**Introduction**

Boron (from the Arabic Buraq or the Persian Burah meaning white, or to glitter or shine). In nature, it is a highly dispersed element - averaging 3-20 ppm in the earth’s upper crust, and 4.6 ppm in seawater. It is both a volatile and mobile element and so tends to be enriched in the later stages of both magmatic crystallization and volcanic eruptions, and a few small economic deposits are found in skarns where late-stage magmas have intruded carbonates. When these primary sources are weathered in arid settings, borate evaporites can form.

Boron is the fifth element of the periodic table and is the only electron-deficient nonmetallic element. Thus, boron has a high affinity for oxygen and so forms strong covalent-bound salts known as borates (Table 1). In the chemical industry, borate salts are defined as minerals containing boric acid or boron-oxygen molecules (Kogel et al., 2006). As such, their purity can be expressed on the basis of B₂O₃, in combination with a major cation (typically Ca, or Na) and so borates as a commodity are sold on the basis of their boric oxide content (Table 12.3). Only a few of the range of naturally occurring borate salts are stable over the long term (Birsoy, 2012).

**Ore salts**

Four minerals comprise more than 90% of the borate ore salts extracted by the borate industry; the sodium borates - borax (tincal), kernite, the calcium borate - colemanite, and the sodium-calcium borate - ulexite (Table 1). Water content of the various borate salts tends to decrease with burial and to increase with exposure and weathering. Borax is the primary mineral in many US deposits, but with burial and dewatering, it converts to tincalconite and kernite. If kernite is exposed to weathering or crossflowing groundwater, it reconverts to borax.

<table>
<thead>
<tr>
<th>Borate Mineral</th>
<th>Composition</th>
<th>B₂O₃ %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Borates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Borax (tincal)</td>
<td>Na₂B₄O₇·10H₂O</td>
<td>36.5</td>
<td>Major ore mineral in USA, Turkey and Argentina</td>
</tr>
<tr>
<td>Kernite (rasorite)</td>
<td>Na₂B₄O₇·4H₂O</td>
<td>51.0</td>
<td>Major ore mineral, can rehydrate to borax</td>
</tr>
<tr>
<td>Tincalconite</td>
<td>Na₂B₄O₇·5H₂O</td>
<td>47.8</td>
<td>Intermediate or accessory mineral + manufactured end product</td>
</tr>
<tr>
<td>Na-Ca Borates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ulexite (cottonball)</td>
<td>NaCaB₆O₁₈·5H₂O</td>
<td>43.0</td>
<td>Major ore mineral particularly in Turkey and South America</td>
</tr>
<tr>
<td>Probertite</td>
<td>NaCaB₆O₁₈·6H₂O</td>
<td>49.6</td>
<td>Secondary/accessory mineral</td>
</tr>
<tr>
<td>Ca-Borates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colemanite</td>
<td>CaB₄O₇·5H₂O</td>
<td>50.8</td>
<td>Major ore mineral, particularly in Turkey, Secondary after inyoite</td>
</tr>
<tr>
<td>Meryehovite</td>
<td>CaB₄O₇·7H₂O</td>
<td>46.7</td>
<td>Intermediate ore mineral, rarely survives at surface</td>
</tr>
<tr>
<td>Priceite (pandermite)</td>
<td>CaB₄O₇·7H₂O</td>
<td>49.8</td>
<td>Ore mineral in Bigadice, elsewhere minor</td>
</tr>
<tr>
<td>Inyoite</td>
<td>CaB₂O₅·13H₂O</td>
<td>37.6</td>
<td>Minor ore mineral</td>
</tr>
<tr>
<td>Danburite</td>
<td>Ca₆B₄Si₂O₁₈</td>
<td>28.3</td>
<td>Ore mineral (borosilicate) in evaporitic skarns in Russia</td>
</tr>
<tr>
<td>Datolite</td>
<td>Ca₆B₄Si₂O₁₈·5H₂O</td>
<td>21.8</td>
<td>Ore mineral (borosilicate) in evaporitic skarns in Russia</td>
</tr>
<tr>
<td>Other Borates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sassolite</td>
<td>B(OH)₃ or B₂O₅·3H₂O</td>
<td>56.4</td>
<td>Natural boric acid (fumarole, hot springs), once extracted in Italy</td>
</tr>
<tr>
<td>Ludwigite</td>
<td>(Fe,Mg)₂Fe₂B₂O₇</td>
<td>17.8</td>
<td>Accessory mineral (meta-evaporitic association)</td>
</tr>
<tr>
<td>Hydroboracite</td>
<td>CaMgB₂O₇·6H₂O</td>
<td>50.5</td>
<td>Secondary ore mineral</td>
</tr>
<tr>
<td>Szabelyite (aschante)</td>
<td>Mg₂B₂O₅·H₂O</td>
<td>41.4</td>
<td>Ore in Russia and China (meta-evaporite)</td>
</tr>
<tr>
<td>Suanite</td>
<td>Mg₂B₂O₅</td>
<td>46.3</td>
<td>Ore mineral Russia/China (meta-evaporite, hydrates to szabelyite)</td>
</tr>
<tr>
<td>Boracite (strassfurite)</td>
<td>Mg₂B₂O₅·Cl</td>
<td>62.2</td>
<td>Associated with potash especially in Zechstein of Europe</td>
</tr>
<tr>
<td>Pinnite</td>
<td>Mg₂B₂O₅·3H₂O</td>
<td>42.5</td>
<td>Secondary to minor ore mineral in some saline lakes, China</td>
</tr>
<tr>
<td>Inderite</td>
<td>Mg₂B₂O₅·15H₂O</td>
<td>37.3</td>
<td>Commonplace in ore from Lake Inder deposit, Kazakhstan</td>
</tr>
<tr>
<td>Howlite</td>
<td>Ca₂SiB₂O₅(OH)₂</td>
<td>44.5</td>
<td>Accessory mineral</td>
</tr>
<tr>
<td>Bakerite</td>
<td>CaB₂(BO₃)(SiO₂)(OH)₂·H₂O</td>
<td>42.1</td>
<td>Accessory mineral</td>
</tr>
<tr>
<td>Tunellite</td>
<td>Sr₂B₂O₇(OH)₂·3H₂O</td>
<td>55.1</td>
<td>Accessory mineral</td>
</tr>
<tr>
<td>Tertschite</td>
<td>Ca₂B₂O₇·2H₂O</td>
<td>65.1</td>
<td>Accessory mineral</td>
</tr>
<tr>
<td>Kumakovite</td>
<td>Mg₂B₂O₅·15H₂O</td>
<td>37.3</td>
<td>Accessory mineral</td>
</tr>
</tbody>
</table>

Table 1. Commonplace sedimentary (and metasedimentary) borate minerals with B₂O₃ equivalents.
Kernite (a source for boric acid manufacture) is present in large tonnages in saline lake beds in the USA and Argentina. It is less suitable as an ore salt than borax or tincalite despite its high B\(_2\)O\(_3\) content. Kernite has excellent cleavage but crushes into fibres that tend to mat and clog handling equipment. It also is much less soluble in water than borax and so is less suitable as a feedstock for the manufacture of pentahydrate. Colemanite is the preferred calcium-bearing ore and is the principal ore mineral in Turkey; it is the least soluble of the borate ore salts and only slowly dissolves in water, but is highly soluble in acid solutions. Szaebelyite, a magnesium borate is the primary ore mineral in the Proterozoic meta-evaporite ores of the Liaoning Province, China, while datolite (a boron silicate) was the principal ore salt in the borate skarns of Dalnegorsk in Russia.

Because most borate salts are soluble in water, most exploitable Neogene deposits of at-surface or near-surface borate salt beds involved lacustrine deposition in arid settings that were strongly influenced by volcanic activity at the time of lake sedimentation. These evaporite deposits, which make up the majority of the world’s borate reserves, tend to have abundant tuff and basaltic interlayers in the drainage basin, to have formed beneath a semi-arid climate and are precipitated from saline continental brines. A protective layer of another impervious less-soluble evaporite salts, such as gypsum or anhydrite, typically forms a carapace that prevents subsequent redissolution of the borate beds.

