

Borate Deposits of Turkey and Argentina; A Summary and Geological Comparison

CAHİT HELVACI¹ & RICARDO N. ALONSO²

¹ Dokuz Eylül Üniversitesi, Mühendislik Fakültesi, Jeoloji Mühendisliği Bölümü, 35100 Bornova, İzmir - TURKEY
(e-mail: chelvaci@izmir.eng.deu.edu.tr)

² Universidad Nacional de Salta and CONICET, Buenos Aires 177, 4400 Salta, ARGENTINA

Abstract: Turkey has the largest borate reserves in the world and Argentina is in third place. Both countries have calcium and sodium borate deposits where colemanite, ulexite and borax are the principal minerals. We present here a comparison of the main borate deposits interlayered in continental Miocene volcanoclastic rocks of the Anatolian plateau (Turkey) and those of the Puna high plateau (Argentina).

The main borate deposits of Turkey are at Emet, Bigadiç, Kestelek and Kırka. Emet is in the western part of the Kütahya province. In Emet, a sedimentary lacustrine sequence rich in tuffaceous materials hosts the colemanite section. There are limestones and marl layers at the base and top of the borate section. Arsenic minerals (realgar and orpiment) are very abundant and spatially related to the borates, indicating a common genetic origin. The principal borate mineral is colemanite with minor ulexite, hydroboracite, meyerhofferite, and rarer species such as veatchite-A, tunellite, teruggite and cahnite. Colemanite occurs as nodules of different sizes, agglomerated in thick beds.

Bigadiç has borates interbedded with tuffs, clay and limestone layers. The borate minerals are formed in two distinct zones, lower and upper, separated by thick tuff beds. Colemanite and ulexite predominate in both borate zones. Other borates include howlite, probertite and hydroboracite in the lower zone, and inyoite, meyerhofferite, pandermite (priceite), terschite, hydroboracite, howlite, tunellite and rivadavite in the upper borate zone.

The Kestelek deposit is 27 km southeast of the town of Mustafa Kemalpaşa in the province of Bursa. The borate zone consists of marl, limestone, tuffaceous limestone, tuff and borate layers. The borate minerals occur interbedded with clay minerals. Colemanite is present as masses from nodule to boulder size (up to 1 m in diameter), and as thin layers of fibrous and euhedral crystals. Colemanite, ulexite and probertite predominate and sparse hydroboracite is also present locally.

The Kırka stratigraphic succession comprises borates that are intimately interbedded with and penetrating marls, claystones, zeolitized tuff and tuffaceous epiclastic material in the lacustrine sedimentary rocks. The main boron mineral is borax with lesser amounts of colemanite, ulexite and other borate minerals.

The volcano-sedimentary rock units in the Sultançayır deposit include borate-bearing gypsum intercalated in a sandy claystone unit. Calcium borates, mainly pandermite (priceite) and howlite, but also colemanite and bakerite, are interspersed within the Sultançayır gypsum.

The borates in all of these districts occur in older playa lake deposits of Miocene age that rest unconformably on a Paleozoic and Mesozoic basement that is comprised of ophiolites, marbles and schists.

Argentina has lacustrine borate deposits restricted to 1) Sijes hill in the Los Andes districts of the Salta province, 2) the Loma Blanca deposits of the Jujuy province and 3) the Tincalayu deposit located on the northwestern margin of the Hombre Muerto Salar. There are also several borate occurrences within salars of the Andes region.

Sijes hill is a topographically positive area of Miocene rocks, 30 km long, along the eastern border of the Pastos Grandes salt pan. Borates occur as interbeds in a very thick lacustrine volcanoclastic sequence. Several evaporitic members, with halite at the bottom and borate and gypsum at the middle and top, are interlayered with tuffs and tuffaceous materials. Colemanite is the main borate mineral at the Monte Verde, Esperanza and Santa Rosa mines. Other deposits are composed principally of mainly hydroboracite, the principal borate mineral in the Sijes district. Colemanite occurs as spherules agglomerated in beds less than 1 m thick and is accompanied by hydroboracite, inyoite and ulexite.

Predominantly borax and trace amounts of colemanite, ulexite and other borate minerals are also present in the Loma Blanca deposit of the Jujuy province, and in the Tincalayu deposit.

Key Words: Borate, Colemanite, Turkey, Argentina, Anatolian Plateau, Puna High Plateau

Türkiye ve Arjantin Borat Yatakları: Jeolojik Bir Karşılaştırma

Özet: Türkiye dünyanın en büyük borat rezervlerine sahip olup, Arjantin ise üçüncü sıradadır. Her iki ülkede de esas mineralleri kolemanit, üleksit ve boraks olan boratlarla birlikte kalsiyum ve sodyum borat yatakları yer alır. Burada, Anadolu (Türkiye) ve Puna (Arjantin) platolarında yer alan, karasal Miyosen volkaniklastik kayalarla ile ardalanmalı önemli borat yataklarının karşılaştırması sunulmaktadır.

Türkiye'deki önemli borat yatakları Emet, Bigadiç, Kestelek ve Kırka yataklarıdır. Emet, Kütahya'nın doğusunda yer almaktadır. Tüf içeren malzemece zengin Emet gösel istif kolemanit düzeyi içermekte, borat düzeyinin tabanında ve üzerinde kireçtaşı ve marn tabakaları bulunmaktadır. Arsenik mineralleri (realgar ve orpiment) çok yaygın olup kökensele olarak boratlarla yakın ilişkilidir. Az miktarda üleksit, hidroborasit, meyerhofferit, veatchit-A, tunellit, teruggit ve kahnit gibi ender boratlar ile birlikte bulunan esas borat minerali kolemanittir. Kolemanit kalın tabakalar arasında değişik boyutlardaki nodüller şeklinde bulunmaktadır.

Bigadiç'te boratlar tüf, kil ve kireçtaşı düzeyleri ile ardalanmalıdır. Borat mineralleri kalın tüf düzeyi ile ayrılmış, alt ve üst zon olarak adlandırılan iki belirgin zonda yer almaktadır. Her iki borat zonunda kolemanit ve üleksit baskın olup, alt borat zonu havlit, probertit, hidroborasit, üst borat zonu ise inyoit, meyerhofferit, pandermite (presit), probertit, hidroborasit, havlit, tunellit ve rivadavit gibi diğer borat minerallerini içermektedir.

Kestelek yatağı, Bursa'ya bağlı Mustafa Kemalpaşa ilçesinin 27 km güneydoğusunda bulunmaktadır. Borat zonu marn, kireçtaşı, tüflü kireçtaşı, tüf ve borat düzeylerinden oluşmaktadır. Bor mineralleri kil mineralleri ile ardalanma gösterirler. Kolemanit blokları (1 m'ye kadar çapa sahip), nodüller veya yığınlar halinde, ayrıca lifsi özşekilli kristallerden yapıları ince düzeyler olarak bulunurlar. Kolemanit, üleksit ve probertit baskın olup, hidroborasit nadiren görülür.

Borat içeren Kırka istif, gösel tortul kayalara ait marn, kiltası, zeolitli tüf ve tüf içeren epiklastik malzeme ile ardalanmalı olarak yerleşmiştir. Az miktardaki kolemanit, üleksit ve diğer borat mineralleri ile birlikte bulunan esas bor minerali borakstır.

Sultançayır yatağındaki volkano-sedimenter kaya birimleri kumlu kiltası birimi ile ardalanmış boratlı jipslerden oluşmaktadır. Esas olarak pandermite (presit) ve havlit, ayrıca kolemanit ve bakeritten yapıları kalsiyum boratlar Sultançayır jipsi ile ardalanmalıdır.

Tüm bu bölgelerdeki oluşumlar, ofiyolit, mermer ve şistten yapıları Paleozoik ve Mesozoik temel kompleksi üzerine uyumsuz olarak yerleşen Miyosen yaşlı playa gölü tortullarıdır.

Arjantin, Salta'da Los Andes bölgesindeki 1) Sijes tepesi ile sınırlanmış borat yatakları, 2) Jujuy'da Loma Blanca yatakları ve 3) Hombre Muerto Salar'ın kuzeyinde yer alan Tincalayu yatağına sahiptir. And bölgesindeki salarlarda çeşitli borat oluşumları bulunmaktadır.

Sijes tepesi, Pastos Grandes tuz havzasının doğu kenarında Miyosen kayalarının oluşturduğu 30 km uzunluğundaki bir yükseltidir. Boratlar çok kalın gösel volkaniklastik istif içinde ardalanmalıdır. Tabanda halit ile başlayan ve orta-üst kesimde borat ve jipsin olduğu evaporitik üyeler tüf ve tüf içeren malzeme ile ardalanma gösterirler. Monte Verde, Esperanza ve Santa Rosa yataklarındaki esas borat minerali kolemanittir. Diğer yataklar ise Sijes bölgesinde ana borat minerali olan hidroborasit içermektedir. Kolemanit oluşumları 1 m'den ince tabakalarda dizilim gösteren nodüller şeklindedir. Kolemanit hidroborasit, inyoit ve üleksit ile birlikte bulunmaktadır.

Tincalayu ve Jujuy'daki Loma Blanca yatakları yaygın olarak boraks, eser miktarda kolemanit, üleksit ve diğer borat mineralleri mevcuttur.

Anahtar Sözcükler: Borat, Kolemanit, Türkiye, Arjantin, Anadolu Platosu, Puna Yüksek Platosu

Introduction

The borate deposits of Turkey occur in western Anatolia, south of the Sea of Marmara, within an area roughly 300 km east-west by 150 km north-south. The main borate districts are Bigadiç, Kestelek, Sultançayır, Emet and Kırka (Figure 1)

These borate deposits were formed in lacustrine environments during periods of volcanic activity which commenced in Early Tertiary time and continued at least to the beginning of the Quaternary. Although the rock types of the borate deposits are somewhat different from each other, they are generally interbedded conglomerate, sandstone, tuff, tuffite, claystone, marl and limestone, and are usually enveloped by, or grade into, limestone or claystone (Figure 1). Sediments in the borate basins exhibit both lateral and vertical facies changes. Volcanic rocks in the vicinity of the ephemeral lakes in which the borate deposits formed are extensive. The volcanic rocks are generally represented by a calc-alkaline series of flows ranging from acidic to basic and by felsic pyroclastic rocks which are interbedded with the sediments.

In South America, there are over 40 borate deposits located along an 885 km trend in the high Andes near the common borders of Argentina, Bolivia, Chile and Peru, of which at least 14 are currently in production (Figure 2). This is an arid segment of the Andean tectonic-volcanic belt, characterized by compressional tectonics and many closed basins with playas, or salt flats, called salars (Figures 2 & 3). For many years (1852-1967), Chile was a major producer of borates, but the industry gradually shifted to adjacent areas of Argentina.

Borate spring deposits are better developed in South America than anywhere else in the world. These deposits consist of cones and aprons of ulexite and, in one case, borax built up around vents from which warm to cool waters and gas are still issuing in some cases. Most deposits are associated with calcareous tufa which occurs as a late-stage capping over the borates, and sometimes with halite and gypsum as well. Recent volcanic activity is indicated by basaltic to rhyolitic flows in adjacent areas, and a hydrothermal waters driven by volcanic source for the borates is presumed. Older rocks in the vicinity of the deposits range from Precambrian to Tertiary and appear to have no genetic relationship to the deposits.

The salar deposits of South America consist of beds and nodules of ulexite with some borax or inyoite,

associated with recent playa sediments – primarily mud, silt, halite and gypsum. The borate-bearing playas occupy individual basins which range in area up to several hundred km² (Figure 3). Springs and seeps appear to be the source of the borates.

The aim of this paper is to report on the genetic relations and comparison between Turkish and Argentinian borate deposits in order to improve our general understanding of borate deposits linked with evaporite formations. The recent evolution of the Andes, along with the development of the volcanic arc and the related geysers and springs provide one of the best natural laboratories for studying the reasons and evidence, which result in the continental borate and other salts formations.

Borate Deposits of Turkey

The western Anatolia borate district contains 5 distinct areas. From the west to east they are: Bigadiç, Sultançayır, Kestelek, Emet and Kırka (Meixner 1965; Baysal 1972; Helvacı 1977) (Figure 1). This district contains the largest borate reserves in the world (Kistler & Helvacı 1994; Helvacı 1989)

All the deposits formed during the Miocene in closed lacustrine basins with abnormally high salinity and alkalinity (Helvacı 1986, 1989; Helvacı & Firman 1976). The pre-Neogene basement of the basins is represented by Palaeozoic and Mesozoic rocks partly belonging to the Menderes Massif. All these basins were partially filled with a series of tuffaceous rocks and lavas. Boron-rich fluids are presumed to have also circulated along faults into these basins (Helvacı 1986, 1989). Although the sediments deposited in the borate lakes show some differences, they are generally represented by tuffaceous rocks, claystones, limestones and Ca-, Na-, Mg-, Sr-borates (Table 1). Sandstones and conglomerates occur near the base of each basin (Özpeker 1969; İnan *et al.* 1973; Helvacı 1989). Generally, the borates are enveloped between tuff and clay-rich horizons (Figure 1). In all of the above areas, intense calc-alkaline volcanic activity took place simultaneously with the borate sedimentation. Volcanic material includes acid to basic lavas and tuffaceous rocks.

