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NEOGENE BORATE DEPOSITS:
Mineralogy, Petrology and Sedimentology;
A workshop with special emphasis on the
Anatolian deposits

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ABSTRACT

Borates constitute a group of mineral deposits of great economic interest. Although several genetic types have been identified (volcanic, hydrothermal, metamorphic and sedimentary), the most important type corresponds to those deposits formed in non-marine, evaporitic settings. Lacustrine basins related to volcanic terrains in which borates have precipitated are known in the stratigraphic record since the Oligocene, although those of Miocene age are most relevant. The borate minerals in all these basins were generated in saline lakes placed in volcanogenic (mainly pyroclastic) terrains with intense hydrothermal influence, under arid to semi-arid conditions, and in some cases at low temperatures.

As in other evaporitic deposits, the origin, composition (chemical and mineralogical) and depositional environments of the borate deposits can be appropriately documented by means of petrologic and sedimentologic approaches (petrography, lithofacies analysis, cyclicity, facies belts, depositional sequences).

The purpose of this workshop is introducing the participants to the Petrology and Sedimentology of the Neogene Borate Deposits in western Anatolia (Turkey) and, to a lesser extent, in the Andean region (Puna, NW Argentina), although references to the deposits in western USA, and in other geological domains will be done.

The workshop is divided in four parts: The first part is an Introduction to the borate deposits and deals with general mineralogical and depositional aspects.

The second part summarizes the Lithofacies and Petrography of the most common borate minerals: ulexite, probertite, inyoite, meyerhofferite, colemamite, priceite, borax, hydroboracite and howlite, among others. Many of them are rock-forming minerals.

The third part presents examples of the depositional Cycles and Successions present in the Neogene and, to a lesser extent, the Holocene deposits involving borates, borates-sulfates, and borates-sulfates-chlorides.

The fourth part discusses aspects of some examples of Neogene Borate Basins in western Anatolia (Bigadiç, Kestelek, Kirka, Sultançayır, and Emet) and in La Puna region (NW Argentina). In the case of the Emet and the Kirka basins, the discussion is mainly based on accurate petrologic observations carried out by direct observation of borehole core samples under an Environmental Scanning Electron Microscope.

Workshop materials consist of: stratigraphic profiles; hand and borehole samples; thin sections; and different types of images (outcrops and quarries, hand and core samples, photomicrographs and SEM images).

Key words: borates, evaporites, lithofacies, petrology, depositional cycles and successions, diagenesis, Neogene, western Anatolia, NW Argentina
PART I: INTRODUCTION

1.1. Purpose

Borates constitute a group of deposits of great economic interest. Although there are several genetic types of borates (volcanic, hydrothermal, metamorphic, sedimentary), the most important type corresponds to those deposits formed in non-marine, evaporitic settings. Lacustrine basins in which borates have precipitated are known in the stratigraphic record since the Oligocene up to the Recent, although those of Miocene age are the most common and important.

The borate minerals in all these basins were generated in saline lakes placed in volcanogenic (mainly pyroclastic) terrains with intense hydrothermal influence, under arid to semiarid conditions, and in some cases at low temperatures. The most important areas of Holocene borate precipitation are shown in Fig. 1.1.

Minor borate occurrences, however, are linked to ancient marine salt formations (Late Permian, Zechstein, Europe; Early Carboniferous, Mississippian Windsor Group, Canada; Early Permian Inder Lake region, Kazakhstan). These occurrences are mainly diagenetic borates dispersed in caprocks of salt domes, and were usually formed by the intrusion of boron-rich geothermal fluids.

In addition to a chemical or mineralogical approach to the description and classification of these lacustrine borate deposits, the composition and genesis can also be appropriately documented by means of petrologic and sedimentologic investigations. Because these deposits constitute a particular type of evaporites, a similar methodology can be applied to them: petrographic study, lithofacies analysis and interpretation of cyclicity, facies belts and depositional successions.

The purpose of this workshop is to introduce the participants to the Petrology and Sedimentology of the Neogene borates and borate-bearing deposits of lacustrine setting. Most of the examples will be taken preferentially from the western Anatolian deposits (Turkey) and, to a lesser extent, from the La Puna region (Central Andes, NW Argentina), although brief references to similar deposits in other regions will be made (California in western USA, Tibet-Qinghai Plateau in China).

1.2. Mineralogy

Boron is never found in the elemental form in nature. The name is derived from the Arabic ‘burak’ or the Persian ‘burah’ words meaning ‘white’. Boron is a minor element in the Earth with an average concentration of 15 ppm in the upper continental crust. It occurs in many metamorphic and acid plutonic rocks in the mineral tourmaline. In sediments, it is present as detrital tourmaline and as a minor element in illitic clays.

In natural waters, boron exists primarily as undissociated boric acid ($\text{H}_3\text{BO}_3$ or $\text{B(OH)}_3$).
Also, boron interacts with water molecules to form the tetrahydroxyborate ion (B(OH)$_4^-$) and a number of polymeric borate ions (polyborates): diborate (B$_2$O$_5^{4-}$); triborate (B$_3$O$_7^{5-}$); tetraborate (B$_4$O$_9^{6-}$); etc. Concentration of boron in water ranges widely: it is from less than 7 ppm in freshwater, averaging 4.5 ppm in seawater, and from 0.3 to 100 ppm in groundwater. Hydrothermal water in some tectonically active regions related to volcanic processes can reach very high concentrations of boron. For instance, it is over 3500 ppm in the volcanic island of Santa Lucia (Lesser Antilles), where hot springs exhibit high temperatures (up to 80°C), low pH (down to pH 2), very high concentrations of sulfates (>6000 ppm) and contain a high anomalous microbial diversity (Stout et al., 2009).

Boron combines with oxygen and other elements to form borates which contain the BO$_3$ (triangular) or BO$_4$ (tetrahedral) structural coordination units (Christ and Clark, 1977; Anovitz and Grew, 1996). These borate units may be polymerized similarly to the SiO$_2$ of the silicate mineral class. This results in more than 230 naturally occurring borate minerals identified until 1996 (Sureda, 1991; Garret, 1998) but the new analytical techniques allow the continuous identification of new borate minerals. Although borates can be formed with any cation, and form double salts with other anions, the most abundant minerals are formed with calcium, sodium or both elements.

Borates are strongly ionic compounds, soluble in hot water, and as the cations are generally alkaline or alkaline earth elements, most of them are transparent and colorless having a glassy luster. Owing to the anisotropy of the anion groups, most borates have a high optical anisotropy and exhibit interference colors of high orders (Jaffe, 1996). A connection can be established between the crystal structures of borate minerals and the conditions of pH and log of [H$_2$O] of their stability field: the proportion of tetrahedrally coordinated B to total boron in the structural unit increases with increasing pH (Schindler and Hawthorne, 2001).

Three different chemical formulation systems (structural, empirical, and oxide-like) are used in borate minerals making in many cases confusing their use and memorization. The main borate minerals present in evaporitic lacustrine deposits with the three formula types are listed in Table I-1: note that only the structural formula contains information about atomic organization although it is not so relevant from the genetic and sedimentologic points of view.

Neogene ore deposits with boron concentrations allowing industrial exploitation are restricted to four groups of major borates: Ca-borates (inyoite, meyerhoffiterite, colemanite and priceite), Na-Ca-borates (ulexite and probertite), Na-borates (borax, kernite) and Mg-Ca-borates (hydroboracite). Other borates occur as minor phases and do not require the presence of the major ones. According to all these, this workshop will be focused on the...
fractures and formed a block close to 650 km. Sierra Nevada Range began to rise along.

- The eruptions increased in frequency, the eastern edge of the modern Range Province. As the eruptions increased in Nevada and the Great Valley, which is bounded was formed in the junction zone of the Sierra Nevada and the Basin and Range Province (western USA).

- The salares of the Central Andean Range (Argentina, Chile, Bolivia, Perú).

- The playas of Konya Karapinar region (central Turkey)

- The saline lakes of the Tibet-Qinghai Plateau.

- Lake Inder (Kazakhstan, to the N of the Caspian Sea).

In these modern environments, either pure borate deposits devoid of significant amounts of other evaporite minerals, or borate deposits in complex parageneses with carbonates, sulfates or chloride may form from the concentrated solutions. The borate precipitation occurs in the following sites:

- In the vicinity to boriferous, hydrothermal sources, where borates form cone or fan-shaped (‘spring-apron’) deposits

- Underneath the dry surface of some saline playas and salars

- On the shore and, less commonly, on the floor of saline lakes.

1.3. Holocene environments

Borate minerals have precipitated during the Holocene in non-marine (endorheic, closed) basins from merely boriferous brines or from more complex solutions. Borate minerals in these basins contain mainly Ca and Na, to a lesser extent Mg, and in some cases Sr and As also.

At present, a number of non-marine regions record significant precipitation of borate minerals in a number of evaporitic environments:

- The playas, marshes, and saline lakes of Great Valley, Sierra Nevada, and the Basin and Range provinces (western USA).

- The salares of the Central Andean Range (Argentina, Chile, Bolivia, Perú).

- The playas of Konya Karapinar region (central Turkey).

- The saline lakes of the Tibet-Qinghai Plateau.

- Lake Inder (Kazakhstan, to the N of the Caspian Sea).

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1.3.1. Holocene borates in North America

Holocene borate deposits in the Western United States are scattered in alkaline lakes and playas from Southern Oregon throughout the states of California and Nevada (Fig. 1.2). All of them are related to the subduction process, started during the Cretaceous, of the Pacific Plate under the North American Plate and the associated plutonism and formation of a volcanic arc in the Sierra Nevada. The proto-Sierra Nevada remained tectonically stable since the Paleocene until the Neogene, when crustal extension caused extensive volcanism in both the Sierra Nevada and the Basin and Range Province. As the eruptions increased in frequency, the eastern edge of the modern Sierra Nevada Range began to rise along fractures and formed a block close to 650 km long and 110 km wide. Uplift of the eastern boundary of the Sierra Nevada continues today. A microplate with rigid behaviour (as a block) was formed in the junction zone of the Sierra Nevada and the Great Valley, which is bounded by the San Andreas Fault on the west and the Eastern Sierra Fault on the east. Most Holocene borate deposits are located along the Sierra Fault System, in both the eastern side of the microplate and the west margin of the Basin and Range Province (Coolbaugh et al., 2006a), although some of them are related to the western edge on the San Andres Fault (Borax Lake, California).

- Borax Lake (California). This lake, located in the San Andreas transform Fault System, is a small alkaline lake which lies in a closed basin separated from the structural basin of the Clear Lake (Lake County, California) by a narrow ridge. With a maximum water depth of 1 m, the lake occupies in spring an area close to 1 km², which decreases up to 0.2 km² in summer, and occasionally disappears for several years. The area consists of a volcanic field containing lava and tuff deposits. A large magmatic chamber provides the geothermal field for the Geysers Steam Field, which was the largest geothermal power-generating system in the world. A number of thermal springs yielding highly boron-rich waters are located just northeast of Borax Lake. According to Garret (1998), the central portion of the lake mud surface is smooth, soft, and plastic with no crystals in its upper 30-40 cm, but at increasing depth, interstitially-grown idiomorphic borax crystals appear within the mud. During the summer of 1934, the lake became almost completely dry due to a prolonged dry period and evolved to a mud playa covered by a white efflorescent crust of halite crystals containing trona (Na₂CO₃·6H₂O), gaylussite (Na₂Ca(CO₃)₂) and glauuberite (Na₃Ca[(SO₄)₂]). Borax was absent in the exposed surface although abundant idiomorphic crystals were found at a depth of 1.5 m.

- Searles Lake (California). Searles Valley is located at the northern edge of the Mojave Desert in the San Bernardino and Inyo Counties (California). In this valley, a number of sedimentary rock units of Tertiary and Quaternary ages and abundant mafic volcanic rocks of Miocene to Pliocene age crop out. The Searles (dry) Lake, in the center of the valley, is about 19 km long and 13 km in its widest point. This lake consists of an extensive mud flat around a salt flat that is periodically flooded by a 2-10 cm deep water body. The Quaternary record of the lake consists of 45 m of evaporites and mud sediments grouped in the Searles Lake Formation (Smith, 2009). Borax was harvested in the surface dried mud. Two non-outcropping saline bodies are composed of a great number of minerals accompanying halite. They can be grouped as Na-bearing carbonates (trona (Na₂CO₃·6H₂O), nahcolite (Na₂CO₃)), Ca-Na-bearing carbonates (gaylussite (Na₂Ca(CO₃)₂), 5H₂O); pirssonite (Na₂Ca(CO₃)₂, 3H₂O), Na-bearing borates (borax; ticalcinite), Na-bearing sulfates (thenardite (Na₂SO₄) and glaserite (KNa₂(SO₄)₂)), and Na-bearing double or triple salts (sulfosalts (Na₈(SO₄)F₄Cl); galeite (Na₈(SO₄)F₄Cl); hanksite (KNa₂(SO₄)₂(CO₃)Cl); burkeite (Na₈(SO₄)₂(CO₃)Cl); tychite (Na₉(SO₄)₄(CO₃)₂Cl)).

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schairerite (Na₃(Bo₄)(CO₃)₂F₂Cl); northupite (Na₃Mg (CO₃)₂Cl). Up to 14 tuff beds containing vitric ash now altered to zeolites, K-feldspars, bentonite and smectite are interbedded with these evaporites (Hay and Gouldman, 1987).

- Saline Valley (California). Saline Valley is a large (48 km long and 32 km wide), arid, dry valley surrounded on the west by the Inyo Mountains (3050 m high) and on the east by the Panamint Range (1830 m). It is located 80 km southeast of the Bishop city, in the Inyo County (California), and takes part of the Mojave Desert and the Death Valley National Park. An extensive (42 km²) dry playa covered by a 0.5 m thick salt crust occupies the center of the valley. Borax occurrences were discovered in 1874 prompting an extensive number of borate land locations up through the 1890. The mineralogy of the recent evaporite crust (Hardie, 1968) is mainly formed by halite mixed with muds and sands. The crust also contains minor amounts of thenardite, mirabilite (Na₂SO₄·10H₂O), glauberite, gypsum, calcite, dolomite and ulexite. Natural hot springs are found in the valley, which belong to a hydrothermal system originated by ascending meteoric water heated at an indeterminate depth. This water, supersaturated with respect to calcium carbonate, is the reservoir of the saline deposit.

- Death Valley (California). Death Valley is located in the Inyo County, southeastern California, on the western margin of the Basin and Range physiographic province. The valley is a pull-apart basin in which strike slip movement has been operating for more than 10 Myr along the Furnace Creek and the Death Valley Fault Zones. The valley currently houses three principal depressions, from north to south: the Cotton-Ball Basin, the Middle Basin, and the Badwater Basin. Inflow waters to Death Valley include streams that enter from the north (Salt Creek) and the south (Amargosa River). Several springs and seeps, associated with faults, discharge along the east and west margins. Seismic reflection profiles in Death Valley have identified a mid-crustal magma chamber, 15 km below the surface of the Badwater Basin which provides potential pathways for upward movement of hydrothermal waters (Lowenstein and Risacher, 2009). Badwater Basin constitutes the lowest point in North America, with an elevation of 86 m below the sea level. In this basin, the Eagle Borax Spring is one of the largest perennial sources located on the southwestern margin of the Death Valley salt pan. East to this spring, in direction to the central salt pan, the surface crust consists of halite and gypsum-cemented silt with ulexite, celestine, thenardite and proberbite (Crowley, 1996). Other minor Mg- and K-bearing borates (aristarainite, hydroboracite, kaliborite, mccallisterite, rivadavite, and pinnoite) have been detected by spectroscopic techniques.

- Salt Wells Marsh (Nevada). The Salt Wells Basin is a closed playa (15 km long, 5 km wide) located 20 km southeast of Fallon Village (Churchill County, Nevada). The basin is surrounded to the north by the volcanic rocks of the Stillwater Range (2680 m high), by the granites of the Sand Spring Range to the southwest and by the Cocoon Mountains to the southeast. The playa is divided into two subbasins (Eight Mile Flat and Four Mile Flat), which are covered by white salt crusts formed by ephemeral salt lakes. Cotton-ball ulexite was harvested from an area of 1.6 km²) of the playa at Salt Wells during 1870 to transform it into borax (Garret, 1998), Coolbaugh et al. (2006b) report tincalconite and borax crusts with mirabilite and thenardite in a more widespread area. Borate occurrences are closely related to the areas of the playa being fed by ascending, thermal groundwater. The intense geothermal field in Salt Wells has allowed the construction of a power plant that taps a shallow geothermal reservoir with an estimated temperature of about 140°C and up to 200°C in the deeper part. Surface indicators of the geothermal activity related to the borate production include opalized sediments, siliceous sinter, argillic alteration, and many ephemeral hot and warm springs (Coolbaugh et al., 2006b).