### Uses

In terms of dollar value, the most commercially valuable boron product is anhydrous borax, which is used directly in the manufacture of boro-silicate glass (fibreglass and heat-resistant glass) as well as, refractories and enamel glazes requiring high colour standards. (Figure 1). Borax (Na\(_2\)B\(_4\)O\(_7\)·10H\(_2\)O; sodium tetraborate decahydrate), is used principally in laundry products. The pentahydrate (Na\(_2\)B\(_4\)O\(_7\)·5H\(_2\)O) is used to neutralize skins/hides in leather tanning, corrects boron deficiency in plants, reduces melting temperature in the glass manufacture process, is a fire retardant in cellulose insulation, and is used to make a bleaching agent for home laundry.

Borax’s mild alkalinity means it can emulsify oil and grease and also reduces the surface tension of water, which aids in the loosening of dirt particles. It also reacts with some organics to produce esters, making it a mild bactericide. This means it has a strong but gentle cleansing action, making it suitable for personal and fabric cleansing (Figure 1). Borax is also used in the manufacture of abrasives and refractories; some boride compounds have a hardness around 9 on the Moh scale and also exhibit high thermal and electrical conductivity. In agriculture, boron is essential to plant growth and one of the 16 necessary plant nutrients, although in higher concentrations it is toxic. Use of borax as a mild antiseptic is minor in terms of both dollars and tons. Amorphous boron is used in pyrotechnic flares to provide a distinctive green colour, and in rockets as an igniter. Other high-grade boron compounds show promise in treating arthritis.

In the field of nuclear energy, boron (the \(^{10}\)B isotope) protects personnel from the harmful effects of reactors. It has the unique property of absorbing neutrons produced by nuclear reaction without the emission of harmful secondary gamma radiation and is sold for nuclear shielding as an organic borate, created by a combination of borate with paraffin. The elemental form of boron is also incorporated into polyethylene and rubber. Ammonium pentaborate is used in a ‘poison’ charge in atomic submarines. Another organo-sodium borate (Liquibor) is now in use in hydraulic brake fluids in cars to provide lower volatility and built-in corrosive protection. Boron, also, confers a low coefficient of expansion, increases the resistance to mechanical and thermal shocks and gives a bright and pleasing appearance to glass. Borax and boric acid are used together in the manufacture of several boro-silicate glasses of low alkali content. Between 15 to 50 parts of borax are applied to every 1,000 parts of a glass-sand batch to give enhanced properties to glass.

Boron nitride can be used to make a material almost as hard as diamond. Cubic boron nitride, commercially called ‘Borazon’ can withstand temperatures that are more than twice the temperature limit of a diamond (about 900°C) and so is used as a flux in the manufacture of artificial gems and the processing of gold ore. The nitride also behaves like an electrical insulator, but conducts heat like a metal. It also has lubricating properties similar to graphite. Boron-hydrides are easily oxidized with considerable energy liberation, and have been studied for use as rocket fuels and igniters for fuels. Demand is increasing for boron filaments, a high-strength, lightweight material chiefly employed for advanced aerospace structures. This form of boron is similar to carbon in that it can form stable covalently bonded molecular networks.

### Current Production

Borate production is dominated by a few nations, with Turkey as the largest producer, followed by the USA, Chile, Argentina and China (Figure 2a,b). All production is from Neogene continental evaporite deposits except the Chinese ores which mine silicified Precambrian meta-evaporites (see Warren 2016, Table 12.4, for a listing of borate salt occurrences, worldwide). Seventy-five percent of the market is controlled by two major producers, Etimine, based in Turkey, and Rio Tinto Borax, with its main mine at Boron in California. The rest of the market is made up of half a dozen or so minor producers. The market is, to all intents and purposes,
a duopoly. Due to economies of scale and other factors, the two leading suppliers have low cost bases, while the other suppliers have higher costs, some significantly so. Although a relatively low-price commodity (Figure 2c) the duopoly competes on a worldwide basis because they can absorb the transportation costs in the high volumes they produce cheaply. Other producers are mostly restricted to their geographical area, again to a greater or lesser degree determined by their underlying production and processing costs. In all world markets, the duopoly is the price setter and can determine local price according to the market penetration to which they aspire. There is one very significant difference between the two major producers. Rio Tinto Borax is well into the latter part of the boron mine life cycle, whereas Etimine’s mines are in the relatively early stages of theirs. According to the Turkish Ministry of Energy and Natural Resources, Turkey has over two-thirds of the world boron resource totalling over 950 million tonnes, while remaining known US resource is somewhere around 80 million tonnes meaning the world is well supplied with borate into the foreseeable future (Figure 2b).

Today, US Borax, a member of the Rio Tinto Borax Group, is perhaps the largest global miner of $\text{B}_2\text{O}_3$, mostly as tincal ore. The company is also the world’s largest manufacturer of refined borate products. US Borax supplies almost half of the world’s demand for industrial and speciality borates from its Kramer borate deposit at Boron in southern California’s Mojave Desert. Turkey is the world’s largest producer of borate ore, mining more than 1 Mt (1.1 million st) of salable product each year (Figure 2a) including refined materials from Kirka and Bandirma. As well as the largest miner, this makes Turkey the second-largest producer of refined boron compounds, after the USA. The government organization, ETI Holding A.Ş., is the sole producer of Turkish borate compounds through its subsidiary Eritban A.Ş. The combined production of Turkey and the US accounts for more than 90% of the global borate output (Figure 2d).
During Kramer ore processing, advantage is taken of the solubility of borate salts, especially borax and kernite, in separating clayey material by water washing and recrystallization. Refined borax is produced by dissolving the crude material in hot water under pressure. The insoluble impurities are filtered off, and the liquor is crystallized to give borax. The ulexite or colemanite mined in Turkey is shipped to many European countries for processing into boric acid and borax. Ulexite and colemanite are treated in the same manner with sulphuric acid to convert them into boric acid. If borax is to be produced, then boric acid is added to a soda ash solution. Borax is also produced from colemanite via boiling the powdered mineral with a sodium carbonate solution for about 3 hours. After filtering, the solution is allowed to crystallize to yield crude borax. Historically, borax is recovered from the Searles Lake deposits as a by-product of potash recovery.

**Historical Production**

Historically, borates (as a component of natron salts) were used 4000 years ago in mummification. Soon after, borax (in a purer form than natron) was imported by the ancient Babylonians from the Far East for use as a gold and silver flux. The word tincal comes from the Babylonian tincar meaning “Far East” or the Malay word tingkal meaning borax. By the 8th century AD, the Arabs around Mecca, Medina and Baghdad were using imported borax (tincar) as a kiln additive or flux to braze or harden precious metals, especially gold. Borax glazes were used in China from AD 300, and boron compounds from Tuscany were used in glassmaking in ancient Rome.

The Crusades ultimately resulted in the introduction of borates into Europe, when Arabic chemistry texts were discovered and translated between 1100 and 1200 AD., stimulating interest in the east and Marco Polo’s subsequent journeys to China along old caravan trade routes. By the 12th Century, borax from Tibet was regularly imported into Europe. At the time borax was very expensive, and this limited its use principally to the precious metal trade where goldsmiths used it as a soldering agent and in the refining of metals and assaying of ores. Quantities traded were small, its method of production was a tightly held secret of the alchemist’s guild, and its source in the borate pavements precipitated in the salt lakes of Tibet remained a mystery until the second half of 18th century.

Marco Polo, a Venetian, voyaged to the Far East and discovered a thriving borate trade between Tibet and India, with borax being harvested from the muds of high mountain lakes in Tibet, traded and accumulated at local bazaars, and transported across the Himalayas in bags tied to the necks of sheep in order to supply several Indian market cities. He must have realized the economic implications of his discovery, for on his return home to Venice he established an exclusive trade agreement between the Venetian glassmakers and the Tibetan borax miners. For centuries, the use of borax as a glaze and flux was a closely held Venetian “trade-secret”.

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Figure 3. Sassolite in the Sasso Pisano region, Castelnuevo Val di Cecina, Tuscany, Italy. A. Typical fumarolic/hot-spring sassolite. B) Sassolite hot spring. C) The valley in the heyday of boric acid production, circa 1920. D) The same valley today (image by Tiberio Bardi).
The price of borax remained high for hundreds of years, with refined borax fetching $3/oz in London, as late as 1790. Border disputes moved control of the Tibetan borates to India in the 17th century, allowing the Dutch to break the Venetian monopoly and create one of their own that lasted until the 1770s. Competition from the French at that time, and about 25 years later by the British, effectively ended the world’s dependence on this single source. Tibetan salt lakes continued to be the source of most borate into Europe until the beginning of the 19th century when sassolite was discovered around fumaroles in Larderello, near Pisa, Italy and production began there in 1808.

