

ORIGIN AND DISTRIBUTION OF EVAPORATE BORATES - THE PRIMARY ECONOMIC SOURCES OF BORON

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Naturally occurring borates are the major economic source of boron. They were first used over 4000 years ago in precious-metal working and are now essential components of modern industry. Although borates have been exploited from other sources, three minerals (borax, colemanite, and ulexite) that are all derived from non-marine evaporates now form the major commercial sources of borate. These deposits are associated with volcanism of Neogene age in tectonically active extensional regions at plate boundaries. The most important continental borate provinces are located in the USA, Argentina, Chile, Peru, and China, with the largest borate reserves in the world being found in western Anatolia, Turkey.

KEYWORDS: economic borate deposits, non-marine evaporates, Turkish borate deposits

INTRODUCTION

Borates are the most important economic source of boron, and have been used for millennia. Borax (see TABLE 1 for borate mineral formulae) was first used in Babylon more than 4000 years ago; indeed, its name is derives from the Persian burah (boorak). At that time, the Babylonians brought borax from the Himalayas for use in

the manufacture of jewelry. The Egyptians used borax in mummifying, and by ~300 AD the Chinese were familiar with borax glazes, as were the Arabs three centuries later. Borax was first brought to Europe in the 13th century by traders from Tibet and Kashmir (Ozol 1977; Travis and Cocks 1984; Kistler and Helvacı 1994; Smith and Medrano 1996; Garrett 1998; Helvacı 2005; 2015).

By the 1770s, the French had sourced borax from Purbet Province, India, and about the same time natural boric acid (sassolite) was discovered in hot springs in the Maremma region of Tuscany, Italy. The discovery and commercial development of borate deposits accelerated in the 19th century. Chile started to mine borate from the Salar de Ascotan in 1852 (accounting for a quarter of the world's annual supply of ~16,000 tonnes), and in 1856 John Veatch discovered borax in Clear Lake, California (Kistler and Helvacı 1994). In Turkey, borate mining extends back to Roman times, but modern mining began in 1865, when borates were extracted from the Aziziye mine (Sultançayır) in Balıkesir province and shipped to France for processing.

ECONOMIC MINERALOGY OF BORON

Borate is defined by industry as any compound that contains or supplies boric oxide (B_2O_3), but of the many known boron minerals only three are currently major commercial sources of borate – colemanite, ulexite, and borax – all of which are found within non-marine evaporates (Smith and Medrano 1996; Garrett 1998) (TABLE 1). Deposits containing these minerals are mined in a limited number of countries dominated by the United States and Turkey, which together furnish 90% of the world's borate supplies (TABLE 2).

Borax is by far the most important mineral for the borate industry. This reflects the fact that borax is the most widely distributed and abundant borate mineral, with large

49 tonnages present in the deposits at Boron (USA), Kırka (Turkey), and Tincalayu,
50 (Argentina) (Kistler and Helvacı 1994). In addition, borax crushes easily and
51 dissolves readily in water, so processing costs are relatively low.

52 Ulexite is a mixed Na-Ca borate that has similar mineral processing properties to
53 borax, and is the usual borate found worldwide near the surface in playa-type lakes of
54 Recent to Quaternary age. However, the only deposits specifically exploited for
55 ulexite are the Neogene deposits in the Bigadiç and Kestelek Basins, Turkey.

56 Colemanite is a Ca-borate that has low solubility in water and requires acid
57 dissolution during processing. It is, however, the preferred source of boron for the
58 production of high-quality sodium-free glass for the fiberglass industry. While
59 colemanite was historically produced in Death Valley, USA, large-scale production of
60 high-grade colemanite is now restricted to the Emet Basin, Turkey (Helvacı 2005;
61 Helvacı and Alonso 2000; Orti et al. 2016).

62 **ORIGIN OF BORATE DEPOSITS**

63 All the world's major economic borates are found in non-marine evaporate deposits
64 located in extensional basins formed during collisional tectonic terrains (FIG. 1) (Ozol
65 1977), and most of the commercial borate deposits in the USA, Argentina, Chile,
66 Peru, and Turkey are associated with continental sediments and acidic volcanism of
67 Neogene age (Smith and Medrano 1996; Helvacı 2005). Many borates in Turkey,
68 USA and Argentina are also covered by carbonate cap rocks that aided their
69 preservation (Helvacı 2005).