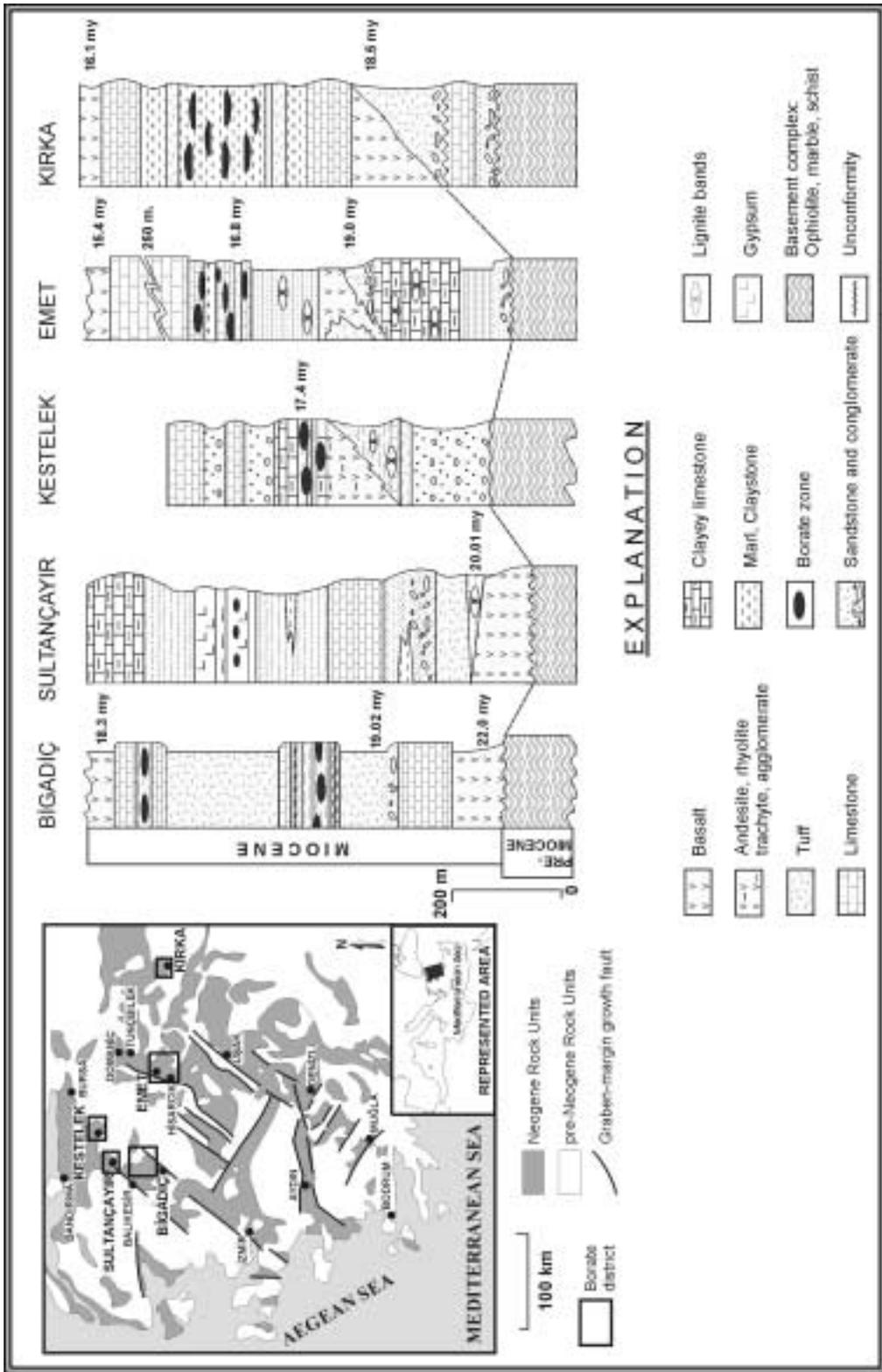


Figure 1 . Location of Miocene borate deposits in extensional rifts, and the stratigraphic sections of borate-bearing Miocene basins in western Turkey.

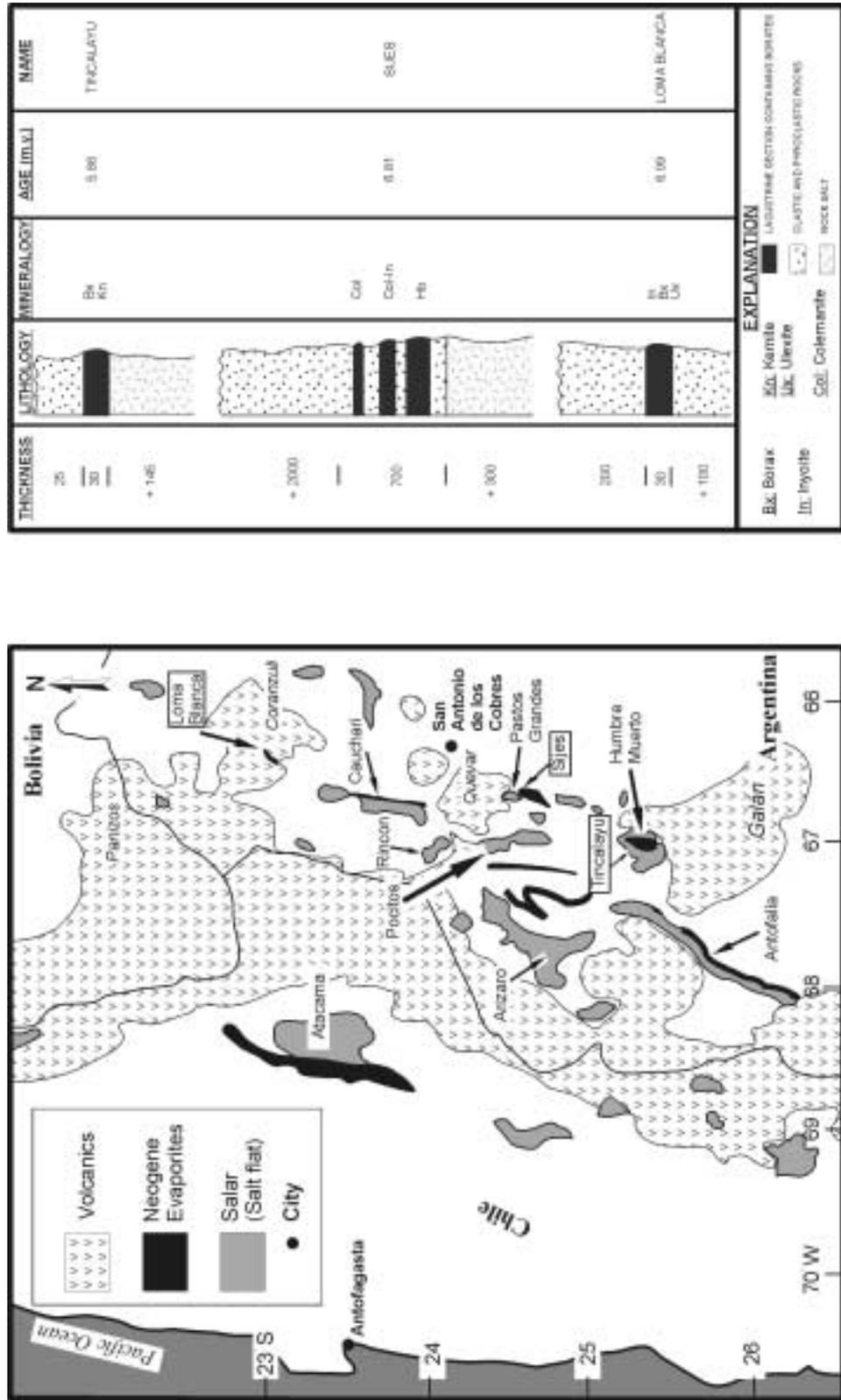


Figure 2. Location of borate deposits and saltars with respect to the volcanic arc of the central Andes, and stratigraphic sections of borate-bearing Miocene basins in the Argentine Puna.

BORATE IN TURKEY AND ARGENTINA

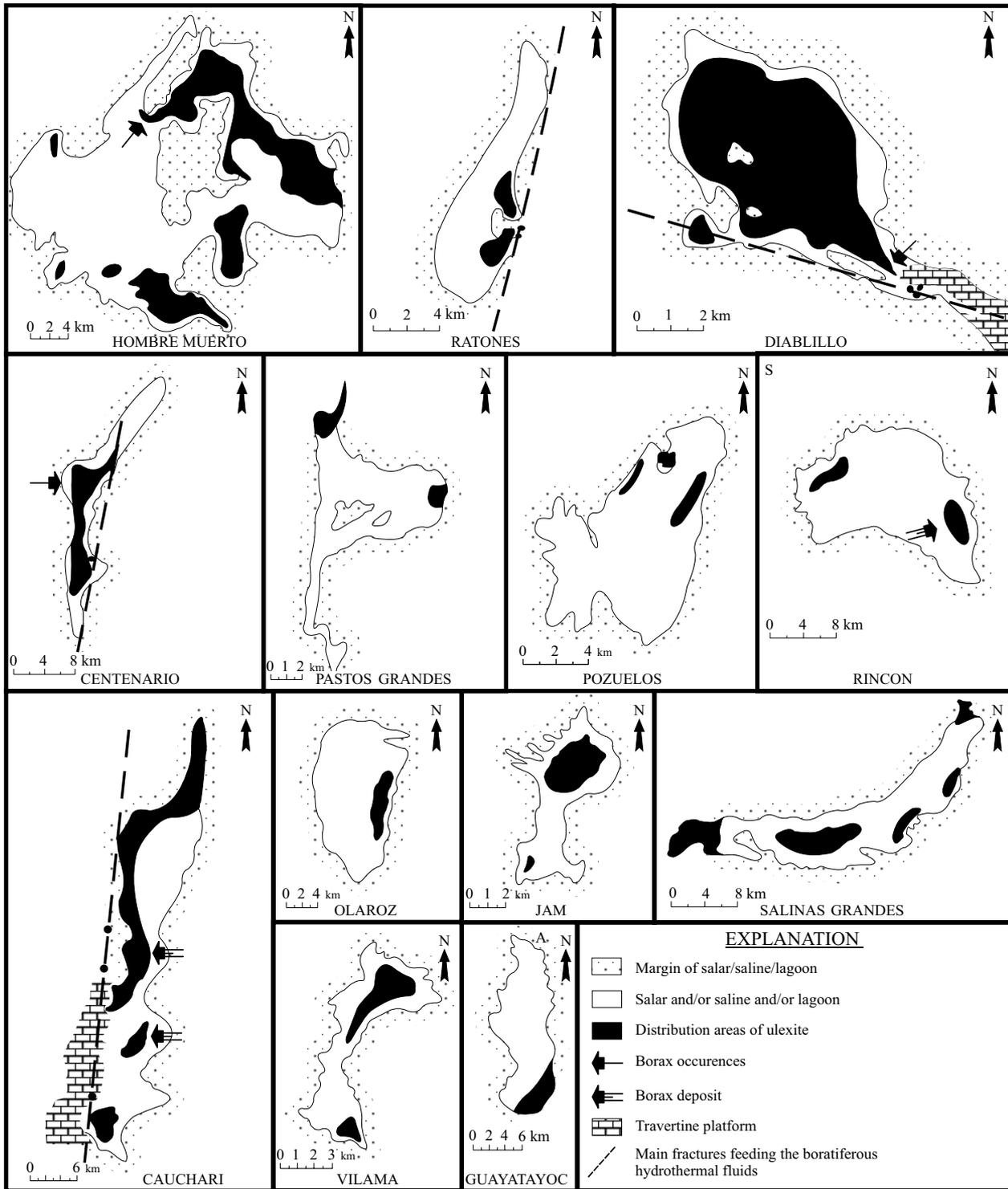


Figure 3. Distribution of borate-bearing salars in the Argentine Puna.

Table 1. Borate minerals occurring in the 5 major Turkish and 3 major Argentine Miocene borate deposits.

Mineral	Formula	Turkish Borate Deposits					Argentine Borate Deposits			
		Bigadiç	Sultançayır	Kestelek	Emet	Kırka	Tincalayu	Sijes	Loma Blanca	
Ca-borates	Inyoite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$	+	-	-	-	+	+	+	
	Meyerhofferite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$	+	-	-	+	+	-	+	
	Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	+	+	+	+	+	-	+	
	Tertschite	$\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 20\text{H}_2\text{O}$	+	-	-	-	-	-	-	
	Pandermite									
	(Priceite)	$\text{Ca}_4\text{B}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$	+	+	-	-	+	-	-	
	Nobleite	$\text{CaB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$	-	-	-	-	-	-	+	
	Gowerite	$\text{CaB}_6\text{O}_{10} \cdot 5\text{H}_2\text{O}$	-	-	-	-	-	-	+	
Ginorite	$\text{Ca}_2\text{B}_{14}\text{O}_{23} \cdot 8\text{H}_2\text{O}$	-	-	-	-	-	+	-		
Ca/Na-borates	Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$	+	-	+	+	+	+	+	
	Probertite	$\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$	+	-	+	-	-	+	+	
Na-borates	Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	-	-	-	-	+	+	-	
	Tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	-	-	-	-	+	+	-	
	Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	-	-	-	-	+	+	-	
	Ezcurrite	$\text{Na}_4\text{B}_{10}\text{O}_{17} \cdot 7\text{H}_2\text{O}$	-	-	-	-	-	+	-	
	Ameghinite	$\text{NaB}_3\text{O}_5 \cdot 2\text{H}_2\text{O}$	-	-	-	-	-	+	-	
Other borates										
(Mg)	Hydroboracite	$\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$	+	-	+	+	+	-	+	-
(Mg)	Inderborite	$\text{CaMgB}_6\text{O}_{11} \cdot 11\text{H}_2\text{O}$	-	-	-	-	+	-	+	-
(Mg)	Inderite	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$	-	-	-	-	+	+	-	-
(Mg)	Kurnakovite	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$	-	-	-	-	+	+	-	-
(Mg)	Rivadavite	$\text{Na}_6\text{MgB}_{24}\text{O}_{40} \cdot 22\text{H}_2\text{O}$	+	-	-	-	-	+	-	-
(Mg)	Mcallisterite	$\text{Mg}_2\text{B}_{12}\text{O}_{20} \cdot 15\text{H}_2\text{O}$	-	-	-	-	-	+	-	-
(Sr)	Tunellite	$\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$	+	-	-	+	+	-	-	-
(Sr)	Veatchite-A	$\text{Sr}_4\text{B}_{22}\text{O}_{37} \cdot 7\text{H}_2\text{O}$	-	-	-	+	-	-	-	-
(As)	Teruggite	$\text{Ca}_4\text{MgAs}_2\text{B}_{12}\text{O}_{28} \cdot 20\text{H}_2\text{O}$	-	-	-	+	-	-	-	+
(As)	Cahnite	$\text{Ca}_2\text{BASO}_6 \cdot 2\text{H}_2\text{O}$	-	-	-	+	-	-	-	-
(Si)	Howlite	$\text{Ca}_4\text{Si}_2\text{B}_{10}\text{O}_{23} \cdot 5\text{H}_2\text{O}$	+	+	-	-	-	-	-	-
(Si)	Bakerite	$\text{Ca}_8\text{B}_{10}\text{Si}_6\text{O}_{35} \cdot 5\text{H}_2\text{O}$	-	+	-	-	-	-	-	-
(Si)	Searlesite	$\text{NaBSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	-	-	-	-	-	+	-	-
(Na-Mg)	Aristarainite	$\text{Na}_2\text{MgB}_{12}\text{O}_{20} \cdot 8\text{H}_2\text{O}$	-	-	-	-	-	+	-	-
(Ca-Sr)	Estroncioginorite	$(\text{Sr,Ca})_2\text{B}_{10}\text{O}_{17} \cdot 7\text{H}_2\text{O}$	-	-	-	-	-	+	-	-

+ Present, - Not present

Bigadiç deposits

The Bigadiç borate deposits are located in 2 different zones and formed within Miocene perennial saline lake sediments within a northeast-trending basin. The Miocene sequence in the region rests unconformably on a Palaeozoic and Mesozoic basement complex (Helvacı 1983, 1989, 1995; Helvacı & Alaca 1991; Meixner 1965; Özpeker 1969).