Sassolite is natural boric acid and is a volcanic product that occurs in association with sulphur in the craters of volcanoes, as in Sassolo Pisano, Castelmuzio Val di Cecina, Tuscany, Italy (Figure 3). As well as the Larderello hot springs and fumarole deposits it was found in the Lipari Islands, southern Italy and the Tuscan lagoons, between Volterra and Massa Marittima. In all cases, the boric acid condenses naturally in water and separates in large sassolite flakes which contain about 50% of the(462,881),(737,894)

The geysers (solfatoni) in Tuscany, were an important source of boric acid in Europe from about 1820 to the 1950s (Figure 3). The Tuscan borate deposits in the Larderello region of Italy are thought to have been the model for Dante’s Inferno. At that time the area was mostly uninhabited and inhospitable, characterized by sulphurous steam vents, poisonous gasses, little vegetation or wildlife, and extreme high acidity of its waters. Boron-rich waters from this area were harvested and concentrated to produce boric acid and crystals. By 1860 an annual production over 2000 tonnes was achieved. Tuscany’s proximity to market and predictability of product quality significantly diminished the demand for Tibetan borax. By today’s standards, this small production would be trivial, but in 1860, this 2,000 tonnes per annum made Tuscany the largest borate-producing region in the world (Bebeeby, 2002).

The borate industry in Turkey commenced in 1865, initially with mining of priceite (Ca₂B₂O₇·7H₂O) from Neogene salt lake beds. At about the same time, several borate deposits were discovered in Quaternary playas in California and Nevada, ore salts encompassed ulexite (NaCa₂B₂O₇·8H₂O) and colemanite (Ca₂B₂O₇·5H₂O) in Death Valley. These minerals were converted to borax by reaction with trona. The Neogene Kramer deposit, at what is now Boron, California, in the Mojave Desert, was discovered in 1913, was first mined as a colemanite ore source. In 1925, tincal ore was found and in 1926, the new mineral kernite (aka rasorite: Na₅B₂O₇·10H₂O) was encountered. Today, the open-pit mine at Kramer is the largest borate deposit outside of Turkey and over the last century has supplied a sizable portion of world borate demand.

The ore can be mined and crushed with water. After a period of time, the majority of the kernite hydrates to crude borax. The borax produced can be processed with an acid to produce a higher purity borax or boric acid by equation 1. The following equation (3) shows an example of kernite being processed into boric acid using sulphuric acid:

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Na₂B₂O₇·10H₂O + H₂SO₄ = 4H₂BO₃ + Na₂SO₄ + 5H₂O</td>
</tr>
<tr>
<td>(2)</td>
<td>5Na₂B₂O₇ + 10NH₄Cl = 10NaCl + 4NH₄B₂O₄ + 6NH₃ + 3H₂O</td>
</tr>
<tr>
<td>(3)</td>
<td>Na₂B₂O₇·4H₂O + H₂SO₄ + H₂O = 4H₂BO₃ + Na₂SO₄</td>
</tr>
</tbody>
</table>

**Kernite**

Kernite is found in large amounts associated with tincal at the Kramer mine. The ore can be mined and crushed with water. After a period of time, the majority of the kernite hydrates to crude borax. The borax produced can be processed with an acid to produce a higher purity borax or boric acid by equation 1. The following equation (3) shows an example of kernite being processed into boric acid using sulphuric acid:

**Natural Brines**

Dissolved sodium borates occur naturally in brines at Searles Lake, CA, where a plant started operation in 1917 and is now owned by Searles Valley Minerals (formerly North American Chemical Corp.). Brine is pumped into carbonation towers where carbon dioxide obtained from calcining limestone is pumped into the towers to precipitate sodium carbonate. The borax-rich brine is blended with lake brine to raise the pH and cool the brine to 38°C. Borax seed crystals are added to precipitate crude sodium tetraborate pentahydrate.
Another process (4) used at Searles Lake requires solar evaporation. Tetraborate reacts with alkaline carbonate to form sodium metaborate as follows:

$$\text{Na}_2\text{B}_4\text{O}_7 + \text{Na}_2\text{CO}_3 = 2\text{Na}_2\text{B}_2\text{O}_4 + \text{CO}_2 \ldots \ldots \ldots \ldots (4)$$

Sodium metaborate is very soluble and will not crystallize under the same conditions as tetraborate. A sodium bicarbonate-borax mixture causes the following reaction (5):

$$2\text{NaHCO}_3 + 2\text{NaB}_2\text{O}_4 + \text{O}_2 = \text{Na}_2\text{B}_2\text{O}_4 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \ldots \ldots \ldots (5)$$

**Datolite**

In Dalnegorsky, a remote township in Russia, datolite (CaO·B₂O₃·SiO₂·B₂O₃·H₂O) ore (skarn) containing between 6% and 12% boron oxide is mined. (Baskina et al., 2009). The ore is crushed and blended to a concentration of 8.6% boron oxide. The datolite is not soluble and the ore is washed to remove gangue after crushing. Decahydrate borax is also produced by the reaction of boric acid with sodium carbonate (soda ash) as follows (6):

$$4\text{H}_3\text{BO}_3 + \text{Na}_2\text{CO}_3 + 4\text{H}_2\text{O} = \text{Na}_2\text{B}_2\text{O}_4·10\text{H}_2\text{O} + \text{CO}_2 \ldots \ldots \ldots \ldots (6)$$

Elemental boron is manufactured by reacting boric anhydride with an alkali metal such as magnesium as follows (7):

$$\text{B}_2\text{O}_3 + 3\text{Mg} = 2\text{B} + 3\text{MgO} \ldots \ldots \ldots \ldots (7)$$

The purity of the elemental boron can be improved by using a hydrochloric acid leach.

**Ulexite**

Some 35 playas are known to contain borates in Argentina, Peru, Bolivia, and Chile at altitudes of 760 to 4,400 meters above sea level. In Chile at the Salina de Surire, Quimica E Industrial Del Borax Ltda., or Quiborax, mines ulexite (NaCaB₅O₉·8H₂O) 1,680 meters above sea level and produces boric acid via a reaction with sulphuric acid (8):

$$\text{NaCaB}_5\text{O}_9·8\text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 = 5\text{H}_3\text{BO}_3 + \text{NaHSO}_4 + \text{CaSO}_4 + 2\text{H}_2\text{O} \ldots \ldots \ldots \ldots (8)$$

**Colemanite**

Colemanite crystals were first discovered in the 1800s in walls of a canyon in Death Valley, USA. Colemanite is insoluble in water and requires a different refining process from the cotton-ball ulexite found in the Death Valley floor. The colemanite ore was converted to a hot solution of sodium borate by treatment with soda ash. The calcium carbonate precipitated to the bottom and borax crystallized on the wall of the vat as the solution cooled. The sodium metaborate was treated with carbon dioxide to produce borax.

$$\text{HCl} + \text{CaB}_2\text{O}_4·5\text{H}_2\text{O} + 2\text{H}_2\text{O} = 6\text{H}_3\text{BO}_3 + 2\text{CaCl}_2 \ldots \ldots \ldots \ldots (9)$$

$$\text{CaCl}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HCl} \ldots \ldots \ldots \ldots (10)$$

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**Borate future markets and prices**

The current borate market is an oligopoly, dominated by output from Rio Tinto’s California operation (through its subsidiary, US Borax), which accounts for 30% of the supply to the world market, and the Turkish-government-controlled Eti Maden, which delivers 43%. In addition, Chinese producers account for around 14%, so supplying a little over a third of the needs of the Chinese domestic market. In total China, the USA and Turkey supply almost 90% of the world market.

Borate salts and associated products, especially boric acid, define a fairly mundane commodity grouping. The stable B₂O₃ price reflects the fact that borate salts have traditionally been used for a variety of everyday products like insulating materials (19% of the end-user market), ceramics (16%), agriculture (13%), specialised glass (11%), and household chemicals and detergents (11%). In this sense, the borate market space and its price have, historically, closely tracked global GDP numbers and the ability of the world’s population to buy more household products (Figure 2c, d).

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 on recent history, the major world consumers of borates will continue to be the developed countries of North America, Europe, and Japan.

