

Borax, Boric acid, and Boron—From exotic to commodity

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Since old times borax has been an important raw material used particularly in the metal and ceramic industries first for soldering and brazing, second as a flux to give certain glazes an appropriate fusibility. Here, we provide the historical background that led to the understanding of the nature and composition of boron compounds, isolation of the element, and establishment of a flourishing industry with an overall annual world output of more than 4.5 million tons of ore.

Boron compounds may have been known for about 6000 years, starting with the Babylonians. The Egyptians, Chinese, Tibetans and Arabians are reported to have used such materials. The Arabic word for borax *baurach*, which also represents a number of other minerals, is found in old manuscripts from Persia and Arabia. Specimens of Chinese pottery utilizing colourful borax glazes made in third century exist today. Tincal, the mineral name for borax decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), derives from tincana, the Sanskrit word for borax. The element boron was not discovered until 1808 when Humphry Davy (1778-1819), Joseph-Louis Gay-Lussac (1778-1850) and Louis-Jacques Thénard (1777-1857) prepared it independently by reducing boron trioxide with potassium and by electrolysis of moistened boric acid. The purity of their products was about 50%. Highly pure boron (~100 %) was not prepared until 1909.

Boric acid deposits were discovered by 1772 in Italy, and about 1836 borates were discovered in Chile and Argentina. These deposits quickly became the major source of borates until the twentieth century when the huge fields discovered in the Nevada and California superseded them.

Borax and boric acid

It is presumed that the Babylonians brought borax from the Far East more than four thousand years ago to be used by the goldsmiths. Archeological evidence shows that tinkar (tincal) was first used in the eighth century around Mecca and Medina, having been brought there (and to China) by Arab traders. The use of borax flux by European goldsmiths dates to about the twelfth century¹. According to Travis² among the medical prescriptions recorded in the Coptic Papyrus,

(dated about the tenth century CE and containing information from Greek and Arabic sources) there are some related to the treatment of eye diseases, which contain borax among their ingredients.

Already Jean-Antoine Chaptal (1756-1832) in his book about chemistry applied to industry³, generalizes without further analysis the names of materials available in different civilizations which he feels is borax, and says: “Le nitron baurake des Grecs, le borith des Hébreux, le baurach des Arabes, le boreck des Persans, le burach des Turcs, le borax des Latins, paroissent exprimer une seule et unique substance, le borate de soude des chimistes” (The nitron baurak of the Greeks, the borith of the Hebrews, the baurack of the Arabians, the boreck of the Persians, the burack of the Turks, the borax of the Latins, all appear to express one and the same substance, the borate of soda). The word *borith* appears in early translations of the Bible, along with other substances like nether, but it is clear that it refers to a cleaning material derived from plants.

For nearly a thousand years prior to the nineteenth century, borax trade was very small, its main use being as a flux in metalworking. It was expensive and this confined it largely to gold and silver smiths, and to jewellers².

Georgius Agricola (1494-1555), in his *De Natura Fossilium*⁴ writes: “Native nitrum is found in the earth or on the surface... It is from this variety that the Venetians make chrysocolla, which I call borax... The second variety of artificial nitrum is made at the present day from the native nitrum, called by the Arabs tinkar, but I call it usually by the Greek name chrysocolla (chrysos = gold; colla = solder). Later on, in his *De Re Metallica*⁵, he mentions borax, usually attached to the word chrysocolla and gives the

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following description of its manufacture: "Native as well as manufactured nitrum is mixed in vats with urine and boiled in the same cauldrons; the decoction is poured into vats in which are copper wires, and, adhering to them, it hardens and becomes chrysocola, which the Moors call borax". According to Agricola's translators, Hoover and Hoover, Agricola used the term chrysocola for borax, but he was always careful to state in every case "chrysocola made from nitrum or chrysocola which the Moors call borax"⁵. Not only that, Hoover and Hoover write that borax was certainly known to Agricola and greatly used in this time, and that his description of the manufacture displays hopeless ignorance. Agricola evidently believed that borax was an artificial product made from nitrum.

Vanoccio Biringuccio (1480-1538) in his book on metallurgy, *De la Pyrotechnica*⁶, states: "Borax is of two kinds. Natural borax is a clear fusible stone of a form like that of sugar candy or rock salt, although Pliny says that it was green and that it served not only to solder gold but also for painting...artificial borax is made from rock alum and sal ammoniac (ammonium chloride). Both kinds have the property of facilitating the melting of metal, and they unit and solder whatever they are put on." Andreas Libavius (1540-1616) described what he calls Venetian borax as made from milk, honey, crocus (yellow oxide of iron), salpêtre and alkaline lye, boiled and evaporated.

In 1640, Alonso Barba (1569? -1661), a Spanish priest in the mining area of Perú, wrote *El Arte de los Metales*⁷, mainly about gold and silver. The work was important and kept secret in Spain, but the British Ambassador, Edward Montagu, Earl of Sandwich (1625-1672), managed to get a copy and translated it in 1669. In page 17 of the original it says: "La Crisocola que llaman Atincar o Bórax, es especie del nitro artificial; hácese de orines meneados al calor del sol en almírez de cobre con mano de lo mismo, hasta que se espesa y cuaja, aunque otros lo componen de almojatre y alumbre" (Chrysocola, called atincar or borax, is an artificial sort of nitre, made of urines stirred together in the heat of the sun, in a copper pan, with a ladle of the same until it thicken and coagulate, although others make it of sal ammoniac and alum).

In 1702, Wilhelm Homberg (1652-1715) noticed that when borax was heated with green vitriol (ferrous sulphate) a new substance was obtained, which he named sedative salt (later to be known as boric acid)⁸. As described by Homberg he heated borax with a

solution of iron vitriol and sublimed off with the water vapour a substance which he called *de sel volatile narcotique du vitriol*. By redistilling the aqueous distillate eight or ten times, Homberg obtained a good yield of sedative salt⁹.

Homberg's discovery started many attempts to resolve the chemical composition of borax. According to Macquer¹⁰ George Ernst Stahl (1660-1734) showed in 1723 that sedative salt could be prepared by treating borax not only with sulphuric acid but also with other acids. Louis Lemery (1677-1743) made the same discovery five years later but thought that the acid merely combined with the borax to form the sedative salt. In 1732, Claude-Joseph Geoffroy (Geoffroy jeune) (1685-1752) showed that borax has the same basis as Glauber's salt and soda and described the resulting green flame when a solution of sedative salt in alcohol was ignited, thus establishing what has ever since been a field test for borax and borate minerals. The mineral sample is treated with sulphuric acid and alcohol; if a borate is present boric acid is formed *in situ* and the alcohol burns with a green flame. Louis Claude Bourdelin (1621-1699) believed that the green colour was caused by the presence of copper in the sedative salt, but in spite of many trials, he was unable to detect the metal⁹.

Up to the eighteenth century, borax was still believed by some to be an artificial material. Caspar Neumann (1648-1715) wrote that "Borax is a saline substance, for which neither the origin nor the component parts are as yet known. It comes from the East Indies in little crystalline masses...The refining of borax was formerly practiced only at Venice, and hence the refined borax was called Venetian, but the Dutch are now the only masters of this manufacture. Serapio calls the rough borax that comes from the Indies tincar; and the dealers in this commodity still distinguish it by the name tincar or tincal, never calling it borax till it is refined." Chaptal³ indicates that the passing of the control to the Dutch was due to the long war the Turks had with Persia; this disrupted the commerce with the Orient, which was dominated by the Venetians.

Hubert Franz Höfer, a chemist at the court of the Duke of Tuscany, first discovered natural boric acid in a boiling hot spring in Tuscany in 1778. Höfer analyzed the water from the hot spring at Monte Rotondo, in the Maremma area of Tuscany, and found it to contain 36 to 72 grains of sedative salt per pound (which he detected by the green flame test) depending

on the season of the year^{9,11}. This finding led to the belief that this was the natural product from which borax was derived and borax was perhaps, after all, an artificial product made from it by some secret process in the Far East or one still being guarded by the Dutch refiners².

In February 1779, Paolo Mascagni (1755-1815) discovered solid boric acid (sassolite) at the lagoni of Montecerboli and Castelnuovo. In a paper published 20 years later he wrote that "if the lagoni are visited long after a rain, the ground is seen to be entirely covered with varying amounts of inflorescences and saline masses¹²". These masses contained boric acid, ammonium borate, sulphates of iron and calcium and, occasionally, magnesium sulphate⁹.

The first stony material found to contain boric acid was one, which Georg Segismund Oton Lasius (1752-1833) described as a cubic quartz from Lüneburg, Hanover¹³. It is known as boracite, $6\text{MgO} \cdot \text{MgCl}_2 \cdot 8\text{B}_2\text{O}_3$. Boracite was analyzed by Johann Friedrich Westrumb (1751-1819) and found to contain magnesia, silica, alumina, iron, and about 60 per cent of sedative salt^{9,14}.

Although, it had been observed for centuries that tincal came from the East, the places and methods by which it was produced remained a carefully guarded secret by those involved in producing borax². Up to the eighteenth century Europe imported crude borax (tincal) from India, China, Ceylon, Persia, Perú, and Tartary in the form of small crystals, which would efflorescence in contact with air, by losing part of their crystallization water. In order to avoid this alteration, which reflected in a loss of weight, the natives coated the crystals with a layer of fatty material that protected them completely. Most of tincal came from Tibet, from a series of Himalayan lakes (Teschu-Lumbu) located at an altitude of 4,000-4,500 meter. The crude borax crystals from Tibetan lakes were transported in bags tied to sheep, which were driven by caravan over the Himalayas to the north of India. From there it reached Calcutta where Arabian, and afterwards European, traders picked it up. In 1787, William Blane gave the following description of the situation: "This saline substance, called in the language of the country *swagah*, is brought into Hindustan from the mountains of Tibet, produced in the kingdom of Jumlate; there in the high mountains there is a hot lake. The water of the lake is put in small reservoirs and let to evaporate into a cake of crude borax. The borax is transported by goats

down to the plains where the material is purified by boiling and crystallization."¹⁵

The protective coating meant that borax had to be purified before its use. The pertinent procedure had been developed by the Venetians and kept secret for many years. By the end of the seventeenth century the Dutch had acquired both the secret of the source of tincal and knowledge of the refining process, so that in a relatively short time Amsterdam had replaced Venice as the center of borax production and monopoly. The Dutch maintained monopoly and secrecy for about one hundred years, although by the middle of the eighteenth century the East Indies and Persia were vaguely specified as sources of tincal. In his book on applied chemistry Chaptal³ reports his experiments on purification of borax; although he was able to remove the fatty coating by calcinations and dissolution, the losses were too large to make the process commercial. The Dutch secrets were eventually revealed by Jacques-Christophe Valmont-de-Bomare (1731-1807) who had visited the Dutch workshops and published the tincal secret in his *Dictionnaire Raisonné Universel d'Histoire Naturelle*¹⁶. According to Anselme Payen (1795-1871), it was the Lécuyer brothers who brought tincal refining to France in 1786.

In 1802, Louis Nicolas Vauquelin¹⁷ (1763-1829) demonstrated that the fatty material that covers tincal could be saponified with caustic soda, and this was the reason why it did not separate by cold or hot dissolution. Treating the material with limewater could separate the fatty material. In 1818, Pierre Jean Robiquet (1780-1840) and Marchand, a chemicals merchant, gave more details^{18,19} about the process and described the material isolated as "une huile consistante d'un brun rouge, d'un saveur rance, très acre...conserve un caractère d'acidité...cette matière grasse...entraîne une certaine quantité de acide borique" (a thick red-brown oil, of rancid taste, very acrid...it has an acid character...and entrains a certain amount of boric acid). They also wrote that they believed that the fatty material was a kind of natural bitumen.

Jacques-François Demachy (1708-1803) was one of the first to give a description of the process used by the Dutch to purify borax. In his book *L'Art du Distillateur d'Eaux-Fortes*²⁰ he wrote that he had learned the details from someone who had visited the Dutch factories. The basic problems were related to obtaining crystals of the proper size and colour. The

Dutch were able to produce large size crystals, which were considered to represent high purity. Less effective refining gave small crystals with a yellow colour imparted by the grease with which the tincal was covered. According to Demachy, the clarification of the hot solution of borax is performed with the “aid of the white of an egg or its equivalent of slaked lime and slate” and slow cooling in copper pots, results in large crystals with the bluish colour “which, in the borax business, is always good to find”².

The secrecy regarding the purification of borax is described very picturesquely by Pierre-Joseph Macquer (1718-1784) in his *Dictionnaire de Chymie*²¹: “We are far from knowing as much concerning borax as is desirable. We are even ignorant of its origin, which might supply the want of a perfect analysis, and light to the nature of this saline substance. As borax is not found in Europe, it is brought from the East Indies in a state that only requires a slight purification, which is given to it by the Dutch and Venetians who are the chief merchants of it. But is not yet known whether this matter be a natural or an artificial substance, not whence, nor how it is obtained. Our ignorance concerning borax is certainly owing to the interest, which they who make a lucrative commerce of it, have to keep everything concerning its origin secret”.

Macquer also gave a detailed description of what was then known about borax: “Borax is a saline matter, with the properties of a neutral salt. When exposed to fire, it first undergoes liquefaction occasioned by the water of crystallization, and is then calcined. If the fire is increased to a melting heat, the borax is pretty easily fused and is converted into a vitreous matter, or saline glass, and when it is mixed with earths of any kind, it acts as a flux, and converts them into more or less transparent glasses according to their nature, Borax is decomposed by sulphuric acid, nitric acid, and hydrogen chloride, and forms the same neutral salts as those which result from the reaction of this acid with caustic soda.”

“Homberg and Lemery obtained sedative salt only by distillation or sublimation. Geoffroy has improved upon their discoveries, by showing the method of obtaining the same salt from borax acid with evaporation and crystallization only. We are also obliged to him for having first demonstrated that borax contains the basis of sea salt. This truth he has firmly established by obtaining a true Glauber’s salt by mixing vitriolic acid with a solution of borax.

Afterwards, Baron proved that sedative salt of borax may be obtained by means of vegetable acids. He also proved that sedative salt is not a combination of an alkaline matter with the acid employed to obtain it, but that it exists ready formed in borax, of which it is a principle or constituent part; that the acids employed to extract it do only disengage it from the alkali with which it is united; that this alkali is entirely similar to that of sea salt; that sedative salt may be reunited with its alkali, and again form borax; which is a complete proof that borax is nothing else than a compound of sedative salt and marine alkali.”

“Borax, when crude, is called tincal. In this state, it consists of small, yellow, glutinous crystals. It is said to be refined by limewater. Refined borax consists of large, white, eight-sided crystals, each of which is composed of small, soft, bitterish scales. It is hardly soluble in water, to which it gives a glutinous quality, and hence it is used by dyers to give a gloss to silk. It is also soluble in spirit of wine, to the flame of which it gives a green colour. By repeatedly moistening it, while it is considerably heated, it may be entirely sublimed. Borax renders all stones and earths fusible by fire, and hence is used for the assaying of ores. It also facilitates the fusion of metals, and is particularly useful when small particles of metal mixed with dirt and ashes are to be melted together as it promotes the fusion of the metal and the vitrification of the other matters. A principal use of borax is to facilitate the soldering of metals, which it does by accelerating the fusion of the surfaces of the metals to be joined, and by clearing them from any calx or other matter by which they might be prevented from being perfectly applied to each other. Borax is also used for the preparation of some fine glasses, and imitations of precious stones, because the glasses prepared by fusing it with earths are very hard, compact, bright, and very transparent; but by long exposure to air they lose much of their luster, become cloudy, and when the quantity employed has been large, even opaque.”

“Borax contains an alkali like the basis of sea salt. This alkali is not perfectly neutralized by the sedative salt, which is also contained in borax; for its alkaline properties are so perceptible as to have led some Chymists to think that borax was only an alkali of a particular kind”²¹.

After Tibet, the next significant stage was utilization of the borax present in the hot springs of Tuscany. The steam vents of Tuscany issuing from the ground, known locally as soffioni, had been

observed for centuries on the slopes of the mountains which separate the valleys of the rivers Cecina and Cornia, south of Volterra, and north of Massa Maritima. In 1818, François-Jacques Larderel (1789-1858), industrialist and merchant of French origin, moved to Tuscany, where he installed the first industrial centre for the extraction of boric acid from the waters of the Lagoons of Montecerboli. Here, geysers of water, called soffioni, fumacchi, fumarole, or mofetti, are released from the ground, at about 205°C and pressures up to 14 bar. The water contains about 0.4% of boric acid, which then crystallizes yielding up to 80% boric acid in the form of decahydrate, $H_3BO_3 \cdot 10H_2O$. These findings were not brought into commercial practice until 1820, and in doing so the Tibetan tincal trade in Europe came almost to an end. Initially, the Tuscany works utilized the local resources of wood and coal as fuel until the dwindling of the timber in the area led to such an increase in costs that the operation became too costly. Harnessing steam from the soffioni as a source of energy was an essential step in the continuing production of boric acid and borax at a cost, which could compete. Giuseppe Gazzeri (1771-1847) and an engineer by the name of Vicente Manteri, developed the first successful drilling methods, and their results were published in 1840. However, it was Larderel who first made commercial use of the technology, which enabled him to increase production ten-fold. Tuscan boric acid began to enter the European markets at the beginning of the nineteenth century. According to Travis² during the ten years 1818 to 1828 production averaged only about 75 tons annually, but thereafter it soon reached 1,000 tons, and began to make a serious impact on the Tibetan tincal trade. By 1860, annual production had reached 2,000 tons, and by the end of the century it was about 3,000 tons. Larderel's plants employed a large number of people, who were guaranteed various social benefits. The Grand Duke of Tuscany, Leopold II (1797-1870) made Larderel Count of Montecerboli to thank him for his contribution to the economy. The residential area of Larderello was thus named by the Grand Duke in 1846, in honour of the founder of the borax industry. Nacini gives a very detailed account of the history of the borax establishment in Tuscany²².

On February 14, 1873 Dennis Searles and E. M. Skillings discovered the great deposits of borax and other soluble salts in San Bernardino County, California, a discovery, which would eventually lead

to the development of the largest reserves in the world (see below).

Many attempts were made to analyze and classify borax. Hyacinthe Théodore Baron (1707-1787) showed that borax was formed by the combination of marine alkali (soda) with sedative salt. The green flame test for borax caused some further confusion. Chemists associated the green flame with copper, and thus the old confusion between borax and the copper compound chrysocholla. Louis-Claude Cadet de Gassicourt (1731-1799), who published a 50-page long paper on borax in 1766²³ believed that “le véritable acide du borax est celui du sel marin, que le acide vitriolique n’entre point dans la composition du borax, que l’acide marin uni à un terre métallique cuivreuse forme un sel particulier bien différent du sel sédatif, et enfin, que est ce sel particulier qui constitue le borax par son union avec la base du sel marin” (the true acid of borax is that of marine salt, sulphuric acid does enter in the composition of borax, marine acid combined with a cupric earth forms a particular salt very different from sedative salt, and it is this particular salt the one that constitutes borax by its union with the base of marine salt).

Chemists now gave increasing attention to the nature of sedative salt from which a whole series of neutral salts in addition to borax could be obtained with bases such as lime, magnesia, potash, ammonia and the metal oxides of zinc, cobalt, lead, etc. Antoine-Laurent Lavoisier (1743-1794) did not include it in his own researches, but he dealt with borax in his *Traité de Chimie*²⁴ as follows: “Borax is a neutral salt with excess of base consisting of soda, partly saturated with a peculiar acid, long called Homberg’s sedative salt, now the boracic acid... The boracic radical is hitherto unknown; no experiments having, as yet, been able to decompose the acid; we conclude from analogy with the other acids, that oxygen exists in its composition as the acidifying principle.” When Louis-Bernard Guyton de Morveau (1737-1816) published his *Méthode de Nomenclature Chimique*²⁵ “sel sédatif” was renamed “acide borique”².

The first borax refinery in Britain dates from 1798, when Luke Howard (1772-1864) started production, based on his own experiments, at the chemical works of Allen and Howard at Plaistow in Essex.

Borax started to be refined in France about 1805, but at the time of Jean-Baptiste-Pierre Payen (1759-1820, the father of Anselme Payen), the French

refineries could only produce small and ill-defined crystals that the commerce refused to accept, in spite of the fact that in 1815 the price of refined borax was about 7-8 francs per kilo.

Jean-Baptiste-Pierre Payen joined the borax refining business in the beginning of the 1800s. When Anselme Payen took over the family business he considered, together with Chartier, the possibility of breaking the Dutch monopoly by preparing borax by the reaction between French sodium carbonate and Tuscan boric acid, using the reaction demonstrated on a laboratory scale by Baron²⁶ in 1750 and the boric acid produced by Larderel from the Italian *soffioni*. Payen succeeded in producing two forms of sodium borate both in his research laboratory and, after scaling up the process, in his borax factory²⁷⁻²⁹. In 1828, he discovered that the reason why artificial borax was of inferior quality than refined tincal was it's being a mixture of octahedral borax (pentahydrate) and prismatic borax (decahydrate), in variable proportions. For this reason, the crystals resulting from the reaction of boric acid with soda were small and without solidity. On the other hand, pure prismatic borax crystals were voluminous and had the qualities preferred by commerce. After a decade of experimentation Payen realized that by careful control of the operating variables, in particular the temperature and density of the solutions, it was possible to guide the process to produce either type of crystals. As explained below, he found that a sodium borate solution of a density of 30°Bé, yielded pure octahedral borax between 79° and 56°, and that below 56°C prismatic borax began to be deposited on the octahedral crystals.

This discovery is quite a feat, considering that at that time there was no knowledge of phase diagrams. It constitutes another proof of Payen's superior analytical qualities.

It did not take long until Payen's factory in Grenelle started offering to the commerce crystals more beautiful than those coming from the best Dutch refineries. In order to introduce in the market, Payen had to fight the conservative attitude of the local users. His crystals were too good to be true, so it seemed "Le nouveau produit était tellement beau, que le commerce commença par le refuser. Pour obtenir qu'on acceptât le borax préparé artificiellement, M. Payen dut lui faire donner la teinte grisâtre qu'avait le borax hollandais; il dut aussi user les angles de ses cristaux par un frottement sur les cribles produisant

des effets semblables à ceux du transport; enfin il fut forcé d'imiter les emballages étrangers, c'est-à-dire d'employer des caisses en bois de Tremble ou Peuplier de Hollande, de donner à ces caisses une contenance de 60 kilogr. et de les doubler intérieurement de feuilles de papier bleu indigo" (The new product was so beautiful that initially commerce refused it. In order to have them accept the borax prepared artificially, Mr. Payen had to impart to it the grayish hue of Dutch borax; he had also to wear down the angles of the crystals by rubbing them against a sieve, thereby producing effects similar to those resulting from transport; he had even to imitate foreign packing, that is to say, boxes made of aspen or Dutch poplar, with a capacity of 60 kg, and lined with sheets of indigo paper)³⁰.

The final result was that France won a new industry and the Dutch lost their monopoly. The price of borax rapidly dropped to less than one third and by 1871 it was already below 2.50 francs per kilo³¹.

Payen described his fabrication process as follows²⁷: "We have used as raw material boric acid from Tuscany, containing between 74 to 83% acid...The preparation of crude borax involves reacting 1000 kg of boric acid with 1200 kg of crystalline sodium carbonate, in about 2000 kg of water... Once all the boric acid has been added the temperature is brought to boiling, at about 105°C, whence the solution has a specific gravity of about 21°Bé [Baumé degrees are related to the specific gravity G by the relation °Bé = 140/ G -130]... The solution is left to rest for about 10-12 h, while a solid deposit is formed at the bottom of the vessel. The clear liquid is drained and left to crystallize in wood basins, where prismatic crystals are formed in a very slow and regular process. After 25 to 30 days, the temperature has dropped to around 27°C and crystallization is complete...Further purification is achieved by re-dissolution and slow crystallization...The principal problem of the refining operation is to obtain voluminous crystals; their volume depends on the mass being treated, the slowness of the cooling, and particularly, on the regularity of the cooling rate. The crude borax to be refined is introduced in a wooden vessel lined with lead and heated by steam. Water is added to dissolve the impure crystals.... For every 100 parts of borax 5 parts of crystalline sodium carbonate are added... The solution is left to rest to clarify it and then...siphoned to a large crystallizer... built in such a way to avoid

vibrations... the process lasts between 16 to 18 days. After this period of time the temperature has dropped to about 27-28°C. Care is taken not to let it go below this range otherwise other substances may also crystallize...The large crystals of borax are dried and packaged. Preparation of octahedral borax is similar, except that the solution is more concentrated, 30°Bé at 100°C. Crystallization of octahedral borax begins at 79°C and ends at 56°C..."

In 1818, Robiquet and Marchand gave the following description of the know-how about borax^{18,19}: "The commercial variety of raw and semi refined borax is tinkal, coming from China. Both require purification in order to acquire the properties required by the different applications. The first variety is in hexahedral prisms, more or less plain and well finished. These crystals, of a few mm length, are colourless or have a yellowish or greenish tint, and are always coated with a pale, earthy material, oily on touch, and smelling as soap. Semi-refined borax comes in masses or crusts 4 to 5 cm thick; their external appearance is similar to that of milk sugar. On their surface we distinguish the points of pyramids, their colour is white, more or less like salt. It can be seen that these crystals were formed in a liquid, which was not transparent. We believe that tinkal has a large proportion of sodium chloride. We have no doubt about the natural formation of borax. The foreign bodies, particularly the small pebbles that it is mixed with; the way its crystals terminate at both ends, etc., are several of the proofs that they have developed and become coated inside earthy sediment. It is more difficult to explain how it is coated with a fatty material. Some have suggested that this substance has been added to avoid efflorescence of the crystals, and we concord with this opinion. Nevertheless, on the one hand, observation that very white tinkal crystals deprived of the fatty material yield, when calcined in a closed vessel, a black glass, and on the other hand, observation that the fatty material is distributed uniformly in the borax semi-refined, make us believe that this fatty material is naturally found. An additional fact is that it is precisely this fatty material the one that prevents crystallization of borax."

"It is said that the acid of borax contains as radical a simple combustible body, which makes it not possible to expect that it can be manufactured easily".

"Valmont de Bomare, who has visited the Dutch industries, claims that no substance is added for borax

purification, that the process consists simply of a series of evaporation stages, and that all the secret rests on cooling the solutions very slowly, using only vessels made out of lead. A Genoa chemist, Mojon, has published a memoir on the subject, and has put forward an opinion that we do not believe is correct. His research on the subject was based on the claim that the Dutch buy their tinkal at Gênes at a price higher than they sell their refined borax. Mojon assumes that tinkal increases in weight during crystallization, and since he assumes that natural and refined borax contain more or less the same water of crystallization, he speculates that the increase in weight comes from the fact that tinkal contains a certain amount of boron as radical, and that the secret of the Dutch consists in transforming this bore into boric acid, and then into borax. Mojon has based his assertion on certain experiments, which are far from being conclusive. He has taken the insoluble residue of tinkal and has fused it, in different runs, with sodium nitrate. In each operation Mojon has withdrawn a new amount of borax; from this he has inferred that the insoluble residue contains a certain proportion of bore. We do not contest his results, which are very exact, but we know from experience that the tinkal residue contains a certain amount of boric acid combined with the fatty material; destruction of the latter with sodium nitrate yields borax. We are left with the question: why is the price of tinkal higher than that of refined borax? We believe that this is not the normal situation; now, for example, its price is 2/3 that of refined borax; the Dutch simply do the sacrifice, sometimes, in order to avoid the entrance of competitors in the field."

"It seems to us that it is convenient to add a certain amount of sodium carbonate to help the crystallization process. We have undertaken the analysis of all the known varieties of borax to see if there is a difference in their composition. We are certain that tinkal, semi refined borax, and commercial borax, have the same amount of crystallization water. In order to determine the amount sodium carbonate present in every type of borax, we have decomposed it with an excess of lead acetate...Our results indicate that all specimens of borax contain the same amount of the base, which shows that the refiners do not utilize alkali in their purification process. Having proven the identity between tinkal and refined borax, we have directed our attention to ways of isolating the substance that incrustates tinkal."

Isolation of boron

The first proof of the composition of boracic acid and isolation of boron the element, was given by independently by Davy and by Gay-Lussac and Thenard in 1808, when they decomposed it by reduction with potassium⁹.

Davy's method of isolating boron was very similar to that of the French chemists. During his experiments on the isolation of potassium and sodium, he had passed a current through boric acid and had noticed a dark, combustible substance at the negative pole, but he had not at that time thoroughly investigated it³². In the following year, however, he placed a mixture of boric acid and potassium in a copper tube and heated it to dull redness for fifteen minutes. When he examined the contents, he found that the potassium had disappeared and had been replaced by an olive-gray powder, which did not effervesce when treated with water or with acids^{9,32}. Davy³² in his Bakerian Lecture on November 19, 1807, reported "that he had obtained a dark coloured combustible matter by the action of electricity on moist boracic acid but researches upon the alkalis have prevented me pursuing this fact, which seems to indicate decomposition." Some months later he produced the same substance by heating potassium and boracic acid in a tube and found that his new product burned brightly in oxygen and returned to boracic acid. In a later lecture on December 15, 1808, he concluded: "There is strong reason to consider the boracic basis as metallic in nature, and I venture to propose for it the name *boracium*".

In 1808, Thenard and Gay-Lussac heated equal weights of potassium and very pure vitreous boracic acid in a copper tube ending in a bent glass tube connected to a flask containing mercury. According to their words^{33,34}: "When the temperature is about 150 degrees, the mixture suddenly glows strongly, which appears in a striking manner if a glass tube is used. Such is the heat produced that the glass tube melts and sometimes breaks and the air is almost always driven out of the vessel with force...The metal (potassium) is used up in decomposing part of the boracic acid and these two substances are converted by their mutual reaction into a olive gray material, which is a mixture of potassium, potassium borate and the radical of boracic acid...Boron can be separated from the mixture by simply washing it with cold or hot water; that which did not dissolve is the radical itself." Gay-Lussac and Thenard recognized in this

substance a new element, which they named *bore* (boron): "Tout nous prouve que ce corps que nous proposons d'appeler bore, est d'une nature particulière, et qu'on peut le placer à côté du charbon, du phosphore, et du soufre et nous sommes portés à croire, que pour passer à l'état d'acide borique, il exige une grande quantité d'oxygène, mais qu'avant d'arriver à cet état, il passe d'abord à celui d'oxide (This proves us that this body that we now propose to call bore, is of definite nature and can be placed beside to carbon, phosphorus, and sulphur, and we are led to think that to transform it into the state of boracic acid requires a great quantity of oxygen, but before arriving at that state it first passes through that of the oxide)". Gay Lussac and Thenard also studied many of boron's chemical reactions and determined some of its physical properties, noting particularly the similarity of the latter with those of carbon, phosphorus, and sulphur³⁵. For example, boron would form borides similar to carbides, phosphides, etc. By burning the new radical in oxygen, or better still, by oxidizing it vigorously with potassium chlorate, potassium nitrate, or nitric acid, Gay-Lussac and Thenard were able to make synthetic boric acid.

Later on the French changed the name of acide boracique to *acide borique* (boric acid). Four years later Davy said that boracium was more analogous to carbon than to the metal, and the name in England was changed from boracium to boron².

In 1856, Henry Sainte-Claire Deville (1818-1881) and Friedrich Wöhler (1800-1882) prepared boron by a modified Thenard and Gay-Lussac's method; substitution of potassium by sodium allowed them to obtain a large amount of amorphous boron and thus thoroughly study its properties^{36,37}. They found, among other new facts, that amorphous boron burns in nitrogen to produce a nitride. By reducing boric oxide with aluminium instead of sodium or potassium, they obtained beautiful crystals of adamantine boron, whose hardness, refractive powers, and brilliance were rivalled only by those of diamond. This is the boron variety known as adamantine boron or boron diamond³⁶. Wöhler and Deville showed that there were three varieties of boron: (a) crystalline boron or boron diamond, extremely hard, transparent, and coloured either garnet or honey yellow. The difference in colour was caused by the presence of small amount of impurities, particularly silicon, carbon, or even amorphous boron. It resists the action of oxygen but it is easily attacked by chlorine yielding

boron chloride. It is not attacked by a concentrated caustic soda, although a dilute solution of NaOH or sodium carbonates dissolves it slowly, (b) graphitic boron, resulting from the dissolution of the element in aluminium. It can be easily prepared by treating potassium fluoroborate with aluminium. It appears in the form of opaque pale red hexagonal blades, having the form of natural graphite and graphitic silicon, and (c) amorphous boron, obtained by heating a small aluminium globule with a large amount of boric acid. This variety has all the properties of the boron reported by Thenard and Gay-Lussac. Contrary to graphitic boron, the amorphous form burns very easily in the presence of a flame.

After his extensive research on fluorine, Henri Moissan (1852-1907; 1906 Nobel Prize for Chemistry) dedicated his efforts to the study of boron and its derivatives. His first results indicated that all the procedures used by Jöns Jacob Berzelius (1779-1848), Gay-Lussac, Thénard, Deville, and Wöhler to prepare the element led to boron that was highly impure. He then studied very carefully the reduction of boric anhydride with magnesium and determined the conditions required to obtain highly pure boron (99%)³⁸. Afterwards, he discovered boron triiodide and boron phosphides^{39,40}. In the same manner, he prepared boron pentasulphide and established for the first time the pentavalence of boron⁴¹. In collaboration with Henry Gautier he measured the heat specific of the element and found that it did not satisfy Dulong-Petit's law⁴².

In 1909, E. Weintraub⁴³ ran high-potential alternating current arcs, fed by a high potential transformer, between water cooled or air cooled copper electrodes in a mixture of boron chloride with a large excess of hydrogen, in a glass or copper vessel, and obtained highly pure boron as a mixture of a powder (99 to 99.5% boron) and partly fused lumps (99.8-100% boron). Weintraub also measured many of the properties of boron, and found, for example, that at room temperature the fused element was a very poor conductor of electricity but heated to dull red its conductivity increased by over 2 million times. Similarly, its electrical resistance varied exponentially with temperature.

Occurrence of boron minerals

Boron, the fifth element in the periodic table, is the only electron-deficient nonmetallic element. It is one of the three elements of low atomic weight, the other

being lithium and beryllium, which are but sparingly represented in the matter of earth and in meteorites. The reason for this scarcity appears to be their instability in the presence of thermally accelerated protons under stellar conditions⁴⁴. Boron has a great affinity for oxygen and for this reasons it appears in nature in the oxygenated state, mainly as borates. It is a ubiquitous element in rocks, soil, and water, it constitutes only 0.001 of the earth's crust; the average soil boron concentration is 10 to 20 ppm, with large areas of the world boron deficient. Boron concentrations in rocks range from 5 ppm in basalts to 100 ppm in shales. Seawater contains an average of 4.6 ppm boron, but ranges from 0.5 to 9.6 ppm. Freshwaters normally range from less than 0.001 to 1.5 ppm, with higher concentrations in regions of high boron soil levels¹.

The volatility of boric acid with steam is believed by geologists to be the primary mechanism for the formation of borate deposits. Boron compounds have been observed (even on commercial quantities) in the gases from volcanic vents and in the waters of thermal springs in volcanic regions, for example as sassolite (H_3BO_3) at Larderello in Tuscany, and on the island of Volcano, where there is also the fluoroboride, avogadrite, $(K,Rb)BF_4$. In many cases the presence of boron compounds in pegmatites, contact zones, and plutonic and volcanic exhalations has been considered by earlier observers to be evidence of igneous magmas being the source of boron compounds. Present knowledge of the geochemical distribution of boron indicates that it is relatively abundant in seawater and in many marine types of sediment as compared with the general scarcity of the element in igneous rocks^{44,45}.

Borax is found mainly in arid regions, since borates are soluble to some degree and in a humid region would have been leached away long ago. These borax-laden waters evaporated in lakes without an outlet in the arid environment that existed then as well as now. Some of these deposits were covered by later sediment and protected from leaching, like the kernite deposits of Boron. The conversion from borax to kernite is a result of mild metamorphism caused by burial under several hundred feet of overburden. In marine evaporate sediments boracite $Mg_6B_{14}O_{26}Cl_2$ is the dominant boron mineral, but others are also known, for example: a magnesium salt of a complex boro-phosphoric acid, lüneburgite⁴⁴. Where seawaters have evaporated instead of continental waters, as at

Stassfurt, Germany, the hard boracite, may be found, associated with halite and gypsum. It is the only hard boron mineral ($H = 7$), though colemanite ($H = 4$) is harder than borax minerals.

In the United States, borax is found in large amounts in California, in Searles Lake brines and in the Mojave Desert. It is also found in Turkey, South America, and other places. The natural deposits are dried-up lakebeds. Molten borax reacts with metal oxides to form borates that dissolve in the melt, so it is a useful as a welding and soldering flux, and in coloured enamels for iron.

Development of natural sources

Borax was first known from the deserts of western Tibet, where it received the name of tincal. In 1777, boric acid was recognized in the hot springs or soffioni near Florence, Italy, and became known as sal sedativum, with mainly medical uses. The rare mineral is called sassolite, which is found at Sasso, Italy. This was the main source of European borax from 1827 to 1872, at which date American sources replaced it. The natural resources of the region of Lardello (lagoons, fumaroles, and hot water springs) were already known to the Etruscans and the Romans, who used the boric salts for pharmaceutical purposes and for the preparation of enamels. In the Middle Ages and the Renaissance, the waters were used for medical purposes. In the second half of the eighteenth century, boric acid was discovered in the lagoons of Volterra, and was developed commercially². These discoveries were followed by others in the Andes of South America, the Anatolia Plain of Turkey, and the Californian and Nevada deserts of the western United States. By the end of the century these, with Italy, were the main producing areas of the world.

The earliest report of borates in South America came in 1787 from a physician, Dr. Antoine Carrère, employed in the mining area of Potosí, Bolivia. This information is quoted by Chaptal as follows³: “Les Indes occidentales contiennent du borax: nous en devons la découverte à Antoine Carrère...Les mines de Riquintipa, celles des environs d’Escapa offrent ce sel en abondance” (There is borax in the occidental Indies, we owe this discovery to Antoine Carrère... The mines of Riquintipa, and those near Escapa, contain this salt abundantly). In 1852, begun commercial operation of borates field in Chile, which became fully operational after 1880. By the end of the century mining was taking place in both Chile and

Perú. Production in Argentina came later and was insignificant in the nineteenth century. Bolivian borates were mined in the twentieth century for short period of time (1901-1905). The borate from South America is a sodium calcium borate, which was named ulexite ($\text{CaB}_4\text{O}_7 \cdot \text{NaBO}_2 \cdot 8\text{H}_2\text{O}$) in 1849 after examination by Georg Ulex (1811-1883). The borate of lime districts of South America are like those in Tibet in that they are of volcanic origin at high altitudes of about 4,500 m, and they exist only between the latitudes of 15 and 18° South. Here, the ulexite mineral is in lumps about the size of a potato and had to be dug out and separated from the sand, so that it was more costly to produce².

The borax industry in Turkey commenced in 1865 with mining of calcium borate pandermite (priceite, $4\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$) at a deposit situated about 65 km south of the port of Panderma on the Sea of Marmara, at Sultancayir, near Susurluk. This deposit was mined continuously until supplies were exhausted in 1955². Sodium borates were discovered at Kirka in 1960 and other deposits have since been found and developed in Anatolia. As a result, today Turkey is the largest producer of borate products in the world, exporting mineral concentrates of tincal, colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), and ulexite, plus refined borax decahydrate, borax pentahydrate ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), anhydrous borax ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$) and borax acid $\text{B}(\text{OH})_3$ ¹.

Borax was found by John A. Veatch in the spring waters of Tehama County, California, in January 1856. John Searles and others discovered borax near Mono Lake in 1870, and this "marsh borax" became the principal source. One of the minerals exploited was ulexite, or "cotton balls," since it is found in soft, fibrous balls. In 1882, colemanite was discovered in the Mojave Desert, and mining began near Daggett in 1887. Colemanite is a calcium borate formed by alteration of ulexite. It is named after the San Francisco merchant who first marketed it.

The Death Valley colemanite mines were the origin of the famous "20-Mule-Team Borax" trade name. The product was hauled 166 miles south to Mojave by teams of 20 mules. The teams worked until 1890, when the company failed and the mine was closed.

Another source of boron minerals is the waters of Searles Lake, which are worked for other minerals as well, such as trona. Kernite is only found in Kern County, California, in the Kramer district about 3 miles north of Boron, California. These deposits were

discovered in 1916. In 1925, tincal ore was found and in 1926, the new mineral rasorite (kernite, $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$) was encountered. Rasorite has been the principal source of borax since 1927 and name comes after Clarence R. Rasor. The Kramer and Searles Lake deposits now constitute the major world source of borax¹.

Perú and Chile produce ulexite concentrates and boric acid, and Boroquímica in Argentina operates a tincal deposit. China and the former USSR also produce some borates¹.

Production and reserves

Today world production of borax minerals has risen from about 10,000 tons a year in the nineteenth century to over 4.5 million tons today.

According to the U.S. Geological Survey, the world production and reserves are as follows⁴⁵:

Table 1—World production and reserves (10^3 tons)

| Country | Production | | Reserves |
|-----------------|------------|-------|----------|
| | 2002 | 2003 | |
| United States | 1,050 | 1,060 | 40,000 |
| Argentina | 510 | 170 | 2,000 |
| Chile | 330 | 430 | NA |
| China | 145 | 140 | 25,000 |
| Russia | 1,500 | 1,500 | 60,000 |
| World (rounded) | 4,540 | 4,300 | 167,000 |

The U.S. is responsible for the bulk of the world's production of borate, coming from the Kramer deposits and the brines at Searles Lake.

Uses and applications

Boron in its combined form of borax has been used since early times. Early uses were as a mild antiseptic and cleaner because of its detergent and water-softening properties. Later it was used as a soldering flux and ceramic flux because of its ability to dissolve metal oxides.

Table 2⁴⁵ lists the uses of boron minerals and chemicals in the US for the year 2002. Glass and related uses consume about one-half of the borates as boric anhydride, B_2O_3 , in the US. Fiberglass accounts for the largest share, comprising about 69% of the total (50% for insulation fiberglass, 19% for textile grade). Small amounts are used in sealing and optical glasses, Vycor, and vitrifying nuclear waste.

Table 2—U.S. consumption in 2002 of boron minerals and compounds, by end use (tons of B_2O_3 content)

| | |
|-------------------------------|---------|
| Agriculture | 12,900 |
| Borosilicate glasses | 19,300 |
| Enamels, frits, glazes | 12,700 |
| Fire retardants | 11,270 |
| Insulation grade glass fibers | 178,000 |
| Metallurgy | 39 |
| Soaps and detergents | 20,900 |
| Textile-grade fibers | 69,300 |
| Miscellaneous | 35,110 |
| Total (rounded) | 359,500 |

Boric oxide can be added to the glass formulation as borax pentahydrate, boric acid, or colemanite, with price and cation compatibility determining which is used. For example, textile fiberglass requires low sodium hence, boric acid or colemanite is used. Glass bath melting is aided by B_2O_3 , which acts as a flux to improve the melting rate of more refractory components. Borax is used to produce a heat-resistant borosilicate glass for the home and laboratory, familiar to many by the trade mark "Pyrex", and is the starting material for the preparation of other boron compounds. Borosilicate glasses, which are 12%-15% B_2O_3 , 80% SiO_2 , and 2% Al_2O_3 , have increased thermal shock resistance because B_2O_3 lowers the expansion coefficient. In fiberglass, boric oxide gives desirable drawing qualities and increases mechanical strength and chemical durability¹.

About 10% of US B_2O_3 is consumed in detergents and bleaches; the percentage is even higher in Europe. Borax can contribute to the softening of hard water by tying up calcium ions, as well as acting as a buffer agent. Sodium perborates, $\text{NaBO}_3\cdot \text{H}_2\text{O}$ or $4\text{H}_2\text{O}$; PBS1 or PBS4, are true persalts that traditionally have been blended into powdered detergents in Europe as bleaching agents. Dilution in alkaline wash water results in hydrolysis of PBS to give hydroperoxide. Borates are employed in welding rods and other fluxes because of their excellent metal oxide solubilizing ability. Borates are used extensively as fire retardants, particularly in shredded cellulosic insulation and zinc borates in plastics^{1,45}.

Borax is necessary in small amounts for plant growth; it is one of the 16 essential nutrients and can be applied either to the soil or to the foliage. The exact role of boron in plant metabolism is not known. Boron deficiency alters the plasmalemma of root cells, which results in reduced absorption of potassium, chloride, and rubidium as well as cessation

of root growth. An adequate supply of boron is essential for proper seed set and normal fruit development. While concentrated borax is toxic to vegetation (borates can be used as non-toxic and non-specific herbicides) its absence in a soil can cause vulnerability to disease and low yield in a crop². Insecticide use of borates is attractive because of their low mammalian toxicity and lack of insect resistance compared to the organic insecticides.

Boric acid has proven to be a very important substance in the ionic equilibrium in seawater, especially the carbon dioxide equilibrium between the ocean and the atmosphere⁴⁴.

Boron trifluoride, BF_3 is not an ionic compound; it is produced in gas form in large quantities for gas tube neutron radiation detectors for monitoring radiation levels in the earth's atmosphere and in space. It is also an important industrial catalyst for many organic reactions, such as polymerization reactions and has also a major role in the electroplating of nickel, lead and tin.

Aluminum boride (AlB_{12}) has been used as a substitute for diamond dust for grinding and polishing. Boron carbide, B_4C , is also used with this purpose and it has found extensive use as a polishing agent, for sandblast nozzles, etc. It is formed by decomposing B_2O_3 with carbon in the electric furnace. Boron nitride, BN , is another very hard compound, used in cutting tools.

Elemental boron is hard and brittle like glass, having similar uses. Boron can be added to pure metals, alloys or to other solids to improve its strength.

The other commonly used boron compounds are orthoboric acid, or simply boric or boracic acid, H_3BO_3 , and boron trioxide, B_2O_3 , its anhydride. Boric acid can be produced from borax by treatment with H_2SO_4 , and boron trioxide by heating boric acid. These are the initial processes in the synthesis of all boron compounds. In aqueous solution, boric acid is a very weak acid, weaker even than carbonic; its first ionization product being 6.4×10^{-10} . Borax hydrolyzes in water to form a slightly alkaline solution that is good for cleaning, since it emulsifies grease and oil. It is not gelatinous like aluminum hydroxide and crystallizes nicely. Boric acid solutions are used as an antiseptic, especially as eyewash.

Chemical and physical properties

Ordinary boron is a brown-black amorphous powder. Pure boron can be made as extremely hard yellow monoclinic crystals that are a semiconductor

resembling silicon, with a band gap of 1.50 or 1.56 eV. Crystalline boron is an insulator at low temperatures, but becomes a conductor at elevated temperatures. The large spectrum of chemical derivatives and its industrial importance is based on the unusual ability presented by borates to form trigonal as well as tetrahedral bonding patterns and to create complexes with organic functional groups, many of biological importance.

Boron is one of the simplest of atoms; it occurs naturally as 80% ^{11}B and 20% ^{10}B . The latter isotope has a high cross section for thermal neutron absorption, 3800 barns. Thermal neutron counters are often filled with BF_3 gas. Boron is also used in reactor control rods.

The electron configuration of boron is $1s^2 2s^2 2p$ and its expected valence is three. It has only three electrons to work with, so the ion does not polarize and does not hydrate. Boron does not donate electrons in an electrovalent bond, and accepts with difficulty. Hence, most of its bonds are covalent, and even forms half-bonds in which only one electron is shared covalently, not the usual two. This gives boron an apparent valence of +6. A boron atom at an icosahedral vertex can make five equal bonds to its nearest neighbors, leaving one bond to stick out radially.

Boron gives a blue-green flame, and the brown amorphous form is often used in pyrotechnical devices for this purpose. The colour can be distinguished from the emerald green of copper. Boron will not form BH_3 . Instead, it forms larger borohydrides called boranes. Tetraborane has a foul smell; diborane, B_2H_6 has no boron-boron bonds, but two bridging hydrogens out of plane in the planar molecule.

Since the Second World War the Nobel Prize for Chemistry has been awarded twice to advances made in boron research, in 1976 to William N. Lipscomb (1919-) for his work on the structure of boranes, and in 1979 to Herbert C. Brown (1912-2005) for his work on development of organic boron and phosphorus compounds².

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