The Bigadiç borates constitute the largest colemanite and ulexite deposits in the world, and the high-grade

colemanite and ulexite ores there should supply a substantial proportion of the world's needs for many years. The volcano-sedimentary sequence in the deposits consists of (from bottom to top) basement volcanics, lower limestone, lower tuff, lower borate zone, upper tuff, upper borate zone and olivine basalt. The borate deposits formed under arid conditions in perennial saline lakes fed by hydrothermal springs associated with local volcanic activity. The deposits are interbedded with tuffs, clays, and limestones (Helvacı 1995; Helvacı & Orti 1998).

The lacustrine volcano-sedimentary sequence of the Bigadiç area is early to middle Miocene in age, with K-Ar values for the biotite and hornblende of the basement (basal) volcanic rocks showing an average age of ~22 Ma (Gündoğdu *et al.* 1989). Biotite from the lower tuff unit has been dated by K-Ar as 19.0 ± 0.2 Ma (Helvacı, 1995). K-Ar dating of the olivine basalt yielded an age of 18.3 ± 0.2 Ma (Helvacı 1995) (Figure 1; Table 2).

Borate minerals formed in 2 zones separated by thick tuff beds that have been transformed to montmorillonite, chlorite, and zeolites (mainly heulandite) during diagenesis. Colemanite and ulexite predominate in both borate zones, but other borates, including howlite, probertite, and hydroboracite, are present in the lower borate zone; inyoite, meyerhofferite, pandermite, tertschite, hydroboracite, howlite, tunellite, and rivadavite are found in the upper borate zone (Table 1). Calcite, anhydrite, gypsum, celestite, K-feldspar, analcime, heulandite, clinoptilolite, quartz, opal-CT, montmorillonite, chlorite, and illite are also found in the deposits. The tuffaceous material is represented by fine-grained ash-tuff. The volcanic glass of the ash-tuffs has been transformed to a series of authigenic silicates, such as boron-bearing K-feldspar, heulandite, clinoptilolite, illite and smectite. Volcanic-derived minerals are quartz and high sanidine. Minor amounts of chabazite and opal-CT were also identified by SEM analysis (Helvacı *et al.* 1993).

Colemanite nodules in both borate zones probably formed directly from solution, within unconsolidated sediments just below the sediment-water interface, and continued to grow as the sediments were compacted. Later generations of colemanite and ulexite are found in vugs and veins and as fibrous margins of early formed nodules. Other diagenetic changes include the partial replacement of colemanite by howlite and hydroboracite, and ulexite by tunellite.

Nodular colemanite and ulexite predominate in both borate zones. Colemanite and ulexite show alternating horizons, and the transformation of 1 mineral to another has not been observed. The boundary between them is always sharp. Because these minerals are readily dissolved, secondary pure and transparent colemanite and ulexite are often encountered in cavities of nodules and cracks. Some colemanite and ulexite is weathered and completely replaced by calcite.

Probertite bands occur in some ulexite horizons, especially in the lower borate zone. It forms in the same chemical environment as ulexite and indicates a period of more extreme desiccation and possibly subaerial exposure within the lakes. Euhedral tunellite formed during dissolution and recrystallization of some Sr-rich ulexite horizons. In the Bigadiç deposits, hydroboracite formed by replacement of colemanite, with Mg^{2+} ions supplied from adjacent tuffs and clays by ion exchange. Howlite grew in clays alternating with thin colemanite bands and

Table 2. Geochemistry, rock types and ages of the volcanic units associated with the 5 major Turkish borate districts.

SAMPLE NAME	STRATIGRAPHIC HORIZONS	ASSAYS (ppm)				ROCK TYPE (Streckeisen 1976)	K-Ar AGE DATE (my) (mineral dated)
		B	Sr	Li	As		
BIGADIÇ							
B-6	100 m above upper ore	267	715	34	45	TRACHYTE	18.3 ± 0.2 (feldspar)
B-2	100 m below lower ore	83	494	19	34	RHYOLITE	19.0 ± 0.2 (biotite)
SULTANÇAYIR							
S-1	450 m below ore					RHYOLITIC TUFF	20.0 ± 0.5 (feldspar)
KESTELEK							
KE-1	within ore zone	127	2370	653	331	TRACHYANDESITIC TUFF	17.4 ± 0.3 (hornblende)
EMET							
E-9	500 m above ore	85	125	10	16	TRACHYTE	15.4 ± 0.2 (feldspar)
E-1	within ore zone	77	38	7	<2	ALKALI TRACHYTIC TUFF	16.8 ± 0.2 (biotite)
E-3	150 m below ore	67	22	<5	64	RHYOLITE	19.0 ± 0.2 (biotite)
KIRKA							
K-1	200 m above top of ore	96	134	14	<2	TRACHYTE	16.1 ± 0.2 (feldspar)
K-2	250 m below base of ore	490	240	600	>2000	RHYOLITE	18.5 ± 0.2 (biotite)

coincided with periods of relatively high Si concentrations. Diagenetic processes also produced small howlite nodules embedded in unconsolidated colemanite nodules. The initial solutions that formed the alkaline perennial saline lake(s) were low in Cl^- and SO_4^{2-} and high in boron and Ca^{2+} , with subordinate Na^+ .

The Bigadiç borates were formed in perennial saline lakes, fed partly by thermal springs and partly by streams draining the catchment areas. In the Bigadiç deposits, all early precipitated minerals seem to have formed within the fine-grained clastic sediments. It is very likely that the brines were never sufficiently concentrated to allow borate precipitation until the lakes partially or wholly dried up, probably until ephemeral-lake conditions developed. The brines were evidently rich in B, Ca, and Na ions in the basins, and Ca and Ca-Na borates are present in every deposit throughout the area (Figure 4). In the deposit, field and textural evidence clearly indicates a precipitation sequence with increasing evaporation as follows: Ca carbonate - Ca borate (+ silica locally) - Ca borate + Ca sulfate (locally) - Ca-Na borate.

Field and geochemical investigations suggest that the most likely sources of B, Na, Ca and S were either the weathering products of Neogene volcanic rocks transported into the borate basins by streams, volcanic ash deposited directly into the borate basins, or thermal springs and hydrothermal solutions.

Sultançayır deposits

The Miocene volcano-sedimentary rocks units which contain borates in the Sultançayır area rest unconformably on a Palaeozoic metamorphic basement complex, the Mesozoic Dışkaya (Karakaya) Formation, and a Palaeogene granodiorite that intruded the basement rock units. The Miocene sequence consists of the following in ascending order: andesite and agglomerate; tuff; sandy conglomerate; limestone; sandy claystone containing boratiferous gypsum, bedded gypsum and tuff; and clayey limestone (Figure 1).

The borates are interbedded with gypsum, claystone, limestone and tuff within the borate zone of the sandy claystone unit. Borate beds, which are predominantly pandermite (priceite), and randomly distributed howlite nodules, alternate with these gypsum horizons. K/Ar age dating of 1 tuff sample taken from the tuff unit yields an age of 20.01 Ma (Figure 1; Table 2).

Pandermite predominates, but other borate minerals include colemanite and howlite (Table 1). Howlite, which has apparently grown in the clays alternating with thin pandermite and colemanite bands, indicates a period of increasing silica concentration. As a result of diagenetic events, some small howlite nodules are embedded in the pandermite and colemanite masses and in the gypsum beds.

Gypsum is abundant, and calcite, zeolites, smectites, illite and chlorite are the other associated minerals in this deposit. Gypsum occurs in independent masses, thin-bedded layers, or as intergrowths with pandermite. Boron-bearing K-feldspar, clinoptilolite and opal-CT are the authigenic silicates. Volcanogenic high sanidine, anorthoclase, quartz, and clay minerals such as illite and smectite are also present in the associated tuffs and claystones. (Helvacı *et al.* 1993).

Calcium borates, mainly pandermite (priceite) and howlite, but also bakerite and colemanite, are intercalated within the Sultançayır gypsum. This lacustrine unit, represented by secondary gypsum in outcrop, is characterized by: (1) a clear facies distribution of depocentral laminated lithofacies and debris-flow deposits, a wide marginal zone of sabkha deposits, and at least one selenitic shoal located toward the basin margin; (2) evaporitic cycles displaying a shallowing-upward trend; and (3) a diagenetic evolution of primary gypsum to (burial) anhydrite followed by its final rehydration. The calcium borates precipitated only in the depocenter of the lake and were partly affected by syndimentary reworking, indicating that they formed during very early diagenesis. The lithofacies, which is made up of a finely laminated host gypsum and borates, indicate that the borates grew interstitially because of the inflow and mixing of borate-rich solutions with basinal brines. Borate growth displaced and replaced primary gypsum beneath a relatively deep depositional floor. Borate formation as free precipitates was much less common. The anhydritization of primary gypsum took place during early to late diagenesis (burial < 250 m deep). This process also resulted in partial replacement of pandermite and accompanying borates (bakerite and howlite) as well as other early diagenetic minerals (celestite) by anhydrite. Final exhumation resulted in the replacement of anhydrite by secondary gypsum, and in the partial transformation of pandermite and howlite to secondary calcite (Orti *et al.* 1998).

In the Sultançayır deposit the initial solutions must have had abundant boron, calcium and sulfate (Gündoğan & Helvacı 1993; Helvacı 1994; Helvacı 1978). The calcium borate deposits of the Sultançayır Basin consist of pandermite (priceite), howlite, bakerite and colemanite that occur mainly as nodules, irregular masses and bands, and as fine laminae to a lesser extent. These borates mainly grew displacing/replacing primary gypsum sediments in the depocenter of a relatively deep lacustrine environment. The growth of borates took place mainly beneath the water-sediment interface of the lake, and the presence of reworked borate clasts and nodules confirms the synsedimentary origin of these occurrences. Also small amounts of laminated pandermite seem to have precipitated primarily from the water column. The relative timing of the growth of the borate minerals was as follows: pandermite, bakerite, howlite and colemanite. The origin of all these borates is related to the mixing of borate-rich solutions with lacustrine brines under progressive evaporation. The gypsum lithofacies is related to the lacustrine subenvironments: a relatively deep central zone, a wide marginal belt and a local selenitic shoal. Sedimentation in the gypsum units reflect cyclicity. In the depocenter, the cycles were controlled by evaporation and gravitational instability and display a shallowing upward trend. Borates are intercalated in the second gypsum cycle.

Kestelek deposit

The Miocene sediments which contain the borates in the Kestelek area rest unconformably on a Palaeozoic and Mesozoic basement complex (Figure 1). The Miocene sequence contains from bottom to top: basement conglomerate and sandstones; claystone with lignite seams, marl, limestone, and tuff; agglomerates and volcanic rocks; the borate zone comprising clay, marl, limestone, tuff and borates; and limestones with thin clay and chert bands (Figure 1). These sediments were deposited during a tectonically stable period accompanied by extensive volcanic activity. During this period, the volcanic activity gradually increased and produced tuff, tuffite and agglomerate, and andesitic, trachytic and rhyolitic volcanic rocks that are interbedded with sediments. A yellow to brown coarse-grained tuff unit, up to a few centimeters thick, occurs within the borate zone. K/Ar age dating of one tuff sample taken from the borate zone yields an age of 17.4 Ma (Figure 1; Table 2). This

sequence is capped by loosely cemented Pliocene conglomerate, sandstone and limestone (Özpeker 1969; Helvacı 1994)

The borate minerals occur interbedded with clay as nodules or masses and as thin layers of fibrous and euhedral crystals. Colemanite, ulexite, and probertite predominate, with hydroboracite being sparse (Helvacı 1978, 1994) (Table 1). Secondary colemanite occurs as transparent and euhedral crystals in the cavities of nodules in cracks and in vugs. Probertite, which forms in the same chemical environment as ulexite in the Kestelek deposit, indicates a period of higher temperature within the ephemeral lake. Calcite, dolomite, quartz, zeolite, smectite, illite, and chlorite are accessory minerals. Clinoptilolite and opal-CT are the only known authigenic silicate minerals occurring within the interbedded tuffs. The tuffs consist of oligoclase, quartz, biotite and smectite. Generally, the particle size of the tuffaceous materials is coarser in the Kestelek area than in the other districts.

In the Kestelek area, the presence of only clinoptilolite and opal-CT seems to indicate lower pH values in the 8 and 9 range (Surdam & Parker 1972; Helvacı *et al.* 1993). This suggests that a standard pH value is not necessary to precipitate borate salts but, rather, a range of values higher than 8 is sufficient. The formation and paragenetic association of authigenic silicates, such as clinoptilolite, analcite and K-feldspar, requires pH values ranging from 8 through 10. This pH range in borate-bearing basins shows that the precipitation of borates starts at a pH around nine and continues at higher alkalinities (Helvacı *et al.* 1993).

There is much geological and mineralogical evidence to show that secondary alteration and diagenetic-mineral formation played an important role in the modification of mineralogical and chemical distributions within this deposit. Diagenetic borate minerals with euhedral crystals, authigenic boron-bearing K-feldspar, zeolites (clinoptilolite and heulandite), and chlorite are good examples of this process. Much of the volcanic ash and glassy matrix of the tuffs has been converted to authigenic minerals, such as K-feldspar, zeolites and clay minerals during diagenesis.