- Teels, Rhodes, and Columbus marshes (Nevada). Teels and Rhodes marshes (Mineral County) and Columbus Marsh (Esmeralda County) are three borate-bearing playas located near the city of Columbus, southwestern Nevada. These playas were the world’s leading sources of mined borate minerals during the 1870’s and lasted for about a decade (Barker and Lefond, 1985). Teels Marsh is an ephemeral saline lake located in a block-faulted valley typical of the Basin and Range geomorphic province. The surrounding mountains consist of a granitic basement and Tertiary volcanic rocks. A tuffaceous deposit correlated to the age of recent volcanism generally occurs about 30 cm below the surface and varies in thickness from 1.3 to 5.1 m. Taylor and Surdam (1981) reported that interstitial waters associated with tuffaceous sediments are alkaline waters essentially of the NaCI-HCO₃-SO₄ type and exhibit a concentration gradient toward the playa center. Saline products at Teels Marsh consist of efflorescent crusts formed by a sandy mixture with halite and ulexite, and minor amounts of dolomite, calcite, trona, gypsum, gaylussite, burkeite (Na₂(SO₄)₂(CO₃)), searlesite and mirabilite. In Rhodes and Columbus marshes ulexite occurs as nodules (cotton-ball) in wet, soft mud underlying the playa surface (Bowser and Dickson, 1966). Field and satellite remote sensing spectroscopy allowed mapping the tincalconite surface distribution (borax in subsurface) on Teels, Rhodes and Columbus marshes (Kraft et al., 2006).

- Fish Lake Marsh (Nevada). Fish Lake Valley is located in the Esmeralda County, Nevada. It is bounded to the west by the White Mountains (California), to the east by the Silver Peak Range, and to the north by the Volcanic Hills. Volcanic Hills are composed of Tertiary basalt flows and tuff deposits. An intense geothermal activity is present in the area (Littlefield and Calvin, 2010). At the northern edge, in contact
with the Volcanic Hills, there is a tuff-hosted mercury deposit with associated chalcedony, sulfur, gypsum and cinnabar. Near surface, groundwater sampling conducted recently by Lithium Corporation (“Lithco”) has discovered lithium-enriched brines with anomalous boron (up to 2500 ppm) and potassium (up to 7200 ppm) concentrations. The northeastern corner of Fish Lake Valley is occupied by a small playa covered by a white saline crust containing borax and cotton-ball ulexite.

-Alvord Valley and Borax Lake (Oregon)

Alvord Valley is a north-northeast-trending graben in the Basin and Range Province (Harney County, southeastern Oregon). The graben is bounded to the west by the tilted fault-block mountains of the Steens and Pueblo Range (2975 m high) and to the east by the Sheepshead and Trout Creek mountains. The Alvord Basin consists of a large playa covering an area of about 250 km² in the north-central part of the valley. It includes the Alvord Desert in the north, the Alvord Lake in the central part, and the small Borax Lake (or Hot Lake) in the south. The Alvord Lake, of about 1 m deep, overflows the Alvord Desert during periods of heavy rainfall. In summer, the lake is quite small and develops a white, surficial alkaline crust. The saline crust surrounding this lake contains a mixture of ulexite and borax (Garret, 1998). The Alvord Basin is placed in a strong geothermal active area with hot springs: about 175 of these springs are distributed along a NE-SW trending normal fault. The discharging water is of the Na-HCO₃-SO₄-Cl type, and has T and pH values ranging from 24 to 95°C and from 5.8 to 8.6, respectively (Colter et al., 2004). Water in the Borax Lake has significant concentrations of boron (Koski and Wood, 2004).

1.3.2. Holocene borates in the Central Andean Range

The Altiplano-Puna Plateau with an average elevation above 3000 m, is the highest plateau in the world associated with abundant magmatism. It extends over an area of 1800 km long and 350-400 km wide of the Central Andean Range occupying parts of northern Chile and Argentina, western Bolivia and southern Perú. The Altiplano-Puna Plateau is bordered on the west by the present-day active volcanic arc of the Western Range, and in the east by the paleo-rift of the Eastern Range, the Santa Bárbara and Sierras Pampeanas system, and by the Subandean thrust belts. Both the western volcanic arc and the eastern volcanic centers have been active from Miocene times to present-day and are the origin of boron-rich fluids (Alonso, 1986). Combination of volcanic chains and faults fragments the Altiplano-Puna area in structural blocks which form endorheic depressions occupied by extensive salt pans or ‘salares’ surrounded by mud flats and alluvial systems (Fig. 1.3).
- **Argentinian salares.** A number of borate-bearing salares are distributed in the volcanic arc (Western Cordillera) and in the La Puna Plateau. In all of them, ulexite and borax (\textit{‘tincal’}) have grown interstitially in salt-crusts and volcanioclastic muds. Ulexite occurs in two lithofacies: (1) isolated nodules usually flattened (‘papas’), which can join together in a chicken-wire structure, and (2) massive beds (‘barras’) up to 2 m thick underlying the efflorescent salt-crust. According to Alonso (1999) and Helvacı and Alonso (2000), a marked transition from marginal travertine limestones to sulfates (gypsum), borates (ulexite, borax) and central chlorides (halite) is usually observed in the Argentinian salares of La Puna. Such a transition, however, is not so clearly observed in the salares of the Bolivia-Perú Altiplano. In the salares where the presence of sulfates (mirabilite, gypsum) is higher (Pocitos, Rincón and Río Grande), the distribution of borates is less important or absent, and those containing borates (Hombre Muerto, Rincón) exhibit lithium-rich brines. In some salares (Diabillilos), borate deposits are more frequent than other detrital or evaporite materials. In some salares (Diabillilos, Ratones, Centenario) a marked relation exist between borates and thermal springs, which are usually placed in travertine deposits along active faults (Alonso and Gutiérrez, 1984). In others (Hombre Muerto), boron is provided by streams and groundwater having leached pyroclastic materials of the surrounding volcanoes (Vinante and Alonso, 2006).

- **Bolivian salares.** Bolivia has a number of borate-bearing salares located in both the Western Andean Range (Chiguana, Empexa and Laguani) and the Altiplano (Chalviri) (Fig. 1.3). In all of them, the ulexite dispersed in salt crusts is exploited as a while. The Bolivian Salar of Uyuni, with an extension >10000 km², is permanently free of superficial water. In summer the brine falls to an interstitial mud bed up to 1 m thick with volcanic ash contains irregular nodules of ulexite and inoyite crystalline aggregates.

- **Chilean salares.** The Chilean salares of Atacama and Punta Negra are placed above 2300 m in the pre-Andean region, in the western side of the Western Range (Fig. 1.3). The Salar of Atacama, the largest salt flat in Chile (3000 km²), is permanently free of superficial water. Although ulexite nodules are recognized in the salt crust, the salar is mainly a great reservoir of lithium, potassium and boric acid concentrated in underground brines. Halite crust with ulexite and minor hydroboracite, gypsum, thernardite, celestine, baritine and orpiment (As₂S₃) has been reported in other Andean salares, as those of Surire and Ascotán (Chong et al., 2000).

- **Peruvian salares.** Laguna Salinas is a borate salar that lies at an altitude of about 4200 m, 64 km east of Arequipa village. The salar occupies an enclosed basin that is underlain by volcanic rocks. The area is flooded in winter and afterward it becomes completely dried forming an efflorescent salt crust of halite, thenardite and glauberite. Beneath the surface, a sandy mud bed up to 1 m thick with volcanic ash contains irregular nodules of ulexite and inoyite crystalline aggregates.

### 1.3.3. Holocene borates in Karapınar-Konya region (central Turkey)

The basin located around the town of Karapınar (Konya) is surrounded by volcanoes which have been active in various phases from the Late Miocene to present. Currently active volcanism is evidenced by the discharge of thermal and mineral waters and magmatic gases. Potentially economic deposits of borate, chloride, sulfate and carbonate salts related to this volcanic activity are forming within the basin. Andesitic lavas of Late Miocene volcanism form Üzecik Mountains are located in the western part of the basin. Karacadağ, which is located in the eastern part of the basin, has a complex domal structure and completed its evolution in a few phases during the entire Pliocene. The lavas which form Karacadağ rise to an elevation of 1995 m are predominantly andesite, but locally trachyandesite, basaltic andesite and dacite are also present. All of them show a highly viscous flow character.

The southern part of the Karapınar Basin is delimited by lava flows and small volcanic cone and maar pyroclastics that formed as a result of several volcanic phases which began in the Early Quaternary and continued up until a few thousands years ago. Trachyandesitic and andesitic lava flows were formed during the first stage of volcanism in the Quaternary. Radiometric determinations done by the K/Ar method give ages between 1.1 and 1.2 Mys for these flows. Later, basaltic lavas, scoria and ash formed small volcanic cones and lava flows. Basaltic volcanic cones reach heights of 250 m. K/Ar radiometric age determinations give ages between 363.000 and 161.000 years for this stage of volcanism.

Later, maars (volcanic craters resulted from explosive eruptions) formed within the basin. Maar pyroclastics, formed successively as products of several different eruptions, are present as concentric rings around the maars. The maars of Meke Öbruğu and Yılan Öbruğu are small in size. As for the Mekegöl and Acıgöl maars, they are larger explosion craters measuring approximately 1.5 km in diameter. Later the maars were filled by waters forming maar lakes. A few thousand years ago, a scoria cone formed within the Meke maar lake during the last phase of basaltic volcanism.

There is evidence of active volcanic activity in the Karapınar Basin, such as the thermal and mineral waters and gases still emitted from the maars and along the major fault line in the eastern part of the basin. The gases contain predominantly CO₂ and have mantle-origin characteristics, based upon helium-and carbon-isotope ratios (\(^{3}He/He = 159.10^{-6}\), \(\delta^{12}C = -1.5\%\)).
Borate, chloride, sulfate and minor amounts of carbonate salts are actively forming in the basin. While NaCl is precipitating in the center of the basin, carbonate and CO₂-bearing waters are being discharged, and carbonates (probably trona) and Na sulfates have precipitated along the fault at the eastern edge of the basin. Ulexite, which is one of the common borate salts, seems to have formed earlier than the other salts and occurs as cauliflower or potato-shaped masses within unconsolidated sediment at depth of <1 m. Thenardite and glauberite are forming within the Acıgöl and Meke maar lakes.

The formation of borate and other salts in the Karapınar Basin is genetically related to the subalkaline volcanic rocks of this region. Na, B, Cl, SO₄ and CO₂ are carried into the basin by thermal and mineral waters related to this volcanism. Through detailed field, geochemical and drilling studies, it is probable that economically important salt deposits will be discovered (Helvacı and Ercan, 1993).

1.3.4. Holocene borates in the Tibet-Qinghai Plateau (China)

The Tibet-Qinghai (Xizang-Qinghai) Plateau lies between the Himalayan Range to the south and the Kunlun Range to the north. It stretches about 1500 km north-to-south and 3500 km east-to-west. With an average elevation exceeding 4500 m and an area over 2.5 10⁶ km², it is the highest, largest and flattest plateau in the world. It formed as a consequence of the collision between the continental crusts of the Indian and Eurasian plates 50 Myr ago. Over 70 saline lakes occur in the Tibet-Qinghai Plateau (Zheng, 1989), although borate minerals are only found in some lakes distributed in two areas: in the Qadam Basin of the Qinghai Province in the southern side of the Quilian Mountains, and in the Xizang (Tibet Province) in the northern side of the Himalayan Mountains (Fig. 1.4). Chemistry of borate-bearing lakes is strongly controlled by boron-rich hot springs related to an intense geothermal activity leaching acid magmatic rocks of the basement in these regions. Since the Würm glaciation more of these lakes remain as perennial and show a chemical differentiation. According to Zheng Mianping et al. (2005) borate precipitation has taken place during dry-cold climatic conditions.

- Qinghai Province. Da Qaidam Salt Lake, with an elevation of 4148 m and located in the north of the Qaidam Basin, is a typical halite-saturated lake enriched in lithium and boron. Two different borate occurrences have been differentiated. The principal orebody, located at the lake bottom, consists of halite, ulexite and pinnoite with minor gypsum, mirabilite, thenardite, glauberite, bloedite (N₂Mg(SO₄)₂·2H₂O) and epsomite (MgSO₄·7H₂O).
Neogene Borate Deposits: Mineralogy, Petrology and Sedimentology: A workshop with special emphasis on the Anatolian deposits

7H₂O). The second is exposed on the lake shores and consists of halite, ulexite, hydroboracite and gypsum with minor Mg-bearing borates (inderite, kurnakovite, mccallisterite and hungchaoite). Xiao Qaidam Salt Lake, with salinity over 279 g/L, is subsaturated in halite, although halite and mirabilite occur around the lake. Ulexite is mined in the surrounding sediments and also occurs with gypsum, mirabilite and pinnoite on the bottom muds (Sun Dapeng, 1990; Sun Dapend and Li Bingxiao, 1993).

-Tibet (Xizang) Province. Changcam Caka Salt Lake has the largest borate operation in the region. Two ore bodies are differentiated: in terraces around the margins of the modern lake and in the lake bottom. In both settings the ore consists of pinnoite and kurnakovite with minor ulexite, indelroite and mirabilite. In the Nier Co Salt Lake, Mg-bearing borates (pinnoite and kurnakovite) mainly occur in several layers up to 4 m thick in the margins and on the bottom of the lake. In some of these layers mirabilite is present as a minor phase. Zabuye Salt Lake, with a salinity ranging between 36 and 44%, is supersaturated with respect to halite. Millions of metric tons of halite, apalhalite ((KNa)₂Na(SO₄)₂), trona and glauberite are deposited on the bottom of the lake. The lake is enriched in lithium and boron. Zabuyite, a lithium carbonate (Li₂CO₃), has been found for the first time and a mineral exploitation plant is conducted by mining lithium carbonate in solar ponds. Although no borate minerals have been found, isothermal evaporation experiments with the lake brine at 25°C produced sylvite (KCl) and borax when 90% of water was removed (Nie et al., 2009).

1.3.5. Holocene borates in Lake Inder (Kazakhstan)

Lake Inder, with a 36 m deep water mass, is a NaCl-saturated lake located north of the Caspian Sea and east of the Ural River. Despite no information is available about the occurrence and genesis of borate minerals in the Inder Lake region, some Mg-bearing borates were described for the first time (inderite, inderborite and kurnakovite). The main borate mineral consists of hydroboracite associated with minor inyoite, colemanite, saibelyite (ascharite), ulexite and priceite. The lake receives drainage from the borate-bearing veins in caprocks of the domes of the Inder Salt, which are Lower Permian (Kungurian) in age. The boron source of Lake Inder as a sump accumulation of water leaching Permian, marine evaporites still remains controversial. Moreover, significant confusion is placed at that point because the same mineral assemblage is attributed to the modern lake and to the Permian salt domes (Garret, 1998; Kistler and Helvaci, 1994).

1.4. Mineralogical differences between Holocene and ancient lacustrine borate deposits

As mentioned above, only a reduced number of borate minerals, as borax and ulexite, are common precipitates in the Holocene occurrences. Other borates, as meyerhoffite, inyoite, problebrite, howlite, hydroboracite, indelroite and kurnakovite are less frequent, and some other borates, as colemanite, priceite and kernite are rare or almost absent (Alonso, 1986). The comparison between these occurrences and the distribution of the various borate minerals in the ancient (Neogene) deposits reveals some important differences (Fig. 1.5). Thus, in the Neogene deposits:

- colemanite is the most common Ca-borate;
- other Ca-bearing borates, as inyoite, priceite, problebrite and howlite, are much more common than in the Holocene occurrences;
- kernite is mainly associated with borax at depth, suggesting the existence of a diagenetic cycle of mineral transformations (primary borax → replacive kernite at depth → secondary borax in exhumation);
- a number of Ca- and Na-bearing borates such as colemanite, priceite and borax can be replaced by secondary calcite close to the surface during exhumation; under these conditions related to groundwater circulation and weathering, calcite pseudomorphs after those precursor borates are commonly preserved.

According to all these differences, colemanite, ulexite, and borax (occasionally kernite) are the most common Ca- and Na-bearing rock-forming borates in the Neogene deposits and those of major petrologic relevance and economic interest as well.

1.5. Mineral zoning in the borate deposits: depositional versus diagenetic patterns

A number of Neogene borate deposits show a mineral zoning both in a lateral (from the margin to the center) and a vertical sense (from the base to the top). In some cases this zoning is symmetrical, while in others it is slightly asymmetrical. In general, this distribution can be assigned to a depositional control. Consequently, the mineral zones in this interpretation reflect the evolution of the brine composition in space and time.

In some cases, however, this zoning has been considered to be diagenetic based on the mineralogic differences recorded between the Holocene and the ancient (Neogene) deposits. Burial (thermal) diagenesis and reaction (with groundwater) diagenesis are the main types proposed in the literature to explain the borate zoning under non-depositional conditions (Smith and Medrano, 1996).

Burial diagenesis refers to dehydration and mineral transformation occurred in the deposits by increasing temperature during progressive burial. This interpretation could explain, in the Neogene deposits, the changes underwent by
minerals in the hydration series of Ca-borates and Na-Ca-borates. For instance, the predominance in the Furnace Creek Fm (Death Valley, Miocene-Pliocene, California) of the less hydrated phases (colemanite, probertite) was related to the dehydration conversions of meyerhofferite-to-colemanite and of ulexite-to-probertite at burial depths of up to 1500 m (Smith and Medrano, 1996; Tanner, 2002).

Reaction diagenesis would occur when groundwater interacts with borate minerals forming these bodies (Smith, 1985). Thus, the presence in many Neogene deposits of a mineral zoning in association with a vein complex of various minerals (ulexite, colemanite, borax) cross-cutting the borate layers, was ascribed by Smith and Medrano (1996) to reaction diagenesis while the deposits were uplifted during the Neogene-Quaternary time.

A discussion on the possible interpretations of a mineral zoning in the Neogene deposits, i.e. depositional controls vs. diagenetic transformations, is out of the scope of this workshop (see comments in Helvacı and Ortí, 1998, 2004). Probably, many factors (geological setting, burial story of the region, sedimentologic and textural characteristics of the borate minerals, isotopic values, fluid inclusions composition, etc.) need to be taken into account for deciphering the prevailing mechanism causing the mineral zoning in a particular deposit.

Barker and Barker (1985) and Crowley (1996) applied the concept of chemical divides to explain the mineral sequences in the borate deposits. In particular, Crowley (1996) assumed the precipitation of rare Mg-borates present in some deposits as the end products of the evolution of the boratiferous brines. This is a sedimentologic alternative to previous interpretations that considered these minerals as late diagenetic and originated from reaction diagenesis (by groundwater action during exhumation). Such a depositional interpretation was assumed by Ortí and Alonso (2000) in the Argentinian hydroboracite deposits and by Helvacı and Ortí (2004) in the Turkish borax deposit.

As regards the assemblage of the Miocene Anatolian deposits, and on the basis of observations on (1) the regional context and (2) the lithofacies, petrography and depositional cycles in the borate units, Helvacı and Ortí (1998) emphasized that these deposits: (a) are mainly formed by high hydrated (borax, ulexite) and less hydrated (colemanite, probertite) minerals; (b) were never buried more than 300-500 m and so, a thermal diagenesis cannot be applied to them; (c) exhibit colemanite which can be largely interpreted as a mineralogically primary (de novo) precipitate that grew interstitially within the sedimentary matrix; and
(d) exhibit other Ca-bearing minerals, as meyerhofferite, priceite and howlite which can also be interpreted as interstitially grown forming mineralogically primary precipitates. All these observations clearly favour a depositional interpretation of the mineral zoning.

It seems likely that various mineralogical and textural transformations affecting the borate minerals in the Neogene deposits occurred from early diagenesis to initial or moderate burial diagenesis. Similarly, it is possible that some of the mineral associations found in the Ca- and Na-bearing borates are the result of total or partial reabsorption of former minerals in the boratiferous brines along the evaporative concentration process. In conclusion, as in other groups of evaporites, detailed studies of petrography, lithofacies and cyclicity can contribute greatly to understand the sedimentary environments and diagenetic transformations in borate deposits, in parallel with other research methods such as geochemical and isotopical determinations.
## TABLE I-1: Borate mineral, formulation and chemical composition

<table>
<thead>
<tr>
<th>Ca-borates</th>
<th>Structural formula</th>
<th>Empirical formula</th>
<th>Oxide like formula</th>
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<tbody>
<tr>
<td>Priceite</td>
<td>Ca$_2$B$_2$O$_7$(OH)$_6$·3H$_2$O</td>
<td>Ca$<em>2$B$</em>{10}$O$_{10}$·7H$_2$O</td>
<td>4CaO 5B$_2$O$_3$ 7H$_2$O</td>
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<tr>
<td>Colemanite</td>
<td>Ca(B$_2$O$_4$(OH)$_2$)·H$_2$O</td>
<td>Ca$<em>2$B$</em>{11}$O$_{11}$·5H$_2$O</td>
<td>2CaO 3B$_2$O$_3$ 5H$_2$O</td>
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<tr>
<td>Meyerhoffrite</td>
<td>Ca(B$_2$O$_4$(OH)$_2$)·H$_2$O</td>
<td>Ca$<em>2$B$</em>{11}$O$_{11}$·7H$_2$O</td>
<td>2CaO 3B$_2$O$_3$ 7H$_2$O</td>
</tr>
<tr>
<td>Inyoite</td>
<td>Ca(B$_2$O$_4$(OH)$_2$)·4H$_2$O</td>
<td>Ca$<em>2$B$</em>{11}$O$_{11}$·13H$_2$O</td>
<td>2CaO 3B$_2$O$_3$ 13H$_2$O</td>
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<td>Probertite</td>
<td>NaCa(B$_2$O$_4$(OH)$_2$)·3H$_2$O</td>
<td>NaCaB$_2$O$_5$·5H$_2$O</td>
<td>Na$_2$O 2CaO 5B$_2$O$_3$ 10H$_2$O</td>
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<td>Ulexite</td>
<td>NaCa(B$_2$O$_4$(OH)$_2$)·5H$_2$O</td>
<td>NaCaB$_2$O$_5$·8H$_2$O</td>
<td>Na$_2$O 2CaO 5B$_2$O$_3$ 16H$_2$O</td>
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<td>Tincalconite</td>
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<td>Na$_2$O 2B$_2$O$_3$ 5H$_2$O</td>
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<td>Borax</td>
<td>Na$_2$(B$_2$O$_4$(OH)$_2$)·8H$_2$O</td>
<td>Na$_2$B$_2$O$_7$·10H$_2$O</td>
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<td>Szalabylite</td>
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<td>Mg$_2$B$_2$O$_5$·15H$_2$O</td>
<td>2MgO 3B$_2$O$_3$ 15H$_2$O</td>
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<td>Na$_2$O SrO SO$_3$ 2B$_2$O$_3$ 4H$_2$O</td>
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PART II: LITHOFACIES AND PETROGRAPHY

**Lithofacies.** In this workshop we are using the word 'lithofacies' in the sense of macroscopic characteristics of the borate rocks, i.e., as a basic description informing on: a) the macroscopic structures/texture of both sedimentary and diagenetic interest, and b) the relationships between the borate and the host-sediment. Many terms of lithofacies, such as laminated, banded, nodular-banded, nodular, massive, enterolithic, brecciated, pseudomorphic, and so on are the same than to those used in other evaporitic rocks.

As regards the sedimentologic interpretations of the borate lithofacies to be found in the literature, they commonly follow the interpretative patterns previously established for the Ca-sulfate lithofacies. Some aspects of the primary (depositional) origin of a particular borate mineral are: the perfect laminations or banding; the lateral stratigraphic continuity; and the alternation with one or several primary, non-borate minerals. Summing up, laminated and banded lithofacies are usually interpreted as subaqueous precipitates, while nodular, nodular-banded and enterolithic lithofacies tend to be interpreted as formed interstitially (within the sedimentary matrix) from underground positions of the water table (under subaerial, exposed conditions). This last point (the nodular lithofacies), however, should not be systematically applied to the borate lithofacies without a detailed sedimentological examination of the depositional cycles formed by the borates alone or in association with other evaporites (see below).

**Crystalline fabrics.** The petrographic observations refer mainly to the description and interpretation of the microscopic textures/structures forming the various lithofacies of borates. In many cases, these fabrics are formed by very small crystals. Not infrequently, however, the fabrics are constituted by coarse-grained crystals attaining up to several centimeters in length. Several petrographic features suggest a diagenetic (secondary) origin for some particular borate minerals: the geometry of grain boundaries; the presence of pseudomorphs of one mineral after a precursor one; and the presence of relics of a (precursor) mineral within the crystals of another. Of particular interest to decipher the diagenetic modifications in a borate paragenesis is the presence of pseudomorphs.

**Primary, early diagenetic, secondary borates.** According to both the modern and the ancient occurrences of borates, some of these minerals as borax, ulexite and inyote are primary, free (subaqueous) precipitates: they form stratified deposits, where the crystals may exhibit fabrics indicating bottom growth conditions. The rest of borates, and also borax in some cases, precipitate interstitially within a preexistent host-sediment or matrix (clay, tuff) under synsedimentary/early diagenetic conditions. This is usually a displacive growth, but the matrix can result embedded and cemented also. Finally, borates can be secondary also: in some cases they replace other preexistent/precursor minerals.

**Studied material.** This workshop is focused on the lithofacies and petrographic features of the most common borate minerals forming the Neogene Anatolian (Turkey) deposits. These deposits were originated in non-marine, evaporitic settings during the Miocene, and are distributed in five mining districts: Bigadiç (colemanite, ulexite), Emet (colemanite, probertite), Kestelek (colemanite, probertite), Kirk (borax, probertite), and Sultançayır (priceite, howlite). At present, the latter exploitation is not active. A number of studies have been devoted to the mineralogy, stratigraphy and genesis of all these deposits (Helvacı and Firman, 1976; Ataman and Baysal, 1978; Helvacı, 1977, 1978, 1994, 1995; Kistler and Helvacı, 1994; Mordogan and Helvacı, 1994; Palmer and Helvacı, 1995; Palmer and Helvacı, 1997; Helvacı and Ortí, 1998, 2004; Ortí et al., 1998; García-Veigas et al., 2011; among many others).

Additionally, some references will be done to the Neogene borate deposits in La Puna region (Central Andes, NW Argentina), from which hand samples and petrographic material is also available.

On the basis of the Neogene borate occurrences in Western Anatolia and Central Andean region, the study of lithofacies and petrography can be separated in two groups: the rock-forming borates and the accessory borates. Only their most significant characteristics are cited in this text, but additional information is given separately in Table II-1. The optical and crystallographic characteristics of most of the borate minerals studied in this workshop are summarized in the Appendix.

2.1. Rock-forming Na-Ca borates

2.1.1. Ulexite

**Lithofacies.** Ulexite is characterized by a white, sometimes silky luster, and a very fine grained texture. Main lithofacies are the following:

- **Nodular, and nodular-banded.** Ulexite nodules display a variety of morphologies, from almost spherical to cauliflower-like (cotton-ball), flattened, irregular or with interpenetrating boundaries. The size of these nodules ranges between <1 cm (micronodules) and up to 30-40 cm (Fig. 2.1A).
- **Vertically elongated (columnar, tooth-shape).** Some ulexite layers are formed by very narrow (usually <1 cm in diameter) nodules elongated vertically up to some tens of centimeters (Fig. 2.1B).
- **Laminated.** In this lithofacies, laminae (<1 cm thick) of ulexite may alternate with carbonate and lutitic laminae. The inner structure of these
ulexite laminae tends to be micronodular and more unfrequently massive.

- **Banded, and banded-massive.** Bands (1 - 10 cm thick) and layers (>10 cm thick) of ulexite are common (Fig. 2.1C). These bands are formed by fibrous, massive to poorly-defined nodular masses of fibrous ulexite, which commonly display radiating fabrics (Fig. 2.1D).

- **Fibrous (satin-spar) veins.** These veins (<1 - 20 mm thick) are very common in the borate units. They can be parallel to bedding (Fig. 2.1A) or crosscut (and cement) all sedimentary materials, both the borate minerals and the matrix, in whatever direction.

---

**Figure 2.1. ULEXITE**

A) Various lithofacies (nodular-banded, columnar, fibrous veins) of ulexite (white, fibrous material) alternating with laminated claystones (dark material) (Kurtpinarı deposit, Bigadiç district, Miocene, Anatolia).

B) View of a vertical trench sectioning the floor of a Holocene salar. The nodules of ulexite ('papas'; fine-grained, white material) have grown in a dark, clayey matrix. The columnar arrangement of the nodules suggests a control by capillary action (Mina Maggi, Salar Centenario, NW Argentina).

C) Banded to massive lithofacies of ulexite. Small crystals at the top corresponds to tunellite. Lens cap: 6 cm in diameter (Bigadiç district, Miocene, Anatolia).

D) Top view of a layer formed by banded to massive lithofacies of ulexite, showing the radiating crystalline fabric. Lens cap: 6 cm in diameter (Bigadiç district, Miocene, Anatolia).

E) Photomicrograph of ulexite micronodules which are surrounded by a dark, clayey matrix. Note the variable size and interlocking character of the micronodules. Bar: 0.32 mm. Crossed nicols.

F) Photomicrograph of fibrous fabric in a micronodular lithofacies of ulexite. Deformation, bending and breakage of the fibers are common and probably occurred during the growth and mutual interaction of the micronodules. Scale bar: 0.32 mm. Crossed nicols.
Crystalline fabrics. Ulexite displays two major crystalline fabrics:
- **Parallel fibers.** The most common fabric is made up of small groups of almost parallel to each other fibers or needles. These fibrous groups exhibit micronodular or fusiform shapes in which the fibers display tangential to fascicular fabrics, as well as bending and breakage features (Fig. 2.1E,F).
- **Radiating fibers.** Less common is a large, fibrous-radiating fabric. This fabric forms large nodules or massive lithofacies in which the fibers reach up to 5 mm in length (Fig. 2.1D).

2.1.2. Probertite

**Lithofacies.** The major lithofacies of probertite are nodular and laminated:
- **Nodular.** Probertite usually occurs as grey, and dirty yellow, or dirty white clusters and nodules, which are composed of fibrous crystals ranging from 5 to 50 mm in length. These fibers are oriented parallel to one another or may display radiating fabrics (Fig. 2.2A,B,C).
- **Lenses and massive beds.** Probertite occasionally forms 20 to 30 cm thick lenses in the ulexite beds, though massive layers up to 1 m thick are encountered in some ulexite beds.

- **Laminated.** In the exploratory boreholes of the Emet district (García-Veigas et al., 2011), probertite forms laminae with variable thickness (from one to some millimeters thick, besides other unusual lithofacies known in this mineral (banded, banded-nodular, nodular, brecciated) (Fig. 2.2A,B).

**Crystalline fabrics.** The crystalline fabrics of probertite are formed by fibrous crystals also of variable sizes, from extremely fine to millimetric arranged in micronodules and micro-bundles (Fig. 2.2A,B).

2.2. Rock-forming Ca-borates

2.2.1. Inyoite

Inyoite occurs rarely as discrete, transparent prismatic to **tabular crystals**, and also as crystal groups and intergrown crystalline masses. Some of these euhedral crystals are up to 2.5 cm in length, but most are microscopic. Locally, inyoite occurs as clear, coarse-grained, euhedral aggregates (Fig. 2.3A,B).

**Replacive inyoite.** In the occurrences with other minerals such as meyerhoffenite, colemanite, ulexite and hydroboracite, replacive inyoite is found scattered within them (Fig. 2.3C,D).
2.2.2. Meyerhofferite

Lithofacies. The main lithofacies of meyerhofferite are the following:
- **Nodular.** Meyerhofferite occurs as nodules up to 15 cm in diameter, which are composed of coarse-crystalline radiating crystals (Fig. 2.4A). These nodules have grown interstitially within a sedimentary matrix. Small vugs in the center of the nodules (Fig. 2.4B) may contain acicular crystals of the same mineral.
- **Crystalline masses.** Yellow-white, coarse-crystalline meyerhofferite usually occurs as a net-texture made up of transparent crystals, regularly oriented in two systems which cross to about 90°.

Crystalline fabrics. Under the microscope, meyerhofferite shows a tabular to prismatic habit (Fig. 2.4C,D). The sections normal to the prisms usually show two cleavage systems which cross almost perpendicularly. In these sections, the optical extinction forms a very low angle with the cleavage (Fig. 2.4E,F).

2.2.3. Colemanite

Lithofacies. The main lithofacies of colemanite are the following:
- **Nodular, and nodular-banded.** Colemanite nodules have variable sizes between <1 cm and >50 cm (meganodules), and display different shapes from spherical to ovoid, hemispheroidal, flattened, discoidal, lenticular, flaser-shaped, cauliflower-like, elongated, and irregular (Fig. 2.5 A,B). Each nodule is a single structure or can be composite, and it occurs isolated or grouped in open or in closely packed patterns deforming and trapping the matrix. Some nodules display growth-bands that are arranged concentrically (zoned growth) (Fig. 2.5C,D). This zoning may involve: a) a coarse-crystalline colemanite core with a blocky, cementing fabric; b) an intermediate zone of radiating fabric; and c) an outer zone with a dendritic fabric. The crystalline core may project through the intermediate zone by means of septaria-like radiating bands. Locally, the center of the nodules may be empty or may have a vuggy texture, where a drusy coat made up of euhedral, coarse-sized crystals of colemanite surrounds the central hollow.
- **Fibrous-banded lithofacies.** The fibrous growth of colemanite in bands and thin layers is a common feature (Fig. 2.5E).
- **Isolated crystals.** Euhedral crystals of colemanite occur interstitially within the...
sediment matrix, either isolated and unoriented or grouped in small, irregular aggregates.

- **Massive, vuggy-breciated lithofacies.** Some colemanite layers exhibit a brecciated texture with vugs, druse cavities and septaria structures, as well as coarse-crystalline masses. Vugs and cavities are commonly coated by coarse euhedral, transparent crystals of the same mineral.

- **Fibrous (satin-spar) veins.** These are veins (<2 mm to >10 cm thick) that are parallel or crosscut the host sediment and the borate units.

  **Crystalline fabrics.** The crystals forming the nodules have several centimeters in length, and are arranged in subgroups with the same optical orientation. Colemanite crystals can also be small in size, either isolated (Fig. 2.5F) or grouped (Fig. 2.5G, H).
Figure 2.5. COLEMANITE
A) Large nodule of colemanite in a nodular-banded lithofacies of this mineral. Note the radiating fabric of the crystals forming the nodule (Kapikaya deposit, Bigadiç district, Miocene, Anatolia).
B) View of a colemanite exploitation front. Note the interlocking fabric of the nodules. Diameters of the nodules range between 10 and 80 cm (Espay deposit, Emet district, Miocene, Anatolia).
C) Close view of a fragment of a colemanite nodule in which the radiating crystals in the central part are totally impregnated by realgar (reddish material). Scale in centimeters (Emet district, Miocene, Anatolia).
D) Close view of a fragment of a colemanite nodule. The central part is formed by radiating crystals of colemanite (light brown), whereas in the external part, a branching-to-dendritic fabric trapping sedimentary matrix prevails (dark grey). Note the zoned pattern (lamination) in the boundary between the two parts. Scale in centimeters (Emet district, Miocene, Anatolia).
E) Colemanite lithofacies grading from isolated nodules to fibrous-banded layers. The colemanite growth is always displacive. Host sediment is grey lutite and tuff horizons (Emet district, Miocene, Anatolia).
Figure 2.6. REPLACIVE COLEMANITE
A) Close view of a fragment of ulexite mass (white, fibrous material) containing centimeter-sized crystals (porphyroblasts) of replacive, secondary colemanite. Lens cap: 6 cm (Acep deposit, Bigadiç district, Miocene, Anatolia).
B) Close view of a block of secondary colemanite (brownish material) replacing a banded lithofacies of fine-grained ulexite (white material). Note that the radiating colemanite crystals preserve both banding and deformation in the ulexite lithofacies (banding can be seen throughout the colemanite masses). Pencil for scale (Acep deposit, Bigadiç district, Miocene, Anatolia).
C) and D) Photomicrographs of replacive colemanite. In normal light (C), the laminated sedimentary matrix and abundant micronodules of (precursor) ulexite can be seen. In crossed nicols (D), two large, anhedral crystals of colemanite (light area on the left and dark area on the right) replace the ulexite and cement poikilitically the matrix. Note that colemanite preserves both the lamination and the micronodular lithofacies of ulexite. Scale bar: 0.32 mm (C: normal light; D: crossed nicols) (Kireçlik mine, Bigadiç district, Miocene, Anatolia).
E) Photomicrograph of a fine-grained mosaic fabric of colemanite forming the center of a nodule. Note the euhedral (rhombohedral) sections. Some crystals show zoned growth and syntaxial overgrowths. The overgrowths tend to be subhedral and to display undulose extinction. Scale bar: 0.32 mm, crossed nicols (Kireçlik mine, Bigadiç district, Miocene, Anatolia).
G) and H) Photomicrographs of the central part of a colemanite nodule. The fabric is formed by a mosaic of euhedral to subhedral crystals with almost the same optical orientation. Some porosity is present. Scale bar: 0.32 mm (G: normal light; H: crossed nicols) (Bigadiç district, Miocene, Anatolia).

F) Photomicrograph of a portion of a colemanite nodule. Large, anhedral crystals of colemanite have replaced and preserved pseudomorphs of a precursor mineral (lenticular gypsum?). Scale bar: 0.32 mm, crossed nicols (Emet deposit, Miocene, Anatolia).
Replacive colemanite. Euhedral crystals (porphyroblasts) of colemanite (Fig. 2.6A) as well as discoidal nodules, radial aggregates, bands and irregular masses of this mineral can replace other borates and are found embedded in their lithofacies (Fig. 2.6B). Fibrous ulexite is the borate which most commonly is replaced by colemanite. Frequently the geometry of the ulexite micronodules is preserved within the colemanite fabric (Fig. 2.6 C, D, E). Colemanite pseudomorphs after other minerals can be easily identified (gypsum, in Fig. 2.6F).

2.2.4. Priceite

Priceite (pandermite) is mainly found as fine-crystalline, milky-white material. It frequently exhibits a hard, hornlike structure with a concoidal fracture, but on exposure to the atmosphere it desintegrates into a kaolin-like mass.

Lithofacies. The main priceite lithofacies are the following:
- Discontinuous bands, lenticular layers, and stratiform masses. These occurrences have a thickness up to several tens of centimeters (Fig. 2.7A).
- Nodular. Nodules and masses displaying a poorly-defined nodular morphology reach sizes comprised between <1 cm and >1 m in diameter.
- Veins. Veins, as well as irregular masses and dykes, are present locally filling discontinuities or crosscutting the host sediment.
- Laminated. Laminae and thin bands (few centimeters in thickness) are made up of extremely fine priceite crystals. These laminae can display micro-convoluted structures.

Crystalline fabrics. Under the microscope, priceite is commonly composed of tiny (<20 µm), equant, unoriented rhombohedrons which form a homogeneous crystalline fabric devoid of sedimentary matrix. These crystals may display an internal fibrous appearance and undulose extinction (Figs. 2.7C, D). Prismatic crystals, either unoriented or arranged in parallel to each other are also present.

Figure 2.7. PRICEITE
A) Banded lithofacies of priceite (white material) intercalated between laminated secondary gypsum (grey material). The priceite mass displaces the laminae of secondary gypsum (Sultançayır deposit, Miocene, Anatolia).
B) Mass of priceite being transformed into secondary calcite. Remains of priceite (fine-grained, massive, white material) can be seen. Calcite displays a porous net-texture. Fallen block in a front quarry; length of the block: 75 cm (Sultançayır deposit, Miocene, Anatolia).
C) and D) Photomicrographs of priceite fabric. Note the rhombohedral sections of the tiny priceite crystals. Some clayey matrix (dark material) is scattered between the dense mass of priceite. Scale bar: 0.32 mm (C: normal light; D: crossed nicols) (Kireçlik mine, Bigadiç district, Miocene, Anatolia).
Figure 2.8. BORAX
A) Banded lithofacies of borax ('tincal', white to transparent material) alternating with clay/tuff matrix (brownish material). Note the coarse size (up to 2 cm) of some borax crystals. (Tincare deposit, Upper Miocene, NW Argentina).
B) Laminated lithofacies of borax (brown material) alternating with dolomitic, marly laminae (white laminae). Palisade fabric (bottom-nucleated, upward-directed, competitively grown crystals) can be seen in some borax laminae. In the lower part, a discoidal nodule of fibrous ulexite is present. The growth of this nodule is early diagenetic, being coeval with the sedimentation of the borax laminae. Under the microscope, the replacive nature of this ulexite nodule can be seen in next photographs E-F. Lens cap: 6 cm (Kirka deposit, Miocene, Anatolia).
2.3. Rock-forming Na-borates

2.3.1. Borax

Lithofacies. The main borax lithofacies are the following:
- Laminated and banded lithofacies. They consist of alternations of planar laminae (<1 cm thick) and bands (1 cm to a few dm thick) of borax, with laminae of sedimentary matrix (Fig. 2.8A,B). Borax crystals are transparent to brownish, and can show a zoning formed by solid inclusions of the matrix. These crystals are euhedral to subhedral, with sizes oscillating between <1 mm and up to 1 cm (Fig. 2.8C,D).
- Interstitial macrocrystals. This lithofacies consists of layers (between 20 and 50 cm thick) rich in marly and clayey matrix, in which displacive, coarse crystals of borax (up to several cm) are present. These crystals are euhedral and transparent, and they are often devoid of internal zoning.
- Massive crystalline. This lithofacies is formed by massive, matrix-free, subhedral to anhedral, transparent crystals of borax, which form layers up to several meters thick. Crystalline sizes range between 1 and 2 cm. No particular orientation of these crystals is observed.

Crystalline fabrics. In the borax laminae of the Kirka deposit (Anatolia), two crystal fabrics may be distinguished:
- Palisade fabric. It is formed by matrix-poor, brown-colored crystals up to 1-2 cm high, which are arranged in a subvertical fabric. These crystals exhibit a planar base and an euhedral apex; dissolution surfaces can be observed at the top of the crystals locally.
- Unoriented fabric. In this fabric, the crystals are euhedral to anhedral in shape, and are surrounded by sediment matrix resulting in a clastic appearance. Locally, some tendency to normal grading is observed. In some laminae, prismatic to tabular crystals are arranged parallel to the lamination suggesting a cumulate character. In the Kirka deposit, borax crystals of the two types of fabrics can be replaced by ulexite (Fig. 2.8E,H).

2.4. Rock-forming Ca-Mg-borates

2.4.1. Hydroboracite

Lithofacies. Hydroboracite usually occurs as nodules and small masses with a conical appearance. These occurrences are formed by radiating needle-shaped crystals, with sizes comprised between 0.5 and 5 cm. Hydroboracite associates mainly with colemanite and ulexite. In the Neogene deposits in NW Argentina, hydroboracite is fine-grained, displays a number of lithofacies, and forms thick deposits of economic interest (Ortí and Alonso, 2000) (Fig. 2.9A,B).

Crystalline fabrics. Under the microscope, the needle-shaped crystals have a fibrous texture resembling ulexite. Groups of these crystals show flow-like arrangements (Fig. 2.9C,D).

Replacive hydroboracite. Hydroboracite can occur also as individual porphyroblastic crystals replacing any preexistent borate mineral in some deposits.

2.5. Accessory borates

2.5.1. Howlite

Lithofacies. This Ca-bearing mineral occurs as white, compact nodules (<1 cm up to 10 cm in diameter), which are dense and structureless resembling unglazed porcelain. These nodular masses may be embedded in clay laminae accompanying the colemanite layers. In the Sultançayır deposit (Anatolia), these nodules displace/replace both the gypsum beds and the priceite lithofacies (Fig. 2.10A). Howlite accompanies priceite, colemanite and gypsum, and can alter to calcite.

Crystalline fabrics. Under the microscope, the crystalline fabric of howlite is homogeneous and fine-grained. It is formed by prisms up to 0.15 mm in length that may be unoriented (decussate fabric) or arranged in small groups of a parallel tendency (Fig. 2.10C,D). Micronodular structures and poorly-defined spherulites can be observed.

2.5.2. Bakerite

Bakerite is visible only under the microscope, forming crystalline aggregates (from ~30 µm to 0.2 mm in size), which display high relief and
variable shapes, from ovoid to perfectly spherulitic (Fig. 2.10B). Poorly-defined radial fabrics are present in these aggregates. Also, unoriented, microcrystalline masses of bakerite are recorded. This mineral replaces both priceite and gypsum, and is replaced by howlite.

2.5.3. Tincalconite

An alteration product of borax is tincalconite. This mineral does not form independent crystals, but occurs as a thin film made up of microscopic, fibrous crystals. These films develop on the borax crystals when they are in contact with dry atmosphere.

2.5.4. Kurnakovite

Kurnakovite is found in the Kirka deposit (Anatolia), where it forms a discontinuous layer at the top of the main borate body. This layer is formed by colorless, grey or pink, elongated (1 to 20 cm long) euhedral crystals (Fig. 2.11D) and also by crystalline aggregates (Inan et al., 1973; Helvacı and Ortı, 2004). These crystals coexist with ulexite, inderite and tunellite, and less frequently with borax also.
2.5.5. Tunellite

Tunellite commonly occurs as individual, thin, flattened or tabular crystals (1 to 5 cm long). Pure tunellite crystals are colorless and transparent, and have perfect cleavages parallel to crystal surfaces (resembling muscovite).

Alternatively, tunellite occurs as small, white, flattened nodules with radiating structures which have grown within the interbedded clays. Some of these nodules may exhibit internal porosity. Tunellite is associated with ulexite, probertite, colemanite and hydroboracite.

**Crystalline fabrics.** Under the microscope, the tunellite nodules are formed by crystalline fabrics exhibiting equant to prismatic sections (Fig. 2.11A,B,C). Prisms show straight extinction and are arranged in fan-shape and radial aggregates. Pores and small vugs are located in the core of some of these aggregates.

2.5.6. Veatchite-A

Veatchite-A occurs rarely in the Emet deposit, where it appears as a white mineral often with clay inclusions, with nodules from 2 to 6 cm in diameter made up of needle-shaped crystals. Locally, very small nodules are grouped together and show mammillar appearance. Veatchite-A associates mainly with colemanite.

Field and textural evidence show that veatchite-A replaces colemanite (Helvacı, 1984).

**Crystalline fabrics.** Veatchite-A occurs as felted masses of very small crystals.

2.6. Facies and petrography of borates and sulfates: a brief comparison

Although lacustrine borates are much less common than sulfates or chlorides, some morphologic and genetic relations exist between all these evaporitic groups. This is particularly valid for sulfates, with which borates exhibit marked similarities in lithofacies, crystalline fabrics, depositional conditions, sedimentary environments, and diagenetic processes including various types of chemical cements. Some of the sedimentological or diagenetic interpretations time ago well established for sulfates, can be applied for a number of borate occurrences. For instance: (1) the sabkha setting of nodular/enterolithic anhydrite for the playa/salar setting of nodular/enterolithic ulexite, and (2) the diagenetic cycle of Ca-sulfates (primary gypsum – replacive anhydrite – secondary gypsum) for the burial-exhumation cycle of Na-borates (primary borax – kernite – secondary borax).

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*Figure 2.10. HOWLITE, BAKERITE*

A) Howlite nodules (white material) displacing laminated (secondary) gypsum (Sultançayıır deposit, Miocene, Anatolia). B) Photomicrograph of spherulites of bakerite cemented by a single poikilitic crystal of secondary gypsum (central part of the photograph). Surrounding this poikilitic crystal many laths (prisms) of anhydrite are still preserved. Average diameter of the spherulites: 0.26 mm. Crossed nics (Sultançayıır deposit, Miocene, Anatolia).

C) and B) Photomicrographs of a portion of howlite nodule. Note the prevalent, decussate fabric of the prisms. Scale bar: 0.16 mm (C: normal light; D: crossed nics) (Kurtpinarı deposit, Bigadiç district, Miocene, Anatolia).
In the Neogene deposits, however, it is worth emphasizing some textural or diagenetic differences which can be found between these two mineral groups:

**Monomineralic deposits.** Several borates may form large deposits of economic interest which are practically monomineralic or in which the presence of other borates is unimportant. This is the case of colemanite, ulexite, borax, priceite, probertite and hydroboracite (see Part IV of this workshop). However, the ability of forming large, practically monomineralic deposits of economic interest in the long list of evaporitic sulfates is limited to gypsum/anhydrite and glauberite.

**Fibrous crystalline fabrics.** Several borates exhibit fibrous textures both to the macro- and the micro-scale as primary, depositional features, a fact that is not at all common in sulfates. The question is that many of the borate microfiber (<10 μm in length) occurrences seem

helvacı, ortı, garcía-veigas, rosell, gündoğan (2012)

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... to be free, subaqueous precipitates. Ulexite, probertite and priceite, among other borates, may form very thin depositional laminae totally integrated by microfibers (Fig. 2.12A,B) either as decussate or oriented individuals, or as groups arranged in tiny bundleless or micronodules. On the one hand, in these thin laminae any non-borate sedimentary matrix can be totally absent, strongly suggesting that microfibers are in fact subaqueous precipitates. On the other hand, microfibers never display palisade fabrics or cumulate textures in these laminae, suggesting that they nucleated directly in the sediment-water interphase, or slightly below it, and that they grew indistinctly from the 'free' brine or the interstitial borate-saturated solution.

Nodular growth. Few sulfate minerals, mainly anhydrite and gypsum, and glauberite to a lesser extent, exhibit nodular lithofacies. In the borate group, however, the nodular growth is extremely common in many minerals. Only in borax and kernite, nodular lithofacies have not been described. The borate occurrence as nodules is mostly valid for those borates which have an accessory character in a particular deposit. This fact could result from a low growth rate of many borates in the precipitating environments.

Subaqueous/burial growth of borate nodules. On the basis of lithofacies description and the characterization of individual depositional cycles made in this workshop (see Part III), some nodular lithofacies in borates could have been formed interstitially below the sediment-water interface (under a free water body) and to variable depths. Such an interpretation has not been formerly well documented for nodular sulfates. Moreover, the extensive development of large nodules (up to >80 cm in diameter) in some borate minerals, as colemanite in the Emet district (Anatolia, see Part IV), suggests that, after its interstitial nucleation close to the surface, the nodules continued growing from shallow to moderate burial depth.

Pseudomorphs and other evidence of diagenetic transformations. The identification of pseudomorphs is one of the best petrographic tools to document these types of transformations. For sulfates this is particularly useful in the diagenetic cycle of Ca-sulfates, in which several types of pseudomorphs are formed. In the case of borates, these transformations are extremely difficult to be characterized between fibrous borates, for instance in the relations between ulexite and probertite. The characterization is more easily recognized in the case of the replacement of a non-fibrous by a fibrous borate, for instance when ulexite replaces borax (Fig. 2.8E,F). In contrast, the total replacement of a fibrous by a non-fibrous borate mineral only can be documented by the preservation in the replacive fabric of (1) the original lithofacies (micronodules, lamination, etc.) (Fig. 2.6C,D), or (2) fiber relics of the precursor borate. In other cases, the difficulty derives from the fact that the attribution to a particular borate mineral of the habit preserved in the pseudomorph is ambiguous. Commonly, however, the replacement of sulfate crystals by a borate mineral can be more easily documented given that the sulfate habitus is better known (Fig. 2.6F).

Figure 2.12. FONTARNAUITE
A) and B) Fontarnauite crystal replacing a fine-grained probertite lamina between two glauberite laminae (A: normal light; B: crossed nicols) (Emet district, Miocene, Anatolia)
TABLE II-1: Additional observations of borate lithofacies and crystalline fabrics; some interpretative aspects.

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<th>ULEXITE</th>
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<th>INYOITE</th>
<th>COLEMANITE</th>
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<tbody>
<tr>
<td>- Nodular and nodular-banded. Nodules may occur isolated within the host sediment (matrix), or in close associations forming layers (nodular-banded lithofacies). They may be single, but frequently they are composite (multinodular).</td>
<td>- Nodular. Micronodules integrated by microfiber groups of probertite can be distinguished surrounding the large fibers that form the nodules. Clay partings may fill the space between some fiber groups.</td>
<td>- Modern deposits of primary inyoite have been described by Muessig (1958) in a saline pan in Perú, and by Helvacı and Alonso (1994) in Lagunita Playa (NW Argentina). İnan et al. (1973) cited in the Kırka deposit the local finding of discrete crystals and masses of inyoite at the top of the colemanite layers, which were interpreted as a primary occurrence of inyoite. Also, some colemanite pseudomorphs after possible inyoite have been described (Helvacı and Orti, 1998). Despite the former observations, inyoite lithofacies clearly indicating a primary origin have not been firmly documented in the Anatolia deposits. In some inyoite occurrences with ulexite, the latter mineral is clearly replaced by inyoite (Fig. 2.3C, D), as proved by the presence of both fiber relicts and pseudomorphic micronodules of (precursor) ulexite, which are retained in the inyoite crystals. In the ulexite-inyoite occurrence of the Pleistocene Blanca Lila Formation (NW Argentina), Vandervoort (1997) interpreted a displacive (diagenetic) lithofacies of inyoite as precipitated from boron-rich brines which percolated downward throughout the sedimentary section during or following the deposition of the overlying ulexite beds.</td>
<td>- Nodular and nodular-banded. The nodules are composed of elongated, straight to slightly curved, fibrous or bladed crystals that radiate from the core outward as stellate clusters. Large nodules are locally flattened suggesting some dissolution by compaction, pressure-solution or mechanical readjustment. In all these nodules, colemanite is transparent to dirty, and white to grey, but locally displays dark tonalities (‘black colemanite’ was cited in the Kırka deposit). Also, some colemanite pseudomorphs after possible inyoite have been described (Helvacı and Orti, 1998). Despite the former observations, inyoite lithofacies clearly indicating a primary origin have not been firmly documented in the Anatolia deposits. In some inyoite occurrences with ulexite, the latter mineral is clearly replaced by inyoite (Fig. 2.3C, D), as proved by the presence of both fiber relicts and pseudomorphic micronodules of (precursor) ulexite, which are retained in the inyoite crystals. In the ulexite-inyoite occurrence of the Pleistocene Blanca Lila Formation (NW Argentina), Vandervoort (1997) interpreted a displacive (diagenetic) lithofacies of inyoite as precipitated from boron-rich brines which percolated downward throughout the sedimentary section during or following the deposition of the overlying ulexite beds.</td>
</tr>
</tbody>
</table>

*UXILETE*

- Nodular and nodular-banded. Nodules may occur isolated within the host sediment (matrix), or in close associations forming layers (nodular-banded lithofacies). They may be single, but frequently they are composite (multinodular). These two lithofacies have grown displacively with dily in the matrix, and can be interpreted as formed interstitially during periods of underground position of the water level in the sedimentary environment.
- Vertically-elongated (columnar, tooth-shaped). This lithofacies forms strong, resistant layers in which the length of the individual fibers can attain up to 1 cm, and the matrix can be absent. Nodules seem to grow upward competitively. The columnar lithofacies has an uncertain interpretation: its formation could be an original (competitive) growth mode; it could also be favored by preexistent plant-root structures on an exposed lake floor; and it could be related to persistent capillary action too.
- Laminated. In the micronodules forming the laminae, fiber fabrics vary from randomly oriented to normal to bedding. This lithofacies corresponds to subaqueous, lake-bottom deposition during shallow lake stages. Some ulexite bands and thin laminae associated with carbonate varves and laminated claystone could represent deeper precipitates.
- Banded, massive-banded. In these lithofacies the proportion of matrix is usually very low.
- Fibrous (satin-spar veins). Fibers attain several cm in length.
- The fibrous veins are cementing (diagenetic) precipitates.
- Replacive ulexite. Locally, some (secondary) ulexite replaces other minerals as borax (Fig. 2.8G,H) and meyerhofferite (Fig. 2.4E,F).

*PROBERTITE*

- Nodular. Micronodules integrated by microfiber groups of probertite can be distinguished surrounding the large fibers that form the nodules. Clay partings may fill the space between some fiber groups.
- Nodular probertite has formed interstitially, in general as a mineralogically primary mineral.
- Laminated. In both the finely laminated and banded lithofacies, probertite is a primary mineral, which has precipitated subaqueously.
- Associations. Probertite is mainly associated with ulexite, colemanite and hydroboracite.
- Replacive probertite. In the parageneses formed by probertite and various ulexite lithofacies, a replacement of ulexite by probertite can be observed locally. This suggests that probertite precipitated at a more advanced concentration stage than ulexite, a possibility that agrees with the theoretical requirement of higher temperature and lower water activity for probertite instead of ulexite precipitation. In this case, following to the ulexite, probertite is indicative of drier, more and conditions in the boratiferous lakes.

*INYOITE*

- Modern deposits of primary inyoite have been described by Muessig (1958) in a saline pan in Perú, and by Helvacı and Alonso (1994) in Lagunita Playa (NW Argentina). İnan et al. (1973) cited in the Kırka deposit the local finding of discrete crystals and masses of inyoite at the top of the colemanite layers, which were interpreted as a primary occurrence of inyoite. Also, some colemanite pseudomorphs after possible inyoite have been described (Helvacı and Orti, 1998). Despite the former observations, inyoite lithofacies clearly indicating a primary origin have not been firmly documented in the Anatolia deposits. In some inyoite occurrences with ulexite, the latter mineral is clearly replaced by inyoite (Fig. 2.3C, D), as proved by the presence of both fiber relicts and pseudomorphic micronodules of (precursor) ulexite, which are retained in the inyoite crystals. In the ulexite-inyoite occurrence of the Pleistocene Blanca Lila Formation (NW Argentina), Vandervoort (1997) interpreted a displacive (diagenetic) lithofacies of inyoite as precipitated from boron-rich brines which percolated downward throughout the sedimentary section during or following the deposition of the overlying ulexite beds.

*COLEMANITE*

- Nodular and nodular-banded. The nodules are composed of elongated, straight to slightly curved, fibrous or bladed crystals that radiate from the core outward as stellate clusters. Large nodules are locally flattened suggesting some dissolution by compaction, pressure-solution or mechanical readjustment. In all these nodules, colemanite is transparent to dirty, and white to grey, but locally displays dark tonalities (‘black colemanite’ was cited in the Kırka deposit). Also, some colemanite pseudomorphs after possible inyoite have been described (Helvacı and Orti, 1998). Despite the former observations, inyoite lithofacies clearly indicating a primary origin have not been firmly documented in the Anatolia deposits. In some inyoite occurrences with ulexite, the latter mineral is clearly replaced by inyoite (Fig. 2.3C, D), as proved by the presence of both fiber relicts and pseudomorphic micronodules of (precursor) ulexite, which are retained in the inyoite crystals. In the ulexite-inyoite occurrence of the Pleistocene Blanca Lila Formation (NW Argentina), Vandervoort (1997) interpreted a displacive (diagenetic) lithofacies of inyoite as precipitated from boron-rich brines which percolated downward throughout the sedimentary section during or following the deposition of the overlying ulexite beds.
The cahnite spherulites contain needle-shaped and fibrous crystals which often show a radial fabric. These crystals tend to be needle-like, and frequently are broken (Fig. 2.11E, F).

Kernite crystals are found in the underground works of the Kırka deposit, in the deeper part of the sodium borate body. Accompanying the small prisms, also equant to rectangular sections of large howlite crystals are seen; commonly these large prisms are bent and broken. Around some nodules, also fine microcrystalline quartz - resembling chert-and opal can be seen in thin, discontinuous films. In these nodules, a partial alteration to calcite is recorded, suggesting that the silica films are by-products of the howlite alteration. In the Sultançayır deposit, where howlite replaces both former sulfates (gypsum) and borates (priceite), no relics or pseudomorphs of a precursor phase are present in the radiating crystals. On the contrary, this lithofacies seems to represent a primary precipitate of meyerhofferite which was formed under synsedimentary conditions.

In the Sultançayır deposit, the local presence of fine lamination indicates that priceite was a (free) subaqueous precipitate.

Howlite crystals are found in the underground works of the Kırka deposit, in the deeper part of the sodium borate body. The crystals forming these nodules are very small and show prismatic habits elongated in the c axis, with pseudohexagonal sections. These crystals tend to be needle-like, and frequently are broken (Fig. 2.11E, F).

Cahnite is white and light brown with a notably glassy lustre. It occurs only rarely in the Emet deposit (Anatolia), both as very small spherulites within the powdery nodules of teruggite, and as a coating on euhedral colemanite crystals present in vugs of colemanite nodules. The spherulites of cahnite rarely exceed 2 mm in diameter. Usually they occur singly, but occasionally two or three of them coalesce together. The crystals of cahnite, characteristic of these nodules, are recognized as very small spherulites within the powdery nodules of teruggite, and as a coating on euhedral colemanite crystals present in vugs of colemanite nodules. The spherulites of cahnite rarely exceed 2 mm in diameter. Usually they occur singly, but occasionally two or three of them coalesce together.

- Massively, vuggy-brecciated. This lithofacies seems to represent mainly a reprecipitation product after partial dissolution of colemanite lithofacies. This could be particularly valid in those deposits in which other borates or evidence of their previous existence- are absent.
- Fibrous (satin-spar) veins. These veins are secondary, cementing features formed by the circulation of fluids throughout the borate formation along fractures and cavities. Differential compaction, deformation by tectonism, or decompression during uplift of the deposit created the necessary net of fractures.
- Replacive colemanite. The replacive crystals of (secondary) colemanite usually retain relics of ulexite fibers and preserve micronodular shapes of this precursor mineral.

Priceite - Discontinuous bands, lenticular layers, and stratiform masses. The bands commonly evolve to isolated patches with irregular morphology, which are embedded in a host rock. These lithofacies are weathered to calcite near the surface. In the Sultançayır deposit, the local presence of fine lamination indicates that priceite was a (free) subaqueous precipitate.

Borax - Laminated lithofacies. In the laminae, it is frequent to notice an upward transition from palisade to unoriented fabrics. The crystals forming these nodules are very small and show prismatic habits elongated in the c axis, with pseudohexagonal sections. These crystals tend to be needle-like, and frequently are broken (Fig. 2.11E, F).

- Nodular. In the Simav deposit, nodules of meyerhofferite form layers in alternation with ulexite beds; small partings of matrix can be found trapped between the large radiating crystals of the nodules. These partings contain small calcite crystals, and tiny crystals of idiomorphic meyerhofferite. The latter crystals contain zones formed by small particles and may display an archeated morphology as an original (not deformational) feature.
- Crystalline fabrics. Accompanying the small prisms, also equant to rectangular sections of large howlite crystals are seen; commonly these large prisms are bent and broken. Around some nodules, also fine microcrystalline quartz - resembling chert-and opal can be seen in thin, discontinuous films. In these nodules, a partial alteration to calcite is recorded, suggesting that the silica films are by-products of the howlite alteration.

- Crystalline fabrics. The crystals forming these nodules are very small and show prismatic habits elongated in the c axis, with pseudoaxial sections. These crystals tend to be needle-like, and frequently are broken (Fig. 2.11E, F).

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Borax - Laminated lithofacies. In the laminae, it is frequent to notice an upward transition from palisade to unoriented fabrics. The crystals forming these nodules are very small and show prismatic habits elongated in the c axis, with pseudoaxial sections. These crystals tend to be needle-like, and frequently are broken (Fig. 2.11E, F).
PART III: CYCLES AND SUCCESSIONS

3.1. Depositional cycles and successions

The sedimentary distribution of the Holocene Ca- and Na-bearing borates in the shallow lakes and playas is mainly controlled by the mineral solubility, which is usually lower for Ca-borates and higher for Na-borates (colemanite: 0.8 g/L; ulexite 7.6 g/L; borax: 47 g/L), and by the lateral gradient of salinity. These two factors contribute to the existence in these deposits of ‘facies belts’, which roughly consist in the precipitation of Ca-borates on the marginal zones of the lacustrine systems, and Na-borates in the central zones (Alonso, 1986; Helvacı, 1995).

In the Neogene deposits, besides the existence of these facies belts, the presence of vertical repetitions (cyclicity) can be clearly observed. Individual cycles have variable thicknesses, from less than one meter to several meters or tens of meters.

Borate successions, with thicknesses from tens to hundreds of meters, refer to the whole stratigraphic section forming the borate units. These successions can be composed by the repetitions of individual borate cycles, or by irregular alternations of borate layers and non-borate host rocks.

The cyclicity shown by the most common borate deposits can be exemplified by some of the Neogene deposits of Anatolia (Turkey) as well as by modern and Neogene deposits of the Andean Region (NW Argentina) and West USA (California). The borate minerals forming these deposits can be grouped in three major chemical (cationic) types: Ca-(Na), Ca-Na, and Na-(Ca). In those deposits involving sulfates and chlorides also, more complex chemical types need to be considered.

In general, the individual cycles selected for examples (Table III-1) can be interpreted as shallowing and with increasing salinity upward. Sedimentological interpretations of these cycles will be done in Part IV. Detailed information on these cycles as well as on the borate successions selected for examples is show in Table III-1.

3.2. Examples of individual cycles

Chemical types: Ca-(Na)-borate and Ca-Na-borate (Fig. 3.1)

Colemanite (Fig. 3.1A):
Emet deposit (Anatolia)

Colemanite (Fig. 3.1B):
Tülü open pit mine (Bigadiç district, Anatolia)
Colemanite (Fig. 3.1C)  
Kestelek district (Anatolia)

Ulexite, inyoite (Fig. 3.1D)  
Lagunita Playa (NW Argentina)

Ulexite, colemanite (Fig. 3.1E,F):  
Acep and Kurtpinar deposits (Bigadiç district; Anatolia).

Ulexite, meyerhoferite (Fig. 3.1G)  
Simav deposit (Bigadiç district, Anatolia)

3.3. Examples of successions with only borates.

Chemical types: Na-Ca-borate and Na-(Ca) borate (Fig. 3.2A-D)

Colemanite – ulexite – proberite – ulexite – colemanite (Fig.3.2A).  
Furnace Creek Fm (California)

Ulexite – borax (+kernite) – ulexite – colemanite (Fig. 3.2B)  
Boron deposit (California)

Colemanite – ulexite – borax – ulexite – colemanite (Fig. 3.2C)  
Kirka deposit (Anatolia)

Colemanite – inyoite – ulexite – borax - (ulyny-ul-bor) – ulexite – inyoite (Fig. 3.2D)  
Loma Blanca deposit (NW Argentina)

?- inyoite-ulexite-borax  
Tincalayu deposit (NW Argentina)

From these examples, the following complete succession of borate intervals can be deduced:  
Ca-borates → Ca-Na-borates → Na-borates → Ca-Na-borates → Ca borates.

This idealized succession can be found complete and symmetrical, as in the Kirka deposit, or assymetrical with several intervals missing (colemanite? ulexite? in the Tincalayu deposit) or with one interval absent (colemanite? in the Boron deposit). Very often, the missing interval is located at the base of the succession, where ulexite occupies the place of the Ca-borates. The absence of the Ca-borate interval in some deposits could be the result of:  
- the great ability of ulexite to precipitate, even under metastable conditions,  
- the early consumption of Ca by calcite/dolomite or gypsum precipitation in the case of higher contribution of carbonate/bicarbonate- or sulfate-rich waters.

Thus, many papers accept the existence of the following general successions, which reflects the most common mineralogic distribution in the borate deposits of the Na-(Ca)-borate chemical type: colemanite – ulexite – borax – ulexite – colemanite (Bowser and Dickson, 1966; İnan et al, 1973; Alonso, 1991; Kistler and Helvacı, 1994; Helvacı, 1995; Helvacı and Ortı, 2004, among others).

Also, repetition of intervals in the succession can be recorded in some particular deposits, as in Loma Blanca (Miocene, Argentina). In this deposit, borax (+kernite) occupies the central position in the succession and prevails volumetrically, being subordinated the rest of borates (ulexite, inyoite, colemanite).

All of the aforementioned successions have a depositional (chemical) origin and are organized according to the solubility of the borate minerals. In the ideal evaporative evolution, a boratiferous brine progressively increases in salinity and alkalinity in order to equilibrate the higher boron concentration. As a result of the different solubility products, the early precipitation of Ca-borates changes the cationic character from Ca- to Na-rich allowing first the ulexite and further the borax precipitation (Palmer and Helvacı, 1995). In detail, the interpretation of the various mineral successions present in the Neogene deposits requires caution, in particular as regards the Ca-borates, whose origin has been a subject of debate in the literature. This is the case for: (a) colemanite, which is considered by many authors to be only a secondary mineral coming from the transformation of precursor phases (inyoite, meyerhoferite, ulexite); and (b) inyoite, which in some cases has been interpreted as formed following the ulexite precipitation; thus, in the Blanca Lila Formation inyoite has been considered an early diageneric mineral precipitated from interstitial solutions underneath the ulexite interval but subsequently to it (Vandervoort, 1997).

3.4. Examples of borate successions with associated sulfates and chlorides

Besides the aforementioned cases in which the precipitating solutions are dominated by borate, some examples are known where borate is accompanied by other anions resulting in evaporitic deposits of more complex parageneses. Apparently, however, examples of genetic relations between borates, sulfates and chlorides are more common in the Holocene than in the ancient deposits.

In the today’s salars of La Puna region (NW Argentina), two opposite facies belts have been documented from the margin to the center:  
- borate - sulfate - chloride (halite) in the Salar of Rincón (Igarzábal, 1991)  

In the Miocene Sijes Formation of the same region, Ortı and Alonso (2000) described a lateral facies change involving sulfates in the margin (gypsum) and borates in the center (hydroboracite) (see Part IV).

In the Neogene formations of Anatolia, a similar facies belt, i.e. sulfate in the margin (gypsum) and borate in the center (priceite) was documented by Ortı et al. (1988) (see Part IV). In the marginal part of the Emet borate district, Helvacı and Firman (1976) interpreted the
following facies belt, from the margin to the center: carbonate - sulfate (gypsum) - borate (colemanite). In the central part of the same district, however, the following facies belts was deduced (García-Veigas et al., 2011) from the margin to the center on the basis of new borehole information: carbonate (dolomite) – borate (colemanite and probertite) - sulfate (glauberite) - chloride (halite).

Apparently, borate minerals can precipitate in a wide range of salinities and chemical types of waters. In the parageneses in which both borates and sulfates are involved, in some cases borates occupy the center of the lake systems while in others occupy the margins. In the parageneses where NaCl is also present, halite always occupies the most central part. Recent borehole information in the Anatolian districts (Emet, Kırka) indicates that borate associations with other evaporitic groups can be more varied and complex than thought up to now (García-Veigas et al., 2011)

In the examples of successions which follow, the chemical types correspond to: Ca-borate-sulfate, Ca-Mg-borate-sulfate and Ca-Na-(K)-borate-sulfate-chloride.

In the examples of successions which follow, the chemical types correspond to: Ca-borate-sulfate, Ca-Mg-borate-sulfate and Ca-Na-(K)-borate-sulfate-chloride.

Gypsum-priceite-gypsum (Fig. 3.2E)  
Sultançayır deposit (Anatolia)

Inyoite-ulexite-gypsum (Fig. 3.2F)  
Blanca Lila Fm (NW Argentina)

Colemanite - gypsum – hydroboracite - gypsum (Fig. 3.2G)  
Monte Amarillo Mb, Sijes Fm (NW Argentina)

Colemanite – probertite – glauberite – halite – glauberite – probertite – colemanite (Fig. 3.2H)  
Emet Basin, central part (Anatolia)

Fig. 3.2. Examples of borate successions with only borates (A-D), and borate successions with sulfates/chlorides (E-H). A: Furnace Creek Fm; B: Boron (Kramer) deposit; C: Kırka deposit; D: Loma Blanca deposit; E: Sultançayır district; F: Blanca Lila Fm; G: Monte Amarillo Mb; H: Emet district, central part. Based on; A: McAllister (1970); B: Bowser (1965); C: Helvacı and Ortí (2004); D: Alonso et al. (1988); E: Ortí et al. (1998); F: Vandervoort (1997); G: Ortí and Alonso (2000); H: García-Veigas et al. (2011). Schemas out of scale: A, B, C, D and F.
**TABLE III-1: Individual cycles and successions in lacustrine borate deposits**

<table>
<thead>
<tr>
<th>COLEMANITE cycles</th>
<th>Depositional intervals</th>
<th>Figure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emet deposit</td>
<td>(1) claystone/tuff layer</td>
<td></td>
<td>Helvacı and Ortí, 1998 (Fig.7A)</td>
</tr>
<tr>
<td>(Anatolia, Miocene)</td>
<td>(2) nodular/meganodular colemanite</td>
<td></td>
<td></td>
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<tr>
<td>Tulů open pit mine, Bigadiç district</td>
<td>(1) alternations of carbonate varves and finely-laminated dark claystone</td>
<td></td>
<td>Helvacı and Ortí, 1998 (Fig. 4A)</td>
</tr>
<tr>
<td>(Anatolia, Miocene)</td>
<td>(2) laminated, pelletal mudstone (and some nodules of colemanite)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kestelet deposit</td>
<td>(1) finely-laminated dark claystone and carbonate varves (some preserved as original</td>
<td></td>
<td>Helvacı and Ortí, 1998 (Fig. 7B)</td>
</tr>
<tr>
<td>(Anatolia, Miocene)</td>
<td>aragonite)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COLEMANITE–ULEXITE–PROBERTITE succession</td>
<td>(2) laminated carbonate (with some lenticular and flaser-shaped nodules of colemanite)</td>
<td></td>
<td></td>
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<tr>
<td>COLEMANITE–ULEXITE–BORAX successions</td>
<td>(3) nodular colemanite bed with minor intercalations of laminated mudstone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ULXITE-INYOITE cycle</td>
<td>Fig. 3.1A</td>
<td></td>
<td></td>
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<tr>
<td>Lagunita Playa (NW Argentina, Miocene)</td>
<td>Fig. 3.1B</td>
<td></td>
<td></td>
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<tr>
<td>ULEXITE–INYOITE cycle</td>
<td>Fig. 3.1C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kestelet deposit (Anatolia, Miocene)</td>
<td>Fig. 3.1C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ULEXITE–MEYERHOFFERITE cycle</td>
<td>(3) nodular colemanite bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simav deposit (Anatolia, Miocene)</td>
<td>Fig. 3.1D</td>
<td></td>
<td>Helvacı and Ortí, 1998 (Fig. 3)</td>
</tr>
<tr>
<td>COLEMANITE–ULEXITE–PROBERTITE succession</td>
<td>Fig. 3.1E,F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furnance Creek Formation, Death Valley (California, Miocene-Pliocene)</td>
<td>colemanite → ulexite → probertite → ulexite → colemanite</td>
<td></td>
<td></td>
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<tr>
<td>KISTLER and Helvacı, 1994 (Fig. 4)</td>
<td>Fig. 3.1A</td>
<td></td>
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<tr>
<td>COLEMANITE–INUITE–ULEXITE–BORAX successions</td>
<td>Fig. 3.1G</td>
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<tr>
<td>Kramer deposit (Boron, California, Miocene)</td>
<td>kolmanite → probertite → glauberite → halite → probertite → colemanite</td>
<td></td>
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<tr>
<td>Kirka deposit (Anatolia, Miocene)</td>
<td>Fig. 3.1B</td>
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<td></td>
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<tr>
<td>BORATE and SULFATE successions</td>
<td>Fig. 3.1E</td>
<td></td>
<td></td>
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<tr>
<td>Sultançayır deposit (Anatolia, Miocene)</td>
<td>gypsum → priceite (pandermite) → gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blanco Lilla Fm. (Argentina, Miocene)</td>
<td>inyoite → ulexite → gypsum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tincalayu deposit (NE Argentina, Miocene)</td>
<td>inyoite → ulexite → borax → inyoite → inyoite → ulexite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BORATE, SULFATE and CHLORIDE successions</td>
<td>Fig. 3.1G</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Doganlar boreholes, Emet district, central part (Anatolia, Miocene)</td>
<td>colemanite → probertite → glauberite → halite → colemanite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Anatolia, Miocene)</td>
<td>Fig. 3.1H</td>
<td></td>
<td>Garcia-Veigas et al., 2011</td>
</tr>
</tbody>
</table>
PART IV: EXAMPLES OF NEogene BORATE BASINS

This last part of the workshop deals with particular petrologic and sedimentologic aspects of selected Neogene borate deposits in western Anatolia (Turkey) and La Puna region (NW Argentina) avoiding comprehensive descriptions and interpretations of the basins. In the Kestelek Basin (Anatolia), mainly colemanite is present. In the Bigadiç Basin (Anatolia), both colemanite and ulexite are exploited in several localities. In the Kirka Basin (Anatolia) borax is actively benefited, and a thick probertite deposit has been recently prospected in the subsurface. In the Sultançayır Basin (Anatolia), Ca-borates (mainly priceite) are interbedded within a thick gypsum succession. In the Emet Basin (Anatolia), a clear distinction can be established between a marginal succession with only borates (mainly colemanite) and a central succession in which a complex paragenesis involving borates (mainly probertite), sulfates (mainly glauberite) and chlorides (halite) is known to exist in the subsurface. In the Neogene Pastos Grandes Basin (La Puna, in NW Argentina), the association of hydroboracite and gypsum contains the largest hydroboracite resources known up to now.

4.1. Bigadiç Basin

In the Bigadiç Basin, the Paleozoic basement is overlain by a thick Neogene succession (Fig. 4-1). The borate deposits form two units (lower and upper borates) separated by thick tuff units. Colemanite and ulexite are the dominant minerals in the two borate units. Minor borates are: howlite, probertite and hydroboracite in the lower borate unit; and inyoite, meyerhofferite, priceite, hydroboracite, howlite and tunellite in the upper borate unit. The Bigadiç Basin has a number of mining localities such as Tülü, Acep, Simav, Kurtpınar and Kireçlik (Helvacı, 1995).

**Individual cycle: interpretation.** In the Part III, some individual cycles in these localities in the Bigadiç Basin were cited (Tülü, Acep, Kurtpınar and Simav). As an example of them, the cycle in the Tülü deposit (Fig. 3.1B) can be selected for a sedimentological interpretation.

Succession in the Tülü deposit is about 65 m thick and is dominated by colemanite layers in alternation with claystone-carbonate beds. The individual cycle in the Tülü deposit involves these depositional stages (Fig. 4.2):

- Stage I: Deep lake (perennial; from few meters to tens of meters). This stage is characterized by the sedimentation of dark, finely-laminated claystone in rhythmic alternations with carbonate varves; these alternations might reflect seasonal climatic changes. Probably the water mass was stratified, the lower mass being anoxic and hypersaline.

Stage II: shallow lake (<1 m to a few meters). This stage represents a drop in the water level, which resulted in the sedimentation of laminae of pelletal carbonate mudstone in a stratified water mass with only minor episodes of subaerial exposure. Some colemanite small...
nODULES COULD DEVELOP WITHIN THE CARBONATE LAMINAE OR WITHIN THE TOP SEDIMENTS OF THE PRECEDING STAGE;

Stage III: Shallow-ephemeral lake to playa-lake. In this stage, the underground position of the water table and the associated brine evolution resulted in the interstitial growth of large nodules, thin layers, and individual crystals of displacive colemanite.

This individual cycle displays a shallowing upwards trend. Colemanite is a mineralogically primary mineral and pseudomorphs of any precursor borate mineral were not found. In other colemanite layers of the Tülü succession, however, some ulexite pseudomorphs can be found (Fig. 4.3). This suggests that, in this particular case, the ulexite growth could locally predate that of colemanite.

**Replacement of ulexite by colemanite.** In contrast to the Tülü deposit, in the Acep deposit some colemanite cycles display features indicating a replacement of precursor ulexite: radial aggregates of colemanite contain remnants of ulexite nodules and micronodules (Fig. 4.4). In the Kurtpınarı deposit, some precursor ulexite micronodules within the replacive colemanite can be also distinguished (Fig. 4.5).
Figure 4.3. Partial stratigraphic succession in the Tülü borate deposit, Bigadiç district, Anatolia. Some individual cycles are shown as well as colemanite layers with particular lithofacies. In these layers it is indicated the petrographic presence of some pseudomorphs after ulexite micronodules, Ps(U), within the colemanite (modified from Helvacı and Ortı, 1998; Fig. 4A).
Figure 4.4. Individual cycle in the Acep borate deposit, Bigadiç district, Anatolia. On the right of the cycle, macroscopic details of colemanite (C) replacement on ulexite (U) are shown. Ps(U) refers to the petrographic presence of some pseudomorphs after ulexite micronodules within the colemanite (modified from Helvacı and Ortí, 1998; Fig. 4B).
Figure 4.5. Partial stratigraphic succession in the Kurtpınarı borate deposit (Bigadiç district, Anatolia), showing an irregular alternation of ulexite, colemanite and carbonate beds. Ps(U) refers to the petrographic presence of some pseudomorphs after ulexite micronodules within the colemanite.
4.2. Kestelek Basin

In the Kestelek deposit (western Anatolia), a Miocene succession rests unconformably on a Paleozoic and Mesozoic basement complex (Helvacı, 1994) (Fig. 4.1). In this succession, a borate unit is intercalated with clay, marl, limestone, tuffaceous limestone and tuff. Colemanite, ulexite and probertite predominate, with rare hydroboracite. A part of the borate succession in this deposit is represented in Fig. 4.6, in which some individual cycles are included. Interval (1) in these cycles is formed by finely-laminated dark claystone and carbonate varves. **Subaqueous colemanite nodules.** The great thickness of interval (1) in the individual cycles indicates a deep-lake stage at the beginning of the cycle. The lenticular and hemilenticular nodules of colemanite included in these cycles can form relatively thin layers. The presence of this type of layers (interval 3) at the top of the cycles suggests that these nodules were formed interstitially under synsedimentary conditions below the sediment-water interface. Likely the depth of the water body was moderate.

![Diagram of Kestelek Basin](image)

**Figure 4.6.** Partial stratigraphic succession in the Kestelek open pit borate mine, Anatolia, showing individual cycles and details of colemanite nodules. Cycle intervals: (1) finely-laminated dark claystone and carbonate varves (some preserved as original aragonite); (2) laminated carbonate (with some lenticular and flaser-shaped nodules of colemanite); (3) nodular colemanite bed (modified from Helvacı and Ortı, 1998; Fig. 7B).
4.3. Kirka Basin

The Kirka Basin contains a non-marine, volcano-sedimentary succession higher than 400 m thick of Miocene age, which rests unconformably on a Paleozoic metamorphic basement, a Mesozoic ophiolitic complex and an Eocene sedimentary cover. The succession is composed of the following units from base to top: volcanic rocks and tuffs (80 m), lower limestone (80 m), lower clay horizon with interbedded marls and tuffs (40 m), borate unit (>70 m), upper claystone with tuff, marl and coal bands (60 m), upper limestone (>50 m), and basalt (>30 m) (Fig. 4.7).

4.3.1. Central part of the basin

In the central part of the basin, a borate unit up to 145 m thick locally crops out. The major borates forming this unit are borax, ulexite and colemanite, which are the ore minerals. Other Ca-, Na-, Mg- and Sr-borates are present in subordinated amounts (İnan et al., 1973; Helvacı, 1978, 1983; Çolak, 1995). Dolomite is the main carbonate, with minor amounts of magnesite and calcite. Strontianite is also present. This borate unit contains the only borax ore body in Turkey, with a B₂O₃ content of 20-25%.

The borate deposit was formed in a lacustrine setting. The boron in this deposit is assumed to have been derived from the hydrothermal activity associated with intense contemporaneous volcanism in the region during the Miocene and with the leaching of country rocks (Kistler and Helvacı, 1994). It is estimated that the borate unit underwent limited burial (300-400 m).

Borate succession. The succession in the borate unit consists of the following layers or intervals, in ascending order (Fig. 4.8): colemanite; ulexite; laminated borax (A); interstitial macrocrystalline borax (B); crystalline massive borax (C); laminated borax with lenticular nodules of ulexite (D); fibrous, columnar ulexite, with Mg-bearing borates (inderite, kurnakovite) (E); nodular to massive colemanite (F). This succession is practically symmetrical.

Borax lithofacies: interpretation. Borax crystals in the various lithofacies range in size between 0.1 and 10 mm. The predominant lithofacies (laminated, banded, massive crystalline) indicate free precipitation on the lake floor. In the middle of the succession, however, a interstitial macrocrystalline borax lithofacies could be interpreted as formed during an exposure episode. Under this point of view, the borax sedimentation reflects an evolution from a predominantly subaqueous setting at variable depths (perennial lake stage) in the lower part, to an interstitial setting (playa-lake stage), and again to a subaqueous setting in the upper part. The evaporative concentration of the boratiferous solutions in the lake together with the periodic changes in temperature of the water mass, are considered to be the main controls on the borax crystallization. Within the borax laminae of interval (D), flattened nodules of ulexite are developed. The growth of these nodules was coeval with the accumulation of the
Figure 4.8. Stratigraphic succession in the central part of the Kirka borate deposit (modified from Helvacı and Ortí, 2004, fig. 4).

Figure 4.9. Interpretative scheme of the lateral facies distribution in the central part of the Kirka borate deposit (modified from Helvacı and Ortí, 2004, fig. 2). 1: central body of laminated borax; 2: nodular and massive ulexite; 3: nodular and massive colemanite; 4: colemanite mine (inactive); 5: marginal lutites and carbonates.
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Figure 4.10. Interpretative scheme of mineral distribution and paleoenvironments in the Kirka borate deposit, Anatolia, till the moment of the deposition of the upper ulexite bed (E) bearing Mg-borates (complete zoning of the deposit is not shown). In this scheme it is interpreted that: (1) synsedimentary, interstitial crystallization occurs in the external zones containing the Na-Ca and Ca borates (margins of the lake and playa-lake settings), and (2) deposition of borax under subaqueous to exposed conditions occurs in Kirka lake (modified from Helvacı and Ortí, 2004, fig. 16).

borax laminae; this growth was also replacive: ulexite pseudomorphs after borax crystals can be observed petrographically.

Mineral zoning. As seen above, the vertical succession of the borate unit is practically symmetrical and constituted by a macrocycle involving these zones: colemanite – ulexite – borax – ulexite - colemanite. The same observation is valid for the lateral facies belt (concentric pattern), which is integrated by: a central body of Na-borate (borax), an intermediate zone of Na/Ca-borate (ulexite) and a marginal zone of Ca-borate (colemanite) (Fig. 4.9).

No petrographic evidence was found in interval (F) for a possible inyoite-to-colemanite transformation, as previously proposed in the literature (İnan et al. 1973). Furthermore, the post-depositional burial of the Kirka deposit is considered to be insufficient for such a generalized transformation related to thermal diagenesis. Beside this, the Mg-borates occurrences in interval (E) probably represent the ultimate evaporitic precipitates from the fractionation of the initial solution (instead of any possible reaction product between pre-existing borates and groundwater).

Thus, mineral zoning in the Kirka deposit can be held as primary, not only for borax and ulexite, but also for the colemanite and the Mg borates overlying the central body. This zoning represents the complete evolution of a Na-rich boratiferous saline lake. In it, the existence of a lateral gradient of salinity would have conditioned the concentric pattern (Helvacı and Ortí, 2004) (Fig. 4.10).

4.3.2. Marginal part of the basin (Göcenoluk section)

Recent petrologic studies of samples coming from two deep boreholes (1100 m depth) drilled in a marginal part of the basin, near the Göcenoluk village, 5 km west of Kirka, have recorded a thick borate succession. The borate succession in the 2008-6 borehole is mainly formed by an upper probertite unit (~300m thick) which overlies a lower borax unit (~100m thick). Abundant small tunellite crystals are scattered throughout the sequence. Ulexite is a very minor phase.

The upper probertite unit consists of nodular probertite interbeded with lavas, tuffs and thin dolomite layers. Only two colemanite intervals, less than 3 m thick, have been identified. Backscattered electron images and X-ray mapping of both probertite and colemanite exhibit an internal zonation pattern as a result of high and variable strontium contents (Fig. 2.2D).

The basal borax unit consists of massive beds formed by anhedral centimetric crystals also interbeded with tuffs and dolomites. In both units, borates show evidence of interstitial growth breaking and deforming peloidal dolomite and stromatolitic layers.

Unlike other contemporaneous borate deposits in the Anatolian region, neither metal sulfides nor arseno-sulfides are present in Kirka. Intense water-rock interaction with volcanosedimentary layers induces the dissolution of feldspars and plagioclases which are usually replaced by probertite. Abundant authigenic zeolites (mainly analcime) and boron-silicates (searlesite) are formed as a consequence of the silica leached from the weathering of silicates.

According to petrographic observations and the internal strontium zonation pattern in both probertite and colemanite crystals, we consider them as primary precipitates which grew interstitially in volcanoclastic sediments and soft dolomitic muds deposited on the bottom of the lake. The absence of well laminated borax in this marginal position suggests that was also formed below the water-sediment interface.
4.4. Sultançayı Basin

The Miocene volcano-sedimentary succession in this basin contains a thick (up to 200 m) sandy claystone formation (Fig. 4.11). In the central part of the basin, this clastic formation contains an evaporitic unit, the Sultançayı Gypsum, of a Middle-Upper Miocene age, which bears a borate deposit (Fig. 4.12). After its formation, this unit was never buried deeper than 300-400 m.

Evaporitic succession. In outcrop, the Sultançayı Gypsum is made up of secondary gypsum and is characterized by the following facies belts: laminated gypsum and intraformational gypsrudites (debris-flow breccias) in the depocenter; pseudomorphic gypsum (after banded selenites) located on shoals in intermediate positions; and nodular gypsum (formerly sabkha anhydrite) in a wide marginal zone.

The gypsum succession in the depocenter, up to 50 m thick, is formed by at least three complete cycles of lutites-gypsum (the oldest forming the Bedded Lower Gypsum and the two younger forming the Bedded Upper Gypsum). These cycles display shallowing-upward trends. The same trend is displayed by the whole gypsum succession (Fig. 4.13): the depositional environment, from which this succession was formed, evolved from deeper (laminated gypsum, debris-flow gypsum) to shallower water (selenitic gypsum on shoals; interstitially-growen nodular gypsum in subaerial conditions). The debris-flow deposits most probably occurred by instability of the depositional surface linked to seismicity in the basin (Ortí et al., 1998) (Fig. 4.14).

Borate occurrences. In the depocenter succession calcium borates, mainly priceite (pandermite) and howlite, and some colemanite and bakerite to a much lesser extent, are found interbedded within gypsum. In the lowermost cycle, at the beginning of the evaporitic episode (Lower Bedded Gypsum), these minerals have been interpreted as the result of mixing the basinal solutions with borate-rich flows ascending through synsedimentary faults. The lithofacies of priceite, the major ore mineral in this deposit are varied: finely-laminated, stratiform masses, discontinuous bands, irregular masses and nodules. Some of these lithofacies indicate that priceite grew not only interstitially within the gypsum host, but also as a primary, free precipitate on the lake floor. In particular, the finely-laminated character of some of the priceite levels in alternation with the laminated gypsum clearly indicates that the two minerals were primary phases.

Howlite is present as compact, interstitially-grown, individual nodules (<1 cm up to 1 dm in diameter), in which the crystalline fabric is fine-grained prismatic. Howlite nodules displace gypsum, and replace priceite in the priceite beds.

The occurrence of fragments of both priceite and howlite embedded in the debris-flow gypsum deposits (Lower Bedded Gypsum) can be interpreted that these two major borates were primary precipitates (priceite) or synsedimentary products (priceite, howlite). Scarcce occurrences of colemanite as small nodules or irregularly-shaped features were formed interstitially within the gypsum host. Bakerite as (microscopic) spherulites is also present.

Interaction between borates and the Ca-sulfate diagenetic cycle. The Ca-sulfates underwent a complete diagenetic cycle: the depositional (primary) gypsum changed to...
anhydrite during moderate burial, and this
diagenetic anhydrite was later re-hydrated into
secondary gypsum during final exhumation of
the deposit. Given that presently all the gypsum
is secondary in this unit (burial anhydritization
was total) the presence of a high geothermal
gradient in the region during the Miocene can be
deduced.

This diagenetic cycle partly affected the
borate minerals: (a) the gypsum-to-anhydrite
conversion during burial resulted in partial
replacement of priceite and accompanying
borates (howlite, bakerite) as well as other early
diagenetic minerals (celestine) by anhydrite; and
(b) final exhumation caused a partial
transformation of priceite and howlite into
secondary calcite (Fig. 2.7B).

Figure 4.12. Geological map of the Neogene Sultançayı Basin, Anatolia (modified from Ortí et al., 1998; Fig. 2).
Figure 4.13. Stratigraphic succession in the central part of the Neogene Sultançayır Basin, Anatolia (modified from Ortí et al., 1998, Fig. 4).
Figure 4.14. Schematic representation of subenvironments during the borate formation (Bedded Lower Gypsum) in the saline lake of the Sultançayı Basin, Anatolia (modified from Ortí et al., 1998; Fig. 5).

Figure 4.15. Diagram of the genetic processes affecting the main minerals (sulfates, borates, carbonates) in the Neogene Sultançayı Basin, Anatolia. Both the sedimentation and the synsedimentary reworking of gypsum and major borates (priceite, howlite) preceding the diageneric phases are not indicated in this diagram. Pandermite is used for priceite (modified from Ortí et al., 1998; Fig. 8).
4.5. Emet Basin

In the Emet Basin (Fig. 4.16), a Miocene lacustrine succession exceeding 1000 m in thickness overlies unconformably a basement formed by Paleozoic rocks and an Upper Cretaceous cover. In ascending order, the Miocene succession is formed by: a basal unit of conglomerates; a clastic unit bearing coal seems; a borate-bearing unit (Hisarcık Fm); and an upper limestone unit with chert, marls and clays. Quaternary sediments discordantly overlie the Miocene materials (Fig. 4.17). Intense volcanic activity began in the Early Miocene in the basin and continued until at least the Late Miocene (Helvacı, 1984; Çolak et al., 2000). Hydrothermal springs, which currently are depositing calcareous travertines and native sulfur, are active in this basin to the west of the Kocaçay River. The dissolution of Neogene
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4.5.1. Marginal part of the basin

The various outcrops and exploitations located to the east of the Kocaçay River (Espey, Gökşipe, Hisarık, Dereköy) are included in a borate succession of up to 150 m in thickness. This succession (Fig. 4.18) is formed by colemanite layers (5-10 m thick) in alternation with clay and tuff beds, and also by minor amounts of ulexite, hydroboracite, meyerhoffiter, realgar and native sulfur (Helvacı, 1984; Helvacı et al., 1993). Colemanite in these layers displays an impressive nodular-to-meganodular, displacive lithofacies, which grew from interstitial brines under synsedimentary conditions in a playa-lake system (Helvacı and Ortı, 1998; Helvacı and Alonso, 2000). Some native sulfur and realgar impregnate or replace the colemanite. Evidence of possible precursor borate phases in these large colemanite nodules is rare: remains of possible ulexite micronodules were observed under the microscope only locally.

4.5.2. Central part of the basin (Doğanlar section)

Two boreholes with continuous rock sampling were drilled near the Doğanlar village by Elı Bor Company (Turkish Government) for exploratory purposes during year 2003 (Fig. 4.19). More than 500 m of a borate-sulfate-chloride succession were intersected by these boreholes. The lithologic cores of this succession show a complex mineral association (García-Veigas et al., 2011). In it, dolomite, probertite, glauberite and halite constitute the major primary phases; other sulfates are anhydrite, gypsum, thenardite, celestine, and kallistrontite; other borates are colemanite, ulexite, hydroboracite, tunellite, kaliborite and aristarainite; sulfides are arsenopyrite, realgar, and orpiment; other carbonate is calcite. Two new minerals (pending of approval by the IMA) have been identified: emetite, Ca₇Na₃K(SO₄)₉ (García-Veigas, et al., 2010a) and fontarnauite, Na₂Sr(SO₄)(B₄O₆(OH)₂)·3H₂O (García-Veigas et al., 2010b) (Fig. 2.12).

Eight units were differentiated in the borehole succession: the basal (C-1) and the top (C-8) units are mainly formed by colemanite; between them, three units of probertite (P-2, P-5, P-7) are found; within these probertite units two glauberite units (G-4, G-5) are interbedded; a halite unit (H-3) occupies the central part. Overall, this succession is dominated by Ca-borates at the base and the top, by Na-Ca borates and sulfates in the intermediate zone, and by Na-chloride in the center (Fig. 4.19).

The main probertite lithofacies are nodular and laminated, while the glauberite and halite lithofacies are basically banded and laminated. Each one of the units identified is characterized by the association of few major minerals (colemanite; probertite-glauberite; probertite-glauberite-halite) and by minor replaceive minerals (various sulfates and borates). Bacterially-induced dolomite appears in the lower part of the succession.

This evaporite succession records a significant change of the parent-waters in the lake from initial Ca-rich solutions precipitating the basal colemanite, to Ca-Na-rich brines from which the probertite and glauberite units formed, and to Na-rich brines from which halite and thenardite precipitated (H-3 unit). According to fluid inclusion compositions, the halite precipitating brine was of the Na-K-Cl-SO₄ type. Although no K-bearing minerals (kaliborite) precipitated as isolated beds in this central part of the basin, their formation during early diagenesis suggests a progressive enrichment of K in the more concentrated Na-brines. After halite precipitation, brines returned to the Na-Ca composition characterized by the precipitation of probertite (P-5 and P-7 units) and glauberite (G-4 and G-6 units), and finished with the colemanite and anhydrite crystallization from terminal Ca-rich type of brines.
Figure 4.18. Partial stratigraphic succession in the marginal zone of the Neogene Emet Basin. Ps(U) refers to the petrographic presence of some pseudomorphs of ulexite micronodules within the colemanite (modified from Helvacı and Ortı, 1998; Fig. 7A).
**Depositional model.** The evaporitic model is envisaged as a saline lake surrounded by an extensive, slightly sloped, marginal saline tuff-flat. In this tuff-flat the nodular colemanite succession of the outcrops/exploitations was formed. In the central lake, the water column evolved from shallow and moderately deeper (saline lake) to very shallow (salt-pond).

During the **saline lake stage**, a marked salinity gradient towards the lake center is evidenced by the Ca-borate (colemanite) precipitation in the outer-most belt and by Ca-Na-borates and sulfates (probertite and glauberite) precipitation in both nearshore (interstitially) and in the center of the lake (subaqueously). Both the bottom water and the underground brines in the surrounding saline mud-flat remained under anoxic conditions that favored the microbial sulfate reduction (BSR) of glauberite. As a result of this, sulfide (from the reduced sulfate) and bicarbonate were produced. Sulfide reacted with Fe and As present in the volcaniclastic matrix yielding the precipitation of colloidal arsenopyrite. At the same time, dolomite was formed by the action of microorganisms. The BSR modified the isotopic composition of the remaining dissolved sulfate enriching the precipitated glauberite in heavy isotopes.

During the **salt pond stage**, the lake remained very shallow and the groundwater level dropped in the surrounding saline tuff-flat. The fall of the water table generated oxidizing conditions in the groundwater of this tuff-flat meanwhile reducing conditions remained in the restricted flooded sector. Increasing salinity related to this restriction resulted in the precipitation of biogenic dolomite and arsenopyrite still formed. The change to oxidizing conditions in the underground brine below the surface of the saline tuff-flat, prevented the bacterial reduction of the dissolved sulfate. Thus, interstitial glauberite precipitated with the original isotopic signal. These oxidizing conditions in the units overlying the halite unit avoided the generation of bio-induced dolomite and colloidal arsenopyrite, and favored the biogenic precipitation of As-sulfide (realgar).

Two complex reactions within the lacustrine sediments were: (1) the synsedimentary replacement of the uppermost probertite unit by ulexite related to the contribution of diluted water at the end of the evaporitic event, and (2) the replacement of previous evaporitic minerals by K-bearing (kaliborite and fontarnauite) and Mg-bearing (hydroboracite) minerals during advanced stages of early diagenesis by means of reaction with interstitial brines.
4.6. Sijes Formation (Miocene, La Puna, NW Argentina)

The Pastos Grandes Neogene Basin displays a sedimentary infilling of up to 5000 m in thickness, which was deposited on a variety of non-marine environments (fluvial, alluvial, saline lake) (Fig. 4.20). One of the Miocene formations in the basin is the Sijes Formation, which contains borate deposits of economic interest. This formation, up to 2000 m thick, is constituted by four members, from base to top: Monte Amarillo Mb (330 m thick), Monte Verde Mb (380 m thick), Conglomerate Mb (0 to 200 m thick), and Esperanza Mb (580 m thick). Overlying the Sijes Fm and the Pliocene Singuell Fm, the Pleistocene Blanca Lila Fm is made up of claystones and evaporites (Fig. 4.21) (Alonso, 1986; Vandervoort, 1997).

The Monte Amarillo Mb contains an inyoite unit (36 m thick) at the base and an upper hydroboracite unit (137 m thick); the Monte Verde Mb intercalates an inyoite-colemanite unit (113 m thick); and the Esperanza Mb has a colemanite unit (37 m thick) (Fig. 4.22). The most important borate deposits are in the Monte Amarillo Mb. The boron source of these deposits seems to be related to the volcanic and hydrothermal activity in the Central Andes during the Miocene. Also, the presence of As-sulfides (realgar, orpiment) in the Sijes Fm suggests a hydrothermal origin for As.
Figure 4.21. General stratigraphic succession in the Neogene Pastos Grandes Basin, La Puna region, NW Argentina (modified from Ortí and Alonso, 2000; Fig. 2).
Recently, 1 m
Blanca Lila Fm 5 m
Esperanza Mb 37 m
Monte Verde Mb 113 m
Monte Amarillo Mb 137 m
Pozuelos Fm >15 m

LEGEND
- borates (C,I,H,U)
- claystone, siltstone, tuff (undifferentiated)
- rock-salt
- gypsum

Figure 4.22. Borate units in the various members of the Sijes Fm, in the Blanca Lila Fm, and in the Holocene Pastos Grandes salar (modified from Ortí and Alonso, 2000, Fig. 2).
Evaporitic succession in the Monte Amarillo Member. The Monte Amarillo Mb of the Sijes Fm contains the largest known hydroboracite reserves in the world. In this member, the sulfate minerals are secondary gypsum and minor anhydrite, and the borate minerals are hydroboracite with subordinate inyoite and colemanite, and minor ulexite. A maximum burial depth of about 1500 m is estimated for this member.

In this member it is possible to distinguish two coeval, shallow, lacustrine subbasins, the Monte Amarillo and the Santa Rosa subbasins (Fig. 4.23) (Ortí and Alonso, 2000). In them, both vertical and lateral zoning is observed: gypsum is preferentially accumulated in the lower and upper parts of the vertical succession and in the marginal parts of the borate units; hydroboracite is preferentially accumulated in the middle of the successions and in the core of the borate unit; the intermediate zones are characterized by mixed gypsum-hydroboracite layers.

The depositional succession of the Monte Amarillo subbasin, up to 317 m thick (section 7, Fig. 4.23), is formed by the following units in ascending order: siliciclastic unit, gypsum unit, gypsum-inyoite unit, hydroboracite unit (without gypsum), gypsum-hydroboracite unit, and gypsum unit. This succession shows a single, gypsum-hydroboracite-gypsum macrocycle, which is slightly asymmetrical (Fig. 4.24).

The depositional succession of the Santa Rosa subbasin is integrated by two gypsum-hydroboracite macrocycles, with individual thickness between 40 and 70 m. Colemanite as micronodules and radial aggregates is associated with the banded-massive facies of gypsum (Fig. 4.25).

Primary, subaqueous hydroboracite. In the two subbasins, hydroboracite is mainly a primary mineral, which display a number of lithofacies: laminated, banded, massive, globular, intraclastic/breciated, nodular, enterolithic, in lenticular masses, and in alternations with gypsum. Hydroboracite crystalline fabrics are: fibrous, prismatic, microgranular, radical, blocky-mosaic (anhderal) and drusy. Moreover, hydroboracite cements are also recorded. Alternations of laminated hydroboracite and laminated gypsum also accounts for a primary, subaqueous origin for the two minerals.

Mineral zoning. Zoning in the two subbasins is chemical (depositional). Lateral zoning corresponding to precipitation belts grades from the margin to the center: Ca-sulfate – Ca-borate – Ca-Mg borate. Vertical zoning allows us to envisage a lacustrine evolution from an initial dry mud flat with a Ca-sulfate solution, to an advanced stage in which the saline lake was oversaturated with respect to hydroboracite (without gypsum), and to a final stage in which the lake brine progressively returned to its initial Ca-sulfate composition. Sodium appears to have been a minor component of the initial solution. In this evolution, colemanite postdated the precipitation of gypsum, whereas inyoite could accompany the precipitation of both gypsum and hydroboracite. The accumulation of gypsum-free hydroboracite could be related to a sulfate decrease in the precipitating lake brines. The environment remained shallow along the evolution of the saline lake.

These conditions of close precipitation of Ca-sulfates and Ca-borates were possible given that the stability ranges of gypsum, colemanite,
Inyoite and ulexite overlap to a considerable degree. Replacements between the various borate minerals during burial diagenesis were not detected.

*Calcium-sulfate diagenetic cycle.* The generalized presence of secondary gypsum in the Monte Amarillo Mb. indicates that the primary gypsum underwent a complete diagenetic cycle. Along this cycle, the primary gypsum: (1) was first transformed into anhydrite by burial (from early diagenesis to moderate burial diagenesis); (2) it changed to secondary gypsum during final exhumation by the groundwater action.

*Interaction between borates and sulfates: gypsum-hydroboracite pseudomorphs.* Within the hydroboracite laminae, pseudomorphs after precursor gypsum can be observed petrographically. The study of these pseudomorphs indicates that: (1) mutual replacements between gypsum and hydroboracite occurred under synsedimentary conditions (Fig. 2.9E,F). These replacements resulted in pseudomorphs of both, gypsum after hydroboracite and hydroboracite after gypsum; (2) these interactions were partly ‘fossilized’ and preserved by the gypsum to anhydrite conversion during burial. In this process, anhydrite replaced the preexistent pseudomorphs to some extent; and (3) final exhumation resulted in secondary gypsum pseudomorphs after several types of precursor pseudomorphs. Thus, it can be deduced that diagenetic processes in borates can be studied in connection with the diagenetic cycle of Ca-sulfates.

![Simplified succession of the Monte Amarillo Mb. in the Monte Amarillo subbasin (Sijes Fm, La Puna region, NW Argentina) (modified from Ortí and Alonso, 2000, Fig. 10).](image-url)
Figure 4.25. Partial stratigraphic succession of the Monte Amarillo Mb in the Santa Rosa subbasin, showing two complete depositional cycles (I and II). The base of the succession is the top of the Pozuelos Fm. (La Puna region, NW Argentina) (modified from Ortí and Alonso, 2000, Fig. 11).
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APPENDIX: Optical characteristics of some borate minerals (modified from Melgarejo and Martin, 2011)

Borax, $\text{Na}_2(\text{B}_3\text{O}_5(\text{OH})_4)\cdot8\text{H}_2\text{O}$

**System and space group:** monoclinic, $C2/c$

**Unit-cell parameters:** $a = 11.885$, $b = 10.654$, $c = 12.206$ Å; $\beta = 106.62^\circ$

**Diffraction lines:** 4.82(100), 5.68(90), 2.56(65) Å

**Optical constants:** $\alpha = 1.447$, $\beta = 1.463$, $\gamma = 1.472$; 2V 39°

**Habit:** euohedral crystals, commonly very large, with a short prismatic habit along [001]; also tabular habit on (100)

**Relief:** marked (-)

**Color:** colorless

**Pleochroism:** absent

**Cleavage:** (100) perfect, (110) good, (010) poor

**Interference colors:** up to second-order greenish blue

**Extinction:** oblique in elongate sections

**Twining:** (100) rare

**Other characteristics:** sections perpendicular to the optic axis display a brown or blue anomalous interference color, with no extinction

**Interference figure:** biaxial negative, $r > v$ strong

Colemanite, $\text{Ca}(\text{B}_3\text{O}_4(\text{OH})_3)\cdot\text{H}_2\text{O}$

**System and space group:** monoclinic, $P2_1/c$

**Unit-cell parameters:** $a = 8.743$, $b = 11.264$, $c = 6.102$ Å; $\beta = 110.12^\circ$

**Diffraction lines:** 3.13(100), 5.64(50), 3.85(50) Å

**Optical constants:** $\alpha = 1.586$, $\beta = 1.592$, $\gamma = 1.614$; 2V 56°

**Habit:** the euhedral crystals are prismatic along [001]; normally in columnar aggregates arranged in radial forms or in nodules; may be a pseudomorph

**Relief:** from low to moderate (+)

**Color:** colorless

**Pleochroism:** none

**Cleavage:** {010} perfect and {001} good, forming 90° angles

**Interference colors:** may reach the upper part of second order

**Extinction:** oblique on elongate sections

**Elongation:** (+)

**Interference figure:** biaxial positive, $r > v$

Howlite, $\text{Ca}_2\text{B}_5\text{SiO}_9(\text{OH})_5$

**System and space group:** monoclinic, $P2_1/c$

**Unit-cell parameters:** $a = 12.93$, $b = 9.34$, $c = 8.60$ Å; $\beta = 104^\circ50'$

**Diffraction lines:** 4.14(100), 6.24(90), 3.10(75) Å

**Optical constants:** $\alpha = 1.586$, $\beta = 1.592$, $\gamma = 1.605$; 2V large

**Habit:** tabular habit {100}; in general, radial aggregates of acicular crystals

**Relief:** moderate (+)

**Color:** colorless

**Pleochroism:** none

**Cleavage:** not evident

**Interference colors:** up to the beginning of the second order

**Extinction:** oblique on elongate sections

**Interference figure:** biaxial negative

Hydroboracite, $\text{CaMg}(\text{B}_6\text{O}_8(\text{OH})_6)\cdot3\text{H}_2\text{O}$

**System and space group:** monoclinic, $P2_1/c$

**Unit-cell parameters:** $a = 11.755$, $b = 6.685$, $c = 8.225$ Å; $\beta = 102.72^\circ$

**Diffraction lines:** 5.77(100), 6.68(85), 3.32(50) Å

**Optical constants:** $\alpha = 1.522$, $\beta = 1.534$, $\gamma = 1.569$; 2V 63°

**Habit:** the crystals have a tabular habit on {010}

**Relief:** low (-) or (+)

**Color:** colorless

**Pleochroism:** none

**Cleavage:** (010) perfect

**Interference colors:** up to the end of the third order

**Extinction:** oblique on elongate sections

**Elongation:** (-)

**Interference figure:** biaxial positive, $r < v$

Inderborite, $\text{CaMg}(\text{B}_3\text{O}_3(\text{OH})_5)\cdot6\text{H}_2\text{O}$

**System and space group:** monoclinic, $C2/c$

**Unit-cell parameters:** $a = 12.137$, $b = 7.433$, $c = 19.234$ Å; $\beta = 90.29^\circ$

**Diffraction lines:** 3.35(100), 3.26(80), 3.07(80), 7.14(10) Å

**Optical constants:** $\alpha = 1.483$, $\beta = 1.512$, $\gamma = 1.530$; 2V 77°

**Habit:** euohedral crystals, commonly large

**Relief:** low, negative

**Color:** colorless

**Pleochroism:** none

**Cleavage:** good on (100), conchoidal fracture
Interference colors: up to yellow of the third order
Extinction: inclined, almost straight
Interference figure: biaxial negative

**Inderite**, Mg (B_2O_3(OH)_5)·5H_2O
System and space group: monoclinic, P2_1/c
Unit-cell parameters: a 11.934, b 13.094, c 6.886 Å; β 104.12°
Diffraction lines: 5.66(100), 3.26(100), 5.01(90), 3.34(80) Å
Optical constants: α 1.488, β 1.491, γ 1.505; 2V 37°
Habit: the crystals are generally granular; also prismatic, acicular and in radial groups
Relief: marked (-)
Color: colorless
Pleochroism: none
Cleavage: (110) good
Interference colors: up to the end of first order
Extinction: oblique
Interference figure: biaxial positive

**Inyoite**, Ca(B_2O_3(OH)_5)·4H_2O
System and space group: monoclinic, P2_1/a
Unit-cell parameters: a 10.621, b 12.066, c 8.408 Å; β 114.02°
Diffraction lines: 3.03(100), 7.59(70), 2.29(25) Å
Optical constants: α 1.490, β 1.505, γ 1.516; 2V 86°
Habit: short euhedral to anhedral prismatic or tabular crystals, forming coarse spherulitic arrays or massive aggregates
Relief: low (-)
Color: colorless
Pleochroism: absent
Cleavage: good on {001} and {010}, irregular fracture
Interference colors: up to second-order blue
Extinction: oblique
Interference figure: biaxial negative, r < v weak

**Kernite**, Na_2(B_2O_3(OH)_5)·3H_2O
System and space group: monoclinic, P2_1/c
Unit-cell parameters: a 7.016, b 9.152, c 15.678 Å; α 90.55, β 101.88, γ 86.62°
Diffraction lines: 8.31(100), 6.47(100), 4.97(25) Å
Optical constants: α 1.500, β 1.535, γ 1.560; 2V 78°
Habit: the crystals have a tabular habit on {001}, in some cases are prismatic or acicular; also allotriomorphic
Relief: low to medium, negative
Color: colorless
Pleochroism: absent
Cleavage: perfect on {010}
Interference colors: low second-order colors
Extinction: oblique
Interference figure: biaxial negative, r > v weak

**Kurnakovite**, Mg(B_2O_3(OH)_5)·5H_2O
System and space group: triclinic, PT (dimorphic relations with inderite)
Unit-cell parameters: a 8.344, b 10.59, c 6.443 Å; α 99.0, β 108.9, γ 87.2°
Diffraction lines: 8.31(100), 6.47(100), 4.97(25) Å
Optical constants: α 1.500, β 1.535, γ 1.560; 2V 78°
Habit: large crystals, commonly in granular aggregates
Relief: low to medium, negative
Color: colorless
Pleochroism: absent
Cleavage: perfect on {010}
Interference colors: high orders
Extinction: oblique
Interference figure: biaxial negative, r > v weak

**Meyerhoffrite**, Ca(B_2O_3(OH)_5)·H_2O
System and space group: triclinic, PT
Unit-cell parameters: a 6.617, b 8.323, c 6.494 Å; α 90.55, β 101.88, γ 86.62°
Diffraction lines: 8.31(100), 6.47(100), 4.97(25) Å
Optical constants: α 1.500, β 1.535, γ 1.560; 2V 78°
Habit: the crystals have a tabular habit on {100}, in some cases are prismatic or acicular
Relief: low (-) or (+)
Color: colorless
Pleochroism: none
Cleavage: (010) perfect
Interference colors: high orders
Interference figure: biaxial negative, r > v weak

**Priceite**, Ca_2(B_5O_7(OH)_5)·H_2O
System and space group: monoclinic, P2_1/c
### Unit-cell parameters

**Probertite**, NaCa(B₂O₇(OH)₄)·3H₂O  
System and space group: monoclinic, *P*₂₁/ₐ  
Unit-cell parameters:  
\[ a = 13.43, \ b = 12.57, \ c = 6.589 \, Å; \ \beta = 100.25° \]  
Diffraction lines:  
12.1(100), 2.79(30), 9.98(20), 8.37(20) Å  
Optical constants:  
\[ \alpha = 1.526, \ \beta = 1.528, \ \gamma = 1.551; \ 2V = 33° \]  
Habit: acicular or platy crystals in rosettes or radial groups; also as massive aggregates  
Relief: low  
Color: colorless  
Pleochroism: absent  
Cleavage: perfect on \{110\}  
Interference colors: high second-order colors  
Extinction: oblique  
Interference figure: biaxial positive, \( r > v \)  

### Unit-cell parameters

**Teruggite**, Ca₄Mg(AsB₆O₁₁(OH)₆)₂·12H₂O  
System and space group: monoclinic, *P*₂₁/a  
Unit-cell parameters:  
\[ a = 15.675, \ b = 19.920, \ c = 6.255 \, Å; \ \beta = 99.33° \]  
Diffraction lines:  
6.57(100), 6.97(30), 5.14(30), 6.21(20) Å  
Optical constants:  
\[ \alpha = 1.519, \ \beta = 1.534, \ \gamma = 1.569; \ 2V = 42° \]  
Habit: coarse prismatic and tabular crystals, and nodules of radiating prisms  
Relief: very low, either positive or negative  
Color: colorless  
Pleochroism: absent  
Cleavage: perfect on \{100\}, distinct on \{001\}  
Interference colors: high third-order colors  
Extinction: oblique  
Twining: possible on \{100\}  
Interference figure: biaxial positive, \( r > v \)
Diffraction lines: 12.2(100), 7.75(80), 6.00(30) Å

Optical constants: α 1.493, β 1.505, γ 1.529; 2V 70-73°

Habit: generally forms subhedral, fibrous crystals grouped in parallel arrays; may transmit images ('mineral television', optic fibers), but also in fibroradial aggregates

Relief: low (-)

Color: colorless

Pleochroism: none

Cleavage: (010) perfect, (100) good, (110) poor

Interference colors: up to the end of the second order

Extinction: oblique in elongate sections

Twining: polysynthetic, common

Interference figure: biaxial positive