Chapter 11
Turkish Borate Deposits: Geological Setting, Genesis and Overview of the Deposits

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Abstract Boron is widely distributed in the earth's crust and the element boron does not exist freely by itself in nature, rather it occurs in combination with oxygen and other elements in salts, commonly known as borates. Boron is a rare element in the Earth's crust, but extraordinary concentrations can be found in places. Four main continental 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. Colemanite is the main calcium borate and large scale production is restricted to Turkey. Main borax (tincal) deposits are present in Anatolia (Kırka), California (Boron), and two in the Andes (Tincalayu and Loma Blanca). 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 and Tibet). The Karapınar playa-lake is located in central Turkey. The formation of borate deposits consisting of 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, 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 faults; thermal springs near areas of volcanic activity; arid to semi-arid climatic conditions; and lake water with a pH of between 8.5 and 11. 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. The main borate districts are located in Bigadiç, Kestelek, Sultançayır, Emet, Kırka and Göcenoluk areas. Most of the world's commercial

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F. Pirajno et al. (eds.), *Mineral Resources of Turkey*, Modern Approaches in Solid Earth Sciences 16, https://doi.org/10.1007/978-3-030-02950-0_11

borate deposits are mined by open pit methods. 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 individuals use their products. Therefore, borates and associated products are critical for the sustainable development of the world.

11.1 Introduction

Borate was first used in Babylon more than 4000 years ago. Its name originated from the Persian burah (boorak), borax was already known to the Babylonians who brought it from the Himalayas some 4000 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 thirteenth century, presumably by Marco Polo, and since that time by traders from Tibet and Kashmir.

Boron is the fifth element of the periodic table and is the only electron-deficient non-metallic 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 four to eight orders of magnitude from <0.1 ppm in primitive mantle to 17 ppm in average continental crust, and to several wt% in pegmatites and evaporites. 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. 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 two 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.

Borates are among the most interesting of the world's 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 (Kistler and Helvacı 1994; Helvacı 2005). Over 250 boron-bearing minerals have been identified, the most common being sodium, calcium and magnesium salts. By the 1770s, the French had developed a source of tincal, the old name for crude borax, in Purbet Province, India, and at 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 the beginning of that State dominance of the borate industry. Demand encouraged exploitation of large-scale deposits in Turkey and the United States.

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 most commercially important worldwide 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, some of which 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, 2015).

The borate deposits of Turkey occur in western Anatolia, south of the Marmara Sea within an area roughly 300 km east-west by 150 km north-south. The main borate districts are Bigadiç, Kestelek, Sultançayır, Emet and Kırka (Fig. 11.1). 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 times. 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 by Dr. 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 a massive borax body, with estimated reserves several times greater than those of Boron, California (İnan 1972;

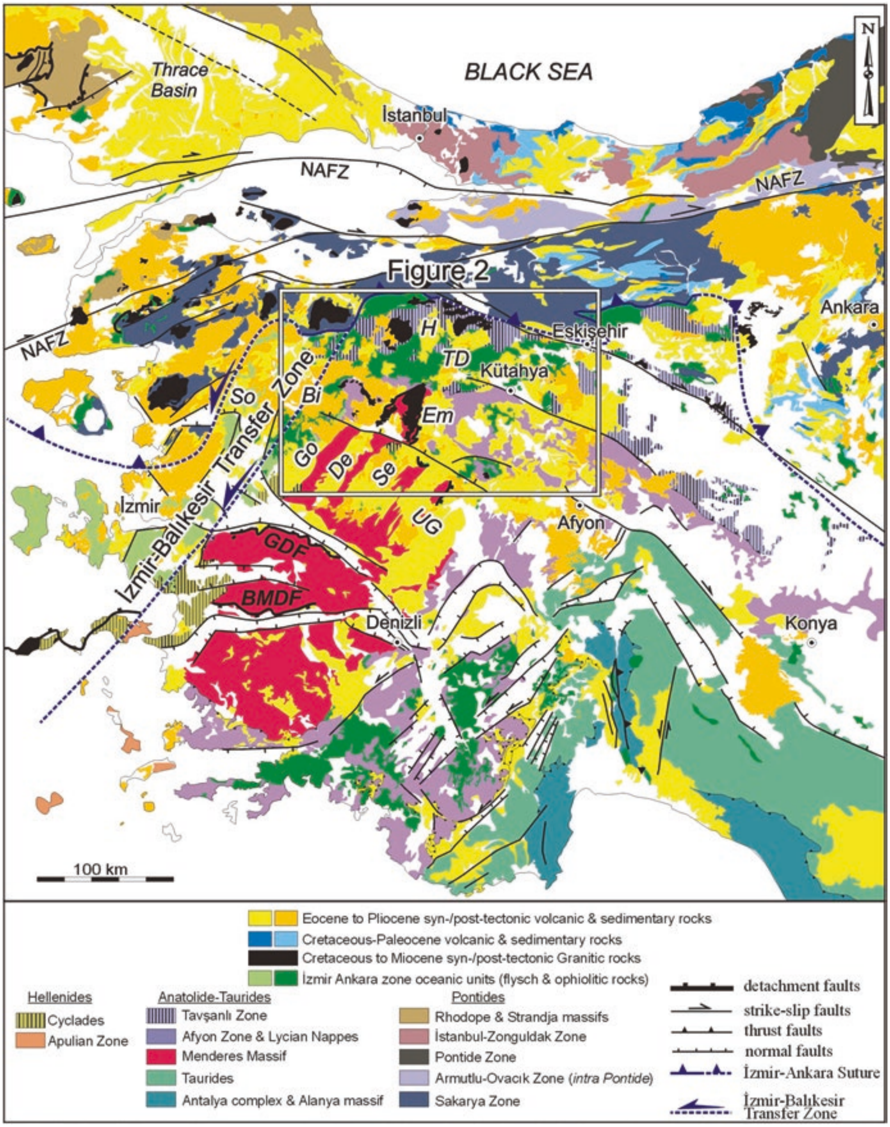

Fig. 11.1 Simplified geological map of western Anatolia showing the main tectonostratigraphic units and major tectonic elements in the region (Compiled from 1/500.000 scaled geological maps of Turkey (MTA 2002). NAFZ: North Anatolian Fault Zone)

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.

Modern borate mining in Turkey 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 (Travis and Cocks 1984). The most important worldwide borate deposits occur in western Anatolia and have been the topic of several papers which dealt with their genesis and ore formation (İnan 1972; Baysal 1972; Helvacı 1983, 1984, 1986, 1995, 2005, 2015; Kistler and Helvacı 1994; Palmer and Helvacı 1995, 1997; Helvacı et al. 1993; Helvacı and Orti 1998, 2004; Helvacı and Alonso 2000). They originated in continental Tertiary lacustrine basins during a period characterized by intense magmatic activity affecting western Anatolia. These borate deposits are interbedded with volcanosedimentary rocks, and the borate deposits and associated sedimentary rocks are deposited within playa lake environments (Floyd et al. 1998; Helvacı and Alonso 2000).

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. Turkey is already the major world producer of colemanite, much of which comes from the Emet valley (e.g. 2500 mt 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.

In this paper, stratigraphic, volcanic and tectonic observations from these basins will be presented in order to outline the main features of the borate bearing basins and the tectono-stratigraphic model for borate formation in western Anatolia.

11.2 Geology

The 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 (Fig. 11.1; 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 (Fig. 11.1, 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; Fig. 11.1). 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)

The geometry, stratigraphy, tectonics and volcanic components of the borate bearing Neogene basins in western Anatolia offer 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 (Figs. 11.1, 11.2, and 11.3). 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 (Fig. 11.1). 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

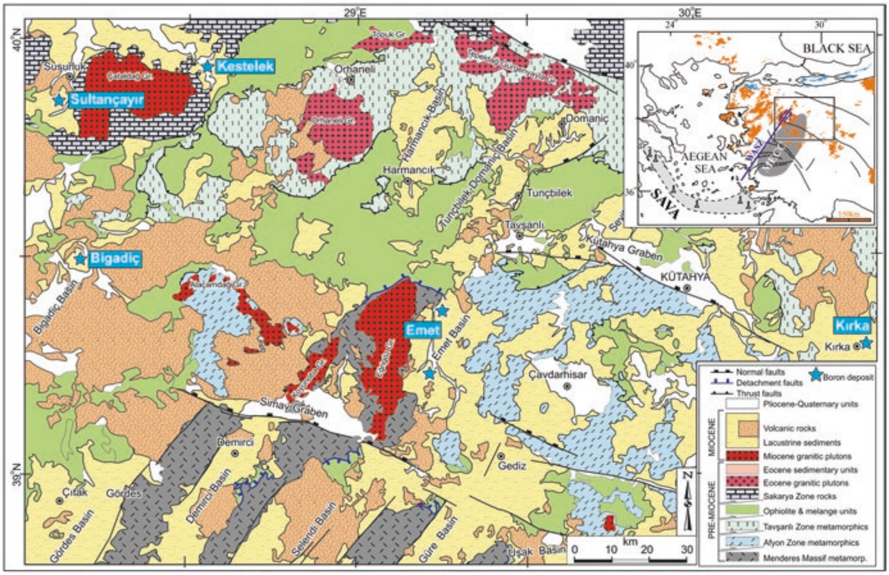

Fig. 11.2 Simplified geological map of the Neogene located NE of the Menderes Massif. The numbers in squares indicate published age data of the Miocene volcanic rocks with the references in parenthesis: (1) Seyitoğlu (1997a, b); (2) Ersoy et al. (2012a, b); (3) Çoban et al. (2012); (4) Ersoy et al. (2010); (5) Karaoğlu et al. (2010); (6) Ercan et al. (1997); (7) Prelevic et al. (2012); (8) Innocenti et al. (2005); (9) Ocakoğlu (2007); (10) Bellon et al. (1979). The age data for the granitic plutons are from Ring and Collins (2005); Hasözbek et al. (2011); Altunkaynak et al. (2012) and references therein

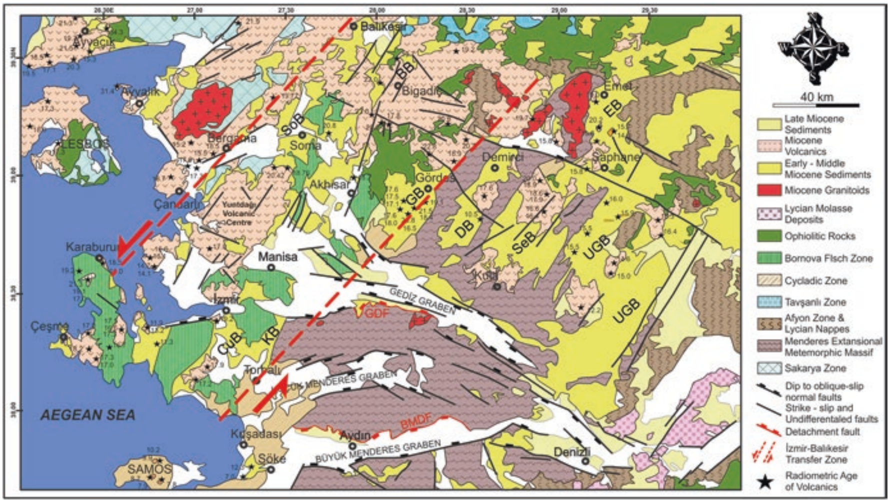

Fig. 11.3 Geological map of western Anatolia showing the distribution of the Neogene basins, radiometric ages of the volcanic intercalations in the Neogene sediments and major structures (Modified from 1/500,000 scaled geological map of Turkey (MTA); and studies cited in the text). Abbreviations for 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)

Anatolides. These two blocks are separated by the İzmir-Ankara zone that is 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 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 with ophiolitic rocks of the Bornova flysch zone, while to the northeast, they are metaclastics, metabasites, and recrystallized limestones of the Afyon zone (Fig. 11.1).

Western Turkey is one of the most famous regions in the world that have been studied in respect of scientific, economic and historical 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 several industrial raw-material deposits (borates, zeolites, clays, coal etc.) and metallic ore deposits (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 (Helvacı and Alonso 2000; Yiğit 2009). The areas located in a region that hosts both gold and borate deposits in the Neogene volcano-sedimentary rock units, and the borate deposits are the subject of this paper.