70 The Precambrian borate deposits of Liaoning Province, China were initially classed as
71 skarn deposits on the basis of their mineralogy (suanite, szaibélyite and ludwigite),

but detailed field studies and boron isotope data indicate that they too are likely metamorphosed non-marine evaporates (Peng and Palmer 2002).

Borates have also been mined from skarn deposits (e.g. datolite from Dalnegorsk, Russia), active geothermal fields (e.g. sassolite from Lardarello, Italy) and marine evaporates (e.g. inderite from the Inder, Kazakhstan), but none of these sources are currently of more than local significance (Kistler and Helvacı 1994).

Borate deposits of Turkey

The world's largest and best-studied borate deposits are those of Western Anatolia, Turkey (Helvacı 1995; 2015; Orti et al. 2016; Helvacı et al. 2017). The borate deposits lie in an area 300 km east-west by 150 km north-south in western Anatolia south of the Marmara Sea (FIG. 2). The main districts include the Bigadiç colemanite and ulexite deposits (Ca and Na borate); Sultançayır priceite deposits (Ca-type); Kestelek colemanite deposits (Ca-type); Emet colemanite deposits (Ca-type) and Kırka borax deposits (Na-type) (FIGS. 2-4) (İnan et al. 1973; Helvacı 1995; Helvacı and Orti 1998; 2004; Garcia-Veigas et al. 2011; Garcia-Veigas and Helvacı 2013; Orti et al. 2016; Helvacı et al. 2017).

Here, the ultimate source of the boron is calc-alkaline volcanic rocks that were enriched in boron as a consequence of metasomatism and melting of the lithospheric mantle during continental collision (Ersoy et al. 2010). The boron was then leached from the volcanic rocks by geothermal waters that collected and evaporated in playa lakes within extensional basins (FIG.5).

The mineralogy of the borate deposits reflects the composition of the geothermal fluids which are, in turn, dependent on the local geology (Helvacı 1995). For example, boron isotope data from the Kırka deposit suggest that colemanite precipitated from

fluids with low pH (~8.2) compared to ulexite (~8.6) and borax (~8.8) (Palmer and Helvacı 1995). While Sr isotope data from across the Turkish borate province indicate that Ca-rich borates likely formed from evaporation of geothermal fluids that had interacted with basement limestone (Palmer and Helvacı 1997; Floyd et al. 1998). Turkey is currently the largest producer of borates and has the world's largest reserves (TABLE 2). Production has more than doubled since 1980 to over one million tonnes per year and further increases (particularly of borax from Kırka) are likely to lead to Turkey dominating world markets. Turkey is already the major world producer of colemanite, much of which comes from the Emet valley.

EXPLORATION

Borate exploration uses all the tools available to the exploration geologist, with recognition of trends of favorable host rocks and structures being an important guide to areas of possible interest. Borates are highly soluble, hence post-depositional dissolution of borate deposits by circulating meteoric water can lead to their dissolution, but this mobility also means that water sampling (from the surface and from wells) and vegetation surveys can yield useful information (Kistler and Helvacı 1994; Floyd et al. 1998; Helvacı 2005).

Geophysical surveys, particularly gravity and magnetics, are used to outline target basins or structures beneath sedimentary basin fill. Once geophysical, geological and geochemical surveys have identified promising targets, soil and rock chip sampling techniques are used in exploration drill programs, with Sr, As, and Li as a common suite of elements to be assayed alongside boron (Helvacı et al. 2004; Palmer et al. 2004). Unlike most other elements, simple field assays of B_2O_3 can be undertaken using the original flame test and the turmeric test. Although bedded deposits of borax, colemanite, and ulexite are not generally sought at depths >500 m, boron-rich

brines, particularly those associated with other salts of value can be extracted from greater depths under certain circumstances (Kistler and Helvacı 1994).

MINING

Borate extraction and transport have a colorful history that includes; workers wading into Himalayan lakes to harvest the “floor” and then transporting the borax in saddlebags on sheep across the Himalayas to markets, extraction from the “Dante’s Inferno” of the Larderello (Italy) boric acid fumaroles, and the famous 20-mule teams used to transport borax from Death Valley to the Pacific coast in the western United States (Kistler and Helvacı 1994).

Most of the world’s commercial borate deposits are mined from open pits (FIG. 4). For example, the Boron mine in Kramer, USA, and the Kırka mine in Turkey are huge open pits using trucks and shovels, and front end loader methods for ore mining and overburden removal. Ores and overburden are drilled and blasted. A belt conveyor is then used to move ore from the in-pit crusher to a coarse ore stockpile from which it is reclaimed by a bucket wheel that blends the ore before it is fed to the refinery.

The Tincalayu deposit, Argentina is also mined from open pits and the ore is transported 400 km by truck and rail to the Salta refinery. Some South American and Chinese salar operations also use hand labor to mine thin salar borates, generally after stripping of the overburden with a small bulldozer.

Borates are mined underground in Liaoning Province, China, and at the Billie and Gerstley mines in Death Valley, CA. Borate brines are recovered at Searles Lake, CA, and in the Qinghai Basin of China. Brines have also been extracted in the Inder region of Kazakhstan.

144 MINERAL PROCESSING

145 Processing techniques for borates are related to the scale of the operation and the ore
146 type, with either the upgraded or refined mineral (borax, colemanite, and ulexite) or
147 boric acid as the final product for most operations. Borax ores (e.g., from Boron,
148 Kırka, and Tincalayu) are generally crushed to ~2.5 cm and then dissolved in hot
149 water/recycled borate liquor. The resultant liquor is clarified and concentrated in large
150 counter-current thickeners, filtered, fed to vacuum crystallizers, centrifuged, and then
151 dried. The final product is refined decahydrate (borax *sensu stricto*), pentahydrate
152 (tincalconite), fused anhydrous borax, or is used as a feed for boric acid production.

153 Colemanite concentrates are used directly in glass melts for the non-sodium fiberglass
154 industry or are used as a feed for boric acid plants. Magnesium borates are generally
155 concentrated, dissolved in acid to remove the magnesium, and then converted to boric
156 acid or sodium borates.

157 Brines from Searles Lake (and also presumably from Qinghai) are recovered by either
158 controlled evaporation or carbonation (Kistler and Helvacı 1994). The remaining
159 borate liquor is fed to tanks containing borax seed crystals which aid in the borate
160 recovery. The resultant slurry is filtered, washed, redissolved, and fed to vacuum
161 crystallizers that produce dehydrate borax products or boric acid.

162 While evaporate borate minerals and brines have relatively low energy (and hence
163 low cost) production methods, borosilicates require much higher energy processing
164 that has led to them becoming largely uneconomic. For example, ores from the Bor
165 deposit, Dalnegorsk, Russia with their relatively low B_2O_3 grades, are crushed, and
166 then run through a complex plant, which includes magnetic separators, heavy media

separators, and flotation cells (Utekhin 1965). The concentrates are then dried, leached, and calcined before being converted to boric acid or to a sodium borate.

USES

Boron is widely used in many industries, so that only a brief summary is possible here, but more extensive details are provided in Crangle (2015). Borax pentahydrate and boric acid are the most commonly traded commodities. Boric acid plants are operated by all 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. Boron fiber-reinforced plastics are used extensively for aerospace frame sheathing where they combine flexibility and light weight with strength and ease of fabrication. Minor uses that will likely increase include those in fertilizers, wood preservatives, alloys and metals, fire retardants, and insecticides (Garrett 1998).

Borates are also used in pharmaceuticals, cosmetics, anti-corrosion compounds, adhesives, abrasives, insecticides, metallurgical processes, and nuclear shielding. More recently, boron has been used in super magnets, where it is combined with rare earths, nickel and iron, to produce alloys to make electromagnets for computer drives, high fidelity speakers, starter motors, and household appliances.