Today, boron market is well supplied and easily capable of coping with an increasing use of boric acid in electronics manufacture to satisfy the expanding middle-class consumers of China, India, and Africa and facilitate increased use of boron as an agricultural fertiliser. Given the lack of players in the market, the relatively slow growth in needs, and an abundance of known reserves there are few companies aside from those already mentioned currently considering bringing new borate volumes onto the market.

Known reserves of borate minerals are enormous, particularly in Turkey, while production from Turkey and the USA will continue to dominate the world market in the next decade. However, given ever-increasing transport costs, borates from other areas may take up an increasing share of their local and world market. This trend is already evident, with boric acid from Chile reaching the Far East and Europe, and both Russia and China are beginning to export.

**Geology of Borates**

The major commercial borate deposits occur in a limited number of Neogene to Holocene non-marine evaporitic settings (Garrett, 1998; Helvacı et al., 2012; Helvacı, 2019). They are always related to volcanic rocks and pyroclastic deposits and closed-basin alkaline lakes or playas fed by hydrothermal sources (Figure 4, Warren 2016). Borax, and to a lesser extent kernite, is open-pit mined today at the Kramer mine near Boron in California, the Sarikaya mine in Kirkα ore district (Eskisehir Province, in Turkey), and Tincalayu in northern Argentina (Figure 4). These three saline lacustrine regions, plus the brines from Searles Lake, California, furnish the majority of the sodium borates used by the chemical industry in the last 100 years. Sodium borates ores are readily soluble in water,
making them preferable feedstock for many end uses. Most of the larger extractive facilities also produce boric acid at nearby refineries. Colemanite is mined from several deposits in the Emet and Bigadic basins of western Turkey, one former Death Valley deposit, and small deposits in northern Argentina. This calcium borate is used in boron endproducts that have a low sodium requirement, and in making boric acid.

Ulexite is the common playa (salar) or hypersaline marsh borate. It is produced commercially from numerous salars in South America and playas in the Provinces of Quinghi and Xizang (Tibet) in western China. Ancient saline lacustrine deposits 5–20 million years old — are the source of Turkish ulexite, it is found in Death Valley and some of the ore produced in Argentina (Figure 4). Much of this material is ground and used as a crude product in agriculture or to manufacture boric acid.

The less easily refined magnesium borates of China occur in the Palaeoproterozoic metasediments of Liaoning peninsula adjacent to North Korea (Figure 4). These are mined by underground methods and refined in small, local plants to produce sodium borates and boric acid for domestic use. A unique borosilicate skarn deposit (datolite and danburite) near Dal’negorsk

Figure 4. Borate deposits. A) Deposits plotted on a world topographic/tectonic base (after Warren, 2016). B) Deposits plotted on a marine evaporite basin base, where brown shading indicates halite-dominant and green indicates megasulphate basin (after Warren, 2010). Plot shows that borate deposits are better developed in volcanic-associated, active orogenic collision belts and zones of fractured continental crust. They do not occur atop or within large marine-fed mega-evaporite basins.
in far-eastern Russia is open-pit mined to produce boric acid. Triassic carbonates were intruded by Cretaceous granodiorites to create the borosilicate skarn. Borates from this source were once shipped by rail to western Russia and eastern Europe, when they were mines operated under the auspices of the Former Soviet Union, but more recently ore products are shipped through local ports to markets in the Far East.

Other borate deposits, some of which were once mined commercially, include saline deposits the Inder region of Kazakhstan, the Stassfurt district of eastern Germany, as well as parts of northern Iran, and Yugoslavia. Numerous smaller lacustrine playa deposits are known in the western United States, western Turkey, and in South America. Some of these Holocene playa deposits were extensively exploited by pioneer producers in the late 19th and early 20th centuries, but are not currently in production (Garrett, 1998; Warren 2010). We shall now discuss the geological detail of three of the more significant regions hosting exploited saline borate deposits (Turkey, South America and USA).

**Turkish borates**

Turkey has the largest known reserves of natural borate salts in the world (Figure 2b). The borate region of western Anatolia has five districts, from west to east they are: Bigadic, Sultancayir, Kestelek, Emet, and Kirka, with the Kirka district containing the most mature borate mining operations, all are open-pit (Figure 5a; Helvaci and Orti, 1998; Helvaci and Alonso, 2000; Helvaci and Orti, 2004; García-Veigas et al., 2011; García-Veigas and Helvaci, 2013; García-Veigas et al., 2016; Helvaci, 2019). Turkish borates have been mined for the last fifteen centuries. Proven borate reserves are 532 million tonnes with a total estimated reserve of some 987 million tonnes. Colemanite is the primary ore mineral at Bigadic, Emet, and Kestelek (Figure 7a), significant ulexite ore occurs at Bigadic and tincal at Kirka. Borax and colemanite ores are refined and concentrated at the Kirka and Bandirma plants. Bigadic borates are extracted from what is likely the largest colemanite/ulexite deposit in the world, with high-grade colemanite and ulexite ores generally running 30% and 29% $\text{B}_2\text{O}_3$, respectively.

The Kirka stratigraphic succession comprises borates that are intimately interbedded with and penetrating marls, claystones, zeolitized tufts and tuffaceous epiclastic materials in bedded lacustrine sediments (Figure 5a). The main boron mineral is borax with lesser amounts of colemanite, ulexite and other borate minerals (Figure 7; Helvaci, 2019). Volcano-sedimentary rock units in the Sultancayir deposit include borate-bearing gypsum intercalated in a sandy claystone unit. Calcium borates, mainly pandernite (priceite) and howlite, but also colemanite and bakerite, are interspersed within the Sultancayir gypsum. The Kestelek deposit is 27 km southeast of the town of Mustafa Kemalpasa in the province of Bursa. Borate ore zones are typically hosted in clays. Colemanite is present as nodule to boulder size masses (up to 1 m in diameter), and as thin sheets of fibrous and euhedral crystals. Colemanite, ulexite and probertite predominate, and sparse hydroboracite is also present locally.
All the exploited Turkish borate ores were initially precipitated as early Miocene (16-20 Ma) perennial saline lake sediment within a series of northeast-southwest-trending elongate basins, which are underlain by a Palaeozoic and Mesozoic basement composed of ophiolites, marbles and schists (Figure 5b; Helvaci, 1995). Tibet-type extensional graben structures host the Bigadic, Emet and Kirkla lacustrine basins of western Turkey. The grabens developed during Miocene continent-to-continent collision along the Izmir-Ankara suture zone, where calc-alkaline volcanism was simultaneous with borate sedimentation. This volcano-sedimentary sequence consists of (from bottom to top) basement volcanics and volcanoclastics, lower limestone, lower tuff, lower borate zone, upper tuff, upper borate zone and olivine basalt (Figure 5b). Borates in the upper zone occur in units up to 30 metres thick beneath a sediment cover that is 25 to 410 metres thick, while the lower borate zone is up to 65 metres thick and is found at depths between 150 and 950 metres.

All these Neogene borate deposits have thin sedimentary covers and have never been deeply buried (Helvaci and Orti, 1998). Borate precipitation occurred mostly in shallow to at-surface brine saturated settings, in saline lake systems encompassing a range of evaporitic settings, from stable playa mudflats to deeper perennial lakes, the latter typically preserve shouling successions, changing from shallow lake to playa and mudflat. Shallowing-upward cyclicity typifies all ore beds in these deposits, which accumulated as lacustrine deposits in a hydrothermally-active volcanicogen terrain (Figure 5b). Colemanite tends to occupy the deposit’s depositional margins, while laminated borax is more common in the centres of the lacustrine basins, with a zone of ulexite separating the two (Figure 7a, b; Inan et al., 1973). This mineral zonation is syndepositional and cannot be ascribed to later burial diagenetic processes.

When details on these primary to very early secondary (sabkha) deposits began to come to the world scientific literature in the mid-1970s, the prevailing notion of borate ore zones as thermal replacements (mesogenetic) began to come to the world scientific literature in the mid-1970s, the prevailing notion of borate ore zones as thermal replacements (mesogenetic) even some of the strongest proponents of the thermal or mesogenetic replacement model for borate ores began to admit the possibility of a primary or syndepositional origin for the ore zonation for most of the world’s borate deposits.