11.2.1 General Outlines of the Neogene Basins Hosting Borate Deposits in Western Anatolia

Western Anatolia has been the focus of many geological studies of the 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 faults during the late Miocene, and by E–W-trending normal faults in the Pliocene–Quaternary. The region has been extended in an N–S-direction since at least the early Miocene, and that this extension occurred episodically in several phases (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 (Bozkurt 2003; Helvacı et al. 2006; Ersoy et al. 2011). There are also NE–SW-trending basins developed along the İzmir-Balıkesir Transfer Zone (İBTZ) (e.g., Kestelek, Sultançayır, Bigadiç and Gördes basins) (Helvacı et al. 2006; Ersoy et al. 2012a, b).

11.2.2 Volcanism of Neogene Basins 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 related basin formation along the İzmir-Balıkesir Transfer Zone in the west of 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, 2012a, b).

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 (Fig. 11.3). The main NE-trending basins 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 (Fig. 11.3). 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. 1997; Seyitoğlu 1997a, b; Yılmaz et al. 2000; Aldanmaz et al. 2000; Helvacı et al. 2009). 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. 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).

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, 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. 2012a, b).

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. 2005b). 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. 2005b; 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 series of volcanic rocks (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 alkaline basaltic (tephrite, basanite, phonotephrite) volcanic activity emplaced on the northern flank of the Gediz graben (Kula volcanics).

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. 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 (Table 11.1).

The Miocene borate deposits of western Turkey are associated with extensive medium- to high-K calc-alkaline 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 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 borate deposits (Floyd et al. 1998).

11.3 Correlations of Borate-Bearing Neogene Basins

The Neogene volcano-sedimentary succession in Bigadiç basin contains the Kocaiskan volcanics (23.6 ± 0.6–23.0 ± 2.8 Ma, Table 11.1) that are composed of andesitic volcanics and the unconformably overlying Bigadiç volcano-sedimentary succession (Fig. 11.4). 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. 2005a, b). These rock units are unconformably overlain by late Miocene–Pliocene continental sediments consisting of detritus and alluvium. The radiometric ages and the stratigraphic relationships clearly indicate that the borate-bearing succession was deposited during the early Miocene.

The NE–SW-trending Gördes basin contains a similar volcanosedimentary sequence to that of Bigadiç basin. These two basins contain an early Miocene volcano-sedimentary sequence. The Bigadiç and Gördes basins are characterized by

Table 11.1 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 tuff	17.4 ± 0.3 (hornblende, K/Ar)	Helvacı and Alonso (2000)
Sultançayır basin				
	S-1	Rhyolitic tuff	20.0 ± 0.5 (feldspar, K/Ar)	
Bigadiç basin				
Kocaiskan volcanics	F-110	Andesite	23.00 ± 2.80 (biotite, K–Ar)	Helvacı and Erkül (2002), Helvacı et al. (2003), and Erkül et al. (2005a, b)
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)	
	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)
Selendi basin				
Eğreltidağ volcanics	SE-1	Rhyolite	18.90 ± 0.60 (biotite, K–Ar)	Seyitoğlu (1997a, b)
	521	Dacite	18.90 ± 0.10 (plagioclase, Ar/Ar)	Helvacı and Ersoy (2006), Helvacı et al. (2012), and Ersoy et al. (2008)
	521	Acidic tuff	20.00 ± 0.20 (amphibole, Ar/Ar)	
Kuzayır lamproite	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 (1997a, b)
	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 age)	Helvacı and Ersoy (2006), Helvacı et al. (2006), and Ersoy et al. (2012a, b)

(continued)

Table 11.1 (continued)

Basin and unit	Sample	Rock type	Radiometric age (Ma), material	References
Emet basin and Gediz–Şaphane region				
Akdağ volcanics	E6	Rhyolite	20.20 ± 0.40 (biotite, K/Ar)	Seyitoğlu (1997a, b)
	E-3	Rhyolite	19.00 ± 0.20 (biotite, K/Ar)	Helvacı and Alonso (2000)
Köprücek volcanics	E-1	Pyroclastic	16.80 ± 0.20 (biotite, K/Ar)	
Dereköy basalt	E9	UK latite	15.40 ± 0.20 ± (feldspar, K/Ar)	
	E3	UK latite	14.90 ± 0.60 (whole rock, K–Ar)	Seyitoğlu (1997a, b)
	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), and Ersoy et al. (2012a, b)
	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 (K1-955.8 m)	Basalt	18.63 ± 0.2 (New Ar/Ar data)	Helvacı and Yücel-Öztürk (2013) and Seghedi and Helvacı (2014)
	2a-2 (K6-1063 m)	Trachyte	18.69 ± 0.04 (New Ar/Ar data)	
	2c	Lamproite lavas	16.91 ± 0.05 (New Ar/Ar data)	
	2d(K-1)	Trachyte	16.1 ± 0.2 (feldspar, K/Ar)	

early Miocene volcano-sedimentary successions which were deposited along early Miocene strike-slip and related normal faults (Ersoy et al. 2012a, b). The Demirci, Selendi, Emet and Güre basins have similar stratigraphic, geochemical and tectonic characteristics. The basin-fill of these Neogene basins are; (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 (Fig. 11.4; Ercan et al. 1978, 1983; İnci 1984; Seyitoğlu 1997a, b; Yılmaz et al. 2000; Ersoy and Helvacı 2007; Ersoy et al. 2010).

The NE–SW-trending Selendi, Emet and Güre basins, which developed on the Menderes Core Complex, have similar lithostratigraphies that comprise two main volcano- sedimentary successions: the Lower Miocene Hacıbekir Group, and the

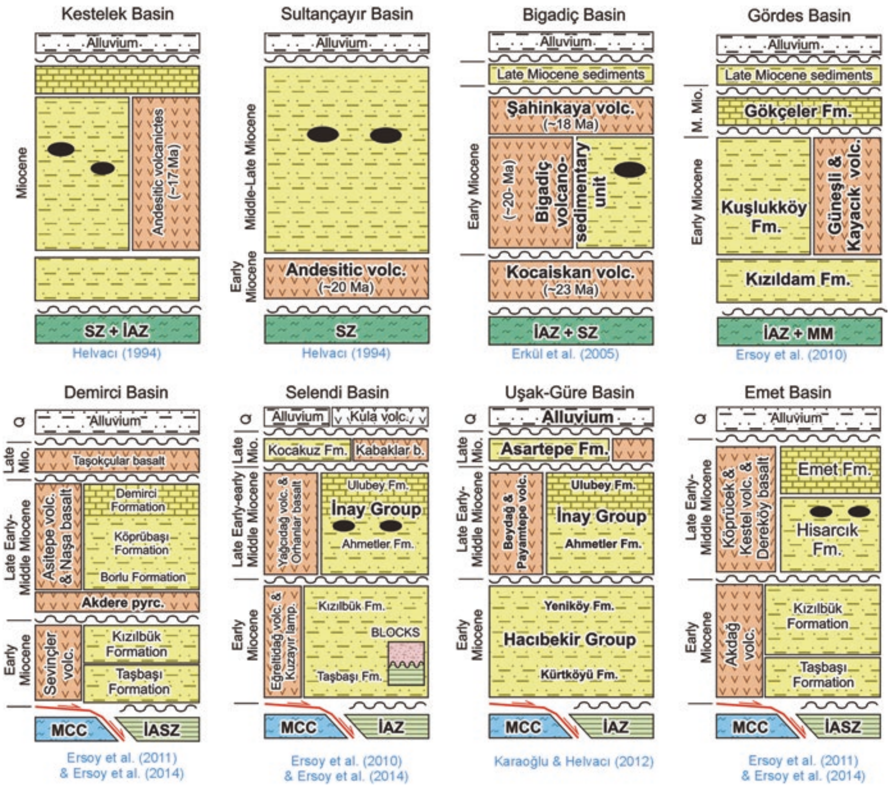

Fig. 11.4 Stratigraphic columns of the borate bearing basins in Western Anatolia. *MM* metamorphic rocks of the Menderes Massif, *İAZ* İzmir-Ankara zone rocks, *SZ* metamorphic rocks of the Sakarya zone, *MCC* Metamorphic Core Complex. (Modified after Ersoy et al. 2014)

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 Kızılbuk 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 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 Köprücek volcanics are overlain by the limestones of the Emet 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. 2012a, b; Figs. 11.3 and 11.4). 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 1997a, b; Helvacı and Alonso 2000; Table 11.1). 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 potential 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 also variably enriched in Li, S, Sr and As. Potential sources for these elements include lacustrine sediments, local basement rocks and volcanics 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 and travertines from hot spring activity. Data from Bigadiç, Emet and Kırka basins show that early volcanism is felsic 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 felsic 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 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 and probertite deposit), Bigadiç (colemanite and ulexite) and Kırka (borax deposit) basins were studied together with a study volcanic rocks associated with the borate deposits of Kırka, Emet, Bigadiç, Kestelek and Sultançayır districts have been performed. The geochemical work 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 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 the 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. Presence of widespread secondary minerals (e.g. zeolites, calcites) supports the hypothesis of interaction with circulating shallow level 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.

11.3.1 Bigadiç, Susurluk and Kestelek Basins

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 volcano-sedimentary associations separated by a basin-wide angular unconformity. Volcanism in the Bigadiç area is characterized by two different rock units that are separated by an angular unconformity. These units are: (1) the Kocaiskan volcanics that gives K/Ar ages of 23.0 ± 2.8 Ma, and (2) the Bigadiç volcano-sedimentary succession within the borate deposits that yields ages of 20.6–17.8 Ma (Fig. 11.4). Both units are Early Miocene in age and are unconformably overlain by Upper Miocene-Pliocene continental deposits (Helvacı 1983, 1995; Erkül et al. 2005b).

The Kocaiskan volcanics, which are andesitic in composition, 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 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. 2005b). 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. 2005b) (Fig. 11.4).

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, and 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. 2005b, 2006; Fig. 11.5). 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 11.1).

Fig. 11.5 Peperitic textures related to plagioclase-phyric trachyandesites of the Kayırlar volcanic unit, Bigadiç deposit, Turkey

The total 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. 2005b) (Fig. 11.6).

Geochemical data from the Bigadiç area are also related to the extensional regime, which was characterized by bimodal volcanism linked to extrusion of coeval alkaline and calc-alkaline volcanic rocks during the second volcanic episode. The formation of alkaline volcanic rocks dated as 19.70.4 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. 2005b). The ages of the intermediate to felsic 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. 2005b). 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. 2012a, b; Seghedi et al. 2015).

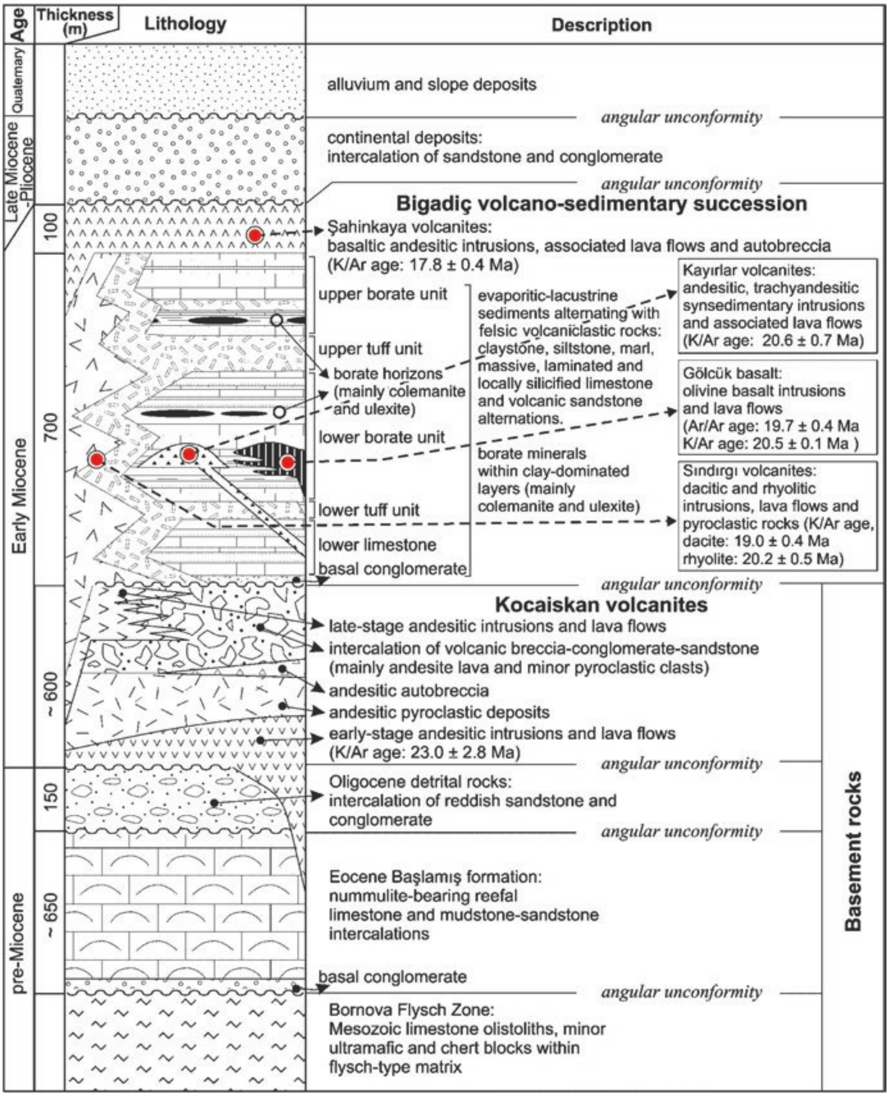

Fig. 11.6 Simplified stratigraphic column of the Bigadic¸ borate basin. Red dot illustrates K–Ar ages of a rock in millions of years. Numbers in parentheses indicate age data sources: Erkül et al. (2005 a,b), (2) Gündoğdu et al. (1989), (3) Krushensky (1976), (4) Helvacı (1995) and (5) Benda et al. (1974)

This early-middle Miocene volcanism continues further NE (towards Susurluk-Çaltıbük; Helvacı 1994; Helvacı and Alonso 2000; Fig. 11.1) with widespread andesitic to rhyolitic lava flows and associated 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 11.1, Figs. 11.3 and 11.4).

11.3.2 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 1997a, b; Ersoy and Helvacı 2007). Three volcano-sedimentary units constitute the Neogene stratigraphy and 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 (Figs. 11.3 and 11.4). 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 (Fig. 11.7). 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 al. 2008; Helvacı 2012).

Fig. 11.7 The vent area of a lava flow, Kula volcanics, Turkey (Location: 38.6 North, 28.7650 East Altitude:551 m above sea)

11.3.3 Emet Basin

The Emet basin (Akdeniz and Konak 1979; Helvacı 1984, 1986; Fig. 11.4), 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 (Figs. 11.1 and 11.2). The stratigraphy of Emet basin comprises two Neogene volcanosedimentary units separated by a regional unconformity (Fig. 11.4). 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 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 (Fig. 11.4). 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 (Fig. 11.4). The Taşbaşı Formation is locally interfingered with rhyolitic pyroclastic rocks of the Akdağ volcanics, and is conformably overlain by the Kızılbük formation. The Akdağ volcanics have yielded 20.3 ± 0.6 (Seyitoğlu 1997a,

b) and 19.0 ± 0.2 Ma (Helvacı and Alonso 2000) K–Ar ages (Table 11.1). 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 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 and the age of the Kestel volcanics is stratigraphically accepted to be early Miocene (Fig. 11.8).

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 (Figs. 11.4 and 11.8). 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 probably probertite in the future (Helvacı and Alonso 2000; Helvacı and Ersoy 2006; Helvacı et al. 2006; Ersoy et al. 2012a, b; Garcia-Veigas et al. 2011).

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

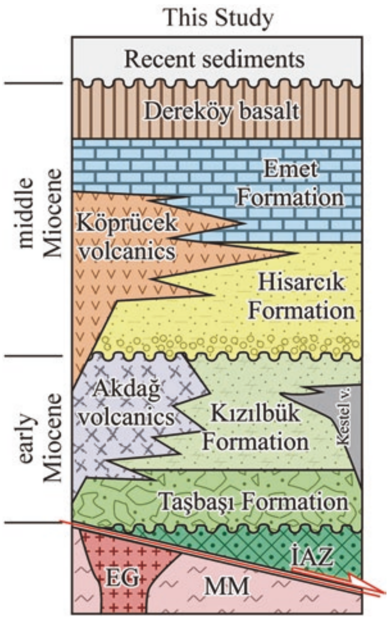

Fig. 11.8 Generalized stratigraphic section of the Emet basin (not on scale). *MM* Paleozoic Menderes Metamorphic basement, *EG* Eğrigöz Granitoid, *IAZ* carbonates and ophiolitic rocks of Izmir-Ankara Zone; Taşbaşi Formation: conglomerates; Kızılbük Formation: clastic unit containing coal; Akdag, Kestel, Köprücek and Dereköy: volcanic units; Hisarcık Formation: carbonates with clastic, and tuff deposits, containing borates; Emet Formation: upper limestone unit. (Modified after Helvacı 1984)

which interfinger with the Hisarcık Formation. 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 11.1). 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 peperitic 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 1997a, b; Helvacı and Alonso 2000) (Table 11.1 and Fig. 11.8).

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 Alonso 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 felsic lavas contain higher B levels than the more recent intermediate alkaline lavas. The Early Miocene felsic 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, 1984; Helvacı and Alonso 2000).

The geological data show that the Emet basin can be correlated with the Selendi and Uşak-Güre basins. In the Uşak-Güre basins, 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 (Ercan et al. 1978; Seyitoğlu 1997a, b; Ersoy and Helvacı 2007; Helvacı et al. 2009; Karaoğlu et al. 2010; Helvacı 2012).

11.3.4 Kırka and Göcenoluk Basin

The Miocene sequence of the Kırka Basin, rests 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) (Fig. 11.9). 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).

The Kırka area, a newly discovered caldera area which was not recognized before (Seghedi and Helvacı 2014), is situated in the northernmost part of the

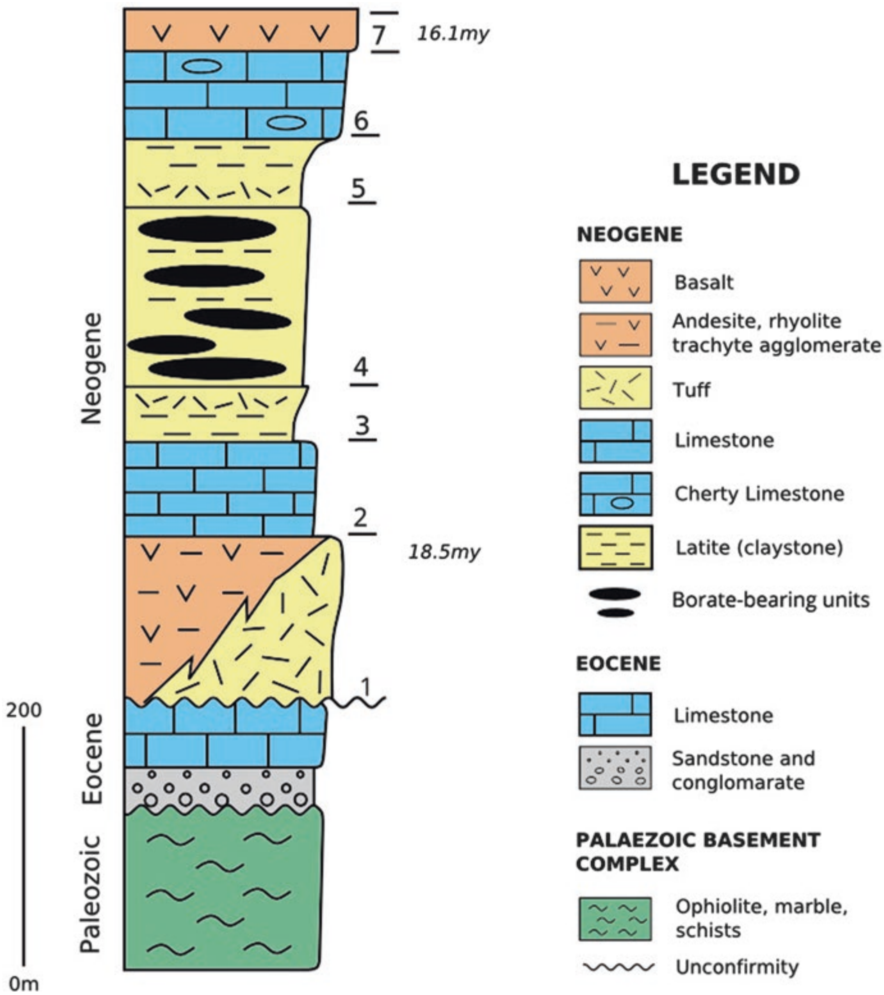

Fig. 11.9 Stratigraphic column of the Kırka borate deposit. Neogene rock units: (1) Tuffs, (2) Lower limestone, (3) Lower clay, marl and tuff, (4) Borate unit, (5) Upper clay, tuff, marl and coal bands, (6) Upper cherty limestone, (7) Basalt. (After Inan et al. 1973; Helvacı 1977; Sunder 1980)

Miocene Eskişehir–Afyon volcanic area (EAV). It is well known and the largest in the world for its borate deposits (e.g., İnan et al. 1973; Helvacı 1977, 2005; Kistler and Helvacı 1994; Helvacı and Alonso 2000; Helvacı et al. 2012; García-Veigas and Helvacı 2013). The caldera, which is roughly oval (24 × 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). 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. Recent exploratory drilling in the Göcenoluk area intersected a thick succession of dolostones, tuffs and three borate-bearing units (Lower, Intermediate and Upper Borate Units) (Fig. 11.10).

The most extensive volcanic deposits related to caldera formations are represented by ignimbrites distributed all around the caldera (Floyd et al. 1998) (Figs. 11.11 and 11.12). However, the most well-preserved outflow pyroclastics 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. 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).

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) (Figs. 11.1 and 11.9). 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". 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 (Fig. 11.9, Table 11.1). 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).

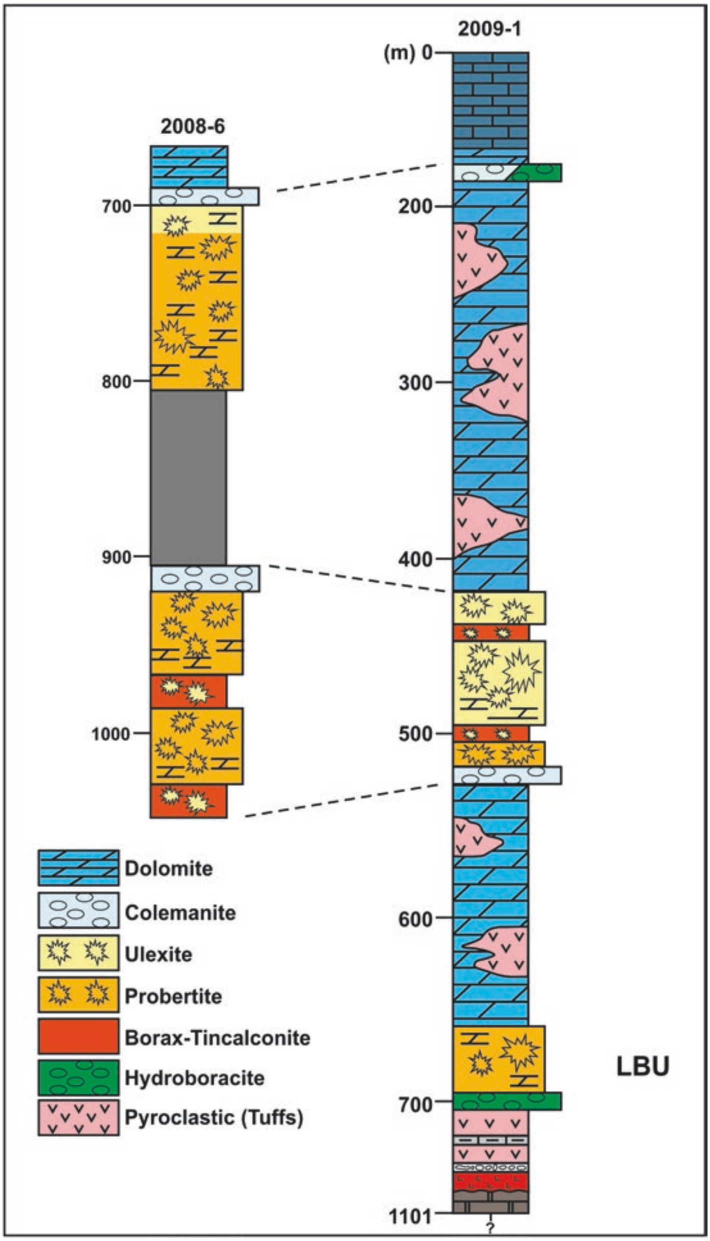

Fig. 11.10 Lithological borehole log correlation of Göcenoluk 2008–6 and Göcenoluk 2009–1 boreholes based on mineral associations. *UBU* Upper Borate Unit, *IBU* Intermediate Borate Unit, *LBU* Lower Borate Unit

Fig. 11.11 Extensive and spectacular ignimbrites outcrops nearby the Kırka borate deposit

Fig. 11.12 Close view of typical ignimbritic rocks near the Kırka area

11.4 Depositional Model and Mineralogy of Borate Deposits

11.4.1 Depositional Model of Borate Deposits

The most important economic deposits are 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. Major borate deposits are found in tectonically active extensional regions associated with collisional plate boundaries (Ozol 1977; Jackson and McKenzie 1984; Floyd et al. 1998; Helvacı 2005, 2015) (Fig. 11.13). Commercial borate deposits in the USA, South America, and Turkey are thought to be associated with Neogene continental sediments and volcanism.

The formation of borate deposits can be tentatively summarized into three main types as follows (Fig. 11.14): (1) a skarn type associated with intrusives and consisting of silicates and iron oxides; (2) a magnesium oxide type hosted by marine evaporitic sediments; and (3) a sodium and calcium borate hydrates type associated with lacustrine (playa lake) sediments (non-marine basins) and explosive volcanic activity.

The borate minerals in the non-marine lacustrine 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. The following conditions are essential for the formation of economically viable borate deposits in playa lake volcanosedimentary sediments (Fig. 11.15): (a) formation of playa lake environment; (b) boron concentration in playa lake sourced from from andesitic to rhyolitic volcanics, direct ashfall into the basin or hydrothermal solutions along graben faults; (c) thermal springs nearby volcanism; (d) arid to semi-arid climatic conditions; and (d) pH of lake water between 8,5 and 11.

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. An arid to semiarid climate also seems to be essential during the deposition and concentration of economic amounts of soluble borates in the basin in which they can collect. 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. 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 in collision-related tectonic events in ancient mobile belts (Figs. 11.13 and 11.15).

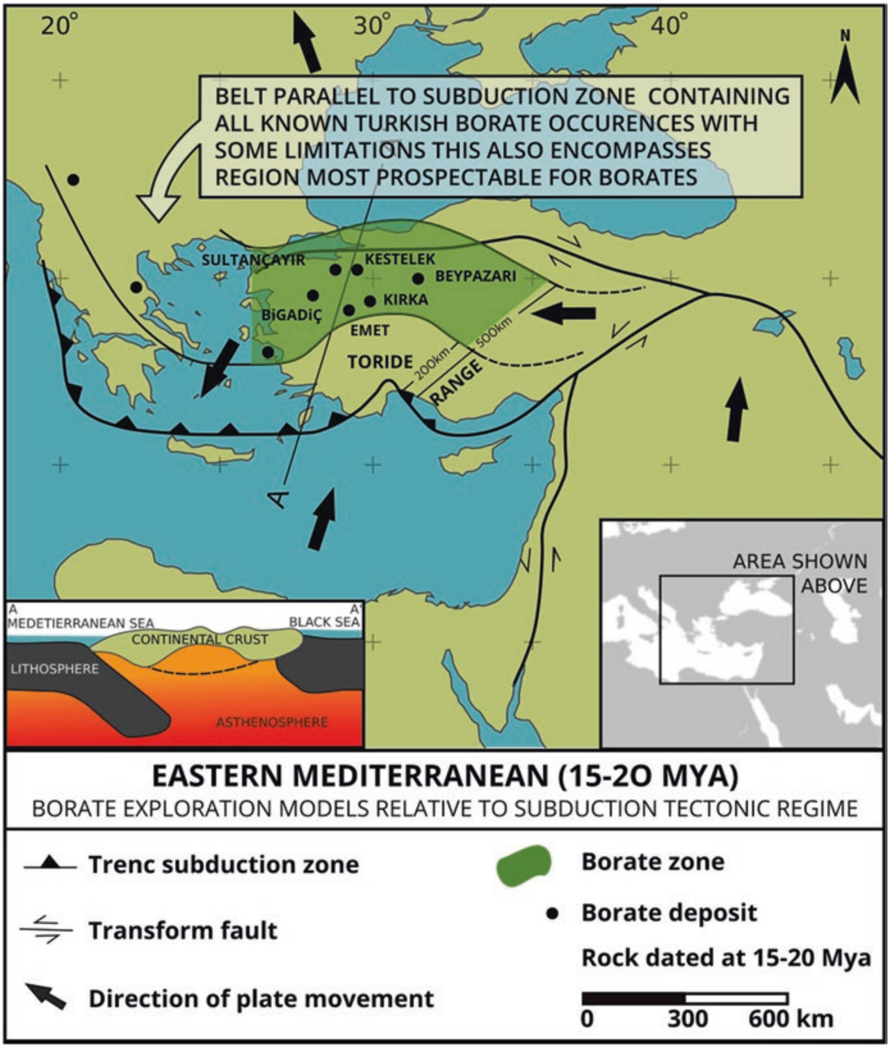

Fig. 11.13 Known deposits and borate exploration model according to the subduction tectonic model for Eastern Mediterranean (15–20 My)

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 (Fig. 11.15). 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

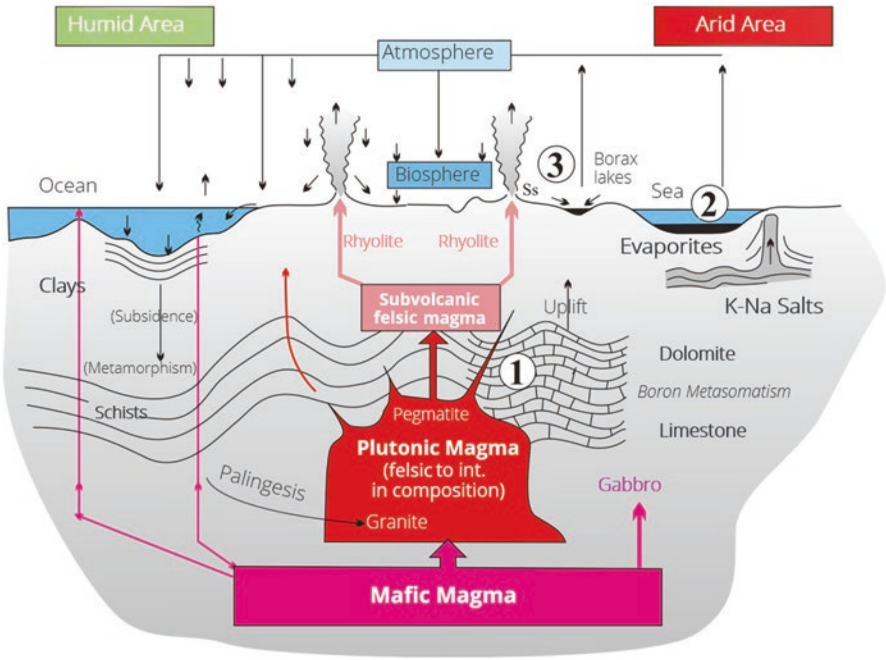

Fig. 11.14 Scheme for the cycle of boron. (1) Skarn deposits; (2) Marine deposites; (3) Playa-lake deposits. (Modified after Watanebe 1964)

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).

11.4.2 Mineralogy

Borax, kernite, colemanite, and ulexite are the main boron minerals, which provide the source for most of the world's production from Turkey, South America, and the United States (Palache et al. 1951; Muessig 1959; Watanebe 1964; Aristarain and Hurlbut 1972; Helvacı 1978, 2005, 2015; Kistler and Helvacı 1994; Grew and Anovita 1996; Garrett 1998).

Borate minerals are formed in various geological environments, over 250 minerals are known to contain boron, and they are found in various 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 (Table 11.2). Borax, ulexite, colemanite and datolite are commercially significant today. Borax or tincal,

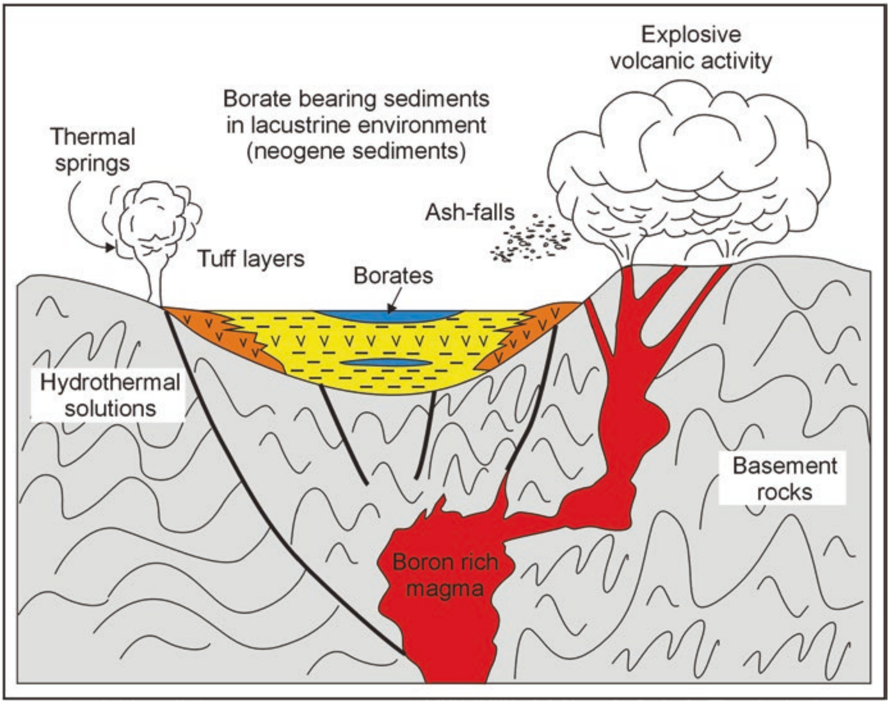

Fig. 11.15 Generalized playa lake depositional model showing the formation of borate deposits in Neogene basins of western Anatolia, Turkey. (After Helvacı 2005)

a natural sodium borate decahydrate, may be regarded as the major commercial source of boron with supplies coming from the United States, Argentina, 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 (Table 11.2).

Borax is by far the most important mineral for the borate industry. 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. Turkey is the world's major source of high grade colemanite. 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. The Salar deposits of South America consist of beds and nodules of ulexite, with some borax or inyoite, associated with Holocene playa sediments, consisting primarily mud, silt, halite, and gypsum.

Table 11.2 Borate minerals, formulas and chemical composition

	Structural formula	Empirical formula	Oxid like formula
Ca-borates			
Priceite	$Ca_{2(}B_5O_7(OH)_{5)}.H_2O$	$Ca_4B_{10}O_{19}.7H_2O$	4CaO 5B2O3 7H2O
Colemanite	$Ca(B_3O_4(OH)_3).H_20$	$Ca_2B_6O_{11}.5H_2O$	2CaO 3B2O3 5H2O
Meyerhofferite	$Ca(B_3O_3(OH)_5).H_20$	$Ca_2B_6O_{11}$.7H2O	2CaO $3B_2O_3$ $7H_2O$
Inyoite	$Ca(B_3O_3(OH)_5).4H_20$	$Ca_2B_6O_{11}$.13H2O	2CaO $3B_2O_3$ $13H_2O$
Ca-Na-borates			
Probertite	$NaCa(B_5O_7(OH)_4).3H_2O$	$NaCaB_5O_9.5H_2O$	Na_2O 2CaO $5B_2O_3$ $10H_2O$
Ulexite	$NaCa(B_5O_6(OH)_6).5H_2O$	$NaCaB_5O_9.8H_2O$	Na_2O 2CaO $5B_2O_3$ $16H_2O$
Na-borates			
Kernite	$Na_2(B_4O_6(OH)_2).3H_2O$	$Na_2B_4O_7.4H_2O$	Na_2O $2B_2O_3$ $4H_2O$
Tincalconite	$Na_2(B_4O_5(OH)_4).3H_20$	$Na_2B_4O_7.5H_2O$	Na_2O $2B_2O_3$ $5H_2O$
Borax	$Na_2(B_4O_5(OH)_4).8H_20$	$Na_2B_4O_7.10H_2O$	Na_2O $2B_2O_3$ $10H_2O$
Mg-borates			
Szaibelyite	$Mg(BO_2(OH))$	$Mg_2B_2O_5.2H_2O$	2MgO B_2O_3 $2H_2O$
Pinnoite	$Mg(B_2O(OH)_6)$	$MgB_2O_4.3H_2O$	MgO B_2O_3 $3H_2O$
Mcasllisterite	$Mg(B_6O_7(OH)_6)_2.9H_2O$	$Mg_2B_{12}O_{20}.15H_2O$	2MgO $6B_2O_3$ 15H2O
Hungchaoite	$Mg(B_4O_5(OH)_4)$.7H2O	$MgB_4O_7.9H_2O$	MgO $2B_2O_3$ 9 H_2O
Kurnakovite	$Mg(B_3O_3(OH)_5).5H_2O$	$Mg_2B_6O_{11}.15H_2O$	2MgO $3B_2O_3$ $15H_2O$
Inderite	$Mg(B_3O_3(OH)_5).5H_2O$	$Mg_2B_6O_{11}.15H_2O$	2MgO $3B_2O_3$ $15H_2O$
Mg-Na-borates			
Aristarainite	$Na_2Mg(B_6O_8(OH)_4)_2.4H_2O$	$Na_2MgB_{12}O_{20}.8H_2O$	Na_2O MgO $6B_2O_3$ $8H_2O$
Rivadavite	$Na_6Mg(B_6O_7(OH)_6)_4.10H_2O$	$Na_6MgB_{24}O_{40}.22H_2O$	$3Na_2O$ MgO $12B_2O_3$ $22H_2O$
Mg-Ca-borates			
Hydroboracite	$CaMg(B_6O_8(OH)_6).3H_2O$	$CaMgB_6O_{11}.6H_2O$	CaO MgO $3B_2O_3$ $3H_2O$
Inderborite	$CaMg(B_3O_3(OH)_5)_2.6H_2O$	$CaMgB_6O_{11}.11H_2O$	CaO MgO $3B_2O_3$ $11H_2O$
Mg-K-borates			
Kaliborite	$KHMg_2(B_{12}O_{16}(OH)_{10}).4H_2O$	$K_2Mg_4B_{24}O_{41}.19H_2O$	K_2O 4MgO $12B_2O_3$ $19H_2O$
Sr-borates			
Veatchite	$Sr_2(B_{11}O_{16}(OH)_5).H_2O$	$Sr_4B_{22}O_{37}.7H_2O$	4SrO $11B_2O_3$ $7H_2O$
Tunellite	$Sr(B_6O_9(OH)_2)$.3H2O	$SrB_6O_{10}.4.H_2O$	SrO $3B_2O_3$ $4H_2O$
Borosilicates			
Bakerite	$Ca_4B_4(BO_4)(SiO_4)_3(OH)_3.H_2O$	$Ca_8B_{10}Si_6O_{35}.5H_2O$	8CaO $5B_2O_3$ $6SiO_2$ $5H_2O$
Howlite	$Ca_2B_5SiO_9(OH)_5$	$Ca_2SiHB_5O_{12}.2H_2O$	4CaO $5B_2O_3$ $2SiO_2$ $5H_2O$

(continued)

Table 11.2 (continued)

	Structural formula	Empirical formula	Oxid like formula
Searlesite	$NaBSi_2O_5(OH)_2$	$NaBSi_2O_6.H_2O$	$Na_2O\ B_2O_3\ 4SiO_2\ 2H_2O$
Boroarseniates			
Cahnite	$Ca_2B(AsO_4)(OH)_4$	$Ca_2AsBO_6.2H_2O$	$4CaO\ B_2O_3\ As_2O_5\ 4H_2O$
Teruggite	$Ca_4MgAs_2B_{12}O_{22}(OH)_{12}.12H_2O$	$Ca_4MgAs_2B_{12}O_{28}.18H_2O$	$4CaO\ MgO\ 6B_2O_3\ As_2O_5\ 18H_2O$
Borophosphates			
Luneburgite	$Mg_3B_2(PO_4)_2(OH)_6.5H_2O$	$Mg_3P_2B_2O_{11}.8H_2O$	$3MgO\ P_2O_5\ B_2O_3\ 8H_2O$
Borosulfates			
Fontarnauite	$Na_2Sr(SO_4)(B_4O_6(OH)_2).3H_2O$	$Na_2SrSB_4O_{11}.4H_2O$	$Na_2O\ SrO\ SO_3\ 2B_2O_3\ 4H_2O$

11.5 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, 2005, 2012, 2015; Kistler and Helvacı 1994; Palmer and Helvacı 1995, 1997; Helvacı and Orti 1998, 2004; Helvacı and Alonso 2000). 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 terrains (Figs. 11.16 and 11.17). Volcanic rocks in the vicinity of the borate basins in which the borate deposits were formed are extensive and are represented by a calc-alkaline series ranging from felsic to mafic 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 (Fig. 11.4). 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. The volcanosedimentary sequences exceed over 1000 m in the deposits. 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 non-marine lacustrine sediments in sedimentary closed basins where fresh water limestone deposition was quite common both before and after borate formation, and are deposited under arid or semi-arid climatic conditions. 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 (Fig. 11.15).

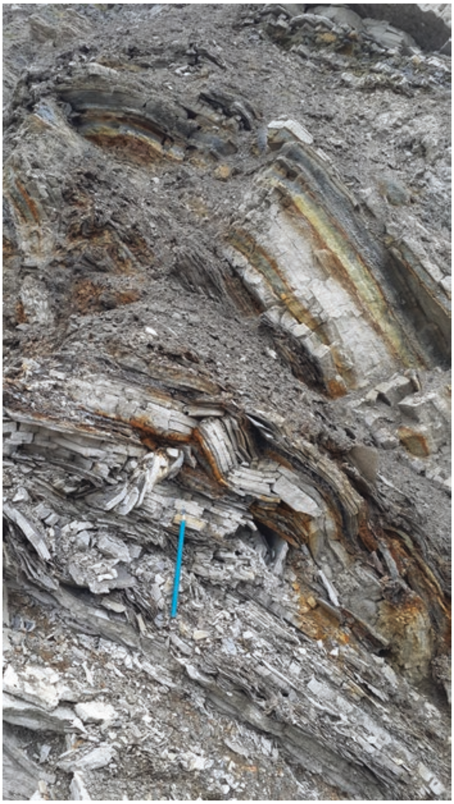

Fig. 11.16 Playa lake volcanosedimentary rocks deformation in the Bigadiç borate deposits, Simav opencast mine, Neogene basins of western Anatolia, Turkey. Neogene basins of western Anatolia, Turkey

Fig. 11.17 Sediments in the borate lake showing clear evidence of cyclicity in the volcaniclastic lacustrine evaporitic sequences associated with borate deposits, Bigadic borate deposit, Turkey

Western Anatolia consists of 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 (Fig. 11.15). The sediments deposited in the borate lakes are generally represented by tuffaceous rocks, claystones, limestones and Ca-, Na-, Mg-, Sr- borates (Table 11.2). The borates are enveloped between clay-rich horizons and limestones respectively (Figs. 11.4 and 11.18).

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-bearing borate has been found at Kırka (Baysal 1972; Helvacı 1977) and Ca-As- and Sr-bearing 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 11.2).

Fig. 11.18 Section of borate zone interbedded with clay and tuff, and limestone overburden, in the opencast mine of the Espey deposit, Emet, Turkey

The known borate deposits of Turkey formed in the Neogene basins, and occur in five distinct areas (Figs. 11.2 and 11.13). These are: 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 and Göcenoluk borax deposits (Na-type).

11.5.1 Bigadiç Deposit

Bigadiç deposit contains the largest colemanite and ulexite deposits known in the world. The borate minerals occur in two distinct zones, lower and upper, seperated by thick tuff beds changed during diagenetic processes to montmorillonite, chlorite and to zeolites (Fig. 11.19). Borate minerals formed in two zones separated by thick tuff beds that have been altered to montmorillonite, chlorite, and zeolites (mainly heulandite) during diagenesis. Colemanite and ulexite predominate in both borate zones (Figs. 11.4, 11.20, and 11.21), but other borates, including howlite, probertite, and hydroboracite are present in the lower borate zone; whereas inyoite, meyerhofferite, pandermite, tertschite, hydroboracite, howlite, tunellite, and rivadavite are found in the upper borate zone. Calcite, anhydrite, gypsum, celestite, K feldspar, analcime, heulandite, clinoptilolite, quartz, opal-CT, montmorillonite, chlorite, and illite are also found in the deposit (Özpeker 1969; Helvacı et al. 1993; Helvacı 1995; Helvacı and Orti 1998; Yücel-Öztürk et al. 2014) (Table 11.2).

The Bigadiç deposits formed within Neogene perennial saline lakes sediments located in a northeast-southwest-trending basin (Fig. 11.19) and were fed by thermal springs associated with local volcanic activity under arid climatic conditions. The volcano-sedimentary sequence in the deposits consists of (from bottom to top) basement volcanics, lower limestone, lower tuff, lower borate zone, upper tuff, upper borate zone, and olivine basalt. The borate deposits formed under arid conditions in perennial saline lakes fed by hydrothermal springs associated with local volcanic activity. The deposits are interbedded with tuffs, clays, and limestones (Figs. 11.19 and 11.22).

Colemanite nodules in both borate zones formed directly from solution, within unconsolidated sediments just below the sediment-water interface, and continued to grow as the sediments were compacted (Fig. 11.23). It is unlikely that the colemanite formed by dehydration of inyoite and/or by replacement of ulexite after burial. Later generations of colemanite and ulexite are found in vugs and veins and as fibrous margins of early formed nodules (Fig. 11.24). Other diagenetic changes include the partial replacement of colemanite by howlite and hydroboracite and ulexite by tunellite. Nodular-shaped colemanite ancl ulexite minerals predominate in both borate zones. Colemanite and Ulexite show alternating horizons, and the transformation of one mineral to another has not heen observed and the boundary between them is always sharp. Because these minerals are readily dissolved, secondary pure and transparent colemanite and ulexite are often encountered in cavities

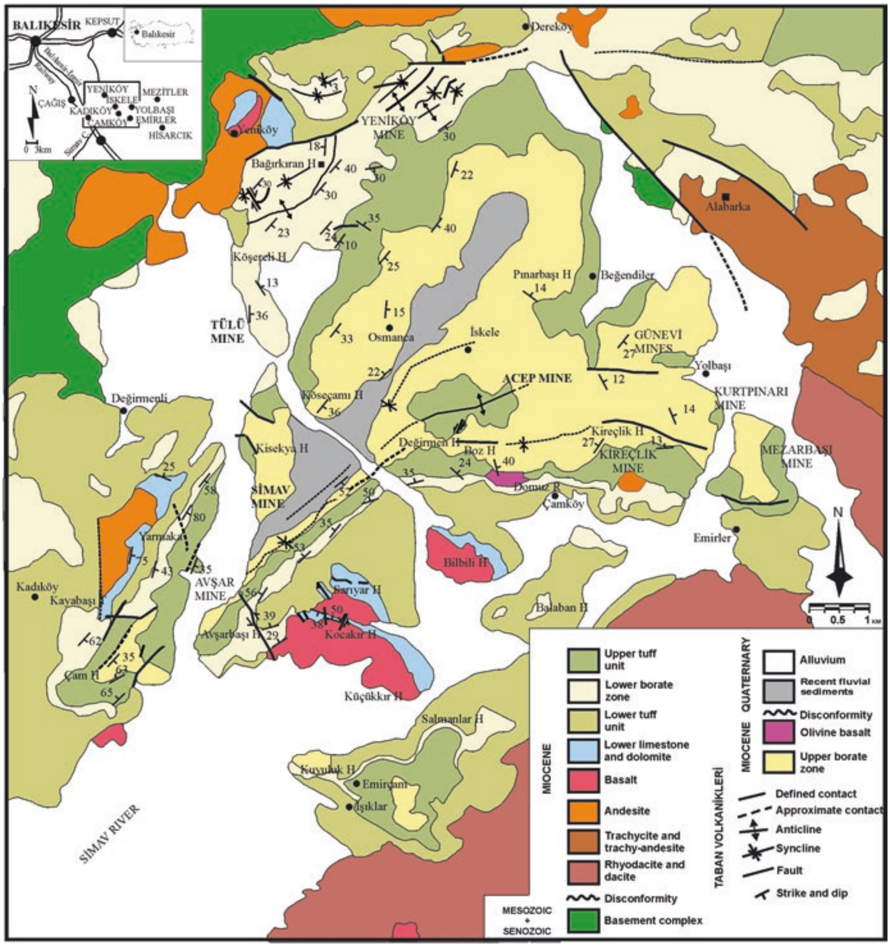

Fig. 11.19 Locality and geological map of the Bigadiç borate district

of nodules and cracks (Fig. 11.24). Some colemanite and ulexite is weathered and completely replaced by calcite.

