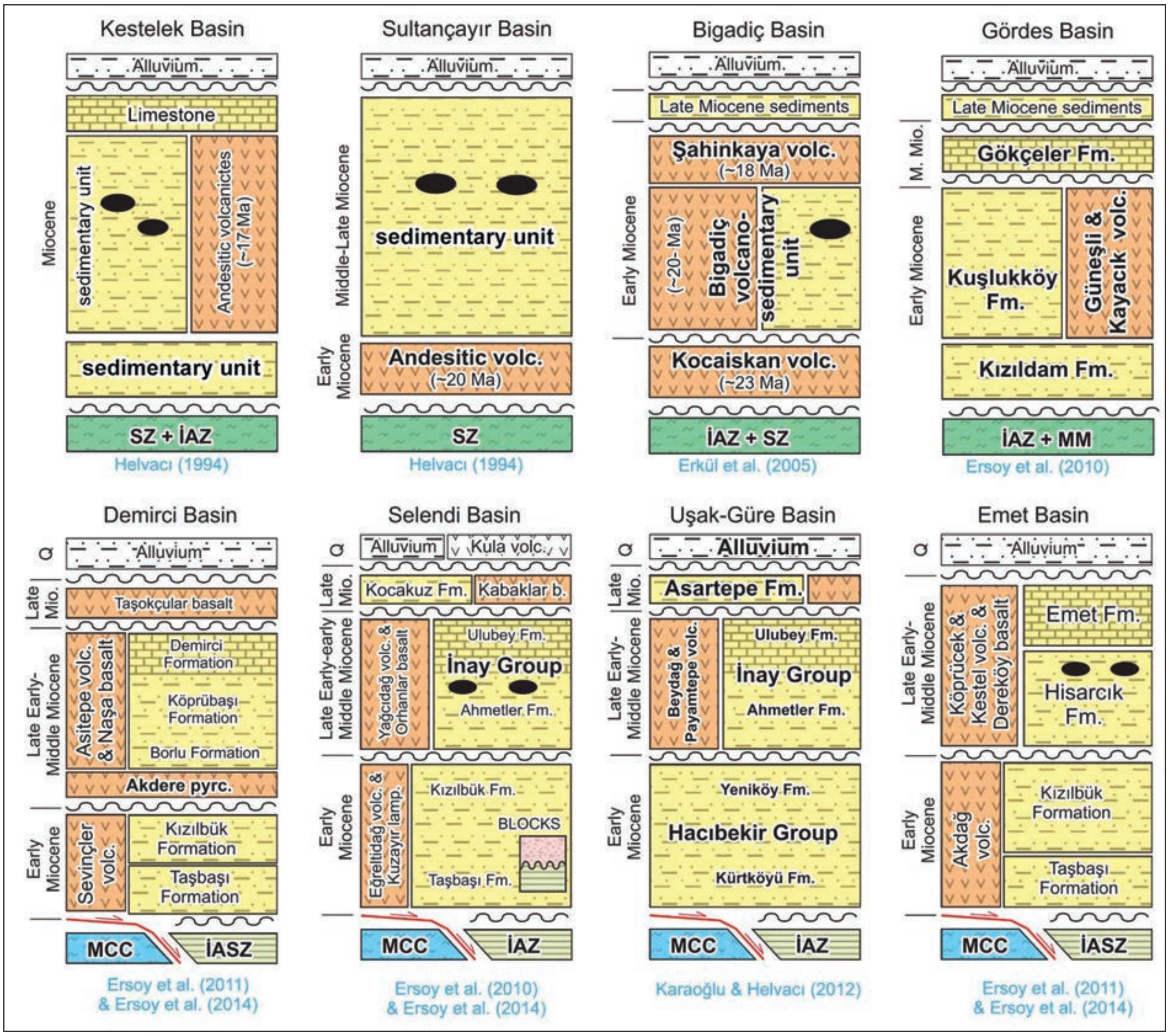

Figure 3- Stratigraphic columnar sections of the borate bearing basins in Western Anatolia. MM-metamorphic rocks of the Menderes Massif, İAZ-İzmir-Ankara zone rocks, SZ-metamorphic rocks of the Sakarya zone, MCC- Metamorphic Core Complex (modified after Ersoy et al., 2014).

number of features that might prove useful in the exploration for borates in similar volcanic domains. In particular, 'fertile' ignimbrites generally belong to a high-K calc-alkali suite, are well-evolved and fractionated (Kr/Rb is low) with a high-silica rhyolitic bulk composition, exhibit a combined high content of B, As, F, Li and Pb, with high Br/La and Br/K ratios, and a mildly fractionated REE pattern and large positive Eu anomaly (Floyd et al., 1998). Other apparent discriminants involving both compatible and incompatible elements are largely a function of different degrees of partial melting and fractionation. It is suggested that the initial source of the B and other associated elements was from LIL-rich fluids released by the progressive dehydration of altered oceanic crust and pelagic sediments in a subduction zone. The absence or presence of sediments in a segmented subduction zone may influence the variable lateral distribution of borates in active margins on a global scale. Once the crust has become enriched in B via previous or contemporary subduction-related calc-alkali magmatism, the effects of tectonic environment, climate and hydrothermal activity influence the local development of the deposits (Floyd et al., 1998).

3. Stratigraphic Correlation of Neogene Borate Bearing Basins

The stratigraphic and structural features of the Selendi, Demirci, Emet and Güre basins are compared with the adjacent Kestelek, Sultançayır, Bigadiç and Güre basins in figure 2 and 3.

The Neogene volcano-sedimentary succession in Bigadiç basin contains the Kocaiskan volcanics (23.6±0.6–23.0±2.8 Ma, table 1) that are composed of andesitic volcanics and the unconformably overlying Bigadiç volcano-sedimentary succession (Figure 3). The latter consists of borate-bearing lacustrine sediments and coeval felsic (Kayırlar, Sındırgı and Şahinkaya volcanics; 20.8±0.7–17.8±0.4 Ma K–Ar and Ar/Ar ages) and mafic (Gölcük basalt,19.7±0.4 Ma K–Ar and 20.5±0.1 Ma Ar/Ar ages) volcanic rocks (Helvacı, 1995; Helvacı and Alonso, 2000; Helvacı and Erkül, 2002; Helvacı et al., 2003; Erkül et al., 2005*a,b*). These rock units are unconformably overlain by late Miocene–Pliocene continental sediments detritus and alluvium. The radiometric ages and the stratigraphic relationships clearly indicate that the borate-bearing succession was deposited during the early Miocene and is very similar to that of Gördes basin (Figure 3).

The NE–SW-trending Gördes basin contains a similar volcanosedimentary sequence to that of Bigadiç basin. These two basins are characterized by a main early Miocene volcano-sedimentary sequence. The early Miocene volcano-sediments of Gördes basin were controlled by NE–SW-trending dextral strike- to oblique-slip and E–W-trending dip-slip normal faults. Gördes and Bigadiç basins are transtensional basins that developed during the early Miocene (Ersoy et al., 2012). The data presented here clearly show that the Demirci, Selendi, Emet and Güre basins have similar stratigraphic, geochemical and tectonic characteristics. The basin-fill of these Neogene basins are characterized by; (a) Lower Miocene Hacıbekir Group, (b) Middle Miocene İnay Group, (c) locally developed late Miocene sedimentary and basaltic volcanic rocks and (d) Quaternary sediments and basaltic volcanics, which are separated by regional-scale major unconformities (Figure 3; Ercan et al., 1978, 1983; İnci, 1984; Seyitoğlu, 1997*a,b*; Yılmaz et al., 2000; Ersoy and Helvacı, 2007; Ersoy et al., 2010). However, the Bigadiç and Gördes basins have distinct stratigraphic and tectonic features from the other NE–SW-trending basins. In that they are characterized by early Miocene volcano-sedimentary successions which were deposited along early Miocene strike-slip and related normal faults.

The NE–SW-trending Demirci, Selendi, Emet and Güre basins, which developed on the Menderes Core Complex, have similar stratigraphies that comprise two main volcano- sedimentary successions: the Lower Miocene Hacıbekir Group, and the unconformably overlying Middle Miocene İnay Group. These two groups are locally overlain by late Miocene volcanic and sedimentary units and recent sediments. The Lower Miocene Hacıbekir Group in the Demirci, Selendi, Emet and Güre basins was deposited in a supra-detachment basin formed on the Simav detachment fault (SDF). The Hacıbekir Group consists of conglomerates of the Kürtköyü formation and sandstone–mudstone alternations of the Yeniköy formation in the Demirci, Selendi and Güre basins and Taşbaşı and Kızılbük formations in the Emet basin. The İnay Group is intercalated with several syn-sedimentary andesitic to rhyolitic lava flows, dykes and associated pyroclastics in the Demirci, Selendi, Emet and Gördes basins.

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 (Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy et al., 2012; figures 2 and 3). The Köprücek volcanics are overlain by the limestones of the Emet formation. In the southern part of the basin, the Hisarcık formation sediments 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; table 1).

The Kırka borate deposit occurs further to the east and is located in completely different geological setting and volcanostratigraphic succession.

As far as the economic potentional of Neogene basins is concerned, a limited number of basins in western Turkey contain world class borate reserves, with mineralization present as stratabound deposits in Neogene volcano-sedimentary successions. These sediments, as well as being enriched in B, are variably enriched in Li, S, Sr and As. Potential sources for these elements include lacustrine sediments, local basement rocks and volcanism with hot spring activity. Volcanism occured throughout the sedimentary infilling of these basins, as shown by the presence of tuffaceous sediments, volcanic clasts in conglomerates, interbedded and cross cutting lavas

Table 1- Radiometric age data from the volcanic rocks associated with the borate bearing Neogene basins in western Anatolia.

Basin and Unit	*Sample*	*Rock type*	*Radiometric Age (Ma), Material*	*References*
Kestelek Basin				
	KE-1	*Trachandesitic tufff*	*17.4±0.3 (hornblend, K/Ar)*	
Sultançayır Basin				*Helvacı and Alonso, 2000*
	S-1	*Rhyolitic tuf*	*20.0 ± 0.5 (feldspar, K/Ar)*	
Bigadiç Basin				
Kocaiskan volcanics	*F-110*	*Andesite*	*23.00 ± 2.80 (biotite, K–Ar)*	
Gölcük Basalt	*F-199*	*Shoshonite*	*19.70 ± 0.40 (groundmass, Ar–Ar)*	
	F-199	*Shoshonite*	*20.50 ± 0.10 (groundmass, Ar–Ar)*	
Sındırgı volcanics	*F-194*	*Rhyolite*	*20.20 ± 0.50 (biotite, Ar–Ar)*	*Helvacı and Erkül, 2002; Helvacı et al., 2003; Erkül et al., 2005b*
	F-197	*Dacite*	*20.30 ± 0.30 (biotite, Ar–Ar)*	
Şahinkaya volcanics	*F-195*	*B. andesite*	*17.80 ± 0.40 (hornblende, K–Ar)*	
Kayırlar volcanics	*F-214*	*Latite*	*20.60 ± 0.70 (biotite, K–Ar)*	
Çamköy basalt	*B-6*	*Basalt*	*18.30 ± 0.20 (feldspar, K–Ar)*	*Helvacı, 1995*
Gördes Basin				
Kayacık volcanics	*LB-1*	*Dacite*	*16.90 ± 0.50 (biotite, K–Ar*	*Seyitoğlu et al., 1992*
	TSB	*Rhyolite*	*18.10 ± 0.50 (biotite, K–Ar)*	
	S2/5	*Rhyodacite*	*20.45 ± 0.38 (feldispat, Ar/Ar)*	*Purvis and Robertson, 2005*
	S2/11	*Acidic tuff*	*21.71 ± 0.04 (biotite, Ar/Ar)*	
Güneşli volcanics	*S2/68*	*Acidic tuff*	*17.04 ± 0.35 (biotite, Ar/Ar)*	
	861	*Rhyolite*	*18.91 ± 0.03 (sanidite, Ar/Ar)*	
Demirci Basin				
Sevinçler volcanics	*721*	*Dacite*	*19.06 ± 0.05 (plagioclase, Ar/Ar)*	*Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy et al., 2012*
	721	*Dacite*	*19.56 ± 0.04 (biotite, Ar/Ar)*	
Asitepe volcanics	*717*	*Andesite*	*17.58 ± 0.09 (plagioclase, Ar/Ar)*	
Naşa basalt	*ÖD-50*	*Shoshonite*	*15.80 ± 0.30 (whole rock, K–Ar)*	*Ercan et al., 1996*
Selendi Basin				
Eğreltidağ volcanics	*SE-1*	*Rhyolite*	*18.90 ± 0.60 (biotite, K–Ar)*	*Seyitoğlu et al., 1997*
	521	*Dacite*	*18.90 ± 0.10 (plagioclase, Ar/Ar)*	*Helvacı and Ersoy, 2006; Ersoy et al., 2008*
	521	*Acidic tuff*	*20.00 ± 0.20 (amphibole, Ar/Ar)*	
Kuzayır lamproiti	*518*	*Lamproite*	*17.90 ± 0.20 (groundmass, Ar/Ar)*	
	518	*Lamproite*	*18.60 ± 0.20 (phlogopite, Ar/Ar)*	
Yağcıdağ volcanics	*SE-3*	*Trachydacite*	*14.90 ± 0.60 (biotite, K–Ar)*	*Seyitoğlu et al., 1997*
	S1/3	*Acidic tuff*	*16.42 ± 0.99 (feldspar, Ar/Ar)*	*Purvis and Robertson, 2005*
	YF-2	*Dacite*	*16.43 ± 0.32 (plagioclase, Ar/Ar yaşı)*	*Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy et al., 2012*
Uşak–Güre Basin				
Beydağ volcanics				
Elmadağ volc. center	*U-31*	*Trachydacite*	*16.28 ± 0.05 (biotite, Ar/Ar)*	*Helvacı et al., 2009; Karaoğlu et al., 2010*
	U-68	*Pyroclastic*	*16.48 ± 0.08 (biotite, Ar/Ar)*	
İtecektepe volkanic center	*UG-63*	*Dacite*	*14.60 ± 0.30 (whole rock, K–Ar)*	*Seyitoğlu et al., 1997*
	U-159	*Dacite dike*	*15.04 ± 0.10 (biotite, Ar/Ar)*	*Helvacı et al., 2009; Karaoğlu et al., 2010*
Beydağ volkanic center	*U-161*	*Daciteik dome*	*12.15 ± 0.15 (biotite, Ar/Ar)*	
	U-2	*Dacite*	*13.10 ± 0.20 (whole rock, K–Ar)*	*Ercan et al., 1996*
Payamtepe volcanics				
Yeniköy dikes	*UG-58*	*Trachydacite*	*15.10 ± 0.40 (whole rock, K–Ar)*	*Seyitoğlu et al., 1997*
	U-153	*Trachyte*	*16.01 ± 0.08 (sanidine, Ar/Ar)*	*Helvacı et al., 2009; Karaoğlu et al., 2010*
Karabacaklar volcanics	*U-144*	*Trachyte*	*15.93 ± 0.08 (groundmass, Ar/Ar)*	
	UG-75	*Trachyte*	*15.90 ± 0.40 (whole rock, K–Ar)*	*Seyitoğlu et al., 1997*
Kıran basalt	*UG-145*	*UK Latite*	*15.50 ± 0.40 (whole rock, K–Ar)*	
Güre lamproite	*IZ-38*	*Lamproite*	*14.20 ± 0.12 (groundmass, Ar/Ar)*	*Innocenti et al., 2005*
	05GÜ02	*Lamproite*	*15.54 ± 0.33 (groundmass, Ar/Ar)*	*Preleviç et al., 2012*
Emet Basin and Gediz–Şaphane Region				
Akdağ volcanics	*E6*	*Rhyolite*	*20.20 ± 0.40 (biotite, K/Ar)*	*Seyitoğlu et al., 1997*
	E-3	*Rhyolite*	*19.00 ± 0.20 (biotite, K/Ar)*	
Köprücek volcanics	*E-1*	*Pyroclastic*	*16.80 ± 0.20 (biotite, K/Ar)*	*Helvacı and Alonso, 2000*
Dereköy basalt	*E9*	*UK latite*	*15.40 ± 0.20 (feldspar, K/Ar)*	
	E3	*UK latite*	*14.90 ± 0.60 (whole rock, K–Ar)*	*Seyitoğlu et al., 1997*
	So7-15	*UK latite*	*15.70 ± 0.50 (whole rock, K–Ar)*	*Çoban et al., 2012*
Kestel volcanics	*821*	*UK latite*	*15.91 ± 0.07 (biotite, Ar/Ar)*	*Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy et al., 2012*
	821	*UK latite*	*15.73 ± 0.11 (biotite, Ar/Ar)*	
Kırka Basin				
	K-2(1)	*Rhyolite*	*18.5±0.2 (biotite, K/Ar)*	*Helvacı and Alonso, 2000*
	K-2	*Rhyolitic ignimbrites*	*19.0±0.2 (biotite, K/Ar)*	
	2a-1 (K1-955.8m)	*Basalt*	*18.63±0.2 (New Ar/Ar data)*	
	2a-2 (K6-1063m)	*Trachyte*	*18.69±0.04 (New Ar/Ar data)*	*Helvacı and Yücel-Öztürk, 2013; Seghedi and Helvacı, 2014*
	2c	*Lamproite lavas*	*16.91±0.05 (New Ar/Ar data)*	
	2d(K-1)	*Trachyte*	*16.1±0.2 (feldspar, K/Ar)*	

and travertines from hot spring activity. Research in this area has involved mapping and sampling of the volcanic successions, K-Ar dating and detailed geochemical analysis of these lavas, as well as determination of the relationships with interfingered sediments. Data from Bigadiç, Emet and Kırka basins show that early volcanism is acidic and largely calc alkaline, although sometimes alkaline, whereas later volcanism is intermediate and exclusively alkaline. K-Ar dating of volcanic samples from the borate basins indicate that the first phase of volcanism occurred in the Early Miocene with the second phase in the Middle Miocene. Field evidence from the basins indicates that the acidic volcanism occurred prior to and during borate mineralisation whilst the intermediate alkaline volcanism occurred later. Correlation of the geochemical characteristics of the volcanic units will help us to understand the interrelationships between the formation of the borate deposit, gold mineralization, and volcanic evolution of the region.