Borate minerals at Bigadic form two ore zones, now separated by thick tuff beds that have been transformed to montmorillonite, chlorite, and zeolites (mainly heulandite) during diagenesis (Figure 6; Gundogdu et al., 1996; Helvaci and Orti, 1998). Colemanite with lesser ulexite predominates in both zones; but other borates, including howlite, proberite, and hydroboracite are present in the lower borate zone; whereas inyoite, meyerhofferite, pandermite, tertschite(?) and hydroboracite, howlite, tunelite, and rivadavite are found in the upper borate zone (Helvaci, 1995). Calcite, anhydrite, gypsum, celestite, K-feldspar, analcime, heulandite, clinoptyliolite, quartz, opal-CT, montmorillonite, chlorite, and illite are also found in the Bigadic deposit.
Nodules of colemanite and ulexite predominate in both borate zones at Bigadic (Figure 6). Agglomerated colemanite and ulexite nodules construct alternating bedded horizons with relatively sharp boundaries. Because these minerals are readily dissolved and reprecipitated, early secondary masses of pure and transparent colemanite and ulexite are often encountered in cavities, nodules and cracks in the same ore hosts. Some nearsurface colemanite and ulexite beds are now so weathered they are entirely replaced by calcite.

Colemanite nodules in both ore zones first formed as widespread secondary syndepositional precipitates in concentrated pore brine within unconsolidated gypsiferous sediments (Figures 6, 7a; Helvaci and Orti, 1998; Helvaci, 2015, 2019). Colemanite and ulexite formed mostly as interstitial growths under synsedimentary conditions, either as mineralogically primary or as displacive and cementing lithofacies. All crystals were later affected by waters tied to progressive compaction and the conversion of gypsum to anhydrite. Heliothermal conditions may have favoured the precipitation of colemanite over ulexite on the shallow bottom or just below the sediment surface in some density-stratified lakes. Locally, some colemanite is a secondary precipitate emplaced during early burial; its precipitation was possibly driven by compactional pore water crossflow via the (macroscopic) replacement of precursor ulexite. Early formed nodules continued to grow as the sediments were compacted to give septarian-like fracture fills. Later generations of colemanite and ulexite are found in vugs and veins and as fibrous margins of early-formed nodules. Burial diagenetic changes in the main borates include the partial replacement of colemanite by howlite and hydroboracite and replacement of ulexite by tunellite. It is unlikely that substantial volumes of Turkish colemanite ever formed by dehydration of inyoite or by a burial driven thermal replacement of ulexite.

Proberite bands at Bigadic are found in some ulexite horizons, especially in the lower borate zone. It formed in the same chemical environment as ulexite, and according to Helvaci (1995) indicates short periods of extreme desiccation and possibly short periods of subaerial exposure within the lake centres. 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 ions supplied from adjacent tuffs and clays by ion exchange. Howlite grew in clay bands alternating with thin colemanite bands and coincided with periods of relatively high silica concentrations. Diagenetic processes also produced small howlite nodules embedded in unconsolidated colemanite nodules.

In contrast to the colemanite-ulexite dominance at Bigadic (Figure 7a), laminated and accretionary lacustrine borax is volumetrically and economically the most important zone in the Kirka borate deposit (Figure 7b; Helvaci and Orti, 2004; García-Veigas and Helvaci, 2013). The deposit is symmetrically zoned in a lateral sense with a central body of Na borate (borax), an intermediate zone of Na–Ca borate (ulexite), and a marginal zone of Ca borate (colemanite; Figure 8). The same mineral zonation is also developed in a vertical sense. However, it is somewhat asymmetrical because of the presence of a discontinuous Mg borate horizon overlying the central body of borax.

Older studies, based on analogies with US borate deposits, attributed the zonation to a diagenetic overprint on the margins of the original syndepositional borax-clay laminates of the lake (Inan et al., 1973). More recent work has shown that the Kirka sequences are depositionally fractionated and that the zonation represents a hydrologically controlled separation of evaporite minerals in a lake basin actively accumulating sediment (Figure8b; Helvaci and Orti, 2004; García-Veigas et al., 2011; García-Veigas and Helvaci, 2013). Lateral gradients in salinity in the mudflats passing into the perennially subaqueous centre conditioned the concentric pattern of the facies at Kirka. Thus, the various borax lithofacies zones (chemical, clastic, mixed) seen in the central ore body reflect surface and near-surface borate precipitation in a lake that evolved with subsidence and climate. Conditions oscillated from predominantly subaqueous with variable brine depths (perennial lake stage), to an interstitial sabkha or mudflat setting (playa-lake stage). The evaporative concentration of the boratiferous waters in the lake, together with the periodic changes in temperature of the water mass, are the main controls on the crystallization of borax.

Helvaci and Orti (2004) found no petrographic evidence for a thermally induced inyoite-to-colemanite transformation, as previously proposed by
the diageneticists and went on to argue that the moderate burial depths in all the various Turkish borate deposits are insufficient for the generalized transformations required by the diageneticists (Figure 8a). Instead, the Mg borates represent evaporitic precipitates from the syndepositional fractionation of the initial boriferous inflow; they are not burial-driven reaction products between pre-existing borates and groundwaters. Thus the mineral zonation in Kirka is primary, not only for borax and ulexite in the subaqueous dominated parts of the lake, but also for both the colemanite forming the marginal playa dominated zones and for the Mg borates overlying the central body of borax in Kirka (Figure 8b). This same argument of syndepositional not burial flushing can be applied to Bigadic, which is then seen to be a deposit accumulating under predominantly playa conditions (Figure 5b).

Almost all workers now accept that the borax-clay laminite texture that dominates the core of the Bigadic deposit is subaqueous. Crystal outlines have a characteristic growth-aligned borax (palisade) texture in mm-cm thick layers separated by clay segregations. This is a texture similar in many ways to the hydroboracites of South American salars and the Kramer deposit in the USA. Borax crystals in the lower portions of the lower borate unit in Kirka show zigzag tops mantled by clay, while borax layers in the upper parts of the same unit show erosional tops. The same textural transition from zig-zag to truncation is seen in meromictic gypsum lakes as the depositional surface aggrades across the zone of saturation in a permanently subaqueous brine lake (Warren, 2016; Chapter 2). The nodular Turkish borate ore of the playa margin is more enigmatic; it may be an early diagenetic playa mudflat precipitate, or it may be an early alteration halo created by centripetal flushing of the borax core by shallow subsurface waters. These same early pore brines that are laterally fractionating the mudflat borates are also driving clay mineral alteration of the volcanic hosts. This creates classic bull’s distributions in the authigenic zeolites. The ultimate products are analcime, and searlesite and processes involved in their formation are discussed in Chapter 12 in Warren (2016).

Initial volcanogenic waters that fed the alkaline perennial saline lake(s) were low in Cl and SO4, and high in boron and Ca, with subordinate Na. Boron isotope data from the Turkish deposits are consistent with colemanite being precipitated from a more acidic brine than ulexite, with borax being precipitated from a brine that was more basic (Helvaci, 1995; Palmer and Helvaci, 1995, 1997). Borax precipitation and replacement to create ore grade beds typically occurred in a laminated gypsiferous glauberitic host, either syndepositionally or in very early burial, perhaps in or immediately beneath stratified brines, where solar-derived brines mixed with upwelling boron-rich hydrothermal solutions. With further burial, the anhydritisation of gypsum began at depths that were less than 250m. At the same time, anhydrite can replace some of the earlier formed more reactive borates (priceite, bakerite and howlite), along with associated celestite precipitation. Subsequent uplift and exposure of some parts of the sequence has rehydrated nearsurface anhydrite to secondary gypsum and partially transformed priceite and howlite into secondary calcite.

**South American Borates**

In South America, there are over 40 borate deposits located along an 885 km trend in the high Andes near the shared borders of Argentina, Bolivia, Chile and Peru, of which at least 14 are currently in production (Figure 4). This is an arid segment of the Andean tectonic-volcanic belt, characterized by compressional tectonics and many closed basins with playas, or salt flats, called salars (Figure 4). For many years (1852-1967), Chile was a significant producer of borates, but the industry gradually shifted to adjacent areas of Argentina. As in Turkey, the Andean borate province sits atop a major plate-suture zone. Most Quaternary borate occurrences are small aprons or cones of borax and ulexite near vol-
canic vents, with reserves measured in thousands of tonnes (Garrett, 1998). But in the drainage sumps of larger endorheic basins, where volcanogenic brines can pond and concentrate, there are beds of ulexite, borax and inyoite in modern and ancient salars ranging up to hundreds of square kilometres in area, with reserves measured in millions to tens of millions of tonnes (Figure 9). They occupy groundwater sumps formed under arid to hyperarid conditions that have prevailed in most of the Andean intermontane lows since the Miocene where even today appropriate sumps continue to focus borate precipitates (Streck et al., 2007; Ovejero-Toledo et al., 2009).

Two main textures typify the South American borate salts, both modern and ancient; 1) Nodular borate locally known as “papas” (potato or cotton-tail borate), and 2) Bedded borates usually interbedded and intermixed with lacustrine muds and locally known as “barras o bancos” (meaning beds or banks). Nodules are the preferred texture to mine as they tend to create a purer product when cleaned and air dried (can be > 28% B₂O₃; Garrett, 1998).

Extraction from modern and Quaternary salar targets ulexite or brine, while ancient (Miocene) ore is dominated by borax or tincal (Figures 9, 10). In the Argentinian Andes the principal ancient borate reserves mostly occur in the Late Tertiary Pastos Grandes Basin, within the 1500-m-thick Neogene volcaniclastic and lacustrine stratigraphic unit known as the Sijes Formations (Figure 10). There were three significant borate pulses during deposition of the Miocene Sijes Formation. These pulses are easily identifiable in the central part of the basin but become indistinct and tend to thin out toward the edges (Helvaci and Alonso, 2000). Along its approximately 30 km outcrop belt, the Sijes Formation is characterized by a string of variably overlapping borate lenses, but not one continuous borate bed. Borate-bearing members of the Sijes formation from the base to top are as follows: Monte Amarillo (Figures 10b, 11; mostly hydroboracite), Monte Verde (colemanite-inyoite) and Esperanza (colemanite). The Tincalayu and Loma Blanca areas are important regions of these older borate salt units (typified by borax (hydroboracite) beds).

Quaternary salar deposits of South America consist of beds and nodules of ulexite with some borax or inyoite along with fracture-fed hydrothermal spring salts (Figure 9). Quaternary-age borate spring deposits are better developed in South America than anywhere else in the world. These deposits consist of cones and aprons of ulexite and, in one case, borax built up around vents from which warm to cool waters and gas are still issuing in some cases. Most deposits are associated with calcareous tuff which occurs as a late-stage capping over the borates, and sometimes with halite and gypsum as well. Recent volcanic activity is indicated by basaltic to rhyolitic flows in adjacent areas, as are hydrothermal waters driven by volcanism; both are likely sources for the boron. Older rocks in the vicinity of the deposits range from Precambrian to Tertiary and appear to have no genetic relationship to the deposits.

Typically, ancient South American salars with substantial borates have a central zone, consisting of a relatively thick halite, surrounded by a thinner marginal sulphate zone consisting of a variety of sulphate minerals, as well as variable amounts of halite, ulexite and other borates (Figure 9a; Ericksen, 1993; Helvaci and Alonso, 2000). Salars that are filled mostly with gypsum lack this zonation. The borate zoning may be symmetrical (bull’s-eye pattern) with sulphate surrounding a central halite core, or asymmetrical with the halite zone crowded against one side of the salar (Figure 9). This is also the situation in modern Salar de Atacama where tectonic tilting has displaced the lowest part of the brine sink to the southern end of the playa. Both the halite and sulphate zones are typically underlain by gypsum and this in turn by siliciclastics. Alternating arid and pluvial climatic episodes in the Andes since the mid-Miocene, means the playas are filled by alternating salt beds and siliciclastics (Warren, 2016; Chapter 3).
Most Neogene borate-rich salar deposits in South America have undergone relatively minor deformation since they were first emplaced. As a result, borates are extracted from several open pit operations in the Andean Altiplano (Alonso, 1991). Borax Argentina, a member of the Rio Tinto Borax Group, extracts sodium borate ores at its Tincalayu Mine, high in the Argentinian Andes Mountains (Figure 10; altitude of 4100 metres). Nearby, hydroboracite is extracted at Sijes, and ulexite from two modern dry lakebeds, Salar Cauchari and Salar Diablillos, all in the Salta province. Initially developed in 1976, Tincalayu is now Argentina’s largest open-pit operation measuring more than 1.5 km (1 mile) across and 100 m (330 ft) deep and extracts ore at a rate of 100,000 tons per year (Figure 10).

In Bolivia, ulexite is also extracted in relatively small volumes from the Salar de Uyuni. In Chile, borates are extracted from Salar de Surire; the largest Quaternary ulexite deposit in the world, with reserves reported to be ≈ 1.5 million tonnes of 35% boron oxide. The salar is located some 4,250 metres above sealevel and within the borders of the Monumento Natural de Surire national park of Chile.

Borate salts occurrences in South America are variously described as depositional or diagenetic, or perhaps syndepositional replacements of gypsum. Across the Neogene borate deposits in the Andes, the dominant portion of bedded hydroboracite is thought to be a primary precipitate in the Sijes Formation (Miocene, central Andes, NW Argentina), which is the primary exploited Neogene ore target (Orti and Alonso, 2000) and in total this region encompasses the largest known hydroboracite accumulation in the world. At outcrop, sulphate minerals in the Sijes Fm, are mostly secondary gypsum and minor anhydrite, while the borate minerals are hydroboracite with subordinate inyoite and colemanite, and some ulexite. Regionally, the Sijes Formation (Miocene) has four members; three of them are fine-grained siliciclastic, tuffaceous, and chemical-evaporitic in nature (the Monte Amarillo Member, the Monte Verde Member, and the Esperanza Member), while the other member is dominantly a coarse-grained siliciclastic (the Conglomerate Member). The overlying Blanca Lila Formation (Pleistocene) is made up of claystone and evaporites (including borates). Much of the exploitable hydroboracite resides in the Monte Amarillo member.

The Monte Amarillo Member accumulated in two coeval, shallow lacustrine Miocene subbasins (Figure 9a; Orti and Alonso, 2000): 1) The Monte Amarillo hydroboracite subbasin, and 2) The Santa Rosa hydroboracite subbasin. In them, both vertical and lateral zoning is observed: gypsum is preferentially accumulated in the lower and upper parts of the vertical succession and the marginal portions of the borate units; hydroboracite preferentially accumulated in the middle of the successions and the core of the borate unit; mixed gypsum-hydroboracite layers characterize the intermediate zones.

The Monte Amarillo hydroboracite subbasin encompasses the borate districts to the south of the Sijes village and is an area where hydroboracite has been mined since 1985. This district is located at an altitude of 3900 m and lies near the paleogeographic centre of the Monte Amarillo subbasin. The Santa Rosa hydroboracite subbasin includes the borate districts to the north of the Sijes village and is located at an altitude of
3900 m. This subbasin occupies a marginal position with respect to the Monte Amarillo subbasin. In these subbasins, the hydroboracite layers are fine-grained, light brown, and difficult to break with a hammer. Because of these characteristics, they had for a long time been confused with limestones. In both subbasins, gypsum accumulated in the margins and the hydroboracite in the centres, the intermediate zones being characterized by mixed gypsum hydroboracite layers.

The type section of the Monte Amarillo Member is 317 m thick, contains an inyoite unit 36 m thick at the base, which is overlain by a hydroboracite unit 137 m thick (Figure 9b; Alonso, 1986). This hydroboracite unit has variable amounts of inyoite and ulexite. Gypsum layers are ubiquitous in the Monte Amarillo Member. Samples of two tuff levels located close to the base and at the top of this section were dated as 6.81 ± 0.18 and 6.25 ± 0.15 Ma, respectively, which indicates a depositional period of about 630,000 years for the Monte Amarillo Member during the Upper Miocene (Alonso, 1986).

Alternations between gypsum and hydroboracite laminae are present in the transition from gypsum units to hydroboracite units in the Monte Amarillo member and contain fabrics that indicate both the borates and the gypsum-anhydrite were primary or syndepositional precipitates. Fine-grained hydro-boracite matrix commonly cements and partly replaces the precursor gypsarenite crystals in the gypsum laminae (Figures 11, 12; Orti and Alonso, 2000; Helvaci et al., 2012). In addition, micronodules of hydroboracite can displace or replace gypsum laminae. Two styles of pseudomorphs after interstitially grown (precursor) gypsum are preserved at the mm-scale in hydroboracite laminae. Type I corresponds to hydroboracite pseudomorphs after euhedral, lenticular or tabular gypsum crystals. Many of these pseudomorphs are thin, curved, lenticular or slightly deformed, and now composed of fine-grained hydroboracite crystals. Others are made up of parallel prisms of hydroboracite that project inward from the boundaries of the pseudomorph with the centre commonly occupied by secondary gypsum bearing anhydrite relics (Figure 11).