Borates are also increasingly used in “green” applications by aiding recovery of heavy metals from industrial waste streams and by removing impurities from polymers used in bleaching wood pulp for paper production.

Medical applications of borates include cancer research, where the large capture cross-section of the ^{10}B isotope makes it an excellent neutron absorber that reacts with low energy neutrons to give off short range alpha particles that can be used for microsurgery in previously inoperable areas of the brain. Current tests on boron

analogues indicate they may also be effective in reducing serum cholesterol and other disease-causing proteins.

Borates were traded at relatively high prices into the late 19th century, but have become a relatively modestly priced industrial mineral commodity in recent years following the development of the large deposits at Boron and Kırka. Prices are directly related to production costs, of which the largest is fuel for drying, dehydrating, and melting the refined ore into the industrial products. Industry prices for most products have held steady with the rate of inflation (Kistler and Helvacı 1994; Helvacı 2005).

Based on recent history, the major world consumers of borates will likely continue to be the developed countries of North America, Europe, and Japan. Consumption of borates is expected to increase, spurred by strong demand in the Asian and South American agriculture, ceramic, and glass markets. World consumption of borates was projected to reach 2.0 Mt B₂O₃ by 2014, compared with 1.5 Mt B₂O₃ in 2010 (Rio Tinto Inc. 2011; Roskill Information Services Ltd. 2010, p. 167; O'Driscoll 2011).

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 world markets (TABLE 2). Very few modern industries can get by without borates, and very few people can get by without their products. Hence, borates and their products will continue to play a vital role in the global economy.

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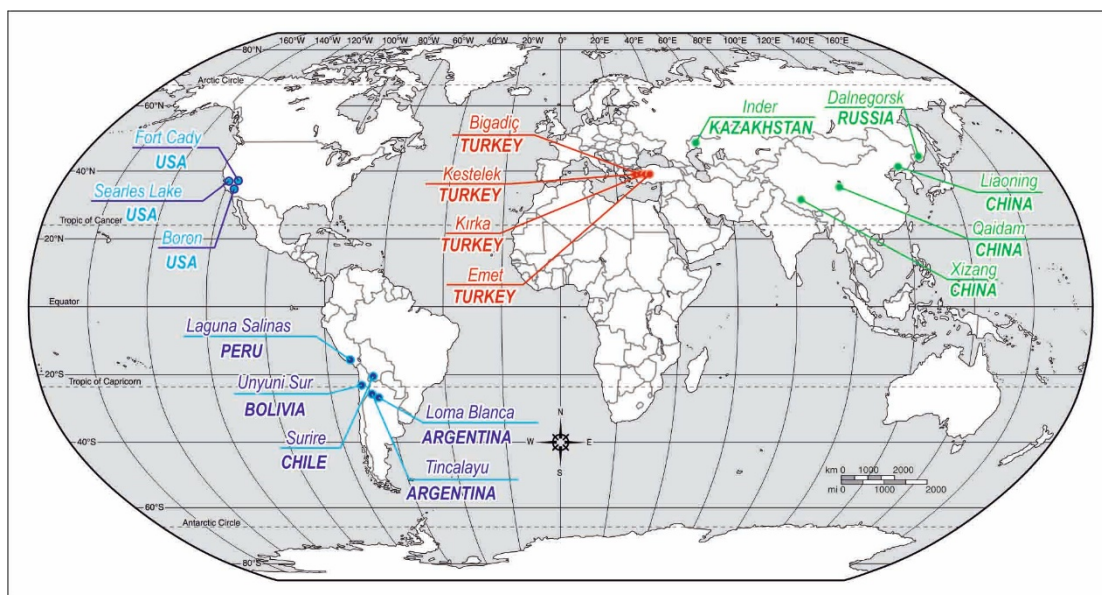
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282 **FIGURE CAPTIONS**



284 **FIG. 1. World's major borate mines**

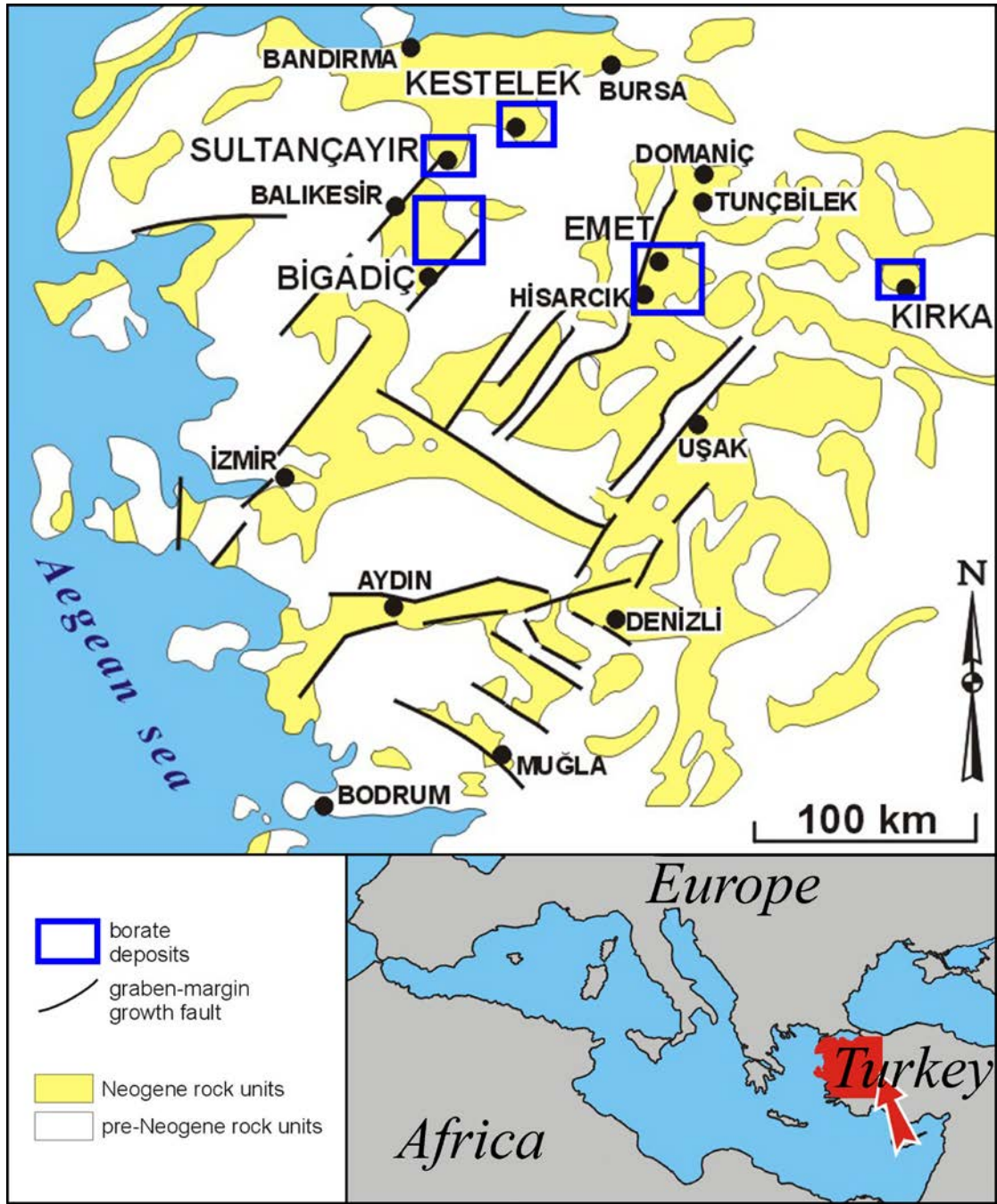
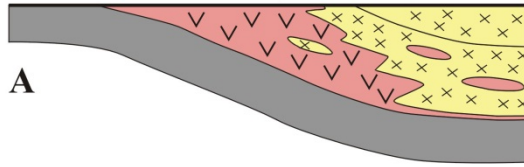
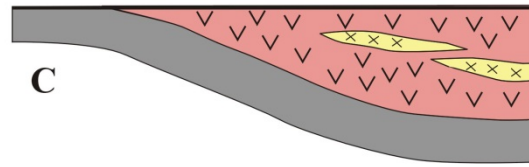


FIG. 2. Map showing borate deposits in western Anatolia, Turkey (after Helvacı 2012).

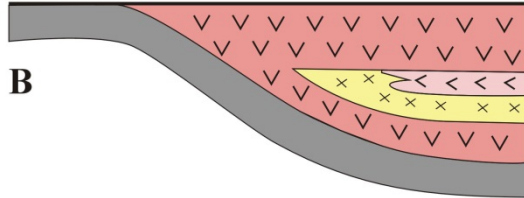
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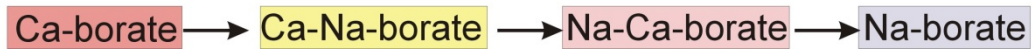
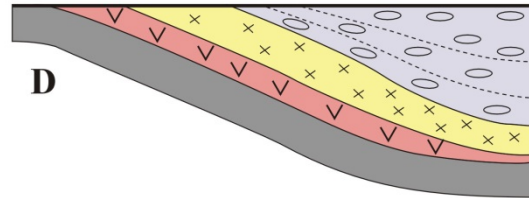
EMET



KESTELEK



KIRKA



287

288 FIG. 3. Sequence of boron mineral formation in Turkish borate deposits (after Helvacı,
289 2015).

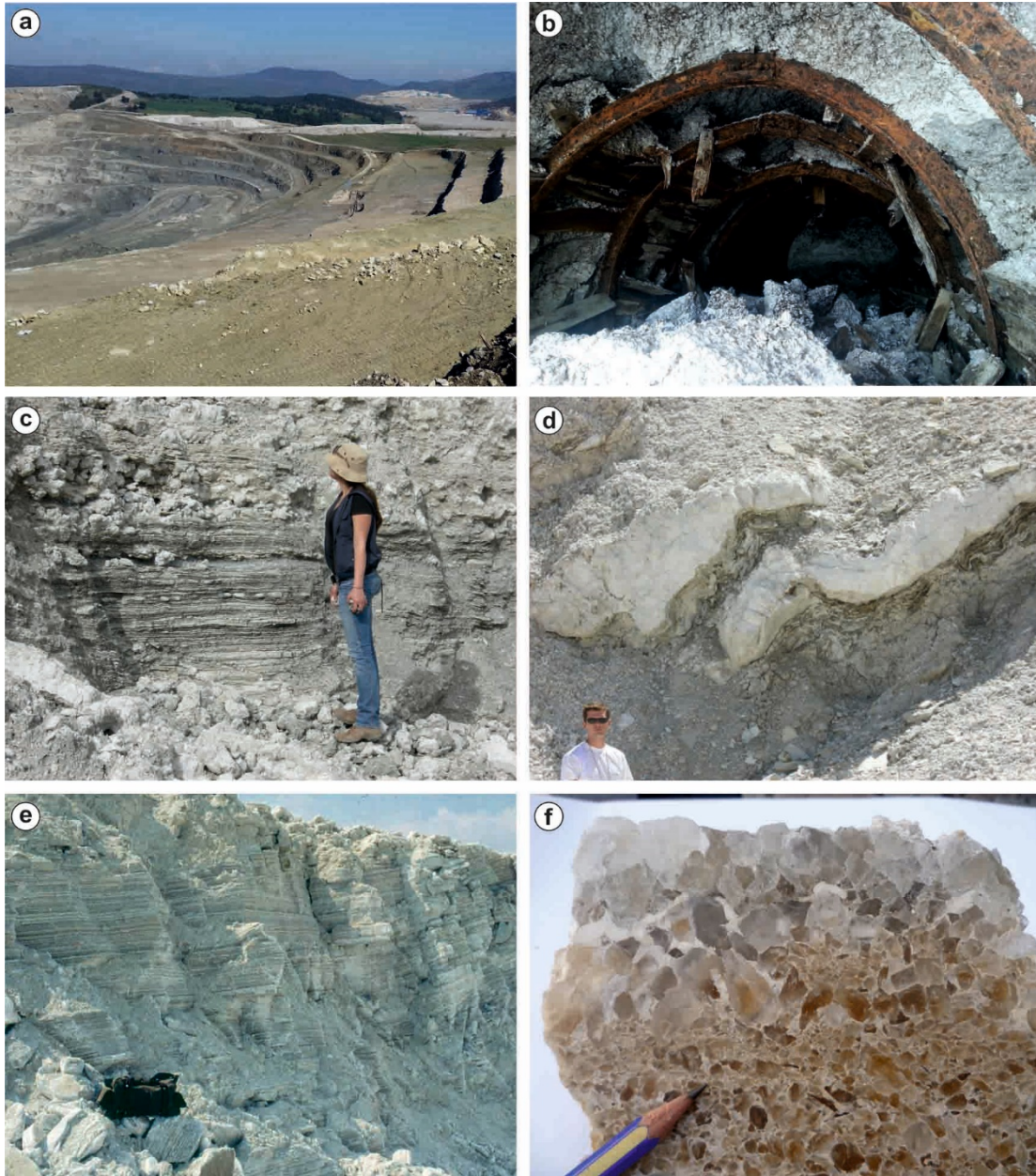
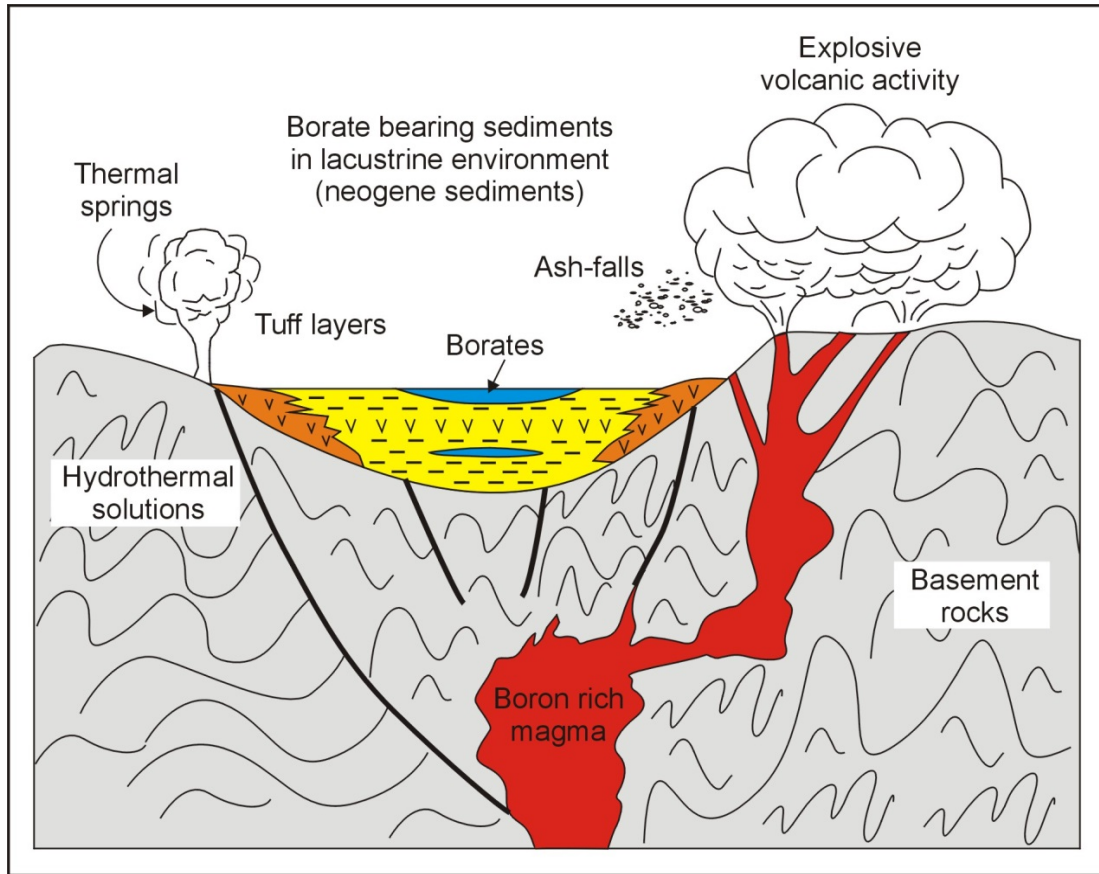


FIG. 4. Turkish borates. a) Simav opencast mine, Bigadiç. b) Old mine adit, Simav mine, Bigadiç. c) Colemanite nodules intercalated with associated sediments, Tülü open pit mine, Bigadiç. d) Ulexite ore lenses intercalated with associated sediments, Kurtpınarı deposit, Bigadiç. e) Borax and dolomitic clay alternations, Kırka opencast borax mine. f) Massive crystalline borax lithofacies. The borax crystals show zone growth at the top. Borax crystals are transparent and rectangular to equant, and are surrounded by a lutitic matrix. (All photographs by C. Helvacı).



298

299 FIG. 5. Generalized playa lake depositional model showing formation of borate
 300 deposits in Neogene basins of western Anatolia, Turkey (after Helvacı, 2005).

TABLES

Table 1: Important borate minerals in commercial deposits (Garrett 1998)

Structural formula	
<i>Boric acid</i>	
<i>Sassolite</i>	$B(OH)_3$
<i>Ca-borates</i>	
<i>Colemanite</i>	$Ca[B_3O_4(OH)_3] \cdot H_2O$
<i>Priceite</i>	$Ca_2[B_5O_7(OH)_5] \cdot H_2O$
<i>Inyoite</i>	$Ca[B_3O_3(OH)_5] \cdot 4H_2O$
<i>Ca-Na-borates</i>	
<i>Probertite</i>	$NaCa[B_5O_7(OH)_4] \cdot 3H_2O$
<i>Ulexite</i>	$NaCa[B_5O_6(OH)_6] \cdot 5H_2O$
<i>Na-borates</i>	
<i>Tincalconite</i>	$Na_2[B_4O_5(OH)_4] \cdot 3H_2O$
<i>Borax</i>	$Na_2[B_4O_5(OH)_4] \cdot 8H_2O$
<i>Kernite</i>	$Na_2[B_4O_6(OH)_2] \cdot 3H_2O$
<i>Mg-borates</i>	
<i>Suanite</i>	$Mg_2B_2O_5$
<i>Szaibélyite</i>	$Mg[BO_2(OH)]$
<i>Inderite</i>	$Mg[B_3O_3(OH)_5] \cdot 5H_2O$
<i>Kurnakovite</i>	$Mg[B_3O_3(OH)_5] \cdot 5H_2O$
<i>Mg-Ca-borates</i>	
<i>Hydroboracite</i>	$CaMg[B_3O_4(OH)_3]_2 \cdot 3H_2O$
<i>Mg-Fe-borates</i>	
<i>Ludwigite</i>	$Mg_2Fe^{3+}O_2(BO_3)$
<i>Borate-chloride</i>	
<i>Boracite</i>	$Mg_3B_7O_{13}Cl$
<i>Borosilicates</i>	
<i>Datolite</i>	$CaBSiO_4(OH)$

306 Table 2. The reserve and life estimates of the world borate deposits (Helvacı 2005).
 307

<i>Country</i>	Economic Reserve (Mt B₂O₃)	Total Reserve (Mt of B₂O₃)	Estimated life of economic reserve (yr)	<i>Estimated life of total reserve (yr)</i>
<i>Turkey</i>	224,000	563,000	155	389
<i>USA</i>	40,000	80,000	28	55
<i>Russia</i>	40,000	60,000	28	69
<i>China</i>	27,000	36,000	19	25
<i>Chile</i>	8,000	41,000	6	28
<i>Bolivia</i>	4,000	19,000	3	13
<i>Peru</i>	4,000	22,000	3	15
<i>Argentina</i>	2,000	9,000	1	6
<i>Kazakhstan</i>	14,000	15,000	10	10
<i>TOTAL</i>	363,000	885,000	253	610

308