In order to establish the role of local volcanism as a source of boron, the relationship between volcanism and associated sediments in the Emet (colemanite deposit), Bigadiç (colemanite and ulexite) and Kırka (borax deposit) basins were studied for comparison. Chemical study of volcanic rocks associated with the borate deposits of Kırka, Emet, Bigadiç, Kestelek and Sultançayır districts have been performed. The geochemical work has focussed on boron and trace elements distribution on volcanics belonging to two main stages of magmatic activity. High boron contents have been found in volcanics coming from outcrops surrounding the borate deposits. The volcanics of Lower-Middle Miocene age are mainly andesites to rhyolites of calk-alkaline affinity and show a range in B from 25 to 270 ppm. Consistently lower values (19-67 ppm) are shown by volcanites of Upper Miocene age (Helvacı, 1977; Fytikas et al., 1984; Floyd et al., 1998; Helvacı and Alonso, 2000) having shoshonitic and potassic affinities. In addition, REE have patterns typically linked to their affinity and degree of evolution, although secondary mobilization can not be exclude in order to explain some negative Ce anomalies observed. Presence of widespread secondary minerals (e.g. zeolites, calcites) supports the hypothesis of interaction with circulating shallow level water. In light of the present data the high B contents in these rocks can be explained by interaction between the volcanics and circulating boron-rich hot water. Magmatic activity may have been responsible for generating a high thermal gradient in the study area which provided the energy to drive thermal circulating water that was able to mobilize boron from sedimentary and volcanic sequences. An alternative hypothesis for generating such borate deposits is suggested by the presence in several deposits of volcanic rocks interfingered with sediments forming peperitic textures. This indicates there may have been direct contributions of volcanics and magmatic volatiles to the lacustrine basins (Erkül et al., 2006).

3.1. Bigadiç, Susurluk and Kestelek Basins

The stratigraphy of these basins was investigated by Helvacı (1983, 1995) and Erkül et al. (2005*b*). The basin-fill that lies unconformably above the basement rocks, includes Upper Cretaceous–Palaeocene Bornova Flysch Zone, Lower–Middle Eocene Başlamış formation and Oligocene detrital rocks (Erdoğan, 1990; Okay and Siyako 1991) and is represented by two distinct volcan-sedimentary associations separated by a basin-wide angular unconformity. Volcanism in the Bigadiç area is characterized by two rock units that are separated by an angular unconformity. These units are: (1) the Kocaiskan volcanics that gives K/Ar ages of 23 Ma, and (2) the Bigadiç volcano-sedimentary succession within the borate deposits that yields ages of 20.6 to 17.8 Ma (Figure 3). Both units are Early Miocene in age and are unconformably overlain by Upper Miocene-Pliocene continental deposits. The Kocaiskan volcanics are related to the first episode of volcanic activity and comprise thick volcanogenic sedimentary rocks derived from subaerial andesitic intrusions, domes, lava flows and pyroclastic-rocks.

The Kocaiskan volcanics, which are andesitic in composition, are the earliest volcanic products of the Early Miocene period, covering an area larger than 800 km^2 within the study area. The K/Ar age data indicate that the Kocaiskan unit is 23.0±2.8 Ma old, consistent with previous measurements (Table 1). The unit comprises andesitic intrusions, lavas, pyroclastic rocks and associated volcanogenic sedimentary rocks, which are unconformably overlain by the Lower Miocene Bigadiç volcano-sedimentary succession (Helvacı and Erkül, 2002; Helvacı et al., 2003; Erkül et al., 2005*b*).

The Bigadiç volcano-sedimentary succession, is a Miocene sequence comprising volcanic (e.g. Sındırgı volcanics, Gölcük basalt, Kayırlar volcanics and Şahinkaya volcanics) and lacustrine rocks (e.g. lower limestone unit, lower tuff unit, lower borate unit, upper tuff unit and upper borate unit) (Helvacı, 1995; Erkül et al., 2005*b*) (Figure 3).

The second episode of volcanic activity is represented by basaltic to rhyolitic lavas and pyroclastic rocks, accompanied by lacustrine–evaporitic sedimentation. Dacitic to rhyolitic volcanic rocks, called the Sındırgı volcanites, comprise NE-trending intrusions producing lava flows, ignimbrites, ash-fall deposits and associated volcanogenic sedimentary rocks. Other NE-trending olivine basaltic (Gölcük basalt - Early Miocene alkali basalt) and trachyandesitic (Kayırlar volcanites) intrusions and lava flows were synchronously emplaced into the lacustrine sediments. The intrusions typically display peperitic rocks along their contacts with the sedimentary rocks (Helvacı, 1995; Helvacı and Erkül, 2002; Helvacı et al., 2003; Erkül et al., 2005*b*, 2006; figure 4).

Figure 4- Peperitic texture of basaltic lava flows in lacustrine sediments, Gölcük locality, Bigadiç deposit, Turkey.

The radiometric age data reveal that the formation of the Bigadiç volcano-sedimentary succession is restricted to a period between 20.6±0.7 and 17.8±0.4 Ma. K/Ar dating of the Sındırgı volcanics yield an age of 20.2±0.5 and 19.0±0.4 Ma from rhyolites and dacites, respectively (Table 1). The total gas age corresponds to a K/Ar age of an olivine-basalt sample, namely 20.5±0.1 Ma, and an Ar/Ar age of 19.7±0.4 Ma. The K/Ar date of the NE-trending dyke of the Kayırlar volcanites is 20.6±0.7 Ma. The K/Ar dating of lavas of the Şahinkaya volcanics gave 17.8±0.4 Ma. (Helvacı and Erkül, 2002; Helvacı et al., 2003; Erkül et al., 2005*b*).

Geochemical data from the Bigadiç¸ area are also related to the extensional regime, which was characterized by bimodal volcanism related to extrusion of coeval alkaline and calc-alkaline volcanic rocks during the second volcanic episode. The formation of alkaline volcanic rocks dated as 19.70 ± 0.40 Ma can be related directly to the onset of the N–S extensional regime in western Turkey. In the Bigadiç basin widespread high-K calcalkaline andesitic to rhyolitic lava flows, domes and pyroclastic rocks are interlayered with borate-bearing lacustrine deposits (Helvacı, 1995; Helvacı and Alonso, 2000; Erkül et al., 2005*b*). The ages of the intermediate to acidic volcanism lie between 23.0 and 17.8 Ma, and interlayered high-K calcalkaline shoshonites within the basin have ages of 20.5–19.7 Ma (Helvacı, 1995; Erkül et al., 2005*b*). The volcanic unit cutting the upper borate zone in the Bigadiç Basin is assigned a late Miocene in age on the basis of its geochemical features. The geochemistry of the shoshonitic rocks in the area is similar to those of other late Miocene mafic rocks in the İzmir-Balıkesir Transfer Zone (İBTZ) (Ersoy et al., 2012; Seghedi et al., 2015).

This early-middle Miocene volcanism continues further NE (towards Susurluk-Çaltıbük; Helvacı, 1994; Helvacı and Alonso, 2000; figure 1) with widespread andesitic to rhyolitic lava flows and related pyroclastic rocks interlayered with lacustrine sediments in Sultançayır and Kestelek basins. The Miocene sequence in the Sultançayır basin consists of the following in ascending order: andesite and agglomerate; tuff; sandy conglomerate; limestone; sandy claystone containing boratiferous gypsum, bedded gypsum and tuff; and clayey limestone (Helvacı, 1994). K/Ar age dating of one tuff sample taken from the tuff unit yields an age of 20.01 Ma (Helvacı, 1994; Helvacı and Alonso, 2000).

The Miocene sequence in the Kestelek basin contains basement conglomerate and sandstones; claystone with lignite seams, marl, limestone, and tuff; agglomerates and volcanic rocks; the borate zone comprises clay, marl, limestone, tuff and borates; and limestones with thin clay and chert bands. The volcanic activity gradually increased and produced tuff, tuffite and agglomerate, and andesitic, trachytic and rhyolitic volcanic rocks that are interbedded with sediments. K/Ar age dating of one tuff sample taken from the borate zone yields an age of 17.4 Ma (Helvacı, 1994; Helvacı and Alonso, 2000) (Table 1, figures 2 and 3)

3.2. Gördes Basin

Gördes basin is confined by the Menderes Massif to the east and by ophiolitic melange units of the

Bornova flysch zone to the west (Figure 2), and has previously been studied by Nebert (1961), Yağmurlu (1984), Seyitoğlu and Scott (1994*a,b*) and Purvis and Robertson (2004, 2005). Seyitoğlu and Scott (1994*a,b*) divided the stratigraphy of Gördes basin into three main sedimentary units. The basal part of the sequence is represented by the conglomerates and sandstones of the Dağdere formation in the north and the Tepeköy formation in the south, which are overlain by the sandstone–mudstone alternation of the Kuşlukköyü formation that is also intercalated with acid tuff (Figure 3). The basin sediments are cut by dacitic–rhyolitic volcanic necks (central volcanics; Seyitoğlu and Scott, 1994*b*). The stratigraphy of Gördes basin has been revised with new field data by Ersoy et al., (2011) and the stratigraphy of the basin begins with Kızıldam formation which is conformably overlain by the Kuşlukköyü formation. The Kuşlukköyü formation interfingers with the Güneşli Volcanics and are also cut by the Kayacık Volcanics in the center of the basin (Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy et al., 2011). These units are unconformably overlain by the Gökçeler formation and late Miocene to Recent sediments. The Kızıldam formation crops out along the basin-bounding faults in Gördes basin.

In the eastern margin of Gördes basin, the Kızıldam formation consists of reddish-brown conglomerates of alluvial fan origin, which are mainly derived from the underlying metamorphic rocks of the Menderes Massif. Here, the Kızıldam formation unconformably overlies the metamorphic rocks and is composed of metamorphic clasts such as gneisses, schists and migmatites. In the western part of Gördes basin, the Kızıldam formation starts with well-lithified carbonate-cemented conglomerates with mainly limestone-dominated clasts derived from the rocks of the İzmir-Ankara suture zone. The type section of the Kızıldam formation is best seen around the Kızıldam village. To the center of the basin, the unit passes laterally into the Kuşlukköy formation. The Kızıldam formation is regionally correlated with the Lower Miocene Kürtköyü formation in the Demirci and Selendi basins, and is equivalent of the lower parts of the Dağdere and Tepeköy formations named by Seyitoğlu and Scott (1994*a,b*). It is also correlated with the alluvial fan facies of Purvis and Robertson (2004) (Figure 3). Seyitoğlu and Scott (1994a) obtained 24.2±0.8–21.1±1.1 Ma K–Ar ages from tourmaline leucogranite pebbles in the Kızıldam formation (Table 1). The age of the Kızıldam formation is accepted to be early Miocene on the basis of radiometric age data from the volcanic intercalations of the conformably overlying Kuşlukköy formation (Ersoy et al., 2011).

3.3. Demirci Basin

The infill of Demirci basin is cut into two sectors by the Pliocene-Quaternary Simav half-graben. The northern sector was named as the Akdere basin by Seyitoğlu (1997*b*) (Figures 2 and 3). The Neogene stratigraphy of this part of Demirci basin rests on the metamorphic rocks of the Menderes Massif that were intruded by the Oligocene–Miocene Eğrigoz and Koyunoba granitoids.

The Demirci basin is composed of two main stratigraphic units separated by an angular unconformity (Figures 2 and 3). The basin-fill starts with early-middle Miocene conglomerates of the Kürtköyü formation that pass upwards into the sandstone–mudstone alternations of the Yeniköy formation. These units are unconformably overlain, in ascending order, by the Mahmutlar formation, the Demirci formation, and the Sevinçler volcanics that crop out in the northeastern part of the basin (İnci, 1984).

Yılmaz et al. (2000) revised the stratigraphy of Demirci basin and proposed that the basin-fill started with boulder conglomerates of the Borlu formation that pass into the sandstones and mudstones of the Köprübaşı formation. The Köprübaşı formation is intercalated with andesitic lavas and pyroclastics rocks of the Okcular volcanics that crop out in the western-central part of the basin. Yılmaz et al. (2000) suggest that these units are conformably overlain by the marls and shales of the Demirci formation and all these units are early-middle Miocene in age. They are unconformably overlain by the late Miocene-early Pliocene Adala formation composed of limestones cropping out around Demirci town.

The stratigraphy of the Demirci basin contains two distinct units separated by a basin-wide angular unconformity (İnci, 1984). The older one is correlated with the Hacıbekir Group in the adjacent Selendi and Uşak-Güre basins (Ercan et al., 1978, 1983), and the data indicates that the younger volcano-sedimentary unit unconformably overlies the Hacıbekir Group and can be correlated with the İnay Group in the adjacent Selendi basin. The Hacıbekir Group in Demirci basin is composed of the Kürtköyü and Yenikoy formations and the rhyolitic volcanic rocks of Sevinçler

Volcanics. The İnay Group comprises the Akdere pyroclastics, sedimentary rocks of the Borlu, Köprübaşı, and Demirci formations which are interfingered by andesitic–dacitic Asitepe Volcanics and the Naşa basalt to the north of the basin (Figure 3). The Kürtköyü formation crops out in the northern part of Demirci basin, with the largest exposures on the southern flank of the Simav half-graben and the unit is composed of reddish-brown to pale yellow boulder conglomerates (with blocks of up to 1 m), pebblestones, cobblestones and sandstones. The conglomerates are derived from the Menderes Massif metamorphics and the Eğrigöz granitoid. The Kürtköyü formation is conformably overlain by rhyolitic pyroclastic rocks and lava flows of the Sevinçler Volcanics and the Yeniköy formation (Figure 3). The Yeniköy formation is composed of yellowish sandstones and mudstones with local laminated limestone and marls, and mainly crop out in the north of Demirci basin.

In Demirci basin, the İnay Group is composed of Akdere pyroclastics, conglomerates of the Borlu formation, sandstone–siltstone alternations of the Köprübaşı formation, and shales, marls and limestones of the Demirci formation. In the northern flank of the Simav half-graben, the İnay Group consists of Akdere pyroclastics, conglomerates and sandstones of the Borlu and Köprübaşı formations, and the Naşa basalt (Figure 3). The Borlu formation of the İnay Group is composed of boulder conglomerates (mainly derived from the Menderes Massif) with sandstone intercalations of alluvial fan origin. The Köprübaşı formation is conformably overlain by the Asitepe Volcanics in the eastern margin of Demirci basin. The Naşa basalt (15.8±0.3 and 15.2±0.3 Ma K–Ar ages of Ercan et al., 1996, table 1) is composed mainly of syn-sedimentary basaltic lava flows that flowed over the sedimentary rocks of the Borlu formation. In Demirci basin, the Köprübaşı formation passes transitionally into the marls, bituminous shales and limestones (with claystone and sandstone intercalations) of the Demirci formation (İnci, 1984, figure 3), which can be correlated with the Ulubey formation in Selendi basin (Seyitoğlu, 1997*a*; Ersoy et al., 2010). The Neogene volcano-sedimentary infill of Demirci basin are very similar to those of the Selendi and Uşak-Güre basins (Figure 3).

3.4. Selendi Basin

The Neogene stratigraphy of the Selendi Basin rests on a basement consisting of both Menderes Massif and İzmir-Ankara zone rocks (Ercan et al, 1978; Seyitoğlu, 1997; Ersoy and Helvacı, 2007). Three volcano-sedimentary units constitute the Neogene stratigraphy, each one was accompanied by different volcanic activities (Ersoy and Helvacı, 2007). At the base, the Lower Miocene Hacıbekir Group tectonically overlies the Menderes Massif and unconformably overlies the İzmir-Ankara zone rocks (Figures 2 and 3). The rocks of the İzmir-Ankara Zone occur also as olistostromal blocks in the Hacıbekir Group. Two contrasting volcanic associations accompanied deposition of the Hacıbekir Group during the Early Miocene: the Eğreltidağ volcanic unit and the Kuzayır lamproite (Ersoy and Helvacı, 2007). The Middle Miocene İnay Group, unconformably overlying the Hacıbekir Group consists of conglomerates, widely exposed claystone-sandstone-marl alternation and limestones. The claystone-sandstone-mudstone horizons include several borate occurrences such as howlite and colemanite (Helvacı and Alonso, 2000). The İnay Group is also interfingered by two contrasting volcanic associations: the Yağcıdağ volcanic unit and the Orhanlar Basalt. These units are unconformably overlain by the Upper Miocene Kocakuz formation and the Kabaklar Basalt. Finally, the Plio-Quaternary sediments and volcanic units unconformably overlie the older units. The final volcanic activity is represented by the Kula volcanics (Figure 5). The stratigraphy of the basin is very similar to the Emet Basin. In particular, the İnay Group can be correlated with the borate-bearing units in the Emet Basin. The Yağcıdağ volcanic unit can also be correlated with the Beydağ volcanics in the Uşak-Güre Basin that include gold mineralization (Kışladağ gold deposit) (Helvacı and Ersoy, 2006; Helvacı et al., 2006; Ersoy and Helvacı, 2007; Ersoy et a., 2008; Helvacı, 2012).

3.5. 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 and 2). The stratigraphy of Emet basin comprises two Neogene volcanosedimentary units separated by a regional unconformity (Figure 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 this basin, the İnay Group hosts the world's biggest colemanite and probertite borate deposits (Gawlik, 1956; Helvacı, 1984, 1986; Helvacı

Figure 5- The vent area of a lava flow, Kula Volcanics, Turkey (Location : 38.6332 North, 28.7650 East Altitude: 551 meters above sea).

and Orti, 1998; Helvacı and Alonso, 2000; Garcia et al., 2010).

The Hacıbekir Group consists of the Taşbaşı and Kızılbük formations and the Akdağ and Kestel volcanics (Figure 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 basal contact of the unit is represented by a low-angle fault with the Menderes Massif, while the unit unconformably overlies the rocks of the İzmir-Ankara zone (Figure 3).

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 the 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 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).

The Köprücek volcanics crop out in the northern part of 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 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 Emet borate deposits were formed in two separate basins, possibly as parts of an interconnected lacustrine playa lake, in areas of volcanic activity, fed partly by thermal springs and partly by surface streams (Helvacı and Alanso 2000). All the lavas at Emet are enriched in B (≤68 ppm), Li (≤55 ppm) and As (≤205 ppm), slightly enriched in Sr (≤580 ppm), but have relatively low levels of S (≤80 ppm). 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 hot meteoric waters, the direct deposition of ash into the lake sediments, or the degassing of magmas. 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 volcanic activity in the Emet basin, which is thought to be the source of the borate deposition, via the thermal springs, also have similar characteristics to with the Middle Miocene volcanic activity in the Uşak-Güre basins. The geological data clearly show that the Emet basin can be correlated with the Selendi and Uşak-Güre basins. These basins, most probably, were interconnected depocenters throughout the Middle Miocene (Ercan et al 1978; Seyitoğlu 1997; Ersoy and Helvacı 2007;).

3.6. Uşak and Güre Basins

The stratigraphy of the Uşak-Güre basin is similar to that of the Selendi Basin. The Uşak and Güre basins accumulated a thick fluvio-lacustrine fill in which three distinct volcanic centers (Elmadağ, İtecektepe and Beydağı) and their deposits can overlap with each other and with the sediments produced by the background sedimentation. The three large complex volcanoes providing a complex mixed siliciclastic and volcaniclastic basin infill in the respective basins where volcanism took place. All three volcanic centres display a complex succession of effusive and explosive volcanism and their reworked deposits, with abundant evidence of magma–water interaction with the lacustrine water-saturated sediment (Figures 2 and 3). All three volcanic centres then experienced a phase of volcano growth and degradation between 17 and 15 Ma ago, most likely related to a combination of tectonic movements on NE–SW-trending basement faults (Helvacı et al., 2009; Karaoğlu et al., 2010; Table 1).

The Lower Miocene Hacıbekir Group is unconformably overlain by the Middle Miocene İnay Group that contain the Middle Miocene latitic volcanics (Beydağ volcanics). The Beydağ volcanics hosted to the biggest porphyry gold deposits (Kışladağ gold deposits) in western Turkey (Helvacı, 2012). The Kışladağ gold deposit was developed in the Middle Miocene latitic Beydağ volcanic rocks (Ercan et al. 1978; Helvacı et al., 2009; Karaoğlu et al., 2010). The Beydağ volcanics interfinger with the Middle Miocene lacustrine sediments including, in ascending order, basal conglomerates, sandstone-siltstone alternation, siltstone-mudstone alternation with marls, tuff horizons and limestones (İnay Group, Ercan et al. 1978; Seyitoğlu 1997; Ersoy and Helvacı, 2007; Helvacı et al., 2009).

3.7. Kırka Basin

The Miocene sequence of the Kırka Basin, rest unconformably on a basement including Paleozoic metamorphics, Mesozoic mélange units and Eocene sediments and consists of volcanic rocks and tuffs, lower limestone with marl and tuff interbeds, borate zone, upper claystone; upper limestone containing tuff and marl with chert bands; and basalt (Arda, 1969; İnan et al. 1973; Helvacı, 1977; Gök et al. 1980; Sunder, 1980; Palmer and Helvacı, 1995). The stratigraphy and mineralogy of the Kırka borate deposit was revealed by (İnan et al., 1973; Helvacı, 1977; Palmer and Helvacı, 1995; Floyd et al., 1998; Helvacı and Alonso, 2000; Helvacı and Orti, 2004; Garcia-Veigas et al., 2011).

Large rhyolitic ignimbrite occurrences are closely connected to the Early Miocene initiation of extensional processes in central-west Anatolia along the Tavşanlı-Afyon zones (Floyd et al., 1998) (Figures 1 and 6). Field correlations, petrographical, geochemical and geochronological data lead to a substantial reinterpretation of the ignimbrites surrounding Kırka area, known for its world-class borate deposits, as representing the climatic event of a caldera collapse, unknown up to now and newly named the "Kırka-Phrigian caldera". The caldera, which is roughly oval (24 km x 15 km) in shape, is one of the largest in Turkey and is thought to have been formed in a single stage collapse event, at ~19 Ma that generated huge volume extracaldera outflow ignimbrites (Floyd et al., 1998; Seghedi and Helvacı, 2014).

Intracaldera post-collapse sedimentation and volcanism (at ~ 18 Ma) was controlled through subsidence-related faults with generation of a series of volcanic structures (mainly domes) showing a large compositional range from saturated silicic rhyolites and crystal-rich trachytes to undersaturated lamproites (Figure 6, table 1). The volcanic rock succession provides a direct picture of the state of the magmatic system at the time of eruptions that generated caldera and post-caldera structures and offer an excellent example of silicic magma generation and associated potassic and ultrapotassic intermediate-mafic rocks in a post-collisional extensional setting (Seghedi and Helvacı, 2014).

The Kırka area, a newly discovered caldera area, is situated in the northernmost part of the Miocene Eskişehir–Afyon volcanic aea (EAV), as recently delineated by Ersoy and Palmer (2013). It is well known for its borate deposits, the largest in the world (e.g., İnan et al., 1973; Helvacı, 1977; Kistler and Helvacı, 1994; Helvacı and Alonso, 2000; Helvacı, 2005; Helvacı et al., 2012; García-Veigas and

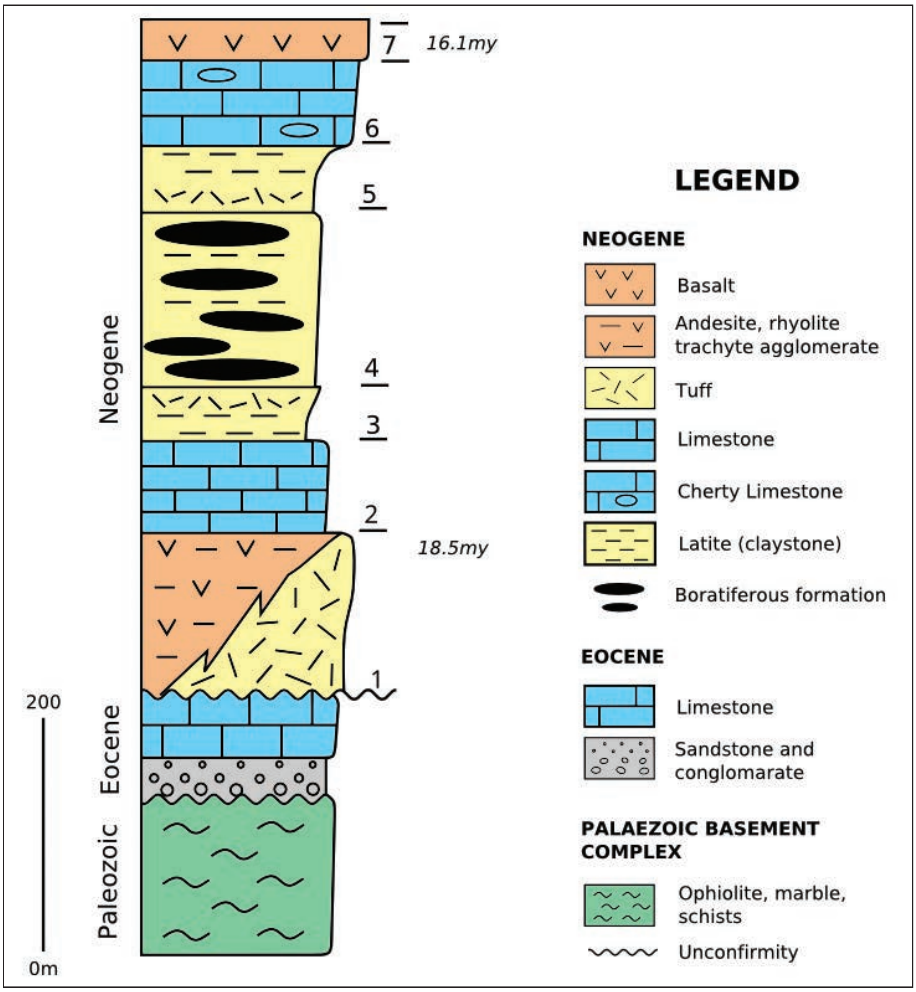

Figure 6- Stratigraphic columnar section of the Kırka borate deposit. Neogene rock units: 1: Tuffs, 2: Lower limestone, 3: Lower clay, marl and tuff, 4: Borate unit, 5: Upper clay, tuff, marl and coal bands, 6: Upper cherty limestone, 7: Basalt (after Inan et al. 1973, Helvacı 1977 and Sunder 1980).

Helvacı, 2013). It was recognized that the borates formed in closed system environments and were connected with thick calc-alkaline volcano-sedimentary successions associated with marls, mudstones, limestones and sandstones; however the caldera system was not recognized before now (Seghedi and Helvacı, 2014).

The most extensive volcanic deposits related to caldera formations are represented by ignimbrites distributed all around the caldera (Floyd et al., 1998). However, the most well-preserved outflow pyroclastic deposits are dominantly distributed toward the south of caldera (Floyd et al., 1998). The base of the volcanic sequence seems to be exposed at the structural margin of the caldera and sometimes associated with lag breccias. The field observations allowed an estimate of the exposed thickness of 160-200 m that includes the caldera-forming ignimbrites (Floyd et al., 1998). The slightly to moderately welded ignimbrite facies is less well-represented toward east, north and west outside of caldera and always associated with thick fall-out deposits. The ignimbrites are also associated with fall-out deposits. The trachyte domes largely developed as two main structures elongated N-S at the northern margin of caldera (10-15 /7 km) and cover the caldera-related ignimbrites and associated deposits, the rhyolite domes, as well the basement deposits. The northern slopes of both the trachytic tuff deposits and lamproitic lava flows are covered by Late Miocene limestones. The reconstruction of intra-caldera deposits are based on the outcrop exposures and drillings (Seghedi and Helvacı, 2014).

4. Depositional Model, Formation and Mineralogy of Borate Deposits

Although boron is one of the rarer and more unevenly distributed elements in the Earth’s crust, there are extraordinary concentrations of boron on an industrial scale in some localized areas (Figure 7). Borate minerals are formed in various environments and in very different conditions. Over 250 minerals are known to contain boron, and they are found in various geological environments (Figure 8 and table 2). The most important economic deposits are very closely related to Tertiary volcanic activity in orogenic belts. They are situated close to converging plate margins; characterized by andesitic-rhyolitic magmas; arid or semi-arid climates; and non-marine evaporite environments. Turkish, United States, South American and many other commercial borate deposits are non-marine evaporites associated with volcanic activity (Ozol, 1977; Jackson and McKenzie, 1984; Floyd et al., 1998; Helvacı, 2005).

Boron is the fifth element of the periodic table and is the only electron-deficient nonmetallic element. Thus, boron has a high affinity for oxygen, forming strong covalent boron-oxygen bonds in compounds known as borates. Because it is strongly fractionated into melts and aqueous fluids, processes that led to formation of continental crust such as partial melting and emission of volatiles, also concentrated boron, resulting in enrichment by 4-8 orders of magnitude from <0.1 ppm in primitive mantle to 17 ppm in average continental crust, and to several wt% in

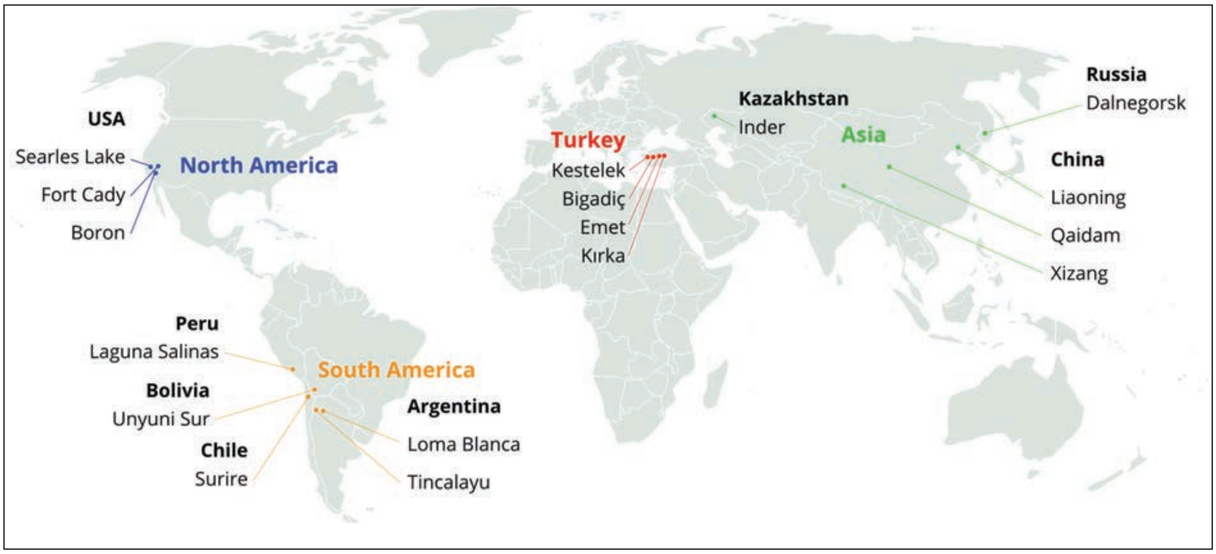

Figure 7- World major borate mines.

Table 2- Borate mineral, formulation and chemical composition.

	Structural formula	**Empirical formula**	**Oxid like formula**
Ca-borates			
Priceite	$Ca_2(B_5O_7(OH)_5).H_2O$	$Ca_4B_{10}O_{19}.7H_2O$	$4CaO5B_2O_3.7H_2O$
Colemanite	$Ca(B_3O_4(OH)_3).H_2O$	$Ca_2B_6O_{11}.5H_2O$	$2CaO3B_2O_3.5H_2O$
Meyerhofferite	$Ca(B_3O_3(OH)_5).H_2O$	$Ca_2B_6O_{11}.7H_2O$	$2CaO3B_2O_3.7H_2O$
Inyoite	$Ca(B_3O_3(OH)_5).4H_2O$	$Ca_2B_6O_{11}.13H_2O$	$2CaO3B_2O_3.13H_2O$
Ca-Na-Borates			
Probertite	$NaCa(B_5O_7(OH)_4).3H_2O$	$NaCaB_5O_9.5H_2O$	$Na_2O2CaO5B_2O_3.10H_2O$
Ulexite	$NaCa(B_5O_6(OH)_6).5H_2O$	$NaCaB_5O_9.8H_2O$	$Na_2O2CaO5B_2O_3.16H_2O$
Na-Borates			
Kernite	$Na_2(B_4O_6(OH)_2).3H_2O$	$Na_2B_4O_7.4H_2O$	$Na_2O2B_2O_3.4H_2O$
Tincalconite	$Na_2(B_4O_5(OH)_4).3H_20$	$Na_2B_4O_7.5H_2O$	$Na_2O2B_2O_3.5H_2O$
Borax	$Na_2(B_4O_5(OH)_4).8H_20$	$Na_2B_4O_7.10H_2O$	$Na_2O2B_2O_3.10H_2O$
Mg-Borates			
Szaibelyite	$Mg(BO_2(OH))$	$Mg_2B_2O_5.2H_2O$	$2MgOB_2O_3.2H_2O$
Pinnoite	$Mg(B_2O(OH)_6)$	$MgB_2O_4.3H_2O$	$MgOB_2O_3.3H_2O$
Mcasllisterite	$Mg(B_6O_7(OH)_6)_2.9H_2O$	$Mg_2B_{12}O_{20}.15H_2O$	$2MgO6B_2O_3.15H_2O$
Hungchaoite	$Mg(B_4O_5(OH)_4).7H2O$	$MgB_4O_7.9H_2O$	$MgO2B_2O_3.9H_2O$
Kurnakovite	$Mg(B_3O_3(OH)_5).5H_2O$	$Mg_2B_6O_{11}.15H_2O$	$2MgO3B_2O_3.15H_2O$
Inderite	$Mg(B_3O_3(OH)_5).5H_2O$	$Mg_2B_6O_{11}.15H_2O$	$2MgO3B_2O_3.15H_2O$
Mg-Na Borates			
Aristarainite	$Na_2Mg(B_6O_8(OH)_4)_2.4H_2O$	$Na_2MgB_{12}O_{20}.8H_2O$	$Na_2OMgO6B_2O_3.8H_2O$
Rivadavite	$Na_6Mg(B_6O_7(OH)_6)_4.10H_2O$	$Na_6MgB_{24}O_{40}.22H_2O$	$3Na_2OMgO12B_2O_3.22H_2O$
Mg-Ca Borates			
Hydroboracite	$CaMg(B_6O_8(OH)_6).3H_2O$	$CaMgB_6O_{11}.6H_2O$	$CaOMgO3B_2O_3.3H_2O$
Inderborite	$CaMg(B_3O_3(OH)_5)_2.6H_2O$	$CaMgB_6O_{11}.11H_2O$	$CaOMgO3B_2O_{3}11.H_2O$
Mg-K-Borates			
Kaliborite	$KHMg_2(B_{12}O_{16}(OH)_{10}).4H_2O$	$K_2Mg_4B_{24}O_{41}.19H_2O$	$K_2O4MgO12B_2O_3.19H_2O$
Sr-Borates			
Veatchite-A	$Sr_2(B_{11}O_{16}(OH)_5).H_2O$	$Sr_4B_{22}O_{37}.7H_2O$	$4SrO11B_2O_3.7H_2O$
Tunellite	$Sr(B_6O_9(OH)_2).3H2O$	$SrB_6O_{10}.4.H_2O$	$SrO3B_2O_3.4H_2O$
Borosilicates			
Bakerite	$Ca_4B_4(BO_4)(SiO_4)_3(OH)_3.H_2O$	$Ca_8B_{10}Si_6O_{35}.5H_2O$	$8CaO5B_2O_{3}6SiO_2.5H_2O$
Howlite	$Ca_2B_5SiO_9(OH)_5$	$Ca_2SiHB_5O_{12}.2H_2O$	$4CaO5B_2O_{3}2SiO_2.5H_2O$
Searlesite	$NaBSi_2O_5(OH)_2$	$NaBSi_2O_6.H_2O$	$Na_2OB_2O_{3}4SiO_2.2H_2O$
Boroarseniates			
Cahnite	$Ca_2B(AsO_4)(OH)_4$	$Ca_2AsBO_6.2H_2O$	$4CaOB_2O_3As_2O_5.4H_2O$
Teruggite	$Ca_4MgAs_2B_{12}O_{22}(OH)_{12}.12H_2O$	$Ca_4MgAs_2B_{12}O_{28}.18H_2O$	$4CaOMgO6B_2O_3As_2O_5.18H_2O$
Borophosphates			
Luneburgite	$Mg_3B_2(PO_4)_2(OH)_6.5H_2O$	$Mg_3P_2B_2O_{11}.8H_2O$	$3MgOP_2O_5B_2O_3.8H_2O$
Borosulfates			
Fontarnauite	$Na_2Sr(SO_4)(B_4O_6(OH)_2).3H_2O$	$Na_2SrSB_4O_{11}.4H_2O$	$Na_2OSrOSO_{3}2B_2O_3.4H_2O$

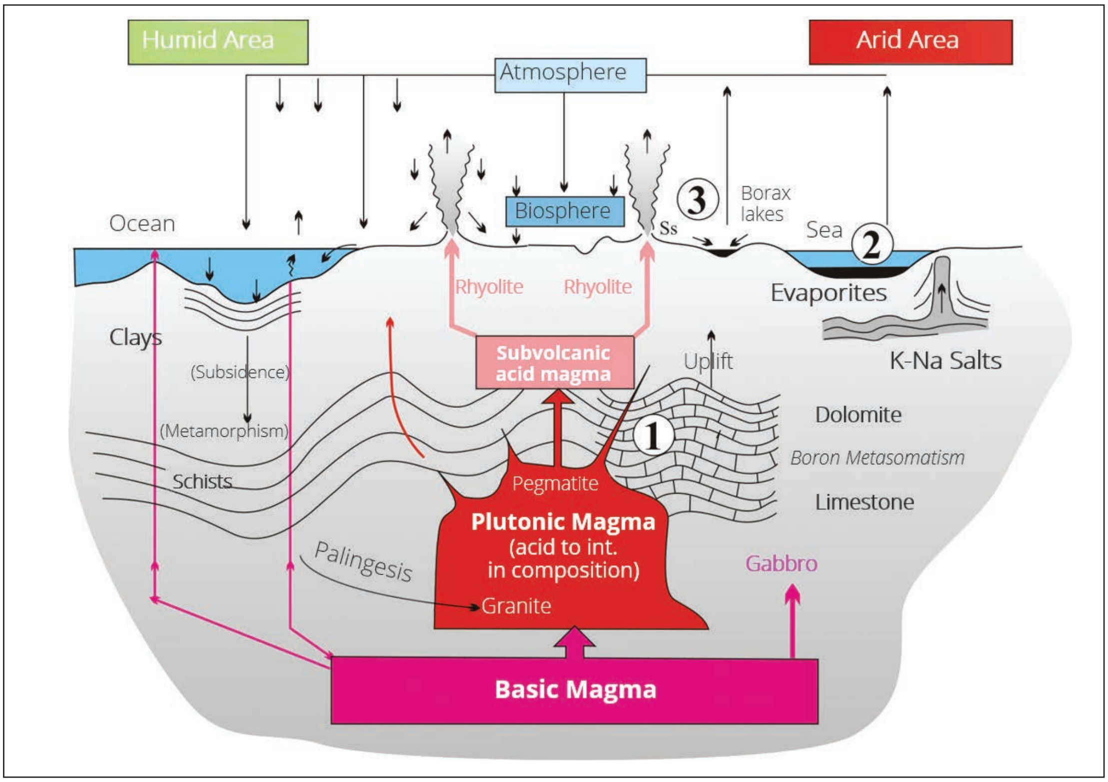

Figure 8- Scheme for the cycle of boron. 1 Skarn Deposits; 2. Marine Deposits; 3. Playa-lake Deposits (Modified after Watanabe, 1964).

pegmatites and evaporites. Major borate deposits throughout the world are found in tectonically active extensional regions associated with collisional plate boundaries (Ozol, 1977; Floyd et al., 1998; Helvacı, 2005). Most of the commercial borate deposits in the USA, South America, and Turkey are thought to be associated with continental sediments and volcanism of Neogene age. Many of the older skarn deposits also appear to be related to continental volcanic sources. Marine borate deposits are apparently the product of evaporation of seawater in a restricted basin, probably associated with a seafloor borate source, and/or progressive decanting that preferentially concentrated the borates to many times natural seawater concentrations, but these are much less abundant than non-marine borates.

Borates associated with igneous and some metamorphic rocks are thought to be an end phase of specialized magmatic segregation or leached from the intruded rocks by associated hydrothermal fluids (Figure 8).

Most of the South American deposits are associated with calcareous tuff, which occurs as a late-stage capping over the borates, and in some cases with halite and gypsum. Recent volcanic activity is indicated by basaltic to rhyolitic flows in adjacent areas, and a volcanic source for the borates is presumed. The Salar deposits of South America consist of beds and nodules of ulexite, with some borax or inyoite, associated with Holocene playa sediments, primarily mud, silt, halite, and gypsum.

Borates can be concentrated in many different ways:

- by chemical precipitation in the neighbourhood of boron-bearing springs in playa-type basins (e.g. the Boron, Searles Lake, and Billie deposits of California, and the Kırka, Sultanayır, Bigadiç, and Emet deposits in Turkey);
- by precipitation from seawater in the closing phase of a salt-forming evaporate cycle (e.g. at Stassfurt in Germany);
- by contact metasomatism with dolomite or magnesite, forming magnesium borates such as ludwigite, kotoite, and ascharite (e.g. the Teazhnoe deposits at Yakutia in Russia, and the Hol-Kol deposit in North Korea);

- by contact metasomatism with limestone, forming boron silicates such as datolite and danburite (e.g. at Ak Akhdar, Pamir, and Dalnegorskoye, Primorsky, Russia); and
- by volcanic exhalations of boric acid, i.e. sublimates (e.g. at Clear Lake, Lake County, California, at Salar de Surire, Chile, and in the Maremma area, Tuscany, Italy).

Borates constitute a group of mineral deposits of great economic interest. Several genetic types have been identified (volcanic, hydrothermal, metamorphic, sedimentary) and the most important corresponds to those deposits formed in nonmarine evaporitic settings. The formation of borate deposits can be tentatively summarized into three main groups as follows (Figure 8):

1. a skarn group associated with intrusives and consisting of silicates and iron oxides;
2. a magnesium oxide group hosted by marine evaporitic sediments; and
3. a sodium and calcium borate hydrates group associated with lacustrine (playa lake) sediments and explosive volcanic activity.

Lacustrine basins related to volcanic domains in which borates have precipitated are known in the stratigraphic record since the Oligocene, although those of Miocene age are the most economically relevant. The borate minerals in these basins were generated in saline lakes emplaced in volcanogenic (mainly pyroclastic) terrains with intense hydrothermal influence, under arid to semi-arid conditions, and in some cases at low temperatures (Figure 9). The following conditions are essential for the formation of economically viable borate deposits in playa-lake volcanosedimentary sediments (Figure 9):

1. formation of playa-lake environment;
2. concentration of boron in the playa lake, sourced from andesitic to rhyolitic volcanics, direct ash fall into the basin, or hydrothermal solutions along graben faults;
3. thermal springs near the area of volcanism;
4. arid to semi-arid climatic conditions; and
5. lake water with a pH of between 8.5 and 11.

4.1. Borate Deposits in Non-Marine Basins

Non-marine continental evaporite deposits are the major economic source of boron. The formation of large economic borate deposits requires a boron-rich source and a means of transporting and concentrating the boron in a restiricted environment. In addition to the concentrated source of the borates and a basin in

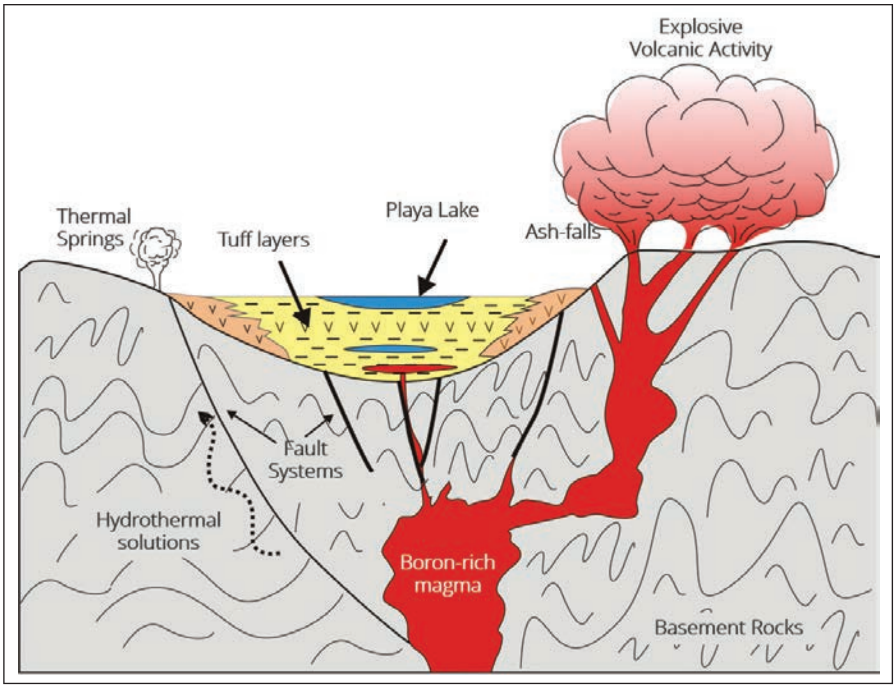

Figure 9- Generalized playa lake depositional model showing the formation of borate deposits in Neogene basins of western Anatolia, Turkey (after Helvacı, 2005).

which they can collect, an arid to semiarid climate also seems to be essential during the deposition and concentration of economic amounts of soluble borates. These soluble borates can, in the long run, be preserved only by burial; however, the lack of deposits of soluble borates older than mid-Tertiary may indicate that even burial is not able to protect borates over long periods of geological time. There are relatively a few occurrences where the element is sufficiently concentrated to be economic use. Where a degree of concentration does occur, it is usually a result of local volcanic activity (as a source of boron), a body of water such as a lake (to dissolve boron compounds), evaporative conditions (to concentrate the solution to the point of precipitation), and the deposition of a protective layer of sediment (to preserve the highly soluble borate minerals).These conditions are present in collisional tectonic settings, for which western Anatolia is a prime example, there have also been significant recent advances in the understanding of the timing of crustal metasomatic processes and collisional and extensional tectonics in this region. Therefore, the formation of borate deposits in western Anatolia is a good example for understanding and identifying boron enrichments in collision-related tectonic events in ancient mobile belts (Figure 9).

The largest borate deposits that originated as chemical precipitates are found interbedded with clays, mudstones, tuffs, limestones, and similar lacustrine sediments. There is a strong evidence that most of these deposits were closely related in time to active volcanism. Thermal springs and hydrothermal solutions associated with volcanic activity are regarded as the most likely source of the boron (Figure 9). Several South American springs in volcanically active areas are currently depositing borates, and the first borax discovered in the USA was found in the muds associated with warm springs at Clear Leak, California, in a volcanically active area. There is, however, another type of borate lake deposit, with mixed salts and/or brine containing borates in sufficient quantity of justify recovery. Searles Lake, California is as a type example of a multicomponent lake formed by evaporation of lake waters. Similarly, the Konya-Karapınar basin (Turkey) is surrounded by volcanes which have been active from the Late Miocene to recent. Active volcanism is evidenced by the discharge of thermal and mineral waters and magmatic gases. Na, B, Cl, SO_4 and CO_2 are carried into the basin by thermal and mineral waters related to this volcanism. Potentially economic deposits of borate, chlorite, sulfate and carbonate salts related to this volcanic activity are presently forming within the basin (Helvacı and Ercan, 1993).

The Italian (Tuscany) steam vents from which sassolite was recovered also represent an active volcanic source. Hydrated borates may accumulate in several ways within a non-marine basin. They may be deposited in layers in a spring apron around a borate spring, with ulexite, borax, or inyoite as the primary borate mineral. Borates may also form in a pool dominantly fed by a borate spring, with borax crystals formed in bottom muds or at the intermittently dried margins (as at Clear Lake, and at Salar de Surire, Chile). The borates found in the large South American salars, such as Uyuni and Atacama, may also have formed by leaching of surrounding rocks and subsequent evaporation (Chong, 1984).

4.2. Marine Evaporites

Borates of marine origin have been found in commercial quantities only in Europe. These are magnesium borates associated with Permian salt deposits. They were produced in Germany as a byproduct of potash mining, and in the Inder region of Kazakhstan. The Inder deposits, where the borates occur as veins in the cap of a very large salt dome complex are reported to be remobilized and concentrated from the salt during the intrusion of the salt dome itself. Some of the Chinese deposits of the Liaoning Peninsula (most likely metamorphosed Precambrian non-marine evaporites) may be of similar origin although they occur as veins in Precambrian metamorphosed limestone and magnesite (Peng and Palmer; 1995, 2002). The Inder Lake brines which are also a source of Kazakhstan production appear to be simply a sump accumulation of borates leached from the huge Inder salt dome complex. The Kara-Boğaz-Göl Lagoon borates on the east shore of the Caspian Sea would also appear to be leached from marine brines (Figure 8).

4.3. Magmatic Sources (Skarn Deposits)

Pegmatites and contact metamorphic rocks contain assemblages of various boron-containing minerals such as datolite, ludwigite, paigeite, and tourmaline (Figure 8, table 2). These represent concentrations of boron that relate more or less directly to the crystallization of intrusive granitic magma. Granites average about 10 ppm boron with a few exceptions ranging up to 300 ppm. The conditions of high temperature, 300 to 400°C and fluids under high pressure at an intrusive contact also provide the possibility that some of the boron may be extracted from the adjacent country rocks. These borate skarn deposits, some associated with iron ores and magnesium deposits of commercial grade, are mined in both eastern Russia and China.

5. Mineralogy

By at least 3.8 Ga, boron had been concentrated sufficiently to form its own minerals, which are thought to have stabilized ribose, an essential component of ribonucleic acid and a precursor to life. Boron has with two abundant isotopes, ^{10}B and ^{11}B; the former has a large capture cross-section that makes it an excellent neutron absorber. These two stable isotopes differ significantly in atomic weight so that boron isotopic compositions of minerals and rocks retain signatures from their precursors and the processes by which they formed. Boron compounds comprise a great diversity of crystal structures. Evaporites constitute the richest concentrations of boron on Earth, and thus are the main source of boron for its many applications in medicine, electronics and the nuclear industry.

Boron is extremely dispersed in nature, averaging 0.1 ppm in land-surface water, 3 ppm in the Earth's crust, and 4.6 ppm in seawater. At low levels, water soluble boron is an essential micronutrient for the growth and viability of plants; the range between insufficient and excess boron is narrow (0.25 to 15.0 ppm) and most soils are usually within this range. Borate has been found in animal tissues at about 1ppm resulting from ingestion of fruits and vegetables; it is not known to have an essential biochemical function, although it may play a role in the body's ability to use calcium. Borate is transported in plants and animals usually complexed with polyalcohols in the aqueous phase (Garrett, 1998; Helvacı, 2005).

Boron minerals commonly form in three main geological environments as skarn minerals related to intrusives, mainly silicates and iron oxides; magnesium oxides related to marine sediment; and hydrated sodium and calcium borates related to continental sediments and volcanic activity (Figure 8, table 2). Some skarn minerals are the source minerals for the Russian and Chinese production, the major ones being datolite and szaibelyite. Borax, kernite, colemanite, and ulexite are the main evaporite minerals, which provide the source for most of the world's production from Turkey, South America, and the United States (Table 3) (Palache et al., 1951; Muessig, 1959; Watanebe, 1964; Aristarian and Hulburt, 1972; Helvacı, 1978; Kistler and Helvacı, 1994; Grew and Anovita, 1996; Grew and Anovita, 1996; Helvacı, 2005; Garrett, 1998; Helvacı, 2012) .

Over 250 boron-bearing minerals have been identified, most commonly as sodium, calcium, or magnesium salts (Table 2). Borax, ulexite, colemanite and datolite are commercially significant today (Table 3). Borax or tincal, a natural sodium borate decahydrate, may be regarded as the major commercial source of boron with supplies coming from the United States, Argentian, and Turkey. The principal commerical mixed sodium-calcium borate, ulexite, is produced in Turkey and several countries in South America, whereas large-scale production of the main calcium borate, colemanite, is restricted to Turkey.

Borax is by far the most important mineral for the borate industry. It crushes freely and dissolves readily in water; its solubility and rate of solution increases with water temperature. Borax in large tonnages is present in the deposits at Boron, California (USA), Kırka, Turkey, and Tincalayu, Argentina. Kernite is present in minor amounts at Kırka and Tincalayu, but it makes up about a third of the total reserve at Boron (California), and has a higher B_2O_3 content than borax.

Colemanite is the preferred calcium-bearing borate used by the non-sodium fiberglass industry. It has low solubility in water, although it dissolves readily in acid. Some colemanite is used in Europe in chemical plants to produce boric acid because the supply from Turkey provides B_2O_3 at lowest cost. Turkey is the world's major source of high grade

Table 3- Commercial borate minerals.

Minerals	**Emprical formula**	**B_2O_3 content (wt.%)**
Colemanite	$Ca_2B_6O_{11}.5H_2O$	50.8
Ulexite	$NaCaB_5O_9.8H_2O$	43.0
Borax	$Na_2B_4O_7.10H_2O$	35.5
Kernite	$Na_2B_{14}O_7.4H_2O$	51
Pandermite	$Ca_4B_{10}O_9.7H_2O$	49.8
Hydroboracite	$CaMgB_6O_{11}.6H_2O$	50.5
Szaybelyite (ascharite)	$Mg_2B_2O_5.H_2O$	41.4
Datolite	$Ca_2B_2Si_2O_9.H_2O$	21.8

colemanite. The United States has important reserves in the Death Valley area, but only limited amounts are produced there at this time as the reserves of main deposits are running out. Colemanite is not known to occur in major deposits outside Turkey and North America, although the higher hydrate, inyoite, is mined on a limited scale in Argentina.

Ulexite is the usual borate found on or near the surface, in playa-type lakes and marshes of Recent to Quaternary age throughout the world, where it occurs as soft, often damp, masses of fibrous crystals. These "cotton balls" or "papas" are collected in major amounts in South America and China. Ulexite of Neogene age, which is mined and produced in Turkey and also occurs lesser amounts at Boron and Death Valley in the United States.

Szaybelyite (ascharite) is a major source of both Chinese and Russian borate material. It is a magnesium borate and like colemanite, has low solubility in water. Although it is less satisfactory, due to its magnesium content, substantial tonnages are utilized in eastern Europe, Russia, and Asia; it is not traded internationally as a mineral concentrate on a major scale. The Russians also produce substantial amounts of borates utilizing the skarn borosilicates, mainly datolite, with some reports of minor amounts of danburite, ludwigite, and tourmaline. Production of datolite, a silicate mineral, is confined to Russia. These minerals must first be liberated, concentrated, and then dissolved in acid to make a usable product because their natural melting points exceed those of the other minerals used in common glass furnaces.

Pandermite (priceite) was mined in Turkey and hydroboracite was mined in Russia and Argentina. Other minerals such as inyoite, howlite, meyerhofferite, and kurnakovite occur intimately associated with the major ores.

Boracite was used in Germany prior to 1945 where boracite and minor magnesium borates were recovered as a byproduct of potash mining. Axinite, suanite, kotoite, and others are listed in the literature as occuring with the Russian borosilicate ores.

Sassolite has only mineralogic interest at most occurences, for the quantity found is generally very small. In the Lardarello region of Italy, however, natural steam carries boric acid recoverable as sassolite, and for a long period prior to 1965, several thousand tons per year were produced.

6. Major Deposits

Four main metallogenic borate provinces, with exogenous deposits in continental environments, as recognized at a global scale and these metallogenic provinces contain the most important borate reserves in the world. They are Anatolia (Turkey), Western America (USA), Central Andes (South America) and Tibet-Qinghai Plateau (Central Asia) (Figure 7). The origin of borate deposits is related to Cenozoic volcanism, thermal spring activity, closed basins and arid climate. With the exception of Tibet-Qinghai Plateau, a collisional plateau, the other provinces were generated in a tectonic framework of non-collisional continental plateaus by plate subduction (Figures 10, 11 and 12).

Anatolia, Tibet-Qinghai Plateau and California are located in the northern hemisphere and the Andes in the southern hemisphere. The age of the borates is Cenozoic, principally, Miocene and Quaternary. Miocene borate deposits are present in Anatolia (ca. 18-14 Ma) (Figure 10), California (ca. 22-6 Ma) (Figure 11) and the Andes (ca. 7-5 Ma) (Figure 12).

Tibet-Qinghai Plateau has only Quaternary borate deposits and Anatolia has mainly Miocene borate deposits, although there are uneconomic Quaternary occurrences as well (Figure 5).

Four major borax deposits are present in the world; Anatolia (Kırka), California (Boron), and two in the Andes (Tincalayu and Loma Blanca) (Figure 7). Kırka, Boron and Loma Blanca have similarities with regard to their chemical and mineralogical composition of the borate minerals, and sequences are Ca/Ca-Na/Na/Ca-Na/Ca (colemanite and/or inyoite//ulexite //borax//ulexite//colemanite and/or inyoite). Borate minerals are enclosed in greenish volcaniclastic lacustrine evaporatic sequences, with minor tectonic deformation (Figure 13). Tincalayu deposit looks very different, as evaporites enveloped within red beds, showing disharmonic deformation, and a lithologic sequence composed from base to top of halite/gypsum/borax/ulexite. Borax textures are different in those four main deposits with chemical fine varves (mm) in Kırka; chemical thick varves (cm) in Boron; massive (m) in Tincalayu; and disseminated evapocrystals (mm to cm) in Loma Blanca (Kistler and Helvacı, 1994; Helvacı and Alonso, 2000; Helvacı, 2005).

Colemanite deposits with or without probertite and hydroboracite are present in Anatolia (Emet), Death Valley, California (Furnace Creek Fm.), and

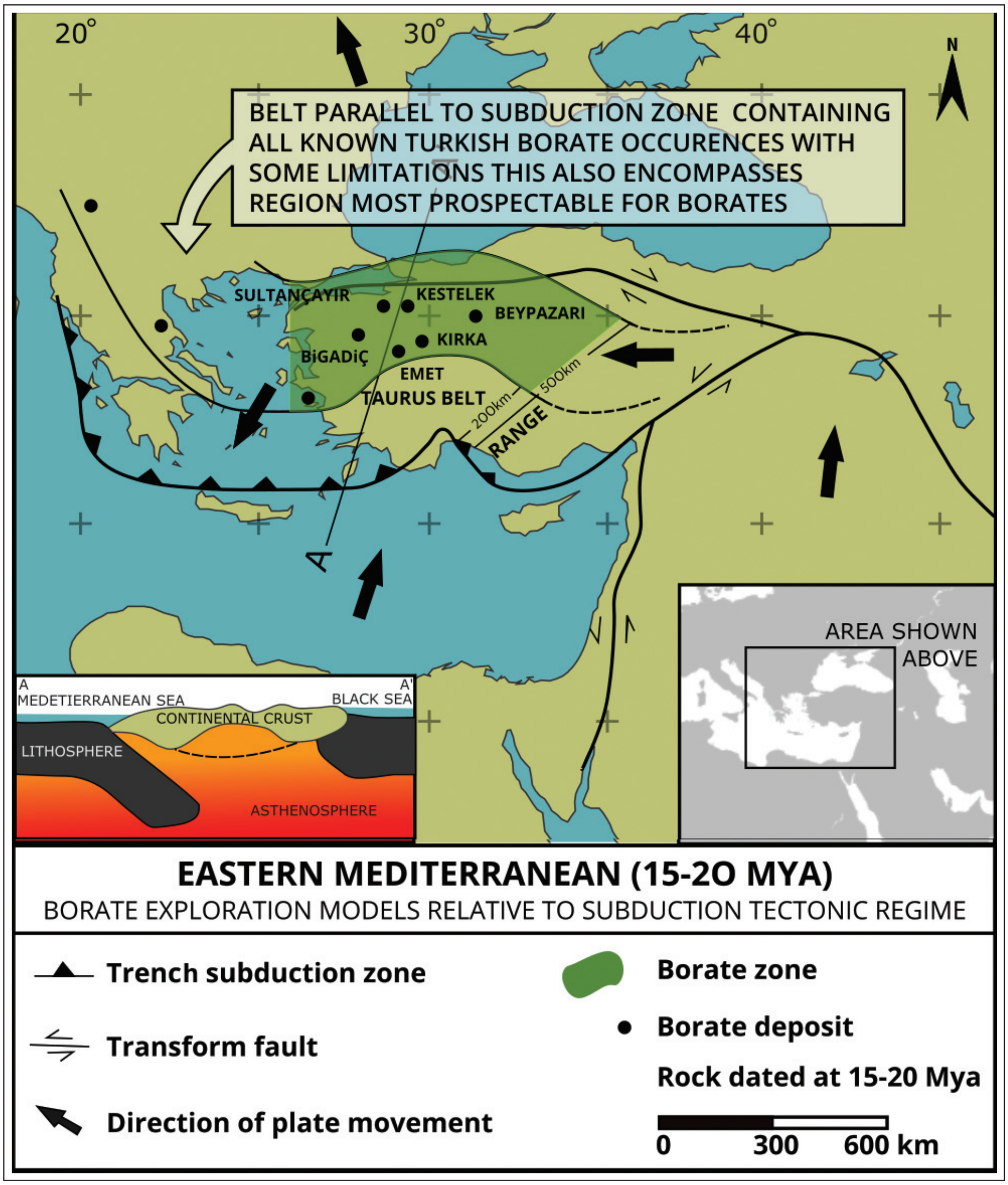

Figure 10- Known deposits and borate exploration model relative to subduction tectonic model for Eastern Mediterranean (15-20 My).

Sijes (Argentina) Quaternary borates are present in salars (Andes) and playa-lakes and salt pans (USA, Tibet-Qinghai Plateau, Central Anatolia). California and Andes have calcium and calcium- sodium borates (ulexite, borax, inyoite), as does the Tibet-Qinghai Plateau (ulexite and Mg-borates). Thermal springs and geysers, producing borate deposits, are common in the Central Andes (Kistler and Helvacı, 1994; Helvacı and Alonso, 2000; Helvacı, 2005).

6.1. Borate Deposits of Turkey

Turkish borate deposits were formed in the Tertiary lacustrine sediments during periods of volcanic activity, forming in separate or possibly interconnected lake basins under arid or semi-arid climatic conditions (Meixner, 1965; Özpeker, 1969; İnan et al., 1973; Helvacı and Firman, 1976; Helvacı, 1986, 1989, 1995; Kistler and Helvacı, 1994; Palmer and Helvacı, 1995, 1997; Helvacı and Orti, 1998; Helvacı and Alonso, 2000; Şaylı, 2003; Helvacı and Orti, 2004; Helvacı, 2005; Helvacı, 2012). Sediments in the borate lakes often show clear evidence of cyclicity, and much of the sediments in the borate basins seem to have been derived from volcanic terrain (Figures 13 and 14). In all the borate areas, intense calc-alkaline volcanic activity took place

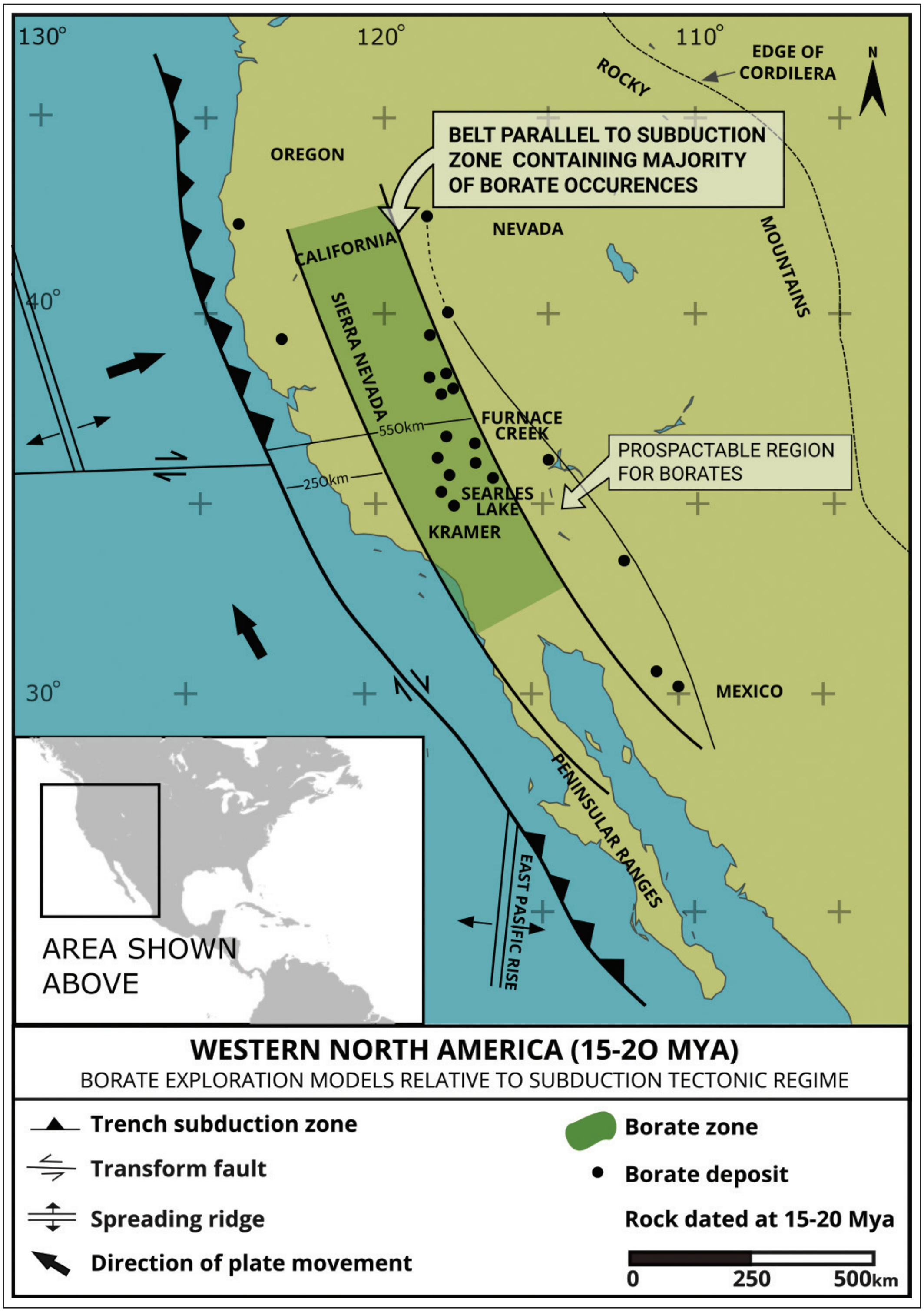

Figure 11- Borate exploration model relative to subduction tectonic model for Western North America (15-20 My).

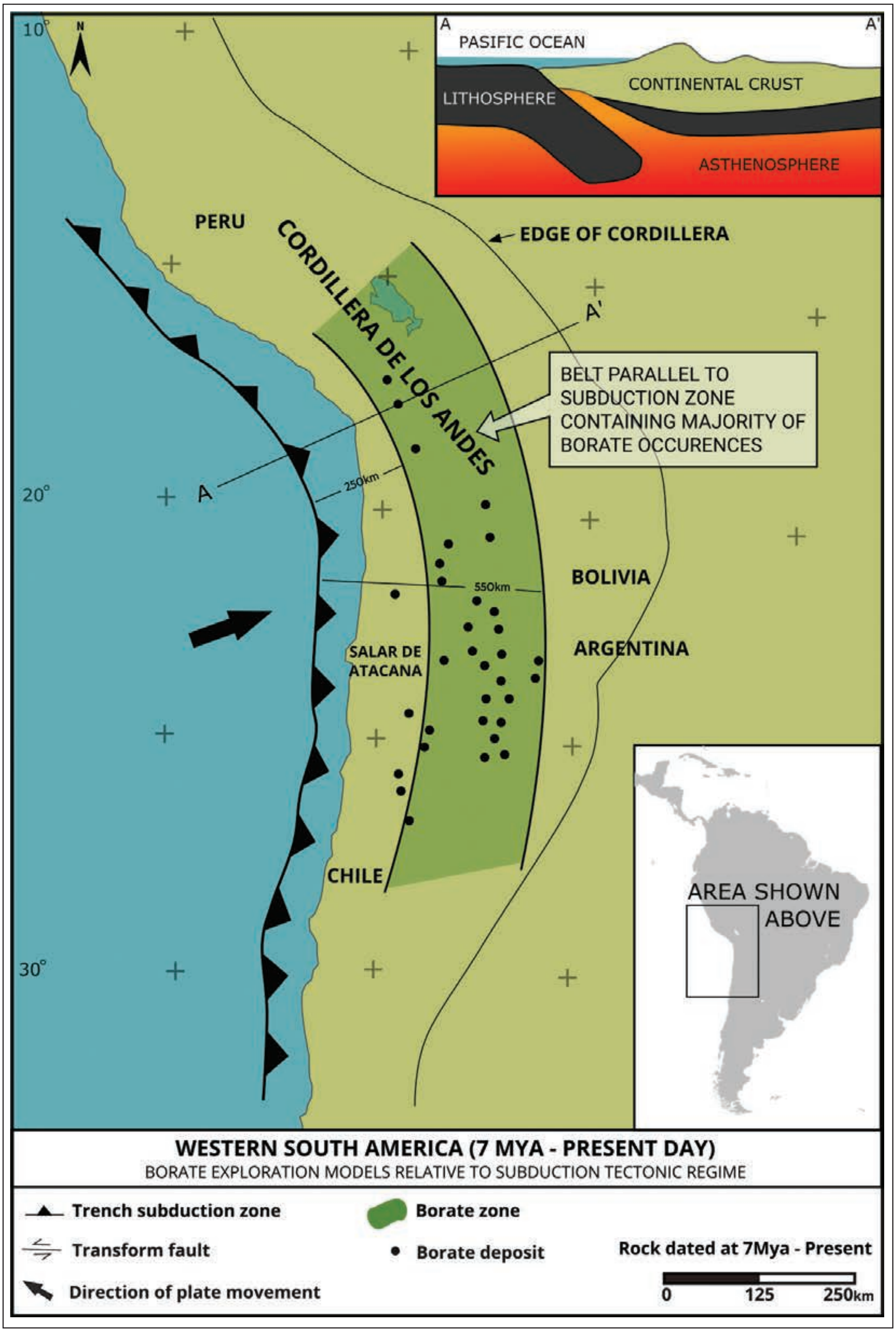

Figure 12- Borate exploration model relative to subduction tectonic model for Western South America (7 My-Present Day).

Figure 13- Volcaniclastic lacustrine evaporitic sequences associated with borate deposits, Bigadiç borate deposit, Turkey.

Figure 14- Sediments in the borate lakes showing clear evidence of cyclicity, and volcanic tuff intercalations with the sediments in the borate unit. Colemanite nodules occuring within clayey-tuffaceous matrix, Hisarcık open pit mine, Emet, Turkey.

simultaneously with the borate sedimentation. Volcanic rocks in the vicinity of the basins in which the borate deposits were formed are extensive and are represented by a calc-alkaline series of flows ranging from acidic to basic and by pyroclastic rocks which are interbedded with the sediments.

Pyroclastic and volcanic rocks of rhyolitic, dacitic, trachytic, andesitic and basaltic composition are interfingered with these lacustrine sediments (Figures 3 and 6). The existence of volcanic rocks in every borate district suggests that volcanic activity may have been necessary for the formation of borates. Thermal springs, which at present precipitates travertine, are widespread in the deposits.

Sedimentary-thickness varies from one deposit to another, probably because of deposition in a chain of interconnected lakes, and volcanosedimentary sequences exceed over 1000 m in the deposits. They are intensively dislocated by NE-SW and NW-SE-trending gravity faults (Figs. 2, 3 and 6). The extreme thickness of the borate zones at Emet, Bigadiç and Kırka indicates that there were somewhat different conditions existing at the time of the formation of these deposits. The borate deposits have the following features in common: They are restricted to lacustrine sediments deposited in a non-marine environment under arid or semi-arid climatic conditions. They were deposited in sedimentary closed basins of limited extent in regions where fresh water limestone deposition was widespread both before and after borate formation. The palaeogeographic scenario seems to have consisted of shallow lakes fed partly by hot springs and partly by streams which carried sediments from the surrounding volcanic, limestone and basement terrain (Figure 9).

Western Anatolia contains the largest borate reserves in the world and all the deposits formed during Miocene time in closed basins with abnormally high salinity and alkalinity. Neogene basins consisting of borate deposits were developed during an extensional tectonic regime in NW Turkey which was marked by NNE trending faults. All these basins were partially filled with a series of tuffaceous rocks and lavas. Boron-rich fluids are presumed to have also circulated along faults into these basins (Figure 9). The sediments deposited in the borate lakes are generally represented by tuffaceous rocks, claystones, limestones and Ca-, Na-, Mg-, Sr- borates. (Table 2). Sandstones and conglomerates occur in marginal parts of each basin. The borates are enveloped between tuff and clay-rich horizons (Figures 3, 6, 13 and 14). In the borate basins, intense calc-alkaline volcanic activity took place simultaneously with the borate sedimentation. The volcanic rocks are represented by a calc-alkaline series of flows ranging from acidic to basic and by pyroclastic rocks which are interbedded with the sediment (Figures 3 and 6).

The mineralogy of the Turkish borate deposits varies considerably and borate minerals recorded from the Turkish deposits are mainly Ca; Ca-Mg; Na and Mg borates. A rare Sr borate has been found at Kırka (Baysal, 1972; Helvacı, 1977) and Ca-As and Sr borates have been reported from the Emet district

(Helvacı and Firman, 1976 and Helvacı, 1977). The Kırka borate deposit is the only Turkish deposit is known to contain any of the minerals borax, tincalconite, kernite, inderite, inderborite and kurnakovite. Borate minerals are associated with calcite, dolomite, gypsum, celestite, realgar, orpiment and sulphur (Helvacı et al., 2012; table 2).

The known borate deposits of Turkey were formed in the NE-trending Neogene basins, and occur in 5 distinct areas (Figures 1 and 10). These are as follows: Bigadiç colemanite and ulexite deposits (Ca and Ca-Na Borate); Sultançayır pandermite deposits (Ca-type); Kestelek colemanite deposits (Ca-type); Emet colemanite deposits (Ca-type); and Kırka borax deposits (Na-type).

6.1.1. Bigadiç Deposits

Bigadiç contains the largest colemanite and ulexite deposits known in the world. The borate minerals formed in two distinct zones, lower and upper, seperated by thick tuff beds transformed during diagenesis to montmorillonite and chlorite and to zeolites. Colemanite and ulexite predominate in both borate zones, (Figures 3,15 and 16), but other borates include howlite, probertite, and hydroboracite in the lower borate zone; inyoite, meyerhofferite, priceite, terschite, hydroboracite, howlite, tunellite, and rivadavite are found in the upper borate zone (Özpeker, 1969; Helvacı, 1995; Helvacı and Orti, 1998; Yücel-Öztürk et al., 2014) (Table 2). The Bigadiç borate deposits were fed by thermal springs associated with local volcanic activity under arid climatic conditions.

6.1.2. Sultanyaçır Deposits

The borates are interbedded with gypsum, claystone, limestone, and tuff. Pandermite (priceite) is abundant, but other borates include colemanite and howlite (Table 2). Gypsum exists abundantly and calcite, zeolite, smectite, illite, and chlorite are the other associated minerals in this deposit (Orti et al., 1998; Gündoğan and Helvacı, 1993; Helvacı, 1994; Helvacı and Alonso, 2000). Howlite, which has apparently grown in the clays alternates with thin pandermite and colemanite bands. As a result of diagenetic events, some small howlite nodules are also embedded in the pandermite and colemanite noludes.

6.1.3. Kestelek Deposit

The borate zone consists of clay, marl, limestone, tuffaceous limestone, tuff, and borate. The volcanic activity produced tuff, and agglomerate, and andesitic and rhyolitic volcanics that are associated with the sediments (Helvacı, 1994; Helvacı Alonso, 2000). This sequence is capped by a unit consisting of loosely cemented conglomerate, sandstone, and limestone. The borate minerals occur interbedded with clay as nodules or masses and as thin layers of fibrous and euhedral crystals. Colemanite, ulexite, and probertite predominate, with hydroboracite

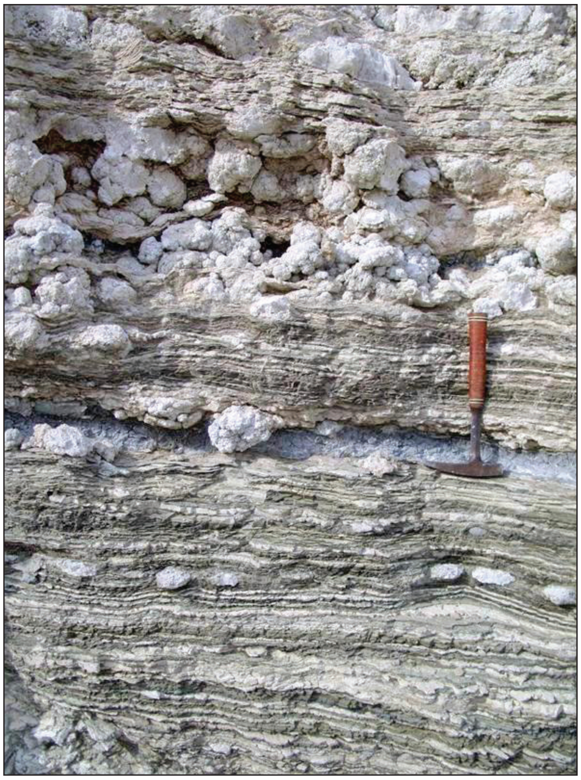

Figure 15- Colemanite nodules in varying sizes intercalated with associated sediments, Tülü open pit mine deposit, Bigadiç, Turkey.

Figure 16- Ulexite ore lenses intercalated with associated sediments, Kurtpınarı deposit, Bigadiç, Turkey.

occuring rarely. Secondary colemanite occurs as transparent and euhedral crystals in the cavities of nodules, in cracks and in vugs (Figure 17, table 2).

6.1.4. Emet Deposits

The Neogene sequence rests unconformably on Paleozoic metamorphic rocks that consist of marble, mica-schist, calc schist, and chlorite schist, and the sediments contains the borate deposits are interclated with clay, tuff, and marl containing the lensoidal borate formations (Figures 3 and 14); The unit consisting of clay, tuff and marl containing the borate deposits has abundant realgar and orpiment at some horizons indicating that arsenic and boron have a genetic relationship and volcanic origin at Emet (Table 2).

The Emet basin is one of the Neogene basins in western Turkey containing significant amounts of borate minerals, mainly colemanite. The borates are interlayered with tuff, clay, and marl with limestone occuring above and below the borate lenses. The principal borate minerals are colemanite and probertite (Figure 18), 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; Helvacı, 1984; Helvacı, 1986; Helvacı and Orti, 1998; Garcia-Veigas et al., 2011).

The petrologic study of core samples from two exploratory wells in the Doğanlar sector, under optical and electron microscopy, eveals a complex mineral association in which probertite, glauberite, and halite constitute the major primary phases (without mineral precursors) precipitated in a saline lake within a volcano-sedimentary context. Other sulfates (anhydrite, gypsum, thenardite, celestite and kalistrontite), borates (colemanite, ulexite, hydroboracite, tunellite, kaliborite and aristarainite), and sulfides (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). A new sulfate-borate mineral (fontarnauite) has been found in the deposit and the paper concerning this mineral is in press in Canadian Mineralogist (Cooper et al., in press). Montmorillonite, illite, and chlorite are the clay minerals that have been identified. Zeolites are abundant along the tuff horizons. Native sulfur, realgar, orpiment, gypsum and celestite occur in the borate zone throughout the area.

6.1.5. Kırka Deposit

The Neogene volcano-sedimentary sequence rests unconformably partly on Paleozoic metamorphics, a Mesozoic ophiolite complex, and Eocene fossiliferous limestone. The Neogene sequence consists of from bottom to top: volcanic rocks and tuffs; lower limestone with marl and tuff interbeds; borate zone; upper claystone; upper limestone containing tuff and marl with chert bands; and basalt (Figure 6). The principal mineral in the Kırka borate deposit is borax with lesser amounts of colemanite and ulexite. In addition, inyoite, meyerhofferite, tincalconite, kernite, hydroboracite, inderborite, inderite, kurnakovite, and tunnelite are found

Figure 17- Secondary colemanite crystals in the cavities of nodules, in cracks and in vugs, Kestelek, Turkey.

Figure 18- Colemanite is principal borate mineral and is interclated with green clay as nodular and elliptical lenses, Espey open pit mine, Emet, Turkey.

(Baysal, 1972; İnan et al., 1973; Helvacı, 1977; Sunder, 1980; Palmer and Helvacı, 1995; Floyd et al., 1998; Helvacı and Orti, 2004; Seghedi and Helvacı, 2014; table 2). This is the only deposit in Turkey that contains the sodium borates (borax, tincalconite, and kernite), together with inderborite, inderite, and kurnakovite. The borax body is enveloped by a thin ulexite facies, followed outward by a colemanite facies (Figure 19). The Mineral formation sequence in the Kırka deposit is Ca/Ca - Na/Na/Ca - Na/Ca (colemanite and/or inyoite / ulexite / borax / ulexite / colemanite and /or inyoite). The borate layers contain minor amounts of celestite, calcite, and dolomite, and the clay partings contain some tuff layers, quartz, biotite, and feldspar. The clay is made up of smectite-group minerals and less frequently, illite and chlorite minerals. Zeolites occur within the tuff horizons. This deposit is distinct from similar borax deposits at Boron and Tincalayu in having very little intercrystalline clay; the clay at Kırka is very pale green to white and is high in dolomitic carbonate (Figure 20). The borax crystals are fine, 10 to 20 mm, and quite uniform in size (Figure 20).

The ore body has thickness of up to 145 m, averaging 20 to 25 % B_2O_3.

6.2. Borate Deposits of USA

In 1856, J.A. Veach discovered borax in the muds associated with a mineral spring at what is now Clear Lake, in Lake County, California. Prospecting soon led to the discovery of larger deposits in the desert areas of western Nevada and southeastern California. Small-scale production began there in 1864. The first 63 years of domestic production saw several changes in both the type and location of the mineral deposits mined, but in general, production increased and the price of borax decreased as larger and better deposits were found and refinery techniques improved. The year 1927 was a benchmark in US borate history as both the large borax deposit at Boron and the Searles

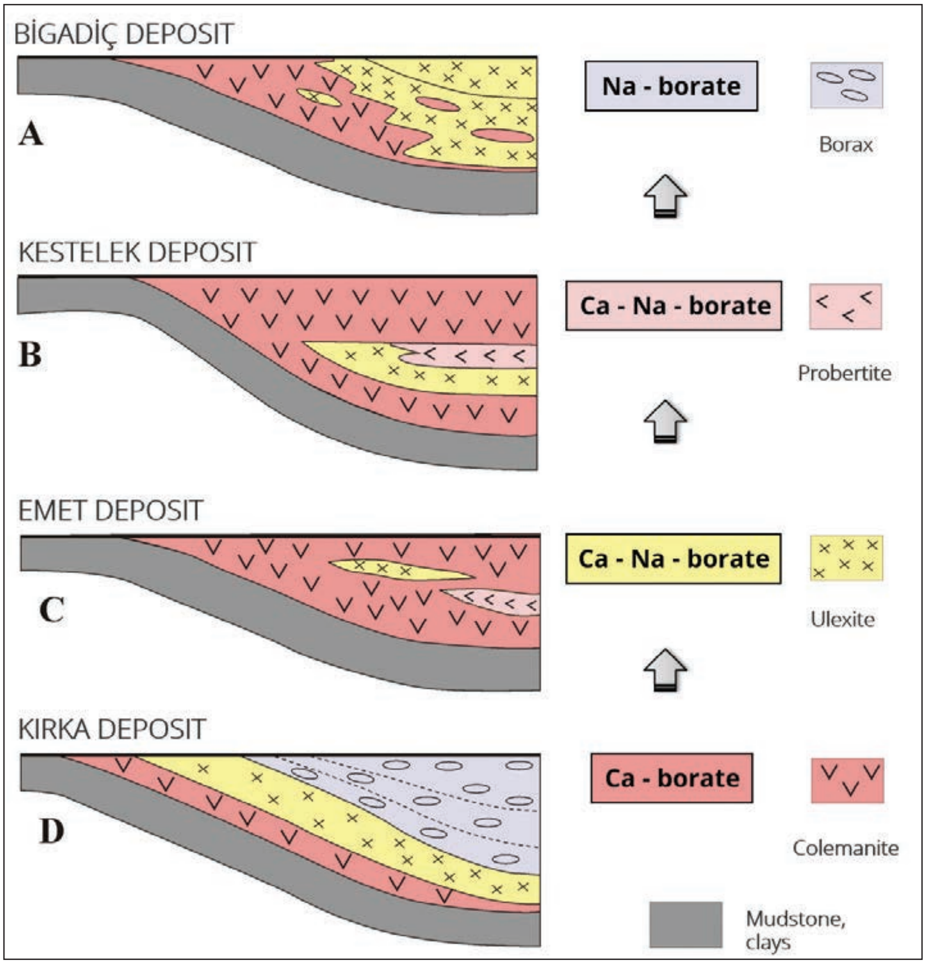

Figure 19- Sequence of boron mineral formations in Turkish borate deposits.

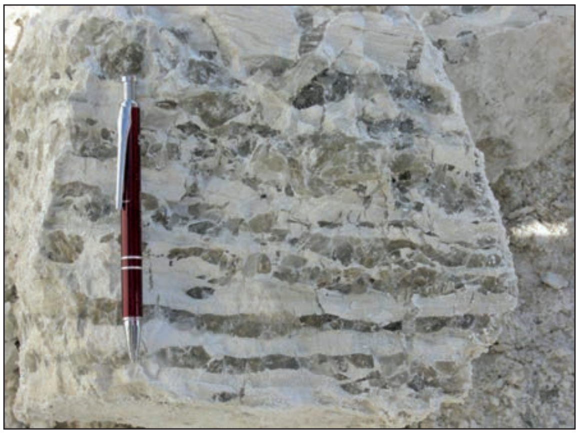

Figure 20- Borax layers and dolomitic clays alternating in Kırka borate deposit, Turkey.

Lake brines with their recoverable borax content were brought into large scale production and soon replaced most of the other domestic sources. Borates are presently produced at three locations in Southern California: Boron, Searles Lake, and, to a lesser extent, the Death Valley area (Bowser, 1965; Kistler and Helvacı, 1994;Garrett, 1998; Grew and Anovita, 1996; Helvacı, 2005; figure 11).

6.2.1. *Boron, California (Kramer)*

This deposit is located between the towns of Mojave and Barstow in the northwestern Mojave desert, 145 km northeast of Los Angeles. The Boron deposit consists of a lenticular mass of borax, kernite, and interbedded montmorillonite-illite clays. It is approximately 1.6 km long, 0.8 km wide, and up to 100 m thick. Outward from this central borax core, there is a facies change to ulexite and clay, which also exists above and below the borax. Colemanite facies are present as very thin lensoidal layers.

6.2.2. *Saearles Lake, California*

The Searles Lake playa occupies the central portion of a small desert valley midway between Death Valley and Boron, in southeastern California. The lake consists of a central salt flat, which overlies a crystalline mass of admixed salts, mainly sodium carbonates, with borax, clays and interstitial brines. The salts and brines are thought to be the end results of concentration, desiccation and decantation in a series of late Quaternary lakes which extended along the east front of the Sierra Nevada. Playa-type borax was discovered on the shores of Searles Lake as early as 1863. Small amounts of borax were produced from the playa surface until 1919, when borax along with trona and various other salts began to be recovered from brine wells sunk into the central portion of the lake, with large scale production beginning in 1927. At the present time, North American Chemicals Co. is the only company producing borates from the lake.

6.2.3. *Death Valley, California*

Death Valley is a long, north-trending valley near the Nevada border with Southern California. It is fault-bounded on both the east and west sides by active faults which have lowered the area near Badwater to 86 m below sea level. The valley contained several lakes during the Pleistocene and over 300 m of salts, mainly halite and gypsum, accumulated in the Badwater area at that time. Minor amounts of the playa borates, borax and ulexite, which occur with these salts, accumulated in the surface muds and seeps and were gathered in the early 1880s. The more productive playa area near Harmony, 32 km north of Badwater near the present National Park headquarters, was the source for the famous 20 Mule Team borates (1883-1897). This area of the Valley floor appers to be enriched by fluids derived from the leaching of the adjacent borate-containing Tertiary beds (Kistler and Helvacı,1994). In the late Neogene, over 2130 m of lake sediments were deposited in what is now Furnace Creek Wash, in and adjacent to the east side of Death Valley. It is these lake sediments of the Furnace Creek formation which contain the bedded borates (Tertiary colemanite-ulexite deposits) that were the main source of domestic borates from 1907 to 1927 and that are currently being mined (Figure 11). The 16 deposits that were commercially worked in the Death Valley area range in size from 181 kt to over 13.6 Mt, averaging 18 to 24 % B_2O_3. Production from the Billie underground mine operated by Newport Mineral Ventures, and from the Gerstley underground mine of US Borax located near Shoshone, California, about 50 km to the southeast of the Billie are presently almost closed down (Kistler and Helvacı, 1994).

6.2.4. *South America*

There are over 40 borate deposits located along an 885 km trend in the high Andes near the common borders of Argentina, Bolivia, Chile and Peru (Figure 12). This is an arid segment of the Andean tectonic-volcanic belt, characterized by compressional tectonics and many closed basins with playas or salt flats, called salars. Reserves are said to total millions of tons of B_2O_3. For many years (1852-1967), Chile was a major producer of borates, but the industry gradually shifted to adjacent areas of Argentina. Recently, Chile has become a major borate producer again (Chong, 1984; Alonso, 1986; Alonso et al., 1988; Alonso and Viramonte, 1990; Helvacı and Alonso, 1994; Kistler and Helvacı, 1994; Helvacı and Alonso, 2000; Helvacı, 2005).

Borate spring deposits are better developed in South America than anywhere else in the world. These deposits consist of cones and aprons of ulexite and in one case borax, built up around vents from which warm to cool waters and gas are still issuing in some cases. Most deposits are associated with calcereous tufa which occurs as a late-stage capping over the borates, and sometimes with halite and gypsum as well. Recent volcanic activity is indicated by basaltic to rhyolitic flows in adjacent areas, and a volcanic source for the borates is presumed (Figure 12). The deposits currently forming are quite small, ranging from a few hundred to approximately 9 kt of borates averaging 20 % B_2O_3.

The salar deposits of South America consist of beds and nodules of ulexite with some borax or inyoite, associated with recent playa sediments, primarily mud, silt, halite, and gypsum. Springs and seeps appear to be the source of the borates. The brines of Atacama, Chile, and Uyuni, Bolivia, contain borates of possible commercial interest.

The borate deposits of Argentina are restricted to a high plateau formed in a non-collisional compressional orogen during the Late Cenozoic (Figure 10). Colemanite is the principal borate at the Monde Verde, Esperanza and Santa Rosa mines, whereas hydroboracite is the predominant borate in the Monte Amarillo deposit. The Tincalayu and Loma Blanca areas are important principally for borax occurences whereas, in salars, borax and ulexite are mainly present (Figure 12) (Kistler and Helvacı, 1994; Helvacı and Alonso, 2000). The borates are found in the Sijes formation of upper Miocene age, and there are at least six small open cut mines in the area which produce colemanite, inyoite, and hydroboracite. The borate deposits of the Pastos Grandes Depression represent the largest reserves of calcium and calcium-magnesium borates of Latin America (Figure 12, table 5). During deposition of the Sijes formation there were 3 major pulses of borate generation. The borate-bearing members of the Sijes formation are from the base to top as follows: Monte Amarillo (hydroboracite), Monte Verde (colemanite-inyoite) and Esperanza (colemanite). The Santa Rosa deposit is composed principally of colemanite and hydroboracite, with appreciable amounts of inyoite and ulexite (Helvacı and Alonso, 2000; Orti and Alonso, 2000).

The Loma Blanca borate deposit was formed in the muds of a playa-lake environment during the Late Miocene and is the fourth commercial Tertiary borax deposit in the world. This deposit consists of colemanite, inyoite, ulexite, borax, tincalconite and teruggite minerals within a mineral sequence that is a unique characteristic sequence of Argentian borate deposits (Alonso et al., 1988). Borax, tincalconite, colemanite, orpiment, native sulfur, montmorillonite, illite and chlorite have been identified in addition to the previously recorded minerals. Borax, inyoite and ulexite are the dominant minerals in the deposit. Arsenic sulfides and native sulfur are present in minor quantities, and are as widely distributed as the borates (Alonso et al., 1988).

Tincalayu is the name of a low hill located in the northwestern corner of the Hombre Muerto Salar that contains an important sodium borate deposit. The peninsula of Tincalayu which hosts the borate deposit of the same name lies in the extreme northwestern part of the Hombre Muerto Salar. The borax deposit lies within the southern part of the peninsula at an altitude of 4100 m (Helvacı and Alonso, 2000; figure 12).

There are more than 100 salars in Argentina, Chile, Bolivia, and Peru, but only about 40 contain borate facies in the chemical and detrital basin deposits (Figure 12). The dominant mineral in the salars is ulexite, and borax occurs in minor proportion (Chong, 1984). The ulexite occurs in 2 types: 1) nodules, the classic "cotton ball" called "papas" (potatoes), and 2) massive beds called "barras" by the miners of the region. The borate deposits in salars are directly related to supplies of boron-rich thermal waters. Ulexite from Chile currently enters the world market from at least five salars. About half of the total production estimated at 31 ktpy, comes from the Salar de Surire, a relatively small salar situated near the border with Bolivia. The ulexite occurs 6 to 14 cm below the surface as irregular masses and in beds that attain up to a meter in thickness and averaging perhaps 30 cm.

The source is Laguna de Salinas, Peru, which occupies a large mountain basin east of Arequipa, reached by 56 km of mountain road that crosses a mountain pass at nearly 5200 m (Figure 12). Ulexite occurs as irregular masses and lenses 25 to 130 cm thick in fine, sandy detritus and green muds, 0.6 to 2.9 m thick, which lie below a surface layer of black to green muds with disseminated ulexite, sulfate, and halite. Very limited production of borates is reported from Bolivia. Reserves of playa borates and brines containing borates in the giant Salar de Uyuni have been known for many years, but supply and transport difficulties have hindered production (Helvacı and Alonso, 2000).

6.3. China

China produces about 27 ktpy of borate minerals and compounds from deposits in Liaoning, Xizang (Tibet), and Qinghai Provinces. The Liaoning production comes from a number of relatively small open pit and upderground mines on the Liaodong Peninsula of northeast China. There are reported to be more than 55 operations on some 112 separate deposits of which 12 contain 98 % of the reserves. The ores are magnesium borates, szaibelyite (ascharite), with ludwigite and suanite associated with magnesite, magnetite, and rare earths. The ores occur as veins in early Proterozoic (2.3 Ga) magnesian marbles of the middle Liaojitite suite. The ore bodies are closely related to, and conformable with, the Liaoji granites. Average grades are low by western standars, 5 to 18 % B_2O_3, and many of the smaller deposits are mined by labor intensive methods.

The Qinghai production comes from three playa lakes in the Tsaidam Basin of south-central China: Da Qaidam, Xiao Qaidam, and Mahai. The main borates are ulexite, pinnoite, hydroboracite, and borax. Recent reports indicate that the surface crusts of ulexite and pinnoite are mainly worked out and that most production is now from the brines. In addition, China has substantial reserves on the Tibetan Plateau where 57 lakes have been identified containing borates. These are not believed to be in large scale production at this time due to transport and supply difficulties (Kistler and Helvacı, 1994; Helvacı, 2005).

6.4. Other

There are a few data on the sources for borate production from Kazakhstan and Russia, which is estimated to be about 200 000 tpy (Ozol, 1977). For many years, the Inder (Gurvey) District of Kazakstan was considered the principal source. Borates, mainly szalbelyite and hydroboracite, occur there as veins and fracture fillings in a large Permian marine salt dome associated with gypsum, carbonate, and clay, and in the nearby brine lakes. Reserves of up to 7 Mt of 20 % B_2O_3 are reported. However, recent exchanges with Russian geoscientists indicate that 95% of the Russian supply now comes from the Bor deposit at Dalnegorsk in Primorsk near the Sea of Japan. The ore is a datolite skarn assemblage formed in Triassic limestones and siltstones intruded by a large pophyry dyke swarm. The borosilicate skarns occur over a length of 2 km and are up to 500 m wide; they have drilled ore grade material to 1000 m. Ore grade is estimated at 8 to 10 % B_2O_3 (30 to 45 % datolite). Minor production of ludwigite has been reported from small pipe-like bodies in North Korea at Khol-don (Hol-Kol) and Raitakuri, southwest of Pyongyang during the 1950s. There have been no recent reports that these deposits are currently in operation (Kistler and Helvacı, 1994). The colemanite body at Magdalena, Sonora, owned jointly by US Borax and Vitro (Mexico's major glass producer) remains on standby status pending an upturn in the market. The development of this deposit has been hampered by processing problems and the relatively high arsenic content of the ore. The occurence of low grade borates, predominantly howlite and colemanite, has been reported from the Jarandol Basin of former Yugoslavia (Figure 21). The borates here apparently lie above the commercial coal seams and are associated with zeolites, tuff, gypsum, calcite, and bitumen. A small colemanite occurrence has been noted on the Greek island of Samos just off the Turkish coast are the first borates reported from the Greek Isles (Helvacı et al., 1993). In the western part of Samos Island (Greece), a small borate lens occurs which is composed of colemanite and traces of ulexite. Layers of gypsum occur below the borates while celestite nodules and lenses occur within and above the borate body, which is hosted in Late Miocene claystone and tuffaceous layers. Hydrothermal vein deposit of borates occur in a fault zone in the northwestern part of Iran (Zencan deposit near Tebriz city).

7. Mining, Mineral Processing and Uses

7.1. Mining

The sodium borates borax (tincal) and kernite, the calcium borate colemanite, and the sodium-calcium borate ulexite make up 90% of the borates used by industry worldwide (Table 3). Most borates were extracted primarily in California and Turkey and to a lesser extent in Argentina, Bolivia, Chile, China, and Peru. Boron compounds and minerals are produced by surface and underground mining and from brine.

Figure 21- Location of borate deposits in Vardar Zone.

Commercial borate deposits in the world are mined by open pit methods (Figure 22). The world's major borate operations, the Boron mine of US Borax at Boron (Kramer), California, and the Kırka mine of Eti Maden in Turkey are huge open pit mines utilizing large trucks and shovels and front end loader methods for ore mining and overburden removal. Ores and overburden are drilled and blasted for easier handling. The boron operation uses a belt conveyor to move ore from the in-pit crusher to a coarse ore stockpile form which it is reclaimed by a bucketwheel that blends the ore before it is fed to the refinery. Kırka utilizes trucks which haul to a crusher near the refenery which is about 0.5 km from the current ore faces.

Smaller operations in Argentina, Chile, China, Turkey, and Russia use similar methods, but on a scale down-sized to the scale of the operation. Some of the South American and Chinese salar operations utilize hand labor to mine the thin salar borates, generally after stripping of overburden with a small dozer on a front end loader (Alonso and Helvacı, 1988; Helvacı, 1989; Kistler and Helvacı, 1994; Helvacı, 2005).

Borates are mined by underground methods in the Liaoning area of northeast China, at the Billie and Gerstley mines in Death Valley, California. Borate brines are recovered at Searles Lake, California, and in the Qinghai Basin of China; brines may also be utilized in the Inder region of Kazakhstan. Borate containing brines are being considered for production from several salars in South America.

7.1.1. Mineral Processing

Processing techniques are related to both the scale of the operation and the ore type, with either the upgraded or refined mineral (borax, colemanite, ulexite) or boric acid as the final product for most operations (Table 4). Borax-kernite ores (Boron, Kırka, Tincalayu) are crushed to 2,5 cm and then dissolved in hot water/recycled borate liquor. The resultant strong liquor is clarified and concentrated in large counter-current thickeners, filtered, fed to vacuum crystallizers, centrifuged, and then dried. The final product is refined borax decahydrate or pentahydrate or fused anhydrous borax, or is used as feed for boric acid production. Colemanite concentrates are used directly in specific glass melts or used as a feed for boric acid plants.

The ulexite from most of the South American salars is air dried, screened, and bagged. It is then combined with locally available sulfuric acid to produce a relatively low grade boric acid or exported as feed for boric acid plants elsewhere. The

Figure 22- Section of borate zone interbedded with clay and tuff, and limestone overburden, Espey deposit, Emet, Turkey.

magnesium borates are generally concentrated, dissolved in acid to remove the magnesium, and then converter to boric acid or sodium borates. The borosilicates of the Bor deposit in eastern Russia with their relatively low B_2O_3 grades, are crushed, and then run through a complex plants, which includes magnetic separators, heavy media separators, and flotation cells. The concentrates are then dried, leached, and calcined before being converted to boric acid or to a sodium borate.

The brines that form Searles Lake, and presumably the Chinese sources, are recovered by either controlled evaporation or carbonation. In the latter process, carbon dioxide produced from lime kilns or flue gas is bubbled through the brine to crystalize sodium bicarbonate; borax is then crystallized in vacuum crystallizers. In the "evaporation" process, a rapid, controlled coolings electively crystallizes the various salts. The remaining borate liquor is fed to tanks containing borax seed crystals which aid in the recovery of borates from the liquor. The resultant slurry is filtered, washed, redissolved, and fed to vacuum crystallizers that produce dehydrate borax products or boric acid (Kistler and Helvacı, 1994).

Boric acid is one of the final products produced from most of the processes (Table 4). The world's largest boric acid facility is located adjacent to the Boron pit and the Emet and Kırka opencast mines. Other smaller facilities around the world make use of smelter acid or other locally available acid feed-stock to produce products acceptable to their local markets.

7.2. Uses

Borate minerals have been employed in a wide range of uses for many centuries, dating from at least the 8th century when they were used primarily as a flux for assaying and refining gold and silver (Figure 23).

Borate was traded at relatively high prices for highly specialized applications into the late years of the 19th century. At that time they were being used for medicines, food preservatives, ceramic glazes, and in expanded applications as metal fluxes. Borate

Table 4- Commercial refined borate productions.

Product	**Formula**	**% B_2O_3**
Borax decahydrate	$Na_2B_4O_7$ $10H_2O$	30,5
Borax pentahydrate	$Na_2B_4O_7$ $5H_2O$	47,8
Boric acit	H_3BO_3	56,3
Borax anhydrous	B_20_3	100,0
Sodium perborate	$NaBO_3$ $4H_20$	22,0
Raw borax anhydrous	$Na_2B_2O_3$	69,2

are often defined and sold by their boric oxide or B_2O_3 content, and most statistical data are listed in tons of B_2O_3. Borax pentahydrate and boric acid are the most commonly traded commodities. Boric acid plants are operated by all of the major borate producers. Glass fiber insulation is the major end use in the United States followed by textile glass fiber and borosilicate glass, detergents, and ceramics. Detergent usage continues to be a major end use in Europe (Figure 24).

Fertilizers represented the third largest application of borates. Ceramics comprise the second largest application of borates after glass, accounting for 10% of world consumption. Borates play an important role in ceramic glazes and enamels, increasing chemical, thermal, and wear resistance. Borax and colemanite are used in ceramics primarily as fluxing agents, with borax being used in higher temperature, and colemanite in lower temperature firings. Borates were incorporated into various materials, such as cellulose insulation, textiles, and timber, to impart flame retardant properties to the materials. Boric acid is incorporated into wood flame-retardants to inhibit the transfer of combustible vapors and reduce the effective heat of combustion, resulting in reduced flame spread. The use of borates in detergents and soaps represented the fourth largest market,

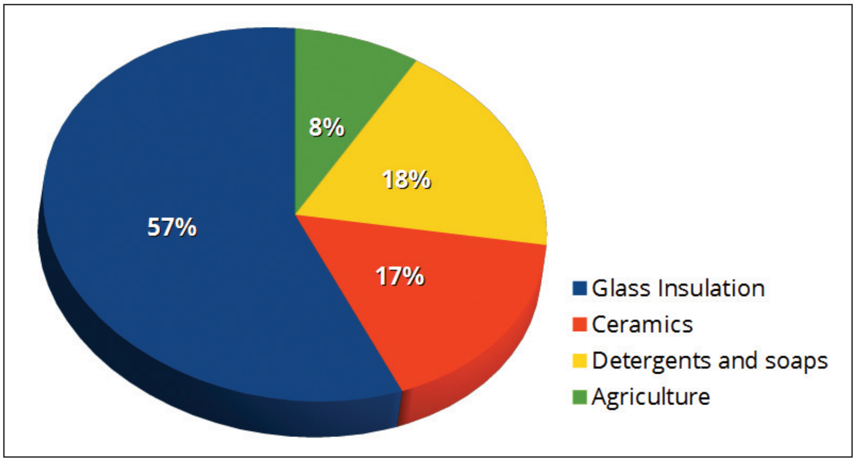

Figure 23- World borate end uses (after Helvacı, 2005).

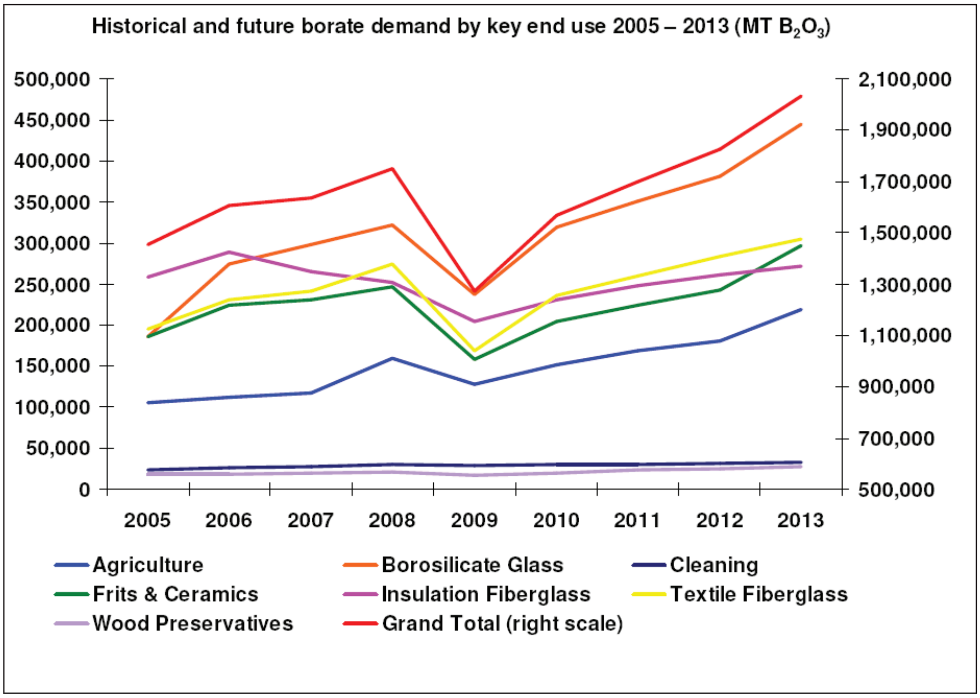

Figure 24- Present and future borate demand by key end use 2005-2013 (MT B2O3)(source: Rio Tinto).

accounting for 4% of world consumption (Kistler and Helvacı, 1994; Helvacı, 2005). Borates are incorporated into laundry detergents, soaps, and other cleaning products because they can be used as alkaline buffers, enzyme stabilizers, oxygen based bleaching agents, and water softeners. Two borates, sodium perborate and perborate tetrahydrate, are used as oxidizing bleaching agents because they contain true peroxygen bonds. The principle market for borates in 2011 was glass, representing approximately 60% of global borate consumption. Boron is used as an additive in glass to reduce thermal expansion, improve strength, chemical resistance, and durability, and provide resistance against vibration, high temperature, and thermal shock. Boron is also used as a fluxing agent, reducing the viscosity of glass during formation to improve manufacturing. Depending on the application and quality of the glass, borax, boric acid, colemanite, ulexite, and sodium borates are typically used. Ferroboron (FeB) is a binary alloy of iron with a boron content between 17.5% and 24% and is the lowest cost boron additive for steel and other ferrous metals. On average, the steel industry consumes more than 50% of the ferroboron produced annually (Eti Maden Inc., 2003). Various boron compounds are used in nuclear powerplants to control neutrons produced during nuclear fission. The isotope boron-10, in particular, possesses a high propensity for absorbing free neutrons, producing lithium and alpha particles after absorbing neutrons. Control rods composed of boron carbide are lowered into a nuclear reactor to control the fission reaction by capturing neutrons. Boric acid is used in the cooling water surrounding nuclear reactors to absorb escaping neutrons (Ceradyne Inc., 2011).

Boron minerals and their products are indispensable industrial raw materials of today. They are widely used from hygiene to health, from durable materials to space industry. Boron minerals and products used in different branches of industry, comprise major industrial utility products such as; fibreglass, medical applications and pharmaceutical materials, for safety purposes in nuclear reactors, artificial fertilizers, in photography, glass and enamel. Used in several compound forms like borax and boric acid, boron creates multi-faceted and useful components. The subject compounds provide an advantage especially in strong soldering, in welding, in reducing friction and in processes of metal purification. Borax and boric acid, with their property to diminish bacteria, to dissolve easily in water and to soften water; are extensively used in the making of soaps, cleansing agents, detergents, office products, textile colouring, protection of different materials, low resistant alloys and agricultural industry. Some boron products, because of their property as a excellent fluxing agents, are essential materials in metal purification and production of steel, atomic reactors, ignition switch fuses, lamps in electronic tools and solar batteries. Boron compounds; diborane (B_2H_6), pentaborane (B_5H_9), decaborane ($B_{10}H_{14}$) and alkali borons are foreseen as the potential jet and rocket fuels of the future (Kistler and Helvacı, 1994; Helvacı, 2005).

The principal uses of borates have not changed much in the past decade and major markets include fiberglass, insulation, textile or continuous-filament glass fibers, glass, detergents and bleaches, enamels and frits, fertilizers, and fire retardants (Figures 23 and 24). Bleaches and detergents are also the major end use; however, sales for glass and glass fibers including fiberglass, are increasing. Boron fiber-reinforced plastics continue to be utilized in quantity for aerospace frame sheathing where they combine flexibility and light weight with strength and ease of fabrication. Relatively minor uses that are expected to increase in the near future include those in fertilizers, wood preservatives, alloys and amorphous metals, fire and flame retardants, and insecticides. However, the promising field of boron-iron-silicon electrical transformers has not developed as rapidly as predicted due to various cost factors.

Miscellaneous uses include pharmaceuticals, cosmetics, anti-corrosion compounds, adhesives, abrasives, insecticides, metallurgical processes, and nuclear shielding. Research is still continuing in many areas. One of the more publicized of these is in super magnets, where borates, combined with rare earths, nickel and iron, produce an alloy that can be used to make electromagnets for computer drives, high fidelity speakers, automobile starter motors, and various household appliances.

Borates can be utilized to protect the environment by aiding in converting heavy metals in industrial waste streams into recoverable free metals and by removing impurities from polymers used in bleaching wood pulp for paper production. Borates also aid in the control of the refractive index in optical fibers for medical research where precise control is needed. Other medical applications include cancer research where the ^{10}B istope reacts with low energy neutrons to give off short range alpha particles that can be used for microsurgery in previously inoperable areas of the brain. Current tests on boron analogues indicate they may be effective in reducing serum cholesterol and other disease-causing proteins. Borates have become a relatively modestly priced industrial mineral commodity in recent years following the development of the large deposits at Boron, and more recently, Kırka. Prices are directly related to the cost of production, of which the major cost is fuel for drying, dehydrating, and melting the refined ore into the products desired by industry. Industry prices for most products have held steady with the rate of inflation.

Borates are a lightweight commodity and are generally sold in bulk by rail carload lots, in IBC's (Intermediate Bulk Containers) or "super-sacks," and by palletized bags. Overseas shipments are made mostly in bulk from special terminals at Los Angeles, California, and from Bandırma on the Marmara Sea in Turkey, to similar terminals in the Netherlands, Belgium, and the United Kingdom, from where it is moved by barge, as well as rail and truck. Other imports to Europe arrive in Italy and Spain. Imports to the Far East are generally sold in small bag lots. Bulk imports to the United States (mainly colemanite) usually land in Charleston, SC, where there are griding facilities; this colemanite is then shipped to easter fiberglass manufacturers. There is no import duty on borates brought into the United States (Kistler and Helvacı, 1994; Helvacı, 2005).

8. Future Forecasts

Known reserves of borate minerals are large, particularly in Turkey, South America, and the United States, and production from Turkey and the United States will continue to dominate the world market. However, borates from other areas will probably take up an increasing share of the world market. This trend is already evident with boric acid from Chile reaching the Far East and Europe, and both Russia and China beginning to export (Figures 25, table 5).

Both western Europe and Japan, neither of which has local borate sources, are major markets for US and Turkish production. South America is largely self sufficient with an increasing amount in excess of their needs which is exported mainly to Europe and Japan. Russia and China both appear to be self sufficient in borates at this time, although their costs of production per ton of B_2O_3 are thought to be relatively high.

Approximately 75-80% of the world's boron reserves are located in Turkey (Engineering and Mining Journal, 2012)(Table 5). The main borate producing areas of Turkey, controlled by the state-owned mining company Eti Maden Inc., are Bigadiç (colemanite and ulexite), Emet (colemanite), Kestelek (colemanite, probertite, and ulexite), and Kırka (borax-tincal). Production of refined borates increased during the past few years owing to continued investment in new refineries and technologies. Eti Maden planned to expand its share in the world boron market from 36% to 39% by 2013, increasing sales to $1 billion by expanding its production facilities and product range. In 2009, Turkey exported 4 Mt of borates valued at $104 million (Uyanik, 2010). Consumption of borates is expected to increase, spurred by strong demand in the Asian and South American agriculture, ceramic, and glass markets. World consumption of borates was projected to reach 2.0 Mt B_2O_3 by 2014, compared with 1.5 Mt B_2O_3 in 2010 (Rio Tinto Inc., 2011; Roskill Information Services Ltd., 2010, p. 167; O'Driscoll, 2011).

The European Union (EU) added borates to a list of banned minerals, which required detergent makers to decrease their use of boron following an EU ruling that determined continuous exposure may be harmful (Lismore, 2012). Demand for boron based fertilizers was expected to rise as a result of an increase in demand for food and biofuel crops. Consumption of

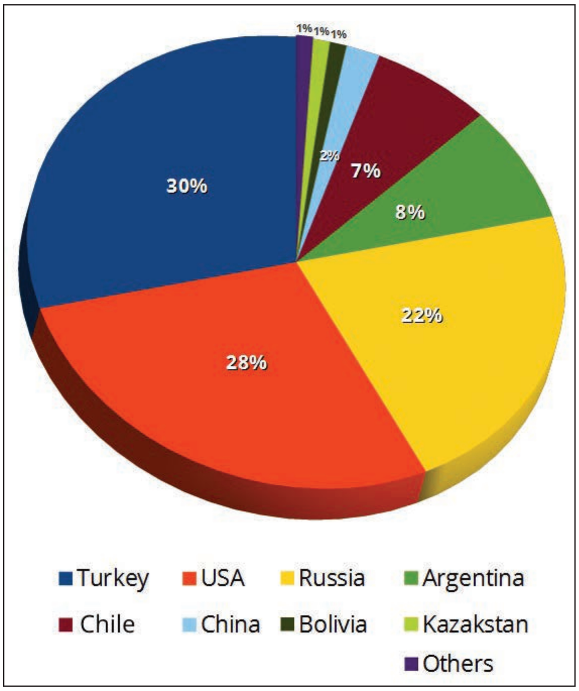

Figure 25- World borate production (Helvacı, 2005).

borates by the ceramics industry was expected to shift away from Europe to Asia, which accounted for 60% of world demand in 2011. Consumption of boron nitride is expected to increase owing to the development of high-volume production techniques coupled with the creation of new technologies. The properties intrinsic to cubic boron nitride, such as hardness (second only to diamond), high thermal conductivity, and oxidation resistance make it an ideal material in a variety of emerging applications. Hexagonal boron nitride is used in additives, ceramics, and intermetallic composites, imparting thermal shock resistance, improved machinability, and reduction of friction.

Turkey, USA, Russia, China, Kazakhstan, Italy, Argentine, Bolivia, Peru and Chile are prominent countries that produce boron minerals and products. Sassolite, borax kernite, ulexite, probertite, pandermite, colemanite, hydroboracite and szaibelyite are economically operated boron mines that have commercial importance. Borax decahydrate, borax pentahydrate, anhydrous borax, boric acid, sodium perborate tetrahydrate, sodium perborate monohydrate and anhydrous boric acid are economically significant chemical boron components. Turkey's borate deposits are the largest and highest grade (respectively 30, 29 and 25% B_2O_3) of colemanite, ulexite and borax (tincal) deposits in the world and have sufficient potential to meet the demand for many years (Table 5).

Boron consumption is directly related to the usage of glass, glass fibers, and ceramics. These materials, along with certain plastics that contain borate products, are seen as having a steady consumer demand in the construction and housewares markets well into the next century. Borates are an essential part of certain plant foods. Their use in nuclear reactor shielding and control is well documented. Other major uses, detergents, plant foods, wood preservation etc. are expected to show a slowly rising demand. Total world borate demand is expected to grow at about 3% per year in the near future, based on industry forecasts (Table 5, figure 26). Future markets are difficult to predict. Based upon recent history, the major world consumers of borates will continue to be the developed countries of North America, Europe, and Japan.

Turkish Scientific and Technical Research Institute (Tübitak- MAM), carried out a project of transforming sodium boron hydride, expected to be the most important potential hydrogen transporter of the future, into industrial production on a pilot-scale, in 2008. The discovery by a Turkish company NNT, through advanced technology of the Borpower engine- lubricant end-product, saves fuel by up to 20% in motor vehicles, expands vehicles' rectification and oil life by a factor of two.

Turkey exports 51% of its boron products to EU contries. Although the EU has recently asserted that boric acid and sodium borates have a negative effect on human reproduction, this is not supported by research in the area covered by the borate deposits and facilities, which show that boron and its products do not have a significant impact on human reproduction (Şaylı, 2003).

Table 5- The reserves and life estimates of the world's borate deposits (Helvacı, 2005).

	Know Economic Reserve (Million tons of B_2O_3)	Total Reserve (Million tons of B_2O_3)	Estimated Life of Known Reserve (year)	Estimated Life of Total Reserve (year)
TURKEY	224.000	563.000	155	389
USA	40.000	80.000	28	55
RUSSIA	40.000	60.000	28	69
CHINA	27.000	36.000	19	25
CHILE	8.000	41.000	6	28
BOLIVIA	4.000	19.000	3	13
PERU	4.000	22.000	3	15
ARGENTINA	2.000	9.000	1	6
KAZAKHSTAN	14.000	15.000	10	10
TOTAL	**363.000**	**885.000**	**253**	**610**

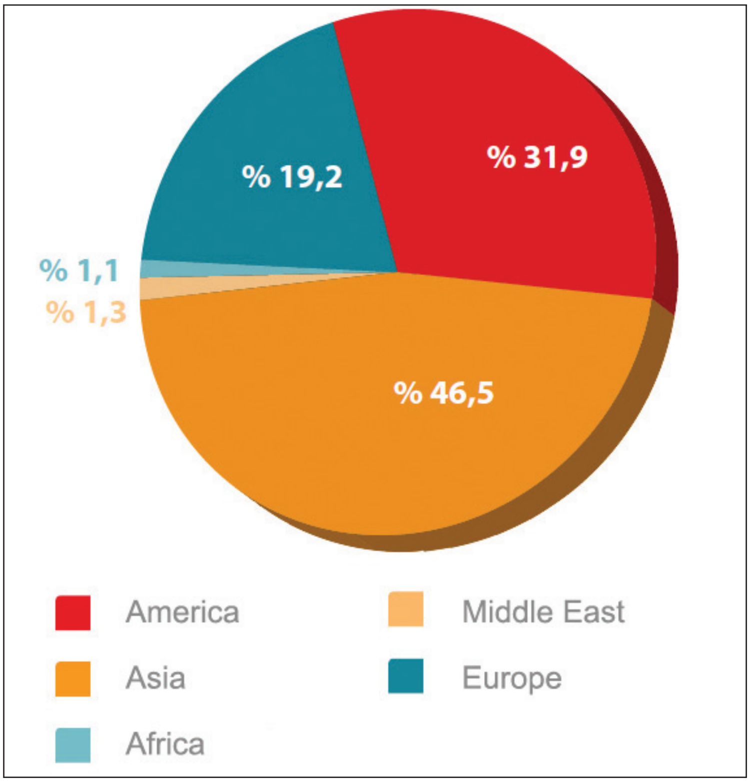

Figure 26- The World Regional Borate Consumption (%)(source: Rio Tinto).

Turkey has the largest boron mines in the world. Turkey has an important share in the world markets with borax (tincal) production in Kırka; colemanite and ulexite production in Emet, Bigadiç and Kestelek regions. Between 1980-2008, Turkey became the biggest colemanite producer in the world. Turkey's visible and potential reserves are greater than its current production. Even the most pessimistic observers are unanimous on the opinion that these borate reserves should be able to meet demands for a couple of hundred years (Figure 22, table 5). The world is dependant on Turkey with its supplies of widely used colemanite and ulexite. All countries in the world extensively using this mineral are dependant on Turkey's boron supplies. Turkey has a substantial potential in the world in terms of both the operation costs of boron mine reserves and it has grade advantages. Borate deposits in Turkey cannot be matched with any other countries in the world, with regard to reserves and grade.

As far as the National Boron Policy is concerned, after the Nationalization Act in 1979, the intensive work has been done on different borate deposits to show the value of boron mineral potential in Turkey. These natural resources, are superior to their equivalents in the world in every respect, are able to bring the country to an unrivalled position in the boron salts sector. Eti Maden Inc. and the private sector should cooperate in producing end products from boron minerals, thus follow marketing and industry oriented research policies.

It is an obligation to operate production of boron minerals towards the country's best interest, in order to hold on against world monopolies and to protect itself from their seperatist influences. In terms of mining, operation of our boron mines are at an advantage with respect to geography, transportation, energy, etc. compared to other countries (especially Latin America, USA and China) and suitable for marketing. For example, the boron deposits in South America are at an altitude of 4000 metres and those in North America are located in the middle of the desert, hence making it very difficult and problematic to operate them.

It is essential for Turkey to form a new national boron policy, so that it can appraise this natural resource with the highest return. The only way to achieve this goal is by operating boron mines towards the best interest of the country and sustaining the advantages it has. The country's resources need to be evaluated in a planned and programmed manner.

Production policy should be grounded on detailed and thorough market research. These important raw-material resources must be restructured and organized to ensure maximum return for the country's economy. In order to protect the advantages to the benefit of our country, research and technological development towards production of end-products with a high added value, should take first place in the fundamental restructuring rather than export of the raw mineral boron raw and semi-manufactured products.

As a conclusions for development of Eti Maden Inc. and Boron Salts Institute, investments and organizations are required. For the purpose of developing all kinds of industrial end-products, production, making short and long-term studies and projects, expert researchers from different fields like material, mechanical, chemistry and electric-electronic, should be employed in these institutions. This will allow closing of the gap between research and implementation and forward-looking, planned research that meets these requirements should be accelerated (Figure 27, table 5).

Today, as economic competition is becoming more intense and many studies are being made on natural resources; the existence of a massive boron reserve potential is a great opportunity for Turkey. Production and marketing of boron minerals should be directed towards end products with a high added-value, instead of raw or semi-finished products, and related investments have to be realized as soon as possible.

Boron products have a high added-value and they have a strategic role in the area they are used. Recently, boron products have been utilized in different fields of industry and shown an increase parallel to technological innovations. Rising standards of living, advancement of scientific and technological discoveries will eventually result in the demand and necessity for advanced boron compounds. Boron operation requires restructuring in a way to provide maximum return on the country's economy.

Ultimately, it is apparent that we face the responsibility and necessity to focus our policies in terms of science and nationwide, on important and strategic minerals, mainly boron. Otherwise, there is stands the possibility of coming up against unfavourable conditions as the destitute keepers of rich natural resources. The main aim here is to sustain the favourable position of our country on boron, which is a duty that relies on each and every citizen.

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Production Capacity : 5.5 million tonnes

Sales Income : 2.5 billion dolars

Profit for the period : 1.6 billion dolars

Figure 27- Eti Maden's 2023 Projection, Turkey.

Turkey (TÜBİTAK, Project No: YDAB.AG-100Y044 and ÇAYDAĞ-103Y124). Mustafa Helvacı is gratefully acknowledged for his typing and drafting assistances which significantly improved the manuscript. I would like to thank the reviews of M.R. Palmer, H.G. Dill, Y.Genç, and H.Mutlu for their constructive comments and suggestions, which have considerably improved the final version of the manuscript.

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