Figure 11. Tincalayu Open Pit, Argentina

Figure 12. Syndepositional formation of hydroboracite pseudomorphs after gypsum in primary hydroboracite successions composed of alternating cm-scale beds of hydroboracite and gypsum precipitates. Most of the hydroboracite is primary, not secondary (after Orti and Alonso, 2000).
Presumably, in these mixed pseudomorphs, the anhydrite replacement also took place in a soft matrix under synsedimentary conditions. Flow deformation of the pseudomorphs that are formed by fine-grained hydroboracite suggest a primary origin for these alternations in which precipitating conditions oscillated from gypsum to hydroboracite. Hydroboracite matrix appears to have precipitated interstitially within the open fabric of the (precursor) gypsarenite under synsedimentary conditions (Orti and Alonso, 2000; Helvaci et al., 2012). This precipitation, together with associated partial replacement of (precursor) gypsum crystals, occurred during the sedimentation of the overlying hydroboracite lamina (Figure 11). In the hydroboracite laminae, type I pseudomorphs seem to correspond to (precursor) gypsum crystals that grew interstitially in the hydroboracite matrix when the borate concentration of the brine was relatively low. It appears that these crystals were very soon (syndepositionally) replaced by hydroboracite matrix.

Flow deformation of the pseudomorphs that are formed by fine-grained hydroboracite occurs between flat laminae suggesting that the replacement process took place in a soft matrix under synsedimentary conditions. However, when this replacement occurred as a growth of prisms along the gypsum cleavage planes, the pseudomorphs remained undeformed and consistent. In general, this mechanism was less penetrative, and many pseudomorphs had a mixed hydroboracite–gypsum composition. Presumably, in these mixed pseudomorphs, the anhydrite replacement of the gypsum postdates the partial hydroboracite replacement. These pseudomorphs changed to hydroboracite–anhydrite during burial, and to hydroboracite–secondary gypsum in the final exhumation. Type II pseudomorphs seem to correspond to (precursor) gypsum crystals that grew interstitially toward the tops of the hydroboracite laminae during precipitation of the overlying gypsarenite layer, once again a syndepositional diagenetic process.

**North American borates**

The United States is the world’s largest producer of boron compounds and the second-largest producer of borate ore, with California’s largest open-pit mine working the Kramer deposit and supplying almost half of the world’s borate needs (Figure 14). Historically, other US producers exploited saline brines and bedded playa deposits, such as Searles Lake in California (Smith, 1979) and the much smaller conventionally mined deposits in the nearby Death Valley area (Kisler and Smith, 1983). An excellent history of the Californian borate industry is given by Beeby (2002).

**Kramer deposit, Boron USA**

The Kramer deposit (aka Boron deposit) is vast and located near Boron, California, in the Mojave Desert, some 140 km north northeast of Los Angeles and midway between the towns of Barstow and Mojave (Figure 14). The total borate area (including the ulexite and colemanite rims) is 8 km (east-west) by 1.6 km (north-south). The deposit within this area is about 1,600 m long, 800 m wide by 100 m thick, and consists of a central lenticular mass of borax/kernite with interbedded mottormillonite-smectite clay (Figure 14a). Borate ore reserves exceed 100 Mt (110 million st). The original borax target was 45-305 metres deep and dipped 10-15° to the south. The deposit was discovered in 1913 and was developed as an underground operation during the 1920s. It was converted to an
The age of the deposit is 19 ± 0.7 Ma, and it defines a small sub-basin in a much larger Tertiary lacustrine basin. It is encased in arkosic sands, silts and minor volcanics and limestones. Sedimentation in the basin was interrupted by flows of acidic lava (olivine basalt to latite) known as the Saddleback Basalt, it constitutes the base to the borate ore zone. It also interfingers with other sediments of the basin fill (Figure 14a, c). The upper part of the basalt in the mine area has fractures filled with ulexite and searlesite and its contact with the overlying sediments is defined by an “apple green” siliceous shale that contains ostracod carapaces. The color of the shale reflects its creation by the basalt reacting with lake waters.

Barnard and Kisler (1966) defined the sedimentology of borate beds above the Saddleback Basalt (Figure 14a). First is a 7.6-15 m thick footwall shale, further divisible into an initial barren (≈3.7m) shale and then a ulexite zone. This is a layer of greenish-grey at times black fissile shale that is thinly laminated, micaceous and at times contorted. Locally it encloses lenses of arkosic sandstone and coarse conglomerate. Above this are the borax beds interbedded with clay and shale along with some beds and lenses of tuff, arkosic sand and conglomerate (Figure 15). The low permeability of these lacustrine shales is thought to have helped preserve the borax by preventing entry of groundwaters. Laterally and vertically away from the deposit’s borax/kernite core, the borate facies changes to ulexite and colemanite, and the levels of shale interbeds and clay impurities in the borates become more significant (Bowser and Dickson, 1966).

The deposit is believed to have formed in a shallow Mid-Miocene saline lake, fed by Na- and B-rich thermal springs, a response to the later stages of volcanism. Saline sodium-borate-bearing thermal spring waters, being denser, sank to the lake bottom, cooled, and precipitated bottom-nucleated growth-aligned borax as they cooled (Figure 15 a). Brine depths at the time the borax was crystallising were likely relatively shallow as single crystals contain many alterations of inclusion-rich and inclusion-poor microlaminae, indicative of rapid temperature changes in the bottom brine (Figure 15b). As discussed in detail in Chapter 2 of Warren (2016) such bottom brine temperature changes indicate brine depths of more than a few tens of centimetres to metres. The tops of some growth-aligned borax beds are truncated likely indicating a freshening episode in the salinities of the bottom brine, once again indicative of shallow to ephemeral bottom waters (Figure 15c). The lack of evidence of subaerial exposure in the laminated clay beds between the borax layers implies bottom brines were likely anoxic, as well as hypersaline.

The original Kramer brine lake position in the regional drainage basin was controlled by faulting contemporaneous with the accumulation of the borax. Continued fault movement, associated with the middle Pliocene uplift of the Mojave Block, later tilted and subsided the lake sediments,
which are now buried by more than 760 m of late Miocene and Pliocene arkosic sediment.

Older models argue that deeply buried portions of the borax deposit were altered, via water loss, to kernite at this time. Renewed movement in late Pliocene–Pleistocene uplifted the deposit and drove some erosion of the original borate so that the outer portions of the kernite facies were rehydrated at that time. The deposit was then covered by 9 to 21 m of Pleistocene and Recent sands and gravels (Barnard and Kistler, 1966, Siefke, 1991).

Death Valley Borates

As well as 19 Ma Kramer deposit, across the Death Valley area, borates were also deposited some 6 Ma, and there are more than 23 known deposits in the Death Valley region (Figure 16; Garrett, 1998). In all, the borate ore is contained in the lower 150 m of the 2,100 m thick Pliocene Furnace Creek Formation. The interiors of most of the Death Valley ore deposits preserve unaltered bedding planes and uniform depositional patterns. There are few to no indicators of syndepositional alteration (slumps, pseudomorphs) in the centres of the deposits but considerable evidence for alteration and replacement about the deposit’s edges. The agglomerated nodular structure composed of masses of acicular crystals in much of the initially exploited ore meant that early miners in Death Valley area described the various exposures of borate ore as cotton ball or cotton-tail (like the fluffy tail of a cottontail rabbit). Regionally a series of projected shoreline features can be traced from the Billie to the Boraxo to the Sigma-White Monster mines, and residues of ancient geothermal spring mantle deposits are locally present (Garrett, 1998).

One of the largest deposits in the Death Valley area was the Billie orebody (an underground mine, now abandoned), a 1,100 m long lens of ulexite, proberite and colemanite, interbedded and surrounded by limey laminated lacustrine mudstone and shale. Fault activity controlled the position of the lake-bed borates, and some beds now have local dips of upwards of 45°. The Billie orebody has an average thickness of 45 - 55 m, a width of 220 m, and a regional dip of 20-30° toward the southeast. Reserves were of the order of 2,700,000 metric tons of ulexite-proberite at 27% B₂O₃ and 11,000,000 metric tons of colemanite at 21% B₂O₃ (Garrett, 1998).

Shales of the Furnace Creek Formation host the borate ore zone at Billie Creek. The deposit is made up of stacked metre-scale units of nodular borate, mainly colemanite, interbedded with laminated mudstones deposited in a saline lacustrine environment during extension of the basin.
The hosting laminites lack features of syndepositional exposure or wave-reworked deposition, indicating that the borate-hosting sediment first accumulated on the floor of a density-stratified perennial lake (Tan-ner, 2002). The presence of interbedded sulphate minerals in this facies suggests that salinity in this lake was elevated. Metre-scale mounds of porous limestone with a clotted-micritic fabric define spring-apron tufas that formed where groundwater discharged along fault-fed outflows about the edge of a more saline water mass.

The exploited massive borate facies in the various Death Valley deposits are made up of thick, massive borate layers, locally containing host rock clasts with sharp to diffuse boundaries (Figure 16). Borate formation first took place at or below the sediment/water interface. The composition of the borate deposits in Death Valley varies from mainly colemanite to zoned accumulations, with colemanite surrounding a core of probertite and ulexite.

Before the 1960s, many older models for the formation of colemanite in the Kramer and Death Valley deposits argue for burial (thermal) replacement of ulexite and inyoite via flushing by “intruding warm borax solutions.” High Ca/Na ratios favoured primary deposition of hydrated Ca-borates, which early workers argued were subsequently transformed by diagenetic dehydration to colemanite (Foshag, 1921; Christ and Garrels, 1959). This meant the gradual depletion of Ca and decreasing Ca/Na ratios in the mother brine resulted in Na-Ca-borate precipitation, while any renewed onset of elevated Ca/Na ratios again caused Ca-borate deposition.

But these older burial/thermal fluid models never clearly addressed a number of textural and conceptual problems (Garrett, 2001), namely: 1) Where did these conversion liquors come from? 2) How did they maintain their chemical uniformity? 3) How did they totally and completely pervade and replace what where impermeable salt units? 4) What was the required voluminous Ca source needed to accomplish the transformation? 5) Where did the residual brine go? In addition, why are there no widespread disruption texture and slumps structures both within and above the bedded salts and why are commonplace colemanite alteration minerals like priceite, ginatorite, nobiletite and gowerite, absent?

A similar set of problems beset the notion that the dehydration of borax to kernite indicates a deep-burial conversion process. The quandary as to deposition versus burial replacement for the Kramer deposit is yet to be resolved to the satisfaction of all. But, given the widespread preservation of depositional features in the Kramer and Death Valley deposits, the primary nature of the various less compacted borate salt beds in Turkish deposits as likely analogues, syndepositional controls for the Kramer and Death Valley deposits are favoured. This argument implies cotton-tail colemanite, for example, forms in the capillary zone of a saline lacustrine mudflat, with inyoite accumulating in the more saline perennial centre of the sump (e.g., Figure 8).

**Searles Lake, California**

Searles Lake in southeastern California is located in the lower central portion of a small block-faulted desert valley with a drainage area of 1600 km² and located midway between Boron and Death Valley (Figure 17). It is a likely Pleistocene counterpart to the lacustrine evaporites that entrain the exploited Neogene deposits of Boron and Death Valley. The central pan, some 103 km² in extent, overlies a crystalline mush of mixed salts dominated by sodium carbonates, but also with borax, clays, and hypersaline interstitial brines. The brine recovery operation is a multi-component chemical system, and borax is only one of the products recovered; others include sodium sulphate, lithium compounds, potash, bromine and other salts. Boron was supplied to the lake via thermal springs along the Sierra Nevada frontal faults in Long and Owens Valleys (Smith, 1979).

There are two main solution-mined salt horizons beneath the central pan: the “upper salt,” some 9 to 27 m thick (averaging 15 m), with a brine content averaging 1.0% B₂O₃; and the “lower salt,” some 8 to 14 m thick, (averaging 12 m), with a brine content averaging 1.2% B₂O₃. The upper salt is overlain by a surficial mud and salt-crust unit some 7 to 9 m thick. It is separated from the lower salt by 3 to 6 m (average 4 m), of relatively impervious clays called the “parting muds” (Figure 18). The upper two salt beds accumulated in the period 3.5–40 Ka. There is also a much deeper salt bed with mineralogy dominated by trona-nahcolite-halite with lesser amounts of burkeite-thenardite.
The salt mush in both the upper and lower salt beds is quite porous (0.35 - 0.40), and the stored brine is pumped via a series of wells into adjacent saltworks where borate, sodium bicarbonate and sodium sulphate salts are recovered. A constant resupply of brine to the mush beds is maintained by natural recharge and percolation of dilute refinery effluent, which is pumped back into the mush beds. The two salt horizons are pumped separately as they differ somewhat in chemical makeup and therefore require different plant treatments. Historically, until 1979, the upper salt was the solution-mining target, since then the lower salt has been mined as a trona target and processed using carbonation (see Warren, 2016, Chapter 12 for detail).

Other borate deposits

Borates in China are found in many salt lakes on the Qinghai-Xizang (Tibet) Plateau, in cold arid conditions in lakes such as Zhacang Caka and Zabuye Caka. These lakes were the original suppliers of borate salts to Medieval Europe. Typical lake waters contain 85 mg/l of boron oxide and are co-associated with elevated lithium levels (Sun and Li, 1993; Zheng and Liu, 2009). The maximum value of boron oxide in such lake brines is around 1,500 mg/l.

However, today the largest economic borate reserves supplying the Chinese borate market occur not in Quaternary/Tertiary saline lakes but in Precambrian meta-evaporitic borosilicate deposits in Liaoning Province. Reported reserves are 44 million tonnes of boromagnesite with 8.4% boron oxide content. Deposits in the Liaoning Province represent 64% of the country’s total boron resources, and 90% of these deposits are associated with banded iron formations. Some 112 separate borosilicate deposits occur in the Liaoning area on the Liaoning Peninsula in northeast China (12 contain 98% of the known reserves). The main ore mineral is szaibelyite (aka ascharite), along with ludwigite, with some suanite (Table 1). All are Mg-borate minerals and are hosted along with magnesite and magnetite in fractured marbles. Deposits are thought to be meta-evaporitic skarns, deposited initially as lacustrine borates interbedded with volcanic tuffs.

Figure 17. Searles lake, California, showing that it is a endorheic basin in the Basin and Range of the USA.

Figure 18. Searles Lake, California showing isopach of the “Upper Salt” in feet as well the stratigraphy of the three salt layers and intervening clays (after Smith, 1979). Note the change in scale in the vertical section at around 50 metres.
The world’s only exploited marine borate deposit is in the Inder district of Kazakhstan (former USSR), north of the Caspian Sea. Now-depleted mined borates formed bedded lenses up to 3 metres thick and hosted in the gypsiferous caprock in the 100+ km² crest of a large Permian salt dome. Ores are magnesian borates, rather than the more commonplace sodium-calcic borates typically found in modern continental salars and playas. Mineralization is centred on fractures near the top of the dome, where borates have precipitated in a matrix of gypsum, clay and anhydrite. The fluids precipitating borate are thought to be derived from geothermal springs (Garrett, 1998). Boron is also periodically extracted from the brines of nearby Lake Inder. This salt lake has a metre-thick surface salt crust, underlain by some 30m of brine-saturated salt, which contains potassium chlorides and bromides as well as borax (Kistler and Smith, 1983). Unlike the other economic borate deposits of the world, this deposit is sourced by dissolving Permian marine salts, hence the association with the magnesian salts, and is not tied to volcanism.

Inder’s marine origin is evident in its boron isotope signature, which is much more enriched in $^{11}$B than nonmarine borate sediments (Figures 19; Swihart et al., 1986). The clear separation of nonmarine and marine borate salts using boron isotopes is also used to define parentage of various meta-evaporitic tourmalines in the meta-evaporites of Liaoning, China. Isotope analysis is a useful technique for determining boron source long after the original salts have evolved into lattice components of high temperature and high-pressure metamorphic minerals (Warren, 2016; Chapter 2).

Borate minerals do occur in marine evaporites other than the Inder deposit but are not known in sufficient amounts to be economic targets. For example, potash ore processing of the Zechstein potash ores in Germany has led to borate-halite saline lake (Miocene, Emet Basin, Turkey): Chemical Geochemistry of Ore Deposits, v. 51, p. 179-196.