Probertite bands are found in some ulexite horizons, especially in the lower borate zone. It forms in the same chemical environment as ulexite and indicates a period of more extreme desiccation and possibly subaerial exposure within the lakes. Euhedral tunellite formed during dissolution and recrystallization of some Sr-rich ulexite horizons. In the Bigadic deposits, hydroboracite formed by replacement of colemanite, with Mg^{2+} ions supplied from adjacent tuffs and clays by ion exchange. Howlite grew in clays alternating with thin colemanite bands and coincided with periods of relatively high Si concentrations. Diagenetic processes also produced small howlite nodules embedded in unconsolidated colemanite nodules. The initial solutions that formed the alkaline perennial saline lake(s) were low in

Fig. 11.20 Colemanite nodules in varying sizes intercalated with associated sediments, Tülü open pit mine deposit, Bigadiç, Turkey. (After Helvacı 2015)

Cl^- and $SO_4{}^{-2}$ and high in boron and Ca^{2+}, with subordinate Na+. The Bigadiç borates are the largest colemanite and ulesite deposits in the world and the high-grade colemanite and ulexite ores (30% and 29% B203 respectively) should supply a substantial proportion of the world's needs for many years (Fig. 11.25).

11.5.2 Sultanyaçır Deposit

In this deposit borates are interbedded with gypsum, claystone, limestone, and tuff. Pandermite (priceite) is abundant, but other borates include colemanite and howlite (Figs. 11.26 and 11.27; Table 11.2). 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).

Calcium-borates, mainly pandermite (priceite) and howlite, but also bakerite and colemanite, are intercalated within the Sultançayır Gypsum in the Miocene Sultançayır Basin (Fig. 11.28). This lacustrine unit, represented by secondary gypsum in outcrop, is characterized by: (1) a clear facies distribution of depocentral laminated lithofacies and debris-flow deposits, a wide marginal zone of sabkha deposits, and at least one selenitic shoal located toward the basin margin;

Fig. 11.21 Ulexite ore lenses intercalated with associated sediments, Kurtpınarı deposit, Bigadiç, Turkey. (After Helvacı 2015)

Fig. 11.22 Depositional cycle in the Tülü deposit (Bigadiç). Facies: tuff layer at the base; (1) alternations of carbonate varves and laminated dark claystones; (2) laminated carbonate; (3) nodular Colemanite, Bigadiç, Turkey. Hammer for scale

Fig. 11.23 Nodular colemanite with radiating structures, Simav open cast, mine, Bigadiç, Turkey

Fig. 11.24 Small white colemanite nodules with radiating structures growing in the cracks during diagenesis, Tülü mine, Bigadiç, Turkey

(2) evaporitic cycles displaying a shallowing-upward trend; and (3) a diagenetic evolution of primary gypsum to (burial) anhydrite followed by its final re-hydration. The calcium borates precipitated only in the depocentre of the lake and were partly affected by synsedimentary reworking, indicating that they formed during very early diagenesis. The lithofacies, which are made up of a host gypsum and borates, indicate that the borates grew interstitially because of the inflow and mixing of borate-rich solutions with basinal brines. Borate growth displaced and replaced primary gypsum beneath a relatively deep depositional floor. Howlite, which has apparently grown in the clays alternates with thin pandermite and colemanite bands. As a result of diagenetic processes, some small howlite nodules are also embedded in the pandermite and colemanite noludes. The anhydritization of primary gypsum took place during early to late diagenesis. This process also resulted in partial replacement of pandermite and accompanying borates (bakerite and howlite) as well as other early diagenetic minerals (celestite) by anhydrite. Final exhumation

Fig. 11.25 Tülü opencast mine, Bigadiç area, Turkey

Fig. 11.26 Pandermite (priceite) nodules within the gypsum beds of the sandy claystone unit, Sultançayırı deposit, Turkey

resulted in the replacement of anhydrite by secondary gypsum, and in the partial transformation of pandermite and howlite into secondary calcite.

11.5.3 Kestelek Deposit

At Kestelek the borate zone consists of clay, marl, limestone, tuffaceous limestone, tuff, and borate. The volcanic activity produced tuff, and agglomerate, and andesitic and rhyolitic lavas that are associated with the sediments (Helvacı 1994; Helvacı Alonso 2000). This sequence is capped by a unit consisting of loosely cemented

Fig. 11.27 Banded lithofacies of priceite (white material) intercalated between laminated secondary gypsum (grey material). The priceite mass displaces the laminae of secondary gypsum, Sultançayır deposit, Turkey

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 occuring rarely. Secondary colemanite occurs as transparent and euhedral crystals in the cavities of nodules, in cracks and in vugs (Fig. 11.29, Table 11.2).

Colemanite, ulexite, and probertite predominate, with hydroboracite occuring rarely. Calcite, quartz, zeolite, smectite, illite, and chlorite are the associated minerals. Secondary colemanite occurs as transparent and euhedral crystals in the cavities of nodules, in cracks and in vugs (Fig. 11.30). Probertite, which forms in the same chemical environment with ulexite in the Kestelek deposit, indicates a period of higher temperature within the playa lake. The initial solutions crystallizing the borates in the Kestelek deposit are deduced to have had a very low concentration of chloride, low concentrations of sulphate and high concentrations of boron and calcium with some sodium.

11.5.4 Emet Deposit

At Emet the borate-bearing 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 (Figs. 11.4, 11.8, and 11.31); The unit consisting of clay, tuff and marl containing the borate deposits has

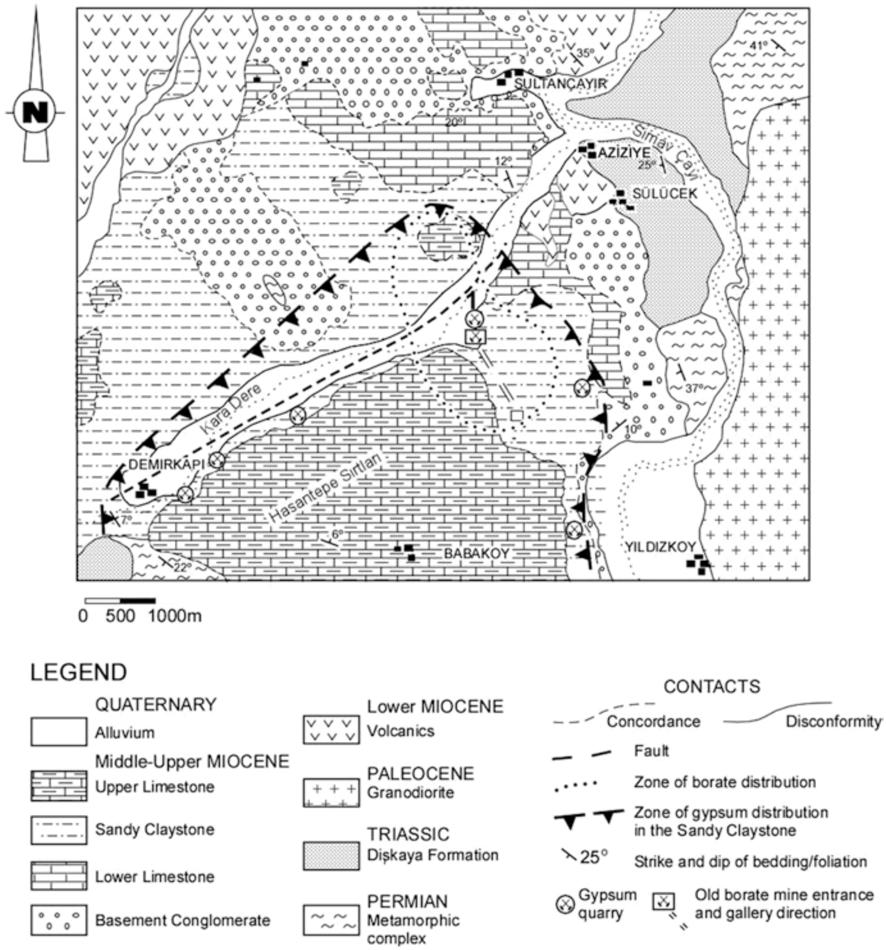

Fig. 11.28 Geological map of the Sultançayır boratiferous gypsum basin

abundant realgar and orpiment at some horizons indicating that arsenic and boron have a genetic relationship and volcanic origin at Emet (Table 11.2).

The Emet borate basin is one of the basins in western Turkey containing significant amounts of borate minerals, mainly colemanite (Fig. 11.32) and probertite with minor ulexite, hydroboracite, and meyerhofferite. The borates are interlayered with tuff, clay, and marl with limestone occuring above and below the borate lenses (Fig. 11.33). The Emet borate deposits contain many of the rare borate minerals such as veatchite-A, tunellite, teruggite, and cahnite (Helvacı and Firman 1976; Helvacı 1977, 1984, 1986; Helvacı and Orti 1998; Garcia-Veigas et al. 2011).

The petrologic study of core samples from two exploratory wells in the Doğanlar sector (Fig. 11.34) using conventional optic and electron microscopy, reveals a complex mineral association in which probertite, glauberite, and halite constitute the

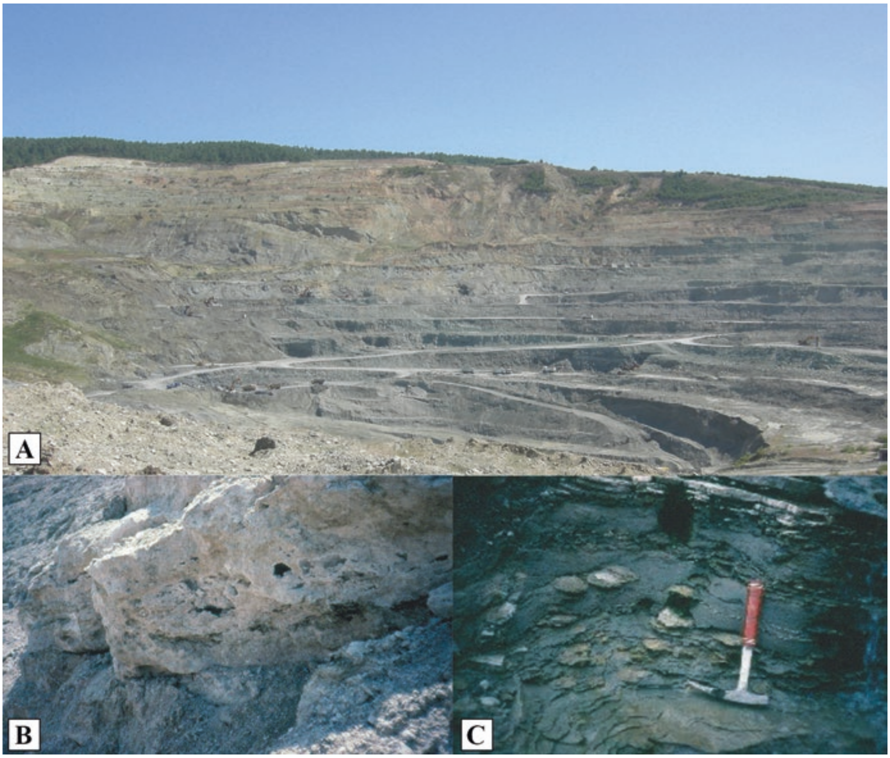

Fig. 11.29 (**a**) Open cast mine in the Kestelek area. (**b**) Euhedral colemanite crystals of massive colemanite zone, growing in cracks and vughs, (**c**) Discoidal Colemanite nodules growing in claystones in the marginal part of the deposit, Kestelek opencast mine

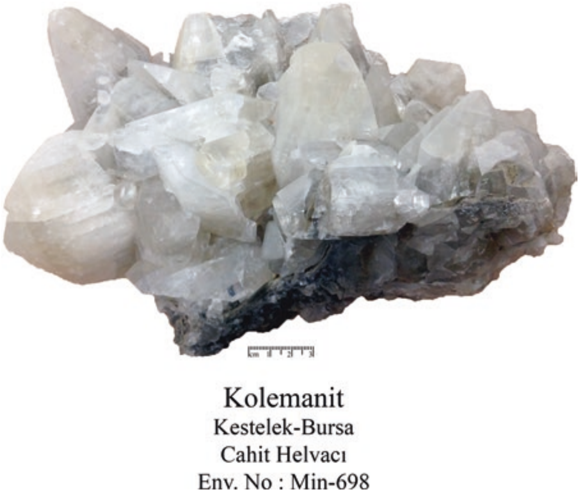

Fig. 11.30 Euhedral colemanite crystals, Kestelek opencast mine, Turkey

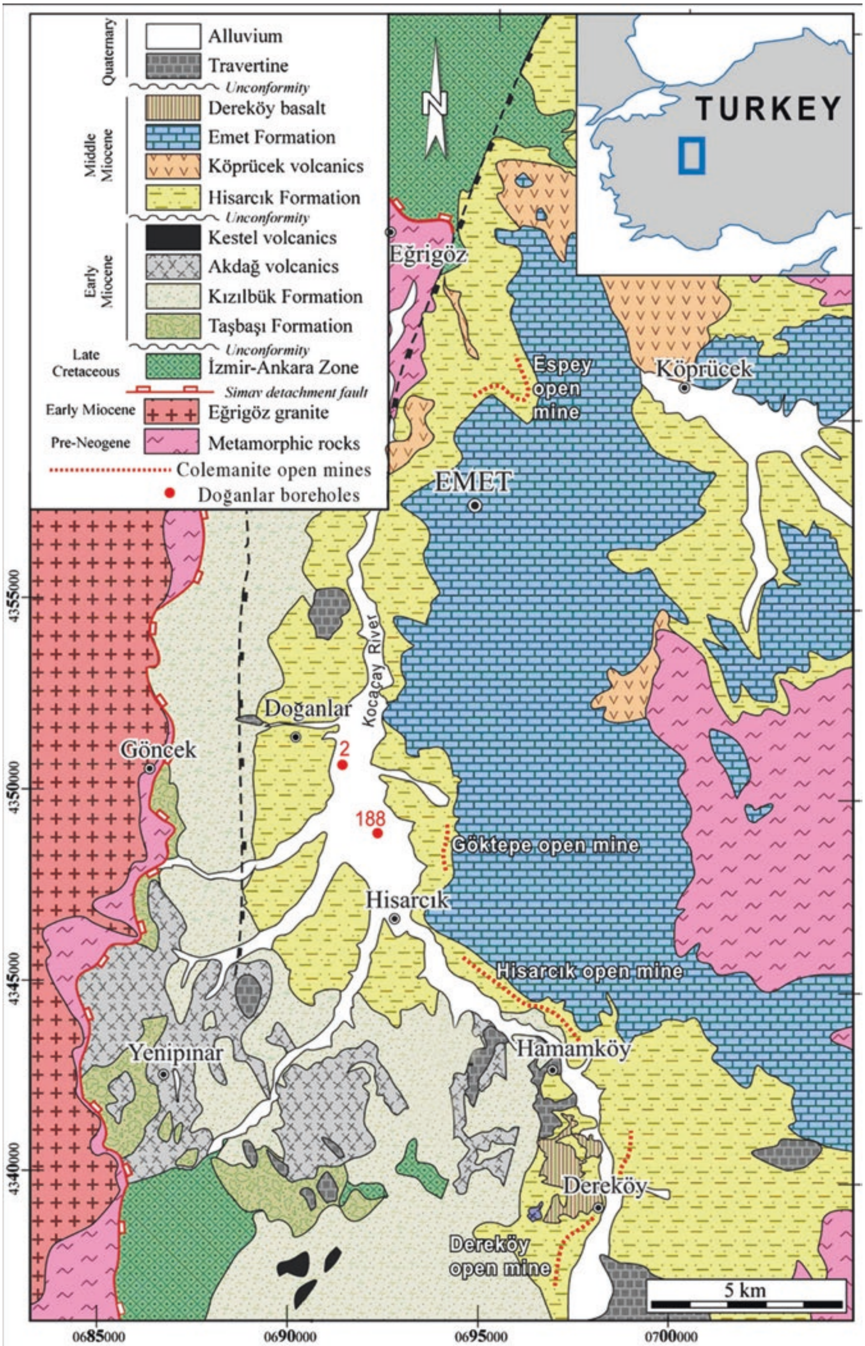

Fig. 11.31 Geological map of the Emet borate district showing the location of the colemanite open pit mines. (Modified after Helvacı 1984)

Fig. 11.32 Colemanite is the principal borate mineral and is interclated with green clay as nodular and elliptical lenses, Hisarcık open pit mine, Emet, Turkey

major primary phases (without mineral precursors) precipitated in a saline lake placed in 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 minetal (fontarnauite) was found in the deposit and reported in the Canadian Mineralogist (Cooper et al. 2016). 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 (Fig. 11.35) occur in the borate zone throughout the area. The Doğanlar deposit is the most important deposit of probertite known up to now. Chemical changes in the groundwater inflow led to the precipitation of Ca-bearing borates (colemanite) in the tuff-flat environment surrounding the lake, while Na–Ca sulfates and borates (glauberite and probertite) precipitated in the center of the lake. Fluid inclusion compositions in halite indicate that the advanced brines correspond to the Na-K-Cl-SO4 type. During restricted stages of the saline lake, the residual brines seeped through the tuff-flat sediments, leading to transformations of previous precipitates that resulted in the formation of K-bearing minerals (Garcia-Veigas et al. 2011).

11.5.5 Kırka and Göcenoluk Deposits

The Neogene volcano-sedimentary sequence rests unconformably partly on Paleozoic metamorphics, Mesozoic ophiolite complex, and Eocene fossiliferous limestone. The Neogene sequence consists of from bottom to top 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. The Miocene Kırka boratiferous district is the most important Na-borate (borax) resource

Fig. 11.33 Hisarcık open cast mine showing borate zone and limestone overburden, Emet area, Turkey

in the world. Two separate deposits in the Kırka district are located near the villages of Sarıkaya and Göcenoluk (Eskişehir Province) (Figs. 11.9 and 11.10).

Borax is intensively exploited in open-pit mines in the Sarıkaya deposit while only small quarries of colemanite are known in the Göcenoluk deposit (Figs. 11.36, 11.37, and 11.38). The ore body has thickness of up to 145 m, averaging 20–25% B_2O_3. 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 (Baysal

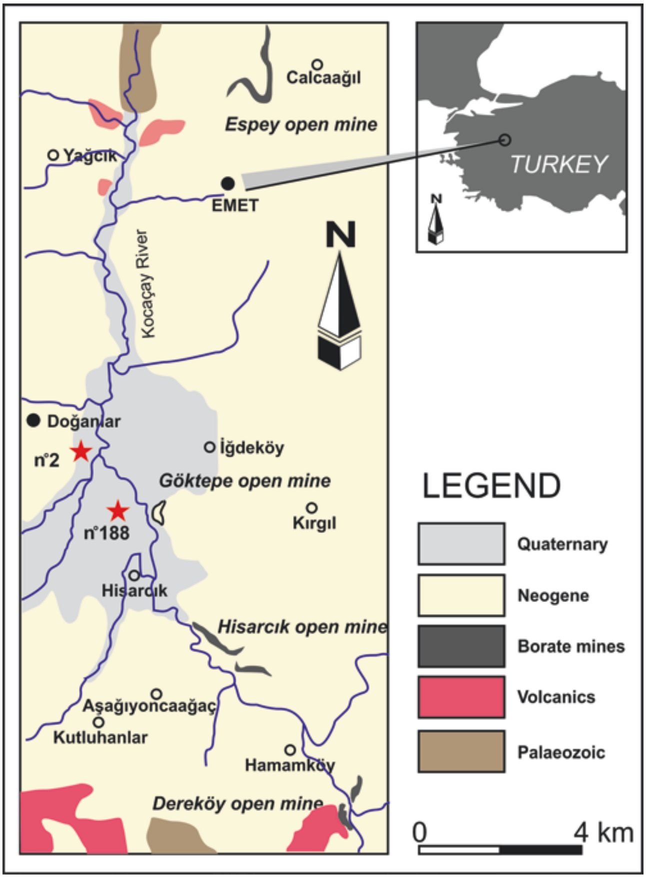

Fig. 11.34 Location of Doğanlar boreholes and geological map of the Emet borate district showing the location of open pit mines and boreholes in western Turkey. (After Helvacı 1986)

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 11.2). This is the only deposit in Turkey that contains sodium borates (borax, tincalconite, and kernite), together with inderborite, inderite, and kurnakovite (Figs. 11.39, 11.40, and 11.41). The borax body is enveloped by a thin ulexite facies, followed outward by a colemanite facies. The whole is enclosed by limestone (Fig. 11.42).

The mineral sequence in the Kırka deposit is Ca/Ca – Na/Na/Ca – Na/Ca (colemanite and/or inyoite/ulexite/borax/ulexite/colemanite and/or inyoite) (Fig. 11.42). 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 (or intracrystal-

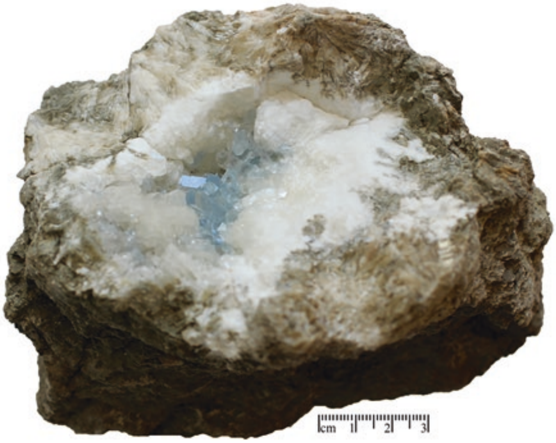

Fig. 11.35 Colemanite nodule with hollow center and cracks filled with secondary generation colemanite and celestine crystals, Hamaköy deposit, Emet area

Fig. 11.36 Kırka opencast borax mine, Kırka deposit, Eskişehir

line) clay; the clay at Kırka is very pale green to white and is high in dolomitic carbonate. The borax crystals are fine, 10–20 mm, and quite uniform in size (Fig. 11.40).

Recent exploratory drilling in the Göcenoluk area intersected a thick succession of dolostones, tuffs and three borate-bearing units (Lower, Intermediate and Upper

Fig. 11.37 Kırka opencast borax mine and mineral processing plant in the background, Kırka deposit, Eskişehir

Fig. 11.38 Overview of the Kırka opencast mine, looking down into the mine area, Kırka deposit, Eskişehir

Borate Units). Here, the most abundant borate mineral is ulexite (Ca-Na-borate) passing at depth to probertite. Borax (Na-borate) is only present in the Intermediate Borate Unit (Fig. 11.10). Minor amounts of colemanite (Ca-borate) and hydroboracite (Ca-Mg-borate) occur at the base, and/or top, of each mineralized unit. Pyroclastic layers within the borate units show intense alteration by alkaline, boron-bearing waters and formation of diagenetic clay minerals (smectites), zeolites (analcime) and borosilicates (searlesite). The Göcenoluk succession is interpreted as a shallow, ephemeral, alkaline lake deposit in which carbonates formed as stromatolites and travertines. Borate precipitation in the Göcenoluk area took place interstitially within muddy and carbonate sediments in a lateral progression from marginal Ca-borates towards Na-Ca-borates and rarely to Na-borates in the center of the lake. Authigenic silicate mineral distribution shows parallel changes toward the center of the lake that reflect increasing pH gradient (Garcia-Veigas and Helvacı 2013).

Fig. 11.39 Laminated lithofacies of borax (brown material) alternating with dolomitic, marly laminae (white laminae). Laminated borax lithofacies with palisade fabric in borax laminae. Clear material corresponds to lutitic matrix and laminae (dolomitic claystone). Dark material corresponds to fresh, crystalline borax

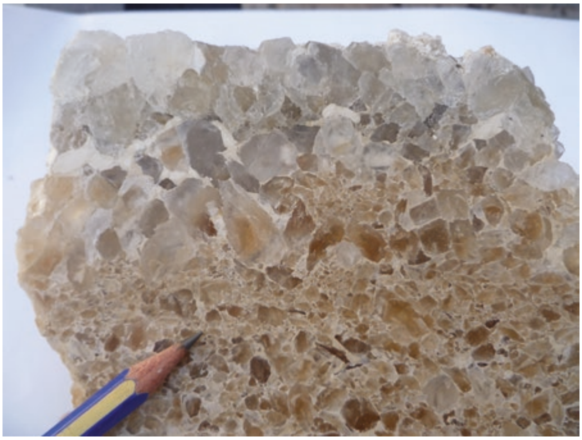

Fig. 11.40 Massive crystalline borax lithofacies. The borax crystals show zoned growth (matrix inclusions) at the top. Borax crystals are transparent and rectangular to equant. These crystals have variable size and are surrounded by an lutitic matrix

Petrologic studies of samples coming from two deep boreholes (1100 m depth) drilled in a marginal part of the basin, near the Göcenoluk village, 5 km west of Kırka, have recorded a thick borate succession. The borate succession in the 2008–6 borehole is mainly formed by an upper probertite unit (~300 m thick) which overlies a lower borax unit (~100 m thick) (Fig. 11.10). Abundant small tunellite crystals are scattered throughout the sequence. Ulexite is a very minor phase. The upper probertite unit consists of nodular probertite interbeded with lavas, tuffs and thin dolomite

Fig. 11.41 View of ulexite layers alternating with nodular and massive lithofacies of colemanite. Crystalline masses, vugh porosity, geodic areas and cemented fractures can be observed, upper section of the Kırka opencast deposit

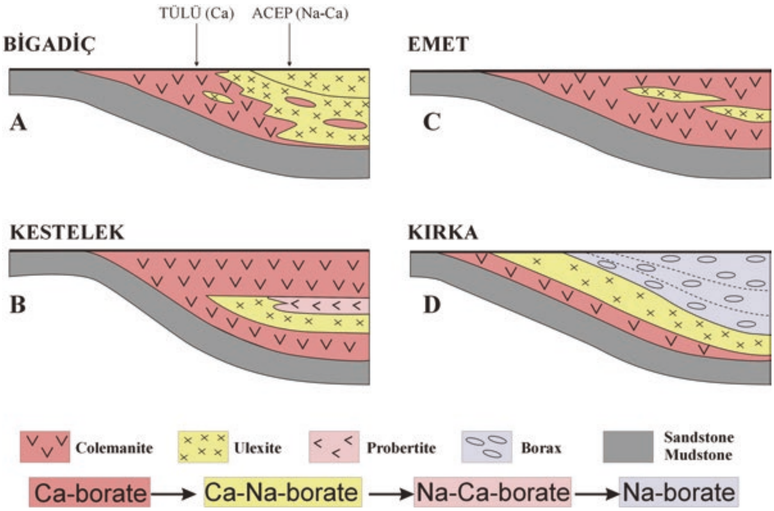

Fig. 11.42 Sequence of boron mineral formations in Turkish borate deposits

layers. Only two colemanite intervals, less than 3 m thick, have been identified. Backscattered electron images and X-ray mapping of both probertite and colemanite exhibit an internal zonation pattern as a result of high and variable strontium contents. The basal borax unit consists of massive beds formed by anhedral cm-size crystals also interbeded with tuffs and dolomites. In both units, borates show evidence of interstitial growth breaking and deforming peloidal dolomite and stromatolitic layers.

Unlike other contemporaneous borate deposits in the Anatolian region, neither metal sulfides nor arseno-sulfides are present at Kırka. Intense water-rock interaction with volcano-sedimentary layers induces the dissolution of feldspars and plagioclases which are usually replaced by probertite. Abundant authigenic zeolites (mainly analcime) and boron-silicates (searlesite) are formed as a consequence of the silica leached from the weathering of silicates. According to petrographic observations and the internal strontium zonation pattern in both probertite and colemanite crystals are considered to form as primary precipitates which grew interstitially in volcaniclastic sediments and soft dolomitic muds deposited on the bottom of the lake. The absence of well laminated borax in this marginal position suggests that was also formed below the water-sediment interface.

11.5.6 Holocene Borates in the Karapınar-Konya Basin

The basin located around the Karapınar town (Konya) is surrounded by volcanos which have been active various phase from the Late Miocene to present. Currently active volcanism is evidenced by the discharge of thermal and mineral waters and magmatic gases. Potentially economic deposits of borate, chlorite, sulfate and carbonate salts related to this volcanic activity are forming within the basin.

Andesitic lavas of Late Miocene volcanism form Üzecik Mountain, located in the western part of the basin. Karacadağ, which is located in the eastern part of the basin, has a complex domal structure and completed its evolution in a few phases during the entire Pliocene. The lavas which form Karacadağ rise to an elevation of 1995 m and are prdominatly andesite, but locally trachyandesite, basaltic andesite and dasite are present and show a highly viscous flow character.

The southern part of the Karapınar basin is delimineted by lava flows, small volcanic cone and maar proclastics that formed as a result of several volcanic phases which began in the early Quaternary and continued up until a few thousand years ago. Trachyandesitic and andesitic lava flows were formed during the first stage of volcanism in the Quaternary. Radiometric age determinations done whith the K/Ar method gives ages between 1.1 and 1.2 my for these flows. Later, basaltic lavas, scoria and ash formed small volcanic cones and lava flows. Basaltic volcanic cones reach hegihts of 250 m. K/Ar radiometric age determinations give ages between 363.000 and 161.000 year for this stage of volcanism (Helvacı and Ercan 1993).

Later, maars (volcanic craters resulted by explosive eruptions) formed within the basin. Maar pyroclastics, formed successively as products of several different eruptions, are present as consentric rings around the maars. The maars of Meke Obruğu and Yılan Obruğu are in small size. As for the Mekegöl and Acıgöl maars, they are larger explosion crates measuring opproximately 1,5 km in diatemer. Later the maars were filled by waters forming maar lakes. A few thousand years ago, a scoria cone formed within the Meke maar lake during the last phase of basaltic volcanism.

There is evidence of active volcanic activity in the Karapınar basin, such as the thermal, mineral waters and gases still emanating from the maars and along the major fault line in the eastern part of the basin. The gases contain predominantly CO_2 and have almost mantle-origin characteristics, based upon helium-and carbon-isotope ratios (3 He/4 He = 159.10^{-6}; 13c/12c = %0–1.5) (Helvacı and Ercan 1993).

Borate, chlorite, sulfate and minor amounts of carbonate salts are actively forming in the basin. While NaCl is precipitating in the center of the basin, carbonate and CO_2 bearing waters are being discharged and carbonates (probably trona) and Na sulfates precipitated along the fault at the eastern edge of the basin. Ulexite, which is one of the common borate salts, seem to have formed earlier than the other salts and occur as coulifflower or potato-shaped masses within unconsilidated sediment at the depth of $\leq$1 m. Thenardite and glouberite are forming within the Acıgöl and Meke maar lakes.

The formation of borate and other salts in the Karapınar basin is genetically related to the subalkaline volcanic rocks of this region. Na, B, Cl, SO_4 and CO_2 are carried into the basin by thermal and mineral waters related to this volcanism. Through detailed field, geochemical and drilling studies, it is probable that economically important salt deposits will be discovered in the area (Helvacı and Ercan 1993).

11.6 Mining, Uses and Future Forecasts

Commercial borate deposits in the world are mined by open pit methods (Figs. 11.18, 11.33, 11.36, 11.37, and 11.38). 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 similarly to the world's major borate operations. 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.

Mineral processing techniques are related to both the scale of the operation and the ore type, with either the upgraded or refined mineral (borax, colemanite, and ulexite) or boric acid as the final product for most operations. Borax-kernite ores in Kırka 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 Boric acid is one of the final products produced from most of the processes. The world's largest boric acid facility is located adjacent to the Boron pit and the Emet and Kırka opencast mines.

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. Borate was traded at relatively high prices for highly specialized applications into the late years of the nineteenth century. At that time they were being used for medicines, food preservatives, ceramic glazes, and in expanded applications as metal fluxes. Borate 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 (Fig. 11.43).

Boron minerals and their products are indispensable industrial raw materials of today. 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 (Fig. 11.43). 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.

Borates have become a relatively modestly priced industrial mineral commodity in recent years following the development of the large deposits at Boron, and more

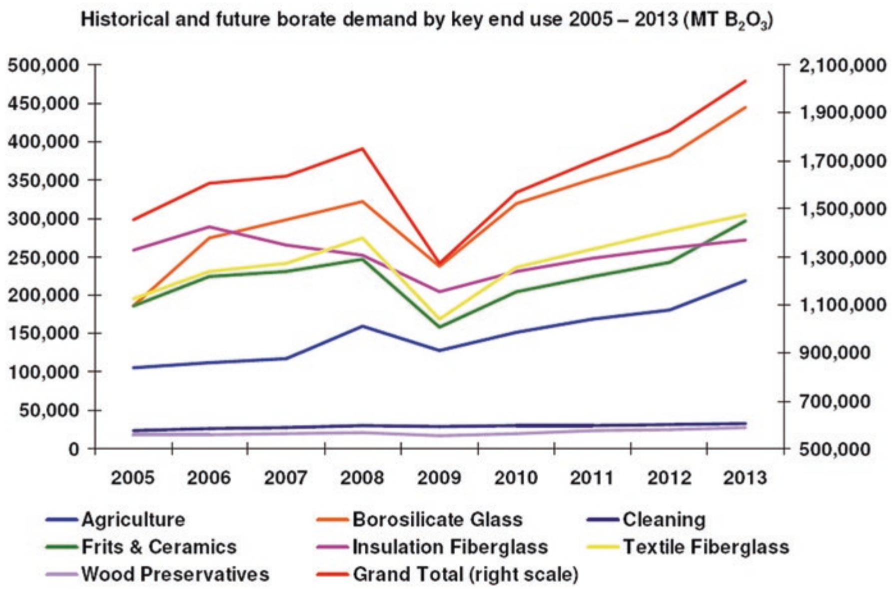

Fig. 11.43 Present and future borate demand by major end use 2005–2013 (MTB2O3). (Source: Rio Tinto)

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. Borates are a lightweight commodity and are generally sold in bulk by rail carload lots, and overseas shipments are made mostly in bulk from special terminals 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, South Carolina, where there are griding facilities; this colemanite is then shipped to Easter fiberglass manufacturers (Kistler and Helvacı 1994; Helvacı 2005).

Known reserves of borate minerals of Turkey are large, particularly in Turkey and production from Turkey will continue to dominate the world market (Table 11.3). Approximately 75–80% of the world's boron reserves are located in Turkey (Engineering and Mining Journal 2012) (Table 11.3). 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 11.3). The borate producing areas of Turkey, controlled by the state-owned mining company Eti Maden AS, are Bigadiç (colemanite and ulexite), Emet (colemanite), Kestelek (colemanite, probertite, and ulexite), and Kırka (borax-tincal). Eti Maden planned to expand its share in the world boron market from 36% to 47% by 2014, 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. Consumption of borates by the ceramics industry was expected to shift away from Europe to Asia, which accounted for 60% of world demand in 2011. 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

Table 11.3 Reserves and life estimates of the world's borate deposits (Helvacı 2005)

	Known economic reserve (million tonnes of B_2o_3)	Total reserve (million tonnes 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
Kazakstan	14.000	15.000	10	10
Total	363.000	885.000	253	610

Information Services Ltd. 2010, p. 167; O'Driscoll 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.

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 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 11.3, Fig. 11.43). Based upon recent history, the major world consumers of borates will continue to be the developed countries of North America, Europe, and Japan.

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 and 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 (Table 11.3). 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.

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 by following marketing and industry oriented research policies. 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 m 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. 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 (Table 11.3).

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. 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.

11.7 Conclusions

Known reserves of borate minerals are large, particularly in Turkey, South America, and the USA, and production from Turkey and the USA 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.

There are few substitutes for borates. In most applications, they provide unique chemical properties at a reasonable price; this is particularly true for glass fibres and in the field of heat- and impact-resistant glass. Borates are an essential part of certain plant foods. Their use in nuclear-reactor shielding and control is well documented. 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.

Today, as economic competition is becoming more intense and many studies are being made on natural resources; the existence of a massive boron resource 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.

Acknowledgments I am especially grateful to Eti Maden and their mine managers for their generosity during fieldwork in Turkey. This study has been encouraged by several research projects supported by the Dokuz Eylül University (Project Numbers: 2005.KB. FEN.053; 2006. KB. FEN.001; 2009.KB. FEN.026; 2010.KB. FEN.009; and 0922.20.01.36) and the Scientific and Technical Research Council of Turkey (TÜBİTAK, Project No: YDAB. AG-100Y044 and ÇAYDAĞ-103Y124). Review comments by Franco Pirajno considerably improved the manuscript. Mustafa Helvacı is gratefully acknowledged for his typing and drafting assistances of the manuscript.

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