Borate minerals in the Kestelek deposit, like the tuffs and clays in the borate zone, are characterized by very low concentrations of As, Sr and S relative to minerals

from the Emet deposits, the Kirka deposit, and certain western U.S. borate deposits (Helvacı 1984; İnan *et al.* 1973; Bowser 1965). Arsenic was present only in trace amounts. Surface streams may have carried Ca, Mg and Sr in solution into the basins as a result of weathering of rocks exposed in the adjacent area, but the major sourcing process is considered to have been leaching of underlying basement metamorphic rocks by thermal springs and surface streams. Volcanic rocks, tuffs and clays interbedded with the borates are the most likely sources for Ca, Mg, Na, Sr, B, As and S. It seems likely that thermal springs were important sources of B, As, S and probably Ca and Na when the borates formed, as similar observations have been made for many other deposits (Helvacı 1984; Alonso *et al.* 1988; Bowser 1965; Alonso 1986; Muessig 1966).

In the Kestelek area, the extensive volcanic rock associations and tuff intercalations with the borates indicate that much of the sediment was derived from a volcanic terrain. Hydrothermal solutions, thermal springs and tuffs associated with local volcanic activity are thought to have been the source of the borates. The initial solutions crystallizing the borates in the Kestelek deposit are deduced to have been very poor in chloride, low in sulfate and to have had abundant boron and calcium with subordinate sodium (Helvacı, 1994) (Figure 4).

Emet deposit

The Miocene sequence in the Emet area rests unconformably on Palaeozoic metamorphic rocks comprising marble, mica schist, calc-schist and chlorite schist. This Miocene sequence consists of the following units in ascending order: conglomerate and sandstone; a thin-bedded lower limestone with lenses of marl and tuff; intermediate and acid volcanics, tuff and agglomerate; a red unit containing conglomerate, sandstone, clay, marl, limestone with coal, and gypsum bands; clay, tuff, tuffite and marl containing the borate deposits; an upper limestone containing clay, marl and chert layers; and a capping basalt (Figure 1). Samples taken from different horizons of the Emet stratigraphic section have been dated by the K-Ar method and the results are shown in Figure 1 and Table 2.

The borates are interlayered with tuff, clay, and marl with limestone occurring above and below the borate lenses. The principal borate mineral is colemanite with

minor ulexite, hydroboracite and meyerhofferite. The Emet borate deposits are the only Turkish deposits known to contain any of the minerals veatchite-A, teruggite and cahnite (Helvacı 1984; Table 1). Montmorillonite, illite, and chlorite are the only clay minerals that have been identified; montmorillonite is the dominant clay mineral in all the samples and occurs as Al, Mg-, or Al-Mg-Fe montmorillonite. Illite is only a minor component and is distributed randomly. Chlorite is widely distributed within the deposits and is relatively abundant near or within the horizon of tuffs and tuffites. Zeolites are abundant along the tuff and tuffite horizons. Native sulfur, realgar, orpiment and celestite occur in the borate zone throughout the area. Gypsum associated with borate minerals has been observed in the southern deposits. Calcite is also found in outcrops and adjacent to faults as a result of recent weathering of borates (Helvacı 1977, 1984, 1986; Helvacı & Firman 1976). Boron-bearing K-feldspar, clinoptilolite, illite and smectite are the authigenic silicates detected in the tuffaceous samples. Volcaniclastic high sanidine and quartz are also present (Helvacı *et al.* 1993).

The Emet borate deposits were formed in 2 separate basins, possibly as parts of an interconnected lacustrine playa lake, in areas of volcanic activity, fed partly by thermal springs and partly by surface streams. Thermal springs associated with local volcanic activity are thought to be the source of the borates. The initial brines from which the borates crystallized are deduced to have been high in sulphite and sulphate, low in chloride, and hence it is assumed that they were fed at all times by abundant calcium and boron with minor amounts of arsenic, strontium and sulfur. Realgar, celestite and native sulfur are almost ubiquitous in borates and sediments, and appear to have formed at all stages during deposition and diagenesis. The unit of clay, tuff, tuffite and marl containing the borate deposits has abundant realgar and orpiment in some horizons indicating that arsenic and boron have a genetic relationship and a volcanic origin at Emet (Helvacı 1984).

The early colemanite, meyerhofferite, ulexite and teruggite nodules were probably formed directly from brines penecontemporaneously within the unconsolidated sediments below the sediment/water interface and continued to grow as the sediments were compacted. Later generations of colemanite occur in vugs, veins and as fibrous margins to colemanite nodules. Tunellite

appears to have formed during diagenesis with enrichment of Sr in some places. Diagenetic alterations include the partial replacement of colemanite by veatchite-A, cahnite, hydroboracite and calcite.

The bulk of the volcanic tuffs and tuffites appear to have been derived from volcanic terrains, but Tertiary limestone might also have been exposed, and erosion of these may have contributed Ca and Sr to the lake waters. Alternatively, Ca and Sr may have been leached from the underlying limestone and basement metamorphic rocks by thermal spring waters.

It may be assumed that the initial brines at all times contained an abundance of calcium and boron with minor amounts of arsenic, sulfur, strontium, magnesium and sodium (Figure 4). All early precipitated minerals seem to have formed within the clastic sediments. The brines were evidently rich in Ca and B in both the northern and southern basins, and Ca borates are present at every horizon throughout the sequence. Field and petrological evidence demonstrates that Ca borates, ulexite and teruggite crystallized within the sediments and did not precipitate from open water. The coprecipitation of ulexite and later diagenetic formation of tunellite apparently occurred infrequently in the northern basin and not at all in the southern area.

Field and textural evidence clearly indicates the sequence Ca borate → Ca-Na borate → Sr borate. Arsenic-bearing borates and Sr/borates do not occur together in the Emet deposits, although arsenic sulfides do occur at the same horizon with Sr borates and sulfate. It is not known whether this condition reflects a genuine incompatibility or merely the scarcity of teruggite and cahnite. Both lateral and vertical changes from calcite-marls to colemanite-bearing clays have been observed and a gross zoning both laterally and vertically from calcite to colemanite and back to calcite seems to be typical of both areas. In the southern area the sporadic occurrence of gypsum suggests that where sulphates are present the sequence is calcite → gypsum → colemanite (Helvacı 1984; Helvacı & Orti 1998).

Kırka Deposit

The Miocene volcano-sedimentary sequence in the Kırka basin rests unconformably on Palaeozoic metamorphics, a Mesozoic ophiolite complex and Eocene fossiliferous limestone. The Miocene sequence consists of from

bottom to top: volcanic rocks and tuffs, lower limestone with marl and tuff interbeds, borate zone, upper claystone; upper limestone containing tuff and marl with chert bands; and basalt (İnan *et al.* 1973; Helvacı 1977; Sunder 1980) (Figure 1). Samples taken from different horizons of the Kırka stratigraphic section have been dated by the K-Ar method and the results are presented in Figure 1 and Table 2.

The principal mineral in the Kırka borate deposit is borax with lesser amounts of colemanite and ulexite. Inyoite, meyerhofferite, tinalconite, kernite, hydroboracite, inderborite, inderite, kurnakovite, pandermite and tunellite also occur (İnan *et al.* 1973; Helvacı 1977, 1978, 1983) (Table 1). This is the only deposit in Turkey that contains sodium borates (borax, tinalconite, and kernite), together with inderborite, inderite, and kurnakovite. The borax body is enveloped by a thin ulexite facies, followed outward by a colemanite facies. The whole is enclosed by calcite and limestones.

The borate layers contain minor amounts of realgar, orpiment, gypsum, celestite, calcite and dolomite, and the clay partings contain some tuff layers, quartz, biotite, and feldspar. The clay is made up of smectite-group minerals and, less frequently, illite and chlorite minerals. Zeolites occur within the tuff horizons (Helvacı 1983; Helvacı *et al.* 1993).

This deposit is different from similar borax deposits at Boron and Tincalayu in having very little intercrystalline clay (Alonso 1986; Bowser 1965); the clay at Kırka is very pale green to white and is high in carbonate. The borax crystals are fine, 10 to 20 mm, and quite uniform in size.

Borax, colemanite and ulexite are the principal ore minerals of the commercial-grade borate bodies of Kırka (Figure 4). Inyoite, tinalconite, kernite, tunellite, kurnakovite and inderite are minor components of the borate paragenesis (İnan *et al.* 1973; Helvacı 1978) The borate minerals are interlayered with claystones and tuffs, while a porcelanous limestone forms a resistant cap-rock for the borate zone. Celestite, gypsum, realgar and orpiment occur in some borate layers.

Boron-bearing K-feldspar, erionite, smectite and illite are the authigenic silicates found in the tuffaceous horizons, accompanied by volcanic-derived high sanidine, albite, anorthoclase, quartz, and calcite (Helvacı *et al.* 1993).

The petrography, composition and replacement relationships of the borates (principally borax, with lesser amounts of colemanite and ulexite) and associated authigenic minerals in the Kirka deposit have been described by İnan *et al.* (1973) and Helvacı (1978). Boron-isotope data for the different borate minerals suggested that they were not coprecipitated, but were deposited from different brines at varying pHs (Palmer & Helvacı 1995). Apart from the borate minerals, authigenic B-rich K-feldspar and clays, together with volcanogenic sanidine, albite, anorthoclase and quartz are common constituents of the lake sediments (Helvacı *et al.* 1993).

The source of the boron is thought to be geothermal springs associated with local volcanic activity, and the borates formed when the springs waters underwent evaporation after flowing into shallow playa lakes (Helvacı 1995). The boron-isotope data are consistent with colemanite being precipitated from a brine of lower pH than ulexite, with borax being precipitated from a brine of higher pH than ulexite (Palmer & Helvacı, 1995, 1997). It is suggested that the Kirka borate deposits represent the end-product of 4 stages of transportation of B: (a) initial concentration in subduction-derived fluids; (b) incorporation in continental crust via arc magmatism; (c) melting of B-enriched continental crust to produce ignimbrites; and (d) selective mobilization of B from ignimbrites by local hydrothermal activity and precipitation in alkaline lakes (Floyd *et al.* 1998). Finally, although the initial enrichment of B in volcanic source rocks is considered a necessary feature for the development of borates, the local climatic, tectonic and volcanic conditions are important secondary features in their eventual genesis (Floyd *et al.* 1998).

Borate Deposits of Argentina

The borate deposits of Argentina are restricted to a high plateau formed in a non-collisional compressional orogen during the Late Cenozoic. The main reserves are in the Pastos Grandes basin within a 1500-m-thick volcanoclastic and lacustrine stratigraphic unit known as the Sijes Formation. Several evaporitic members, with halite at the bottom and borate-gypsum in the middle and at the top are interlayered with tuffs and tuffaceous materials. Colemanite is the principal borate at the Monte Verde, Esperanza and Santa Rosa mines (Table 1),

whereas hydroboracite is the predominant borate in the Monte Amarillo deposit. The Tincalayu and Loma Blanca areas are important principally for borax occurrences whereas, in salars, borax and ulexite are mainly present (Table 1). References to the geology, Tertiary rocks, evaporites and borates of the Puna region include: Aristarain & Hurlbut 1972; Jordan & Alonso 1987; Alonso & Helvacı 1988; Alonso *et al.* 1988, 1989, 1991; Alonso & Viramonte 1990; Helvacı & Alonso 1994; Kistler & Helvacı 1994; Vandervoort *et al.* 1995.

Borate deposits in the Pastos Grandes Basin

The Pastos Grandes basin has the most complete Tertiary sequence of the Puna high plateau. Of the Tertiary formations (Geste, Pozuelos, Sijes, and Singuel), only the Pozuelos and Sijes formations contain borates (Figure 5). The borates of the Pozuelos Formation (ulexite and minor inyoite) might be considered to be occurrences of little economic value, while those of the Sijes Formation are the main deposits with large apparent reserves. The borate deposits of the Pastos Grandes Depression represent the largest reserves of calcium and calcium-magnesium borates of either Latin America or the Southern Hemisphere (Alonso 1986; Sureda *et al.* 1986) (Figures 2 & 5).

During deposition of the Sijes Formation there were 3 major pulses of borate generation. These pulses are easily identifiable in the central part of the basin but become indistinct and tend to thin out toward the edges. Along its approximately 30 km outcrop, the Sijes Formation is characterized by a string of borate deposits and occurrences which both set it apart from the under and overlying formations and cause it to have an enormous mineral potential. The borate-bearing members of the Sijes formation are from the base to top as follows: Monte Amarillo (hydroboracite), Monte Verde (colemanite-inyoite) and Esperanza (colemanite). We describe here the most important colemanite deposits in the middle (Monte Verde) and top (Esperanza) members, as well as the Santa Rosa deposit.

Monte Verde deposit (Colemanite - Inyoite)

The deposit is composed primarily of colemanite and inyoite with lesser amounts of secondary disseminated hydroboracite and ulexite. At present, the property is

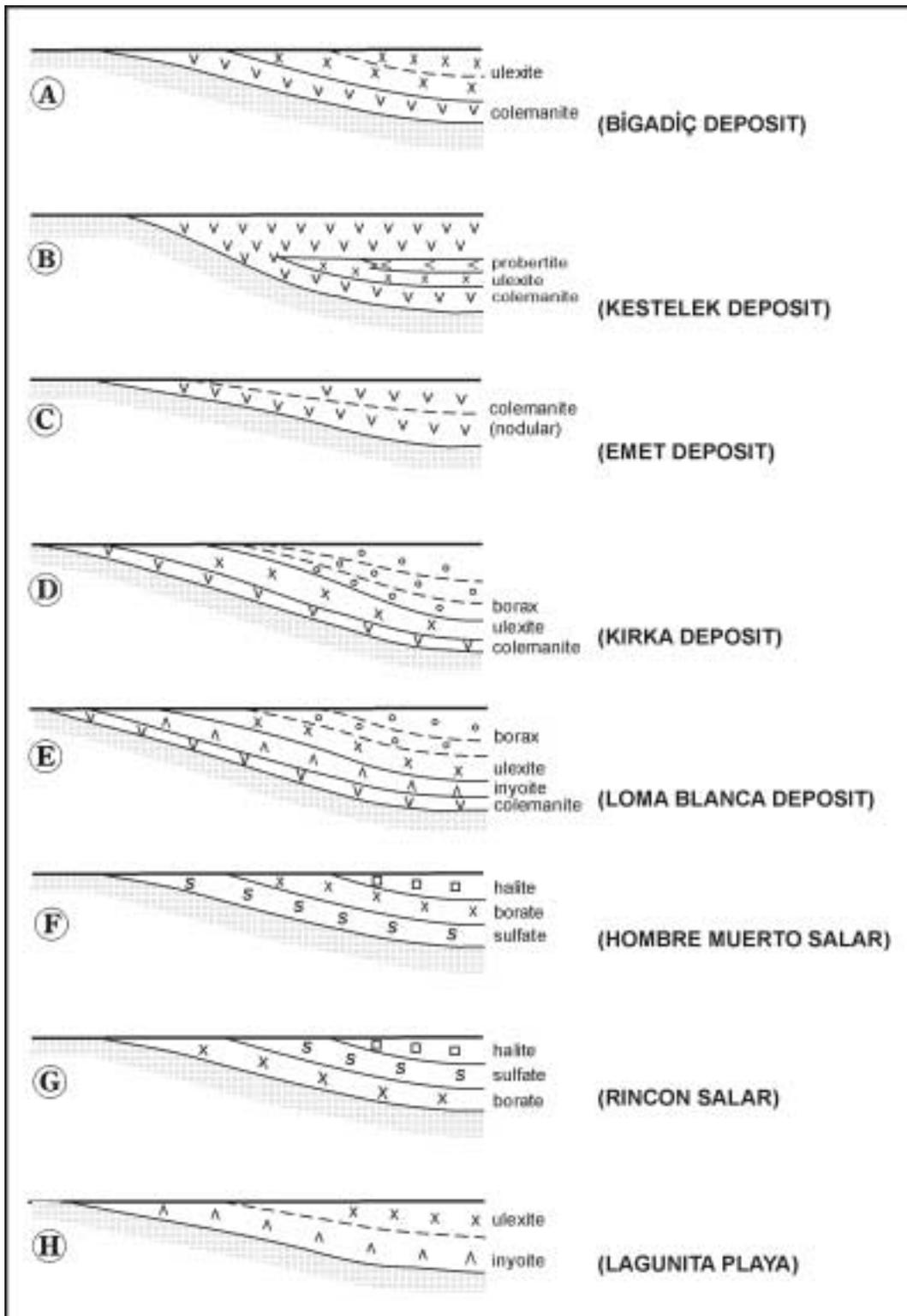


Figure 4. Representation (not to scale) of the simplified borate distribution and depositional models for the basins studied in Turkey and Argentina.

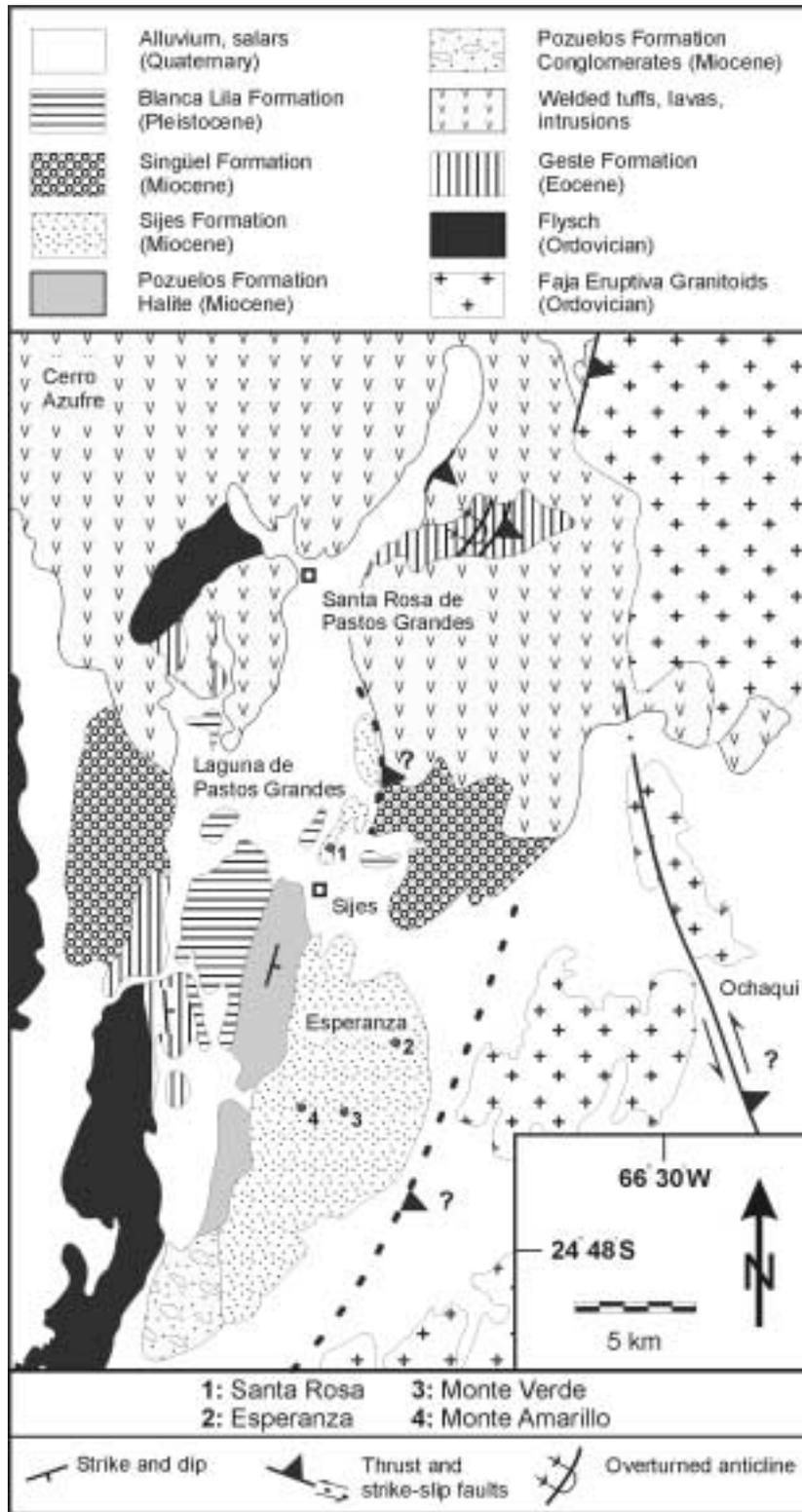


Figure 5. Geologic map of the Salar de Pastos Grandes area, Puna, Argentina.

inactive but small amounts of mining have been carried out in the past. The area is reached by a treacherous pathway from the workings at Monte Amarillo (Alonso 1986, 1992; Alonso and Gonzalez-Barry 1990).

The principal beds of colemanite and inyoite lie interbedded within the middle part of the Sijes Formation in the Monte Verde member. This member corresponds to the middle third of the Sijes Formation and is bound on the base and top by the Monte Amarillo and Esperanza members of that formation, respectively. The thickness, including the upper part which is covered by unconsolidated material, is 378 m of which 113 m embrace the colemanite-inyoite section. The mineralization extends for some 3 km, most of which is along a north-south homocline with an average dip of 35 °E. Small folds are common throughout the section. There are also faults 500 to 1000 meters apart of the same orientation with throws of some tens of meters and with small parallel faults between them.

The mineralized beds have well-defined contacts, principally with green clay gangue. The materials enclosing the borate are brown and green claystones, siltstones, and gray tuffs, with a few sand and white tuff interbeds. Gypsum is also important, generally as greenish and brownish gypsiferous sandstones. Anhydrite is practically absent. The typical thickness of a pair of alternating beds of borate/non-borate is about a meter. The borate-bearing levels vary from stringers of a few millimeters thick to beds of up to 2 meters. The beds have good continuity and maintain their thickness, which allows them to be followed along the surface in the area of the deposit, even though they do not have the pronounced morphological expression as do those of Monte Amarillo.

The lateral continuity of the individual mineralized beds allows for the characterization of important changes in their internal compositions. Some beds are composed entirely of colemanite, others of inyoite, and some are a mixture of greater or lesser volumetric proportions of the 2 minerals. Also, hydroboracite occurs in a facies relationship with colemanite and inyoite. Following a given bed over a distance of 400 meters one can observe the repetition - every 50 meters or so - of a change between colemanite and hydroboracite, and locally gypsum. Toward the edges of the mineralized area, the borate beds tend to become lens-like and become

increasingly interfingering with fine sands, clays, and pyroclastics of the playa facies.

If the borate pulses are also analyzed vertically, from base to top, some significant variations can be recognized. The first section is predominantly colemanite alternating with sediments, gypsum, and 2 white tuff layers. The colemanite is generally impure, except for 2 beds, and occurs as either nodules within the sediments or with abundant gypsum. The second section has borate beds on an average of 1 per meter alternating with sediments and gypsum, and there are 2 important gray tuffs which serve as marker beds. This is the richest part of the ore body in terms of volume of borates. Besides colemanite, there is also abundant inyoite and lesser amounts of hydroboracite. Secondary ulexite is disseminated widely through the section, as is gypsum in varying proportions. The third section corresponds to a barren lithologic unit. The fourth section has 2 important borate beds, 1 at the base, the other at the top, between which there are alternating beds of tuffs, sediments, and gypsum with 1 thin stringer of inyoite. One unit is especially notable as a thick bed of massive inyoite with lenses and veins of hydroboracite and colemanite. The uppermost section is a sandy siltstone with isolated tuff beds and thin stringers of inyoite and colemanite. The date obtained from a tuff sample at the top of the underlying Monte Amarillo member indicates that the Monte Verde beds are between 6.3 ± 0.2 and 5.4 ± 0.8 Ma.

The Monte Verde succession can be considered a bimineralic deposit, composed of approximately volumetrically equivalent amounts of colemanite and inyoite, with minor amounts of hydroboracite and ulexite (Table 1). Colemanite is found in various forms. These are following: 1) massive, compact crystalline beds interfingering with sediments, gypsum, and inyoite; 2) colemanite disseminated and/or intergrown with sediment, gypsum, or inyoite; 3) colemanite in small nodules of about 5 mm average size within a silty or sandy gangue; 4) colemanite spherules, 0.2 to 2 cm in size, isolated or in aggregates, composed of crystals radiating from a nucleus, sometimes hollow. The spherules may be perfectly round, or flattened parallel to the stratification producing ovoid structures. They may be packed so densely that there is no space between them, or contain open spaces within which new crystals grow.

Small transgressive veinlets are common, as are drusy fissures. These fissures can form a more or less complex polygonal network which resembles a skeletal web when the enclosing gangue material is weathered away. Colemanite geodes containing clean and transparent crystals are also abundant. Black colemanite also occurs, which may be caused by impregnations of todorokite (Muehle 1974). Yellowish or orange arsenic sulfides (orpiment, realgar) in the cores of spherules or as intercrystalline phases are common. In general, colemanite occurs as fragile crystalline material, either transparent or with variegated colors.

Inyoite is found as discrete, continuous layers or associated with colemanite or gypsum, either disseminated or in lenses of various sizes. It occurs in massive form as a granular, crystalline mosaic; in lenses or interstratified beds of pseudorhombic crystals; as crystalline agglomerates in small nests or pockets; as transgressive veinlets; or in thin fibrous layers with crystals grown perpendicular to the stratification, in a manner very similar to that of gypsum. It locally contains lenses, beds, or veinlets of colemanite, gypsum, hydroboracite, or sediments. In general, it is a fragile, transparent material with a light yellowish or greenish tone, and it most commonly occurs as intergrowths with colemanite.

Hydroboracite predominates in the underlying Monte Amarillo member, but also is found in much smaller amounts in the Monte Verde member. It occurs locally in massive beds in a facies relationship with inyoite, colemanite, or gypsum, or as lenses within any of these materials. It is a whitish-yellow, fibrous, massive, tough mineral constituting less than 10% of the total borates in this deposit.

Ulexite is found widely distributed within the weathered surface covering the mineralized section. It occurs as a surficial alteration product of the borate beds. It is not found within fresh rock or within the primary borates. The ulexite formed from borate solutions evaporating in the clayey-saline capping material, and has a typical thickness of a few centimeters to half a meter. It occurs as white, pure, finely disseminated nodules, transgressive veinlets, or thin coatings.

Gypsum commonly accompanies the borate minerals, but there is very little anhydrite. Arsenic minerals are also present locally, principally as realgar and orpiment.

Coatings and patinas of iron and manganese oxides are also common.

Esperanza deposit

The Esperanza borate deposit consists primarily of colemanite with minor amounts of hydroboracite, inyoite and ulexite. The Esperanza district is located on the east flank of the Sijes hill, some 8 km SE of the Sijes mining camp in the small valley of the dry Esperanza River at an average altitude of 3850 meters (Figure 5). It is accessed via a precarious side route from the Sijes-Tincalayu road. At present, the district is inactive, but for many years it was an important supplier of borate minerals (Schalamuck *et al.* 1983; Alonso 1986; Gonzalez-Barry and Alonso 1987; Alonso & Gonzalez-Barry 1990).

The borate beds lie intercalated within the lower middle part of the Esperanza member. This member passes lithologically from conglomerates at the bottom to evaporites in the middle and finally to tuffs in the upper part. The Esperanza member constitutes the upper third of the Sijes Formation. It is the thickest member of the Sijes Formation, reaching 780 meters of which 37.15 meters is the colemanite section. The mineralized belt is 3 km long and consists of a north-south homocline dipping an average of 20°E.

The colemanite beds lie between mudstone layers with flat, well-defined contacts. They are predominantly dark brown, with a few minor isolated greenish layers and one yellowish-ocher layer. The greenish layers and yellowish layer are most conspicuous near the base, have well defined contacts, and good lateral continuity. The colemanite section lies between 2 tuffs, a lower gray tuff, which is a good marker bed, and an upper white one. As opposed to the aforementioned members (Monte Amarillo and Monte Verde), the Esperanza colemanite section has relatively thin borate beds that average about 30 cm thick, and none of which exceed 60 cm. Likewise, tuffaceous layers are practically absent and gypsum beds are much subordinated, although some gypsum layers lie at the edges of the deposit in a facies relationship with the borates. In addition to the colemanite beds, there are several polyborate layers where the more conspicuous contain hydroboracite, colemanite, inyoite, and ulexite, in proportions which vary laterally.

A vertical survey of the composition of the borate section shows its simple format to be an alternating,

rhythmic clastic-evaporitic sequence composed basically of mudstone-borate pairs. The borate mineral composition is nearly constant throughout the section.

No precise data are available concerning the age of the Esperanza member. On the basis of its stratigraphic position and the age of the Monte Amarillo member, its deposition occurred during the Late Miocene. The count of detrital-chemical pairs indicates a duration of 300,000 years for the borate-depositing event.

The borate section of the Esperanza member might be considered a monomineralic colemanite deposit, even though hydroboracite, inyoite, and ulexite are present in minor amounts.

Colemanite is the principal mineral species of the deposit. Locally, it is brown or greenish, depending on the gangue which may be clastic or of gypsiferous materials. The mineral is most commonly found in lenses or small beds, either massive or in spherules, normally tinged with iron or manganese oxides which give it an internal dark coloration. Black colemanite is very common, probably due to impregnations of manganese oxide (todorokite?). The spherules vary between a few millimeters and 2-3 centimeters in diameter and tend to grow either freely within the sediment or in densely packed layers, locally compressed into ovoid forms. Nodular aggregates of spherules with an average diameter of 0.5 cm are also abundant. In some levels, particularly in the polyborate beds, there are numerous small veins which form networks on weathered surfaces. The walls of these networks are locally covered with millimeter sized crystals. This texture is particularly evident in vertical veinlets (up to 4 cm wide) in 1 of the polyborate units.

Hydroboracite forms more than 90% of the Monte Amarillo deposit, is found in lesser amounts at Monte Verde, and is uncommon in the Esperanza deposit. It occurs in some layers as very pure massive beds or lenses, and in transgressive veinlets with colemanite and fine intercalations of inyoite.

Inyoite which forms around 45% of the mineralization in the underlying Monte Verde member is not significant at Esperanza. It occurs in 1 of the lithologic units as a thin layer of fibrous crystals growing perpendicular to the stratification, bordered by hydroboracite and crossed by transgressive colemanite veins. It also occurs in the polyborate layers, along with hydroboracite and colemanite.

Ulexite is very scarce. As in the underlying members, it occurs primarily disseminated within the surface clay-saline weathered cap that typically covers borate beds. It appears as very pure and millimeter-sized nodules.

Although gypsum is less abundant than in the lower members, it is a common accompanying gangue, while anhydrite is completely absent. Iron and manganese oxides occur as impregnations and patinas. Notable amounts of realgar are also present in some layers.

The special position of the borate section at Esperanza indicates that the center of deposition moved toward the north with time relative to the underlying members. The center of deposition shifted toward the south between Monte Amarillo and Monte Verde time. These migrations are possibly evidence of the differential warping of the underlying basement in the mechanics of basin development during deposition of the Sijes Formation.

From the lithologic analysis, it is apparent that as sedimentation of the Esperanza member began, the nearby positive areas were uplifted and their accumulated detrital material carried into the basin. Next came a stage of reactivated explosive volcanism, the force of which is demonstrated by pumice fragments up to 3 cm across in some of the layers. This context (erosion of upraised areas and active volcanism) preceded the conditions of slow sedimentation in permanent bodies of shallow water in a closed basin, with alternating stages of oxidation and reduction, into which reactivated geothermal systems began discharging their mineralized waters.

The characteristics of colemanite which show it to be a primary mineral, as described above, may be best expressed in this deposit as the mineralized sediments have been little deformed. The mineral occurs as massive beds within that gangue. Some of the spherules show flattening due to the weight of the overlying sediments, becoming oval-shaped with their long axes parallel to the stratification. The spherules grew from distinct centers of crystallization, and their abundance is a direct consequence of the amount of boric anhydride available within the sedimentary medium. The development of the spherules is equivalent to that of the "potatoes" of ulexite in the present-day salares.

A lithologic unit at the top of the sequence is a special case within this deposit, being composed principally of hydroboracite with very scarce inyoite, and crossed by thick veins of colemanite of transverse orientation. The

composition of the Esperanza member exhibits again the prevalence of the calcium borates which dominated the geochemical system during Monte Verde time, with a notable attenuation of the borate-depositing pulse as is shown by the reduction in number and thickness of the mineralized layers.

Santa Rosa deposit

The Santa Rosa deposit is composed principally of colemanite and hydroboracite, with appreciable amounts of inyoite and ulexite. It is located approximately 2 km NE of the Sijes mining camp and formed part of the extreme north end of the Sijes range (Figure 5). The topography of Santa Rosa is formed by small island-hills which rise up 50 meters or so from the floor of the Pastos Grandes Salar. The Santa Rosa deposit was the subject of a careful study by Rusansky (1985) in which he describes principally hydroboracite occurring in the central and western sector of the area. Alonso (1986) delineated important new reserves of colemanite, with subordinate ulexite and inyoite, along the eastern flank of the range.

The Monte Amarillo and Monte Verde members, although reduced in thickness, can be clearly recognized by their position at the near edge of the sedimentary basin. The Monte Amarillo member crops out on the west side and along the crest of Santa Rosa Hill. Its facies relations show hydroboracite intercalated with sands, muds, clays, tuffs, gypsum, anhydrite, and inyoite in minor proportions in its lower part. The dominant coloring is yellowish (hydroboracite), greenish (clastics), and grayish (pyroclastics). Toward the base, the strata become pinkish, marking the transition to the underlying Pozuelos Formation, which was found by various drill holes to have its clastic rock-salt facies within the deposit. At the top, it grades evenly into the overlying Monte Verde member. The hydroboracite beds form conspicuous layers that protrude at the surface. The structural trend of the sequence is approximately NNE-SSW, is inclined toward the east, and the sequence is cut by numerous minor transverse faults and shows gentle internal folding.

The Monte Verde member lies along the eastern flank of Santa Rosa Hill and comprises colemanite beds intercalated with brown and greenish clastic layers. Tuffs are more poorly represented than in the underlying

member. Gypsum occurs in some levels as thick facies variations with colemanite; anhydrite is absent. With respect to borates, although monomineralic layers of colemanite exist, the beds tend to be polyborate containing varying proportions of ulexite and inyoite.

The section is geomorphically low and covered by weathered material, which long impeded the discovery of these reserves. The mineralized system presents internal complications in that it is part of a large syncline upon which has been imposed disharmonic internal folding related to the great plasticity of the deformed material. Locally, this folding caused the tectonic thickening of some borate beds. The top of the Monte Verde member is covered by present-day evaporites of the Santa Maria Salar. Both the Monte Amarillo and Monte Verde members are composed of beds with a typical thickness of 0.5 to 1.0 m. The thickness of the entire group does not exceed 300 meters.

The principal borates of the deposit are colemanite and hydroboracite. Colemanite was mined intensively during the period 1983-1985, while hydroboracite was extracted only sporadically and to a minor degree. Both ulexite and inyoite are present in appreciable amounts either in discrete beds or forming part of polyborate layers. There were some small ulexite workings on the extreme south of Santa Rosa Hill. Other borate species that have been mentioned as occurring rarely are meyerhofferite, nobleite, and gowerite (Rusansky 1985).

The principal modes of hydroboracite were dealt within the description of the section Monte Amarillo member, and hydroboracite appears similarly here. It occurs principally in massive strata as a hard yellowish-white material which forms sharp ridge-like crests upon weathering. Hydroboracite may either make up an entire bed, or be intercalated with, or in a facies relationship with, beds of sandstone, gypsum-anhydrite, clay-siltstone, or tuff, or mixed in varying proportions with these materials. Facies changes between hydroboracite and inyoite and/or ulexite are common in the lower part of the Monte Amarillo member. In the Monte Verde member, there are 2 hydroboracite beds, 1 of which is a polyborate occurrence with colemanite, ulexite, and inyoite. The other bed is a dark brown muddy claystone with balls and flattened nodules of hydroboracite up to a maximum of 0.5 m in diameter. The mineral is of high purity, hard, and has a fibrous internal appearance.

Colemanite is presently the principal economic mineral of the deposit and is restricted almost entirely to the Monte Verde member. Some of its forms of occurrence as described in the Monte Verde section also occur here (e.g., massive, spherulitic, nodular, intergrown, disseminated, veins, in geodes and druses). The predominant mode contains abundant geodes and druses, and is partly massive crystalline and partly spherules of radiating crystals mixed with a green tuffitic gangue.

Cavities filled with selenite crystals up to 20 cm long are present locally within some beds. Another common occurrence is that of small spherules of colemanite distributed within the sediment, mainly brown tuffaceous sandstone, which gives a nodular appearance to the bed. It is worth noting that the colemanite beds also contain other borate minerals, principally ulexite and inyoite, and lesser amounts hydroboracite, as products of postgenetic transformations.

Inyoite is found primarily in the lower part of the Monte Amarillo member and in the Monte Verde member. In both cases, it forms either 1) massive beds that change to ulexite, colemanite, and hydroboracite or 2) as a product of postgenetic transformation. In the latter case, it commonly forms transgressive veins in colemanite or hydroboracite where it occurs as either transparent crystals or as secondary nodules up to 25 cm in diameter grown within ulexite. Inyoite as euhedral rhomboid crystals grown within green tuffaceous claystone occurs on the extreme southeastern part of Santa Rosa Hill.

There are minor amounts of ulexite in the deposit, but it is widely distributed. Beds of massive ulexite, comparable to the "barra" (massive ulexite) in present-day salares are found on the extreme southeastern part of Santa Rosa Hill where they have been mined in the past. The ulexite occurs there as beds associated with tuffs and claystone. There are also polyborate beds in which ulexite occurs with other borate minerals.

Anhydrite and gypsum are plentiful within the Monte Amarillo and Monte Verde members, respectively. Impregnations of yellowish and orange arsenic sulfides (orpiment and realgar) occur in many of the borate beds.

The general outlines of primary borate genesis as described below may be applied to the Santa Rosa area, as they apply to an identical stratigraphic unit here. It need only be added that south of Santa Rosa near the

Sijes River, some excellent examples of fossil thermal springs have been found, concordantly deformed within the Sijes Formation and composed of travertines which show facies changes laterally to borates (Alonso 1986).

The aspects of paleogeographic evolution which differentiate the Santa Rosa deposit from those dealt with above are that, at Santa Rosa, there are small hills which acted as barely emergent islands during the development of the Pleistocene lake which covered the region. During the greater part of the Pleistocene, there was a permanent body of water in the salar which affected the sediments of Santa Rosa Hill and caused important diagenetic transformations in the borate beds. There are, for instance, dissolution features which form cavities within which have grown large transparent crystals in a perfect state of preservation. Likewise, the numerous transformations within mineralized beds containing several coexisting borate minerals show secondary features indicating that the environment was propitious for the dissolution and later recrystallization of evaporitic materials.

According to Rusansky (1985), petrographic and microscopic studies in the hydroboracite section are not sufficient to resolve such genetic problems as whether certain borate beds are a product of syngenetic chemical sedimentation or of epigenetic incorporation from adjacent beds followed by diagenesis.

Loma Blanca deposit (Jujuy Province)

The Loma Blanca borate deposit was formed in the muds of a playa-lake environment during the Late Miocene and is the fourth commercial Tertiary borax deposit discovered within the borate districts of the world. It is the only South American deposit known to contain all of the minerals colemanite, inyoite, ulexite, borax, tinalconite and teruggite within a mineral sequence that is unique and characteristic sequence within the other Argentinian borate deposits (Figure 2). The Loma Blanca deposit is characterized by abundant Ca, Na and B, very low Cl and relatively high As, S and Mg concentrations compared to other borate deposits. Thermal springs and hydrothermal solutions associated with local volcanic activity are thought to be the source of the borates. The early colemanite, inyoite, ulexite, borax and teruggite nodules appear to have been formed directly from brines penecontemporaneously within the unconsolidated

sediments, and they continued to grow as the sediments were compacted. Later generations of borate minerals occur in vugs, veins and as thin layers. Diagenetic alterations include the partial replacement of borax by ulexite and tincalconite; when weathered, borates are typically almost completely replaced by calcite.

The Loma Blanca borates were formed in a playa-lake in a seismically active area, fed partly by streams draining the catchment areas. The bulk of the interbedded clastic sediments appear to have been derived from a volcanic terrain. The borates of the Loma Blanca area are part of the Neogene playa-lake volcano-sedimentary sequence which rests unconformably on Lower Ordovician graywackes, pelites and black shales which represent the oldest rocks in the region (Figure 2).

The sediments, predominantly volcanoclastic, of the Loma Blanca area consist of the following sequence, in ascending order: 1) yellowish lower pyroclastic rocks, predominantly ignimbrites and surges, ca. 50 m; 2) lacustrine sediments, green in color, predominantly tuffite, claystone and tuff with borate deposits and travertine overburden, ca. 113 m; 3) gray upper pyroclastic rocks, ca. 106 m (Figure 2).

The red conglomerate and sandstone in the lower part of the section do not crop out in the Loma Blanca area, but occur between ignimbrites of the lower pyroclastic rocks and the Ordovician basement outside the study area.

Mineralogical studies have shown that the borate deposit is far more complex than was first thought by Aristarain and Hurlbut (1968) who recorded only teruggite, inyoite and ulexite with non-borate minerals calcite, aragonite and realgar. Borax, tincalconite, colemanite, orpiment, native sulfur, montmorillonite, illite and chlorite have been identified by Alonso *et al.* (1988) in addition to the minerals previously recorded (Aristarain & Hurlbut 1968) (Table 1). New exploration and mining indicate that the district is to become the second major Ca-Na and Na-borate deposit in Argentina. Borax, inyoite and ulexite are the dominant minerals in the deposit (Alonso *et al.* 1988).

Borate minerals in the Loma Blanca deposit occur as: 1) euhedral disseminated crystals in the claystones, mudstones and tuffite matrix; 2) thin layers interbedded with claystones, mudstones, tuff and tuffites; 3) small nodular forms with radiating structures; 4) cauliflower-

like nodules, and often "cotton ball" textures in a clay matrix; and 5) vein and vug fillings (Alonso *et al.* 1988).

Since Ca, Ca-Na and Na borates make up over 95% of the deposit, it is reasonable to assume that the original brines were enriched in sodium, calcium and boron. Arsenic sulfides and native sulfur, although present in minor quantities, are as widely distributed as the borates, and hence it may be assumed that the initial brines, at all times, were concentrated to allow borate precipitation until the lakes partially or wholly dried up. Brines in the basin were evidently rich in Ca and B; and Na borate (borax) did not crystallize from solution until Ca borates (colemanite and inyoite) and Na-Ca borate (ulexite) had been precipitated. Field and textural evidence clearly indicates the sequence Ca borate → Ca-Na borate → Na borate. (Figure 4). Arsenic-bearing borate (teruggite) occurs with Ca borates.

Tincalayu deposit

Tincalayu is the name of a low hill located in the northwestern corner of the Hombre Muerto salar that contains an important sodium borate deposit. The deposit lies between 67° 3' W and 25° 16' S at an altitude of 4100 m. Among the most important references describing this deposit are: Muessig & Allen (1957), Aristarain & Hurlbut (1967 a, b), Hurlbut *et al.* (1973), Hurlbut & Erd (1974), Igarzábal & Poppi (1980), Cornejo & Raskovsky (1981), Alonso *et al.* (1984), Alonso (1986), and Alonso & Viramonte (1990).

The peninsula of Tincalayu which hosts the borate deposit of the same name lies in the extreme northwestern part of the Hombre Muerto salar. The borax deposit lies within the southern part of the peninsula. The peninsula is about 10 km long by 2 km wide and has a generally rectangular form. It is bounded on the west by the Gallego Range from which it is separated by a long, narrow saline tongue; on the north by the southern foothills of the Bequeville Range; on the east by Farallon Catal Island, from which it is separated by a short stretch of salar; and on the south by the white polygonated crust of the Hombre Muerto salar (Figure 2).

It consists geologically of a basement of rock salt covered by sediments, principally reddish claystones, claystones and tuffs, with a few gypsum layers. The color is generally reddish brown with isolated greenish layers.

The borax deposit lies between the rock salt and overlying sediments. The entire complex is strongly folded and can be generally assigned to the Sijes Formation or its equivalent.

Clastic and evaporitic rocks of the Upper Miocene Sijes Formation, unconformably overlain by Pleistocene sediments and basaltic flows, constitute the principal geologic features of the deposit. A thick borate bed is conformably interlayered between salt rock at the base and overlying pelites (Figure 2). These units can be identified as stratigraphic members of the Sijes Formation.

The rock salt substratum was drilled as far as 145 m in depth and the base was still not reached. The borate member is 30 m thick and is integrated with massive borax in pure beds or with argillaceous or tuffitic matrix in several ratios. There are also thin stratified layers of claystones, siltstones, sandstones, tuffs, and tuffites. The borate section is covered by reddish brown siltstones, claystones, and sandstones with a thickness of 25 m (Figure 2). The Sijes Formation is strongly folded and faulted in the borate deposit area.

A tuff sample near the top of the borate section yielded a K-Ar age of 5.86 Ma (Alonso & Viramonte 1990), indicating a Late Miocene age for the deposit. This borate section is composed of borax and minor kernite. There are also several rare mineral species such as ulexite, tinalconite, probertite, macallisterite, strontioginorite, ginorite, inyoite, inderite, kurnakovite, searlesite, and some minerals exclusively from Tincalayu, such as ezcurrite, ameghinite, rivadavite, and aristarainite (Table 1).

Borate minerals are found in a playa lake fed by thermal springs carrying boron solutions related to Ratonés stratovolcano, located a few kilometers northeast of the deposit. Borate-crystal formation took place both within the mud and at the water-mud interface at the bottom of the lake. Deposition occurred due to saturation of boron in water as a consequence of evaporation in the arid climate.

Genesis of colemanite

Colemanite is known to form numerous deposits in California (USA) and in Anatolia (Turkey), always stratabound in Tertiary rocks. It does not seem to be

forming in recent deposits, although in some places such as the nitrate fields of Chile it has been mentioned at the level of a mineralogical curiosity (Chong 1984). It also occurs in the salars of Argentina (Catalano 1926) and Bolivia (Cadima & Lafuente 1969). This is one of the reasons that several authors accept a secondary origin for colemanite (e.g., Foshag 1921; Muessig 1959; İnan *et al.* 1973; Kistler & Smith 1983). In this sense, a great majority of the deposits in the USA and Turkey show characteristics that give the impression that colemanite is a secondary mineral brought about by post-depositional transformations. Nevertheless, Helvacı & Firman (1976) and Helvacı (1977) put forth the idea that at least some of the colemanite at Emet (Turkey) is of primary origin.

In this work, we base our observations regarding genesis of colemanite, strictly on the field evidence. The Monte Verde colemanite has mixed characteristics, giving the appearance of a primary mineral in some cases and secondary in others. Thus, for example, features that indicate a primary origin are: 1) Normal stratification, that is, the colemanite beds are interstratified regularly with the beds of sediments and other evaporites, maintaining contacts that are flat, sharp and laterally regular and continuous; nowhere has it been observed that colemanite beds penetrate the under or overlying beds (transgressive phenomena are very common within a given colemanite bed, but not between such beds); 2) The presence of massive colemanite beds intercalated with sediments or with other evaporites, all within a larger colemanite unit; and 3) The presence of nodules and spherules of colemanite grown during diagenesis within the sediments which locally show ovoid deformation due to lithostatic pressure.

In accordance with the above, it would seem necessary to accept that at least some of the colemanite is of primary origin, that is, that it formed penecontemporaneously within the unconsolidated sediments, beneath the water-sediment interface in the case of the nodules, or at the interface in the case of the crystalline massive beds. It should be noted that due to the distinct sedimentary characteristics of the Monte Verde section, such as the great amounts of greenish clay and the scarcity of sedimentary features such as desiccation cracks, raindrop impressions, bird tracks, paraclastics, etc., the beds carrying the colemanite seem to have been laid down in deeper water than the borate beds of the Monte Amarillo member. Other

manifestations of the colemanite show clearly and definitively its secondary origin, for instance, transgressive veins and stringers, colemanite crystals within geodes and druses, and colemanite spherules with hollow cores.

The large colemanite deposits of the southwestern United States show abundant evidence of their secondary origin via transformation of pre-existing borates such as ulexite, inyoite, or meyerhofferite. One such expression is the beautiful pseudomorphs of colemanite after inyoite, some of which preserve the complete passage from inyoite through meyerhofferite to colemanite (Muehle 1974). There are also masses of ulexite with cores or patches of colemanite forming within them, both in the USA and on a limited basis in Turkey. Nevertheless, there is also evidence in both regions indicating a primary origin. The authors of this work carried out studies of the deposits in California and Nevada and came to the conclusion that the majority of them have features indicating a primary genesis for some occurrences of colemanite. In some cases the colemanite has undergone limited changes since its original deposition, as at "Anniversary", "Lila-C", "Gerstley", and "Cerro Blanco" in the USA.

Inyoite in the Monte Verde deposit, although it may not be an easy genetic problem to resolve due to the large amounts involved, at least it has already been described as a primary mineral (Muessig 1958; Aristarain & Erd, 1971; Alonso *et al.* 1988).

Various alternatives might be considered for the formation of colemanite as a secondary mineral, by transformation of pre-existing borates:

1. Colemanite derived from ulexite. This occurs abundantly in deposits in the USA, but not in Argentina where interstratified ulexite is notably absent and is found only as an alteration product in the surface weathering zone. Thus, neither relicts nor pseudomorphic replacements of ulexite are found, although it occurs in thick primary beds in other parts of the Sijes Formation (Santa Rosa, Sorpresa, etc.). It must also be considered that the total replacement of ulexite by colemanite would require the reduction of water of crystallization and removal of sodium. The loss of water carries with it a reduction in volume and a consequent abundance of internal openings. Such openings are

found in many beds, although it is not possible to tell whether they are due to dehydration or to leaching of soluble material.

2. Colemanite derived from inyoite. This is also abundant in some North American deposits but is very limited in Turkish deposits. In Argentina, we have not observed such replacements, although they may have occurred in restricted areas. Inyoite is the highest hydrate in the Ca-borate series, and its transformation to colemanite requires only a loss of water. There is, however, an intermediate state, meyerhofferite, which is found to occur frequently in such transformations. Meyerhofferite has not been found in the deposits of the Sijes Formation, although it has been noted at the level of a mineralogical curiosity (Rusansky 1985).

The genesis of the other borate present, hydroboracite, was dealt with at length in Alonso (1986), where it was concluded to have been fundamentally of primary origin. In the Monte Verde case, there seem to be 2 alternatives: primary, where hydroboracite forms independent beds or where it is observed in a facies relationship with inyoite, gypsum, or colemanite; and secondary via a transformation from colemanite which requires only the substitution of magnesium for calcium and the addition of water (Helvacı & Firman 1976). A few small, diffuse patches of hydroboracite within colemanite may have had this secondary origin.

Gypsum beds are an additional factor in the analysis of genesis. They show the stratification and structures of a normal chemico-evaporitic deposit, formed at ambient temperature and pressure in a body of water enriched in calcium sulfate. Gypsum beds are found in some localities at Monte Verde intercalated between beds of colemanite and, in others, in a lateral facies relationship with borates. A gypsum bed between beds of colemanite and composed of gypsum rosettes within a gypsiferous clay gangue, is found to be exactly the same as in present-day salars. The preservation of the original features in this unit is a clear indication of the lack of any important epigenetic transformations.

In accordance with the above, the conclusion of this section is that the borate beds of the Monte Verde member are substantially of primary origin, with only minor changes after deposition. Thus, either the geothermal systems which had operated during Monte

Amarillo time were reactivated during Monte Verde deposition, or new systems were formed over a wide area which produced and carried borate solutions into the nearby closed basins. These solutions poured into, and crystallized within, a perennial shallow lake. Due both to supersaturation in boric anhydride and the reigning physico-chemical conditions, there was direct deposition of colemanite, inyoite, hydroboracite and perhaps small amounts of other borate minerals. With burial and later deformation, there may have been some diagenetic and postdiagenetic changes consisting of dehydration and dissolution, with resulting textures such as geodes and druses.

Borate in salars

This is the most common occurrence of borates in the Andes. There are more than 100 salars in Argentina, Chile, Bolivia, and Peru, but only about 40 contain borate facies in the chemical and detrital basin deposits (Figure 3). The main references of information on borate in salars of the Central Andes are Muessig (1959, 1966), Chong (1984), Alonso (1986), Alonso & Viramonte (1990) and Alonso & Helvacı (1996).

Basins containing salars were formed by block tectonics during Quaternary times after the Diaguite diastrophic phase (Pliocene-Pleistocene boundary). The concurrence of the N-S-trending Cordillera and slightly oblique NNW-SSE volcanic chains caused the closed system of basins (Viramonte *et al.* 1984). The borates occur in the upper part of salars, either cropping out or below an overburden composed of salts and clastic materials no more than 0.5 m thick. The thickness of borate beds reaches 1.5 m, but normally is 0.2 to 0.4 m.

The substrata of borate beds vary from place to place; clastic material, evaporites, or travertines occur. The substratum can be black clays with abundant organic matter. The water table is normally near the surface and below the borate facies (Figure 3). Although deep boreholes have been made in salars, borates have not been found at depth. However, these holes are scarce and the presence of borate at depth is still a possibility.

The dominant mineral in the salars is ulexite, and borax occurs in minor proportion (Figure 3). The ulexite occurs in 2 types: 1) nodules, the classic "cotton ball" called "papas" (potatoes), and 2) massive beds called "barras" by the miners of the region. The size of the

nodules is from 1 to 30 cm in diameter, but the most typical diameter is around 5 to 10 cm. Borax occurs in euhedral evapocrystals, grown in mud, that average 1 to 2 cm long but reach 25 cm in exceptional cases. The matrix where borax crystals are enclosed is normally grayish green or reddish brown. In addition, inyoite has been found in 2 places, Laguna Salinas in Peru (Muessig 1958) and Lagunita in Argentina (Helvacı & Alonso 1994).

The borate deposits in salars are directly related to supplies of boron-rich thermal waters. In general, the deposits occur in situ around the vents of thermal springs. Other boron and salt supplies are from the weathering and leaching of volcanic rocks as well as elements adsorbed from fresh volcanic ash. Such sources of elements probably contributed to the saturation of the brines in the salars (Figure 3). Travertine deposits usually indicate the locations of fossil thermal springs. Hot waters ascend along graben boundaries and then evaporate and precipitate. The sizes and shapes of borate deposits are directly related to the configuration of the original lake where they were formed (Figure 3).

It is possible to see in some salars a gross lateral zonation from travertines to different ulexite types (Alonso and Gutierrez, 1984). The evapofacies zonation in the Andean salars is not clear; however, the borates are located between lateral gypsum and salt facies. The travertines generally occur along the edges of the basins (Figure 3). A generalized distribution of facies from the border to the center of a basin is travertine, gypsum, borate, and halite (Figure 4).

Comparison Between Turkish and Argentine Borate Deposits

- During the Miocene, similar environmental conditions were present in Anatolia (Turkey) and in Puna (South America). The geological setting of both regions included volcanism, thermal springs rich in boron, aridity and closed basins with internal drainage. Volcanism and extensional basins in a special plate tectonics framework were responsible for the endogenetic and exogenetic conditions favorable to chemical deposition. The final result was the formation of evaporite depocenters, where borates played an important role as dominant evapofacies.

- The basement rocks for the borate deposits in two countries are different. The basement of the Turkish deposits comprises Precambrian-Mesozoic metamorphic rocks, including ophiolites, marbles and schists. The basement of the borate deposits in the Argentine Puna consists of Ordovician marine rocks of very low metamorphic grade, mainly graywackes and pelites.
- The Turkish deposits according to some radiometric ages and other chronologic evidence are Early Miocene (ca. 16-20 Ma), while the Argentine deposits are Late Miocene (5-7 Ma).
- Both regions have borate beds interlayered in a lacustrine volcanoclastic sequence where tuffs, tuffaceous siltstones, tuffaceous claystones, limestones and travertines are the basic lithologic units.
- Calcium carbonate facies (limestones, cherty limestones, etc.) are abundant and widely distributed in the Turkish borate sections, while they are sparse in the Argentine deposits.
- Sodium chloride (halite) and calcium sulfate (gypsum) are very common minerals and form thick evaporite facies in the sections of the Argentine Puna deposits, while, in contrast, they are poorly represented in the Anatolia deposits.
- The borates have different presentations in two countries. In the Turkish deposits, borates (mainly colemanite, occasionally ulexite and other borate minerals) are associated in beds forming thick sequences with minor non-borate materials and are present in boulders and nodules up to 1 m in diameter and often in massive layers. In Argentina, the borates occur as spherules of a few centimeters and thin, massive layers forming strata less than 1 m thick where beds are separated 1 or 2 m non-borate materials. So, more rapidly changing lacustrine environments are present in the Puna region.
- From the mineralogical point of view, the borate associations have some differences in two countries. In Turkey, colemanite is associated with ulexite, probertite and hydroboracite while other borate species (howlite, inyoite, meyerhofferite, priceite, veatchite-A, tunellite, teruggite, terschite, cahnite and rivadavite) are poorly represented. In Argentina, colemanite is associated with inyoite, hydroboracite and ulexite while other borate species (such as probertite, inderite, meyerhofferite, nobleite and gowerite) are very scarce.
- Borax is by far the most important mineral for the borate industry and it tends to have different modes of formation in the Kirka deposit (Turkey), and the Tincalayu deposit and Loma Blanca deposits, (Argentina). Stratigraphic sequences, associated rocks and the internal texture of the ore body are also different in the Kirka and Argentine deposits.
- The Turkish deposits consist of high-grade borate ores and should supply a substantial proportion of the world's needs for many years, whereas the Argentine deposits are made up of smaller and low-grade borate ores.

Acknowledgment

We are especially grateful to Etibank and Industrias Químicas Baradero and their mine managers for their generosity during fieldwork in Turkey and Argentina, respectively. K-Ar dating was carried out at the University of Arizona. We also thank Dr. S. K. Mittwede and 2 referees (Barry N. Watson and Iain C. Scarr) for their critical reviews of the manuscript, and Fuat Erkül, Filiz İncedere and Nesrin Bayrak of the Dokuz Eylül University for drafting and typing assistance, respectively. One of the authors (R. N. Alonso) wishes to thank CIUNSA and CONICET where he is developing a program to study borate deposits of Argentina and the Central Andes.

References

- ALONSO, R.N. 1986. *Occurrence, Stratigraphic Position and Genesis of the Borate Deposits of the Puna Region of Argentina*. PhD Thesis, Universidad Nacional de Salta [in Spanish, unpublished].
- ALONSO, R.N. 1992. Geology of the Monte Verde mine (colemanite-inyoite), Salta, Argentina. *Proceedings of IV Argentine Congress and I Latin America Congress of Economic Geology*, Cordoba, Argentina, 241-252 [in Spanish].
- ALONSO, R.N. & GONZALEZ-BARRY, C.E. 1990. Geology and distribution of borate deposits in the Sijes district, Salta. *IV Argentine Congress of Mining Engineering II*, 55-64, Jujuy, Argentina [in Spanish].

- ALONSO, R.N. & HELVACI, C. 1988. Mining and concentration of borates in Argentina. In: Aytekin, Y. (ed), *Proceeding of the II International Mineral Processing Symposium*, İzmir, Turkey, 551-558.
- ALONSO, R.N. & HELVACI C. 1996. Salt pan borate deposits of Argentina. 30th *International Geological Congress, Beijing, China, 4-14 August 1996, Abstract Books*, **2**, 692.
- ALONSO, R.N., HELVACI C., SUREDA, R.J. & VIRAMONTE, J.G. 1988. A new Tertiary borax deposit in the Andes. *Mineralium Deposita* **23**, 299-305.
- ALONSO R.N., JORDAN, T.E. & TABBUTT, K. 1989. Neogene sedimentary basins of Argentine Southern Puna Plateau, Central Andes Mountains. 28th *International Geological Congress, Washington D.C.* **1**, 33-34.
- ALONSO, R.N., JORDAN, T.E., TABBUTT, K. & VANDERVOORT, D. 1991. Giant evaporite belts of the Neogene Central Andes. *Geology* **19**, 401-404.
- ALONSO R.N. & VIRAMONTE, J.G. 1990. Borate deposits in the Andes. In: FONTBOTE, L. et al. (eds), *Stratabound Ore Deposits in the Andes*, Springer Verlag, 721-732.
- ALONSO, R.N., GUTIERREZ, R.V. & Viramonte, J.G. 1984. Megacuerpos salinos cenozoicos de la Puna Argentina. *IX Congreso Geológico Argentino* **1**, 25-42.
- ALONSO, R.N. & GUTIERREZ, R.V. 1984. Zonacion de ulexita en los salares de la Puna Argentina. *Argentina Association of Geological Review* **39**, 52-57.
- ARISTARAIN L.F. & ERD, R. 1971. *Inyoita, 2CaO.3B₂O₃. 13H₂O de la Puna Argentina*. Anales de la Sociedad Científica Argentina. Tomo CXCI, Entrega V-VI. Buenos Aires.
- ARISTARAIN, L.F. & HURLBUT, C.S.JR. 1972. Boron, minerals and deposits. *Mineralogical Record* **3**, 213-220.
- ARISTARAIN, L.F. & HURLBUT, C.S.JR. 1968. Teruggite, a new mineral from Jujuy, Argentina. *American Mineralogist* **53**, 1815-1827.
- ARISTARAIN, L.F. & HURLBUT., C.S.JR. 1967a. Ameghinite, Na₂O.3B₂O₃. 4H₂O, a new borate from Argentina. *American Mineralogist* **52**, 935-945.
- ARISTARAIN, L.F. & HURLBUT, C.S.JR. 1967b, Macallisterite, 2MgO.6B₂O₃. 15H₂O, from Salta, Argentina. *American Mineralogist* **52**, 1776-1784.
- BAYSAL, O. 1972. *Mineralogic and Genetic Studies of the Sarıkaya (Kırka) Borate Deposits*. Ph.D. Thesis, Hacettepe University, Turkey [in Turkish, unpublished].
- BOWSER, C.J. 1965. *Geochemistry and Petrology of the Sodium Borates in the Non-marine Evaporitic Environment*. PhD Dissertation, University of California, Los Angeles [unpublished].
- CADIMA, J. & LAFUENTE, F. 1969. *Prospeccion General de Algunas Borateras Particulares (Provincias Nor y Sud Lipez, Dto. Potosi)*. Ministerio de Minería y Metalurgia, Division Tecnología Minera, La Paz. Informe No. 647.
- CATALANO, L. 1926. *Geología de los Yacimientos de Boratos y Materiales de las Cuencas*. Salar de Cauchari, Puna de Atacama. Dirección General de Minas, Geología e Hidrología, Buenos Aires, Publicacion No. **23**.
- CHONG, G. 1984. Die salare in Nordchile-Geologie, Structure und Geochimie. *Geotektonische Forschungen* **67**, 1-146.
- CORNEJO, R. & RASKOVSKY, M. 1981. Proyecto minero y explotación a cielo abierto del yacimiento Tincalayu. *II Jornadas Argentinas de Ingeniería en Minas, San Juan* **1**, 232-242.
- FLOYD, P.A., HELVACI, C. & MITTWEDE, S.K. 1997. Geochemical discrimination of volcanic rocks, associated with borate deposits: an exploration tool? *Journal of Geochemical Exploration* **60**, 185-205.
- FOSHAG, W. 1921. The origin of the colemanite deposits of California. *Economic Geology* **16**, 194-214.
- GONZALEZ-BARRY, C. & ALONSO, R. 1987. El deposito Neoterciario de boratos Esperanza. *X Congreso Geológico Argentino, Tomo II, Tucuman*, 63-66.
- GÜNDOĞAN, İ. & HELVACI, C. 1993. Geology, mineralogy and economic potential of Sultançayır (Susurluk-Balıkesir) boratiferous gypsum basin. *Bulletin of the Geological Society of Turkey* **36**, 159-172 [in Turkish].
- GÜNDOĞDU, M.N., BONNOT-COURTOIS, C. & CLAUER, N. 1989. Istopic and chemical signatures of sedimentary smectite and diagenetic clinoptilolite of a lacustrine Neogene basin near Bigadiç, western Turkey. *Applied Geochemistry* **4**, 635-644.
- HELVACI, C. 1977. Geology, mineralogy and geochemistry of the borate deposits and associated rocks and the Emet Valley, Turkey. PhD Thesis, University of Nottingham, England [unpublished].
- HELVACI, C. 1978. A review of the mineralogy of the Turkish borate deposits. *Mercian Geology* **6**, 257-270.
- HELVACI C. 1983. Mineralogy of the Turkish borate deposits. *Geological Engineering* **17**, 37-54.
- HELVACI C. 1984. Occurrence of rare borate-minerals: veatchite-A, tunellite, teruggite and cahnite in the Emet borate deposits, Turkey. *Mineralium Deposita* **19**, 217-226.
- HELVACI C. 1986. Geochemistry and origin of the Emet borate deposits, western Turkey. *Faculty of Engineering Bulletin, Cumhuriyet University, Series A, Earth Sciences* **3**, 49-73.
- HELVACI C. 1989. A mineralogical approach to the mining, storing and marketing problems of the Turkish borate production. *Geological Engineering* **34-35**, 5-17.
- HELVACI, C. 1994. Mineral assemblages and formation of the Kestelek and Sultançayır borate deposits. Proceedings of 29th *International Geological Congress, Kyoto Part A*, 245-264.
- HELVACI, C. 1995. Stratigraphy, mineralogy, and genesis of the Bigadiç borate deposits, Western Turkey. *Economic Geology* **90**, 1237-1260.

- HELVACI C. & ALACA, O. 1991. Geology and mineralogy of the Bigadiç borate deposits and vicinity. *Bulletin of Mineral Research and Exploration Institute of Turkey* **113**, 31-63.
- HELVACI C. & ALONSO, R.N. 1994. An occurrence of primary inyoite at Lagunita Playa, Northern Argentina. Proceedings of 29th International Geological Congress, Kyoto **Part A**, 299-308, Japan.
- HELVACI C. & FIRMAN, R.J. 1976. Geological setting and mineralogy of Emet borate deposit, Turkey. *Transactions/section B, Institute of Mining and Metallurgy* **85**, 142-152.
- HELVACI C. & ORTI, F. 1998. Sedimentology and diagenesis of Miocene colemanite-ulexite deposits (western Anatolia, Turkey). *Journal of Sedimentary Research* **68**, 1021-1033.
- HELVACI C., STAMATAKIS, M.G., ZAGOUROGLOU, C. & KANARIS, J. 1993. Borate minerals and related authigenic silicates in northeastern Mediterranean Late Miocene continental basins. *Exploration Mining Geology* **2**, 171-178.
- HURLBUT, C.S. JR., ARISTARAIN, L. F. & ERD, R.C. 1973. Kernite from Tincalayu, Salta, Argentina. *American Mineralogist* **58**, 308-313.
- HURLBUT, C.S. JR. & ERD, R.C. 1974. Aristarainite, a new mineral from Salta, Argentina. *American Mineralogist* **59**, 647-651.
- IGARZÁBAL, A. & POPPI, R. 1980. El salar del Hombre Muerto. *Acta Geologica Lilloana, Tucuman, Argentina* **15**, 103-117.
- INAN, K., DUNHAM, A.C. & ESSON, J. 1973. Mineralogy, chemistry and origin of Kirka borate deposit, Eskişehir Province, Turkey. *Transactions/section B, Institution of Mining and Metallurgy* **82**, 114-123.
- JORDAN, T. & ALONSO, R.N. 1987. Cenozoic stratigraphy and basin tectonics of the Andes Mountains, 20-28 South latitude. *American Association of Petroleum Geologists Bulletin* **71**, 49-64.
- KISTLER, R.B. & SMITH, W.C. 1983. Boron and borates. In: LEFONDS, S.J. (ed), *Industrial Mineral and Rocks*. 5th Edition, Society of Mining Engineers of AIME, 533-560.
- KISTLER, R.B. & HELVACI, C. 1994. Boron and borates. In: CARR, D.D. (ed) *Industrial Minerals and Rocks*. 6th Edition, Society for Mining, Metallurgy and Exploration Inc., Littleton, Colorado, 171-186.
- MEIXNER, H., 1965. Borate deposits of Turkey. *Bulletin of the Mineral Research and Exploration Institute of Turkey* **125**, 1-2.
- MUEHLE, G.H. 1974. Colemanite pseudomorphs from the Corkscrew mine, Death Valley, California. *Mineralogical Record* **5**, 174-177.
- MUESSIG, S. 1958. First known occurrence of inyoite in a playa at Laguna Salinas, Peru. *American Mineralogist* **43**, 1144-1147.
- MUESSIG, S. 1959. Primary borates in playa deposits: minerals of high hydration. *Economic Geology* **54**, 495-501.
- MUESSIG, S. 1966. Recent South American borate deposits. In: RAU, J.L. (ed), *2nd Symposium on Salt, Northern Ohio Geological Society, Cleveland* **1**, 151-159.
- MUESSIG, S. & ALLEN, R.D. 1957. Ezcurrite, a new sodium borate from Argentina: Occurrence, mineralogy and associated minerals. *Economic Geology* **52**, 426-437.
- ORTI, F., HELVACI, C., ROSELL, L. & GÜNDOĞAN, İ. 1998. Sulphate-borate relations in an evaporitic lacustrine environment: the Sultançayır Gypsum (Miocene, Western Anatolia). *Sedimentology* **45**, 697-710.
- ÖZPEKER, İ. 1969. *Western Anatolian Borate Deposits and Their Genetic Studies*. PhD Dissertation, Istanbul Technical University [in Turkish, unpublished].
- PALMER, M.R. & HELVACI, C. 1995. The boron geochemistry of the Kirka borate deposits, western Turkey. *Geochimica et Cosmochimica Acta* **59**, 3599-3605.
- PALMER, M.R. & HELVACI, C. 1997. The boron isotope geochemistry of the Neogene borate deposits of western Turkey. *Geochimica et Cosmochimica Acta* **61**, 3161-3169.
- RUSANSKY, J. 1985. *Geology of the Santa Rosa Borate Mine, Los Andes Department, Salta*. PhD, Universidad Nacional de La Plata, Buenos Aires [in Spanish].
- SCHALAMUCK, I., FERNANDEZ, R. & ETCHEVERRY, R. 1983. Los yacimientos de minerales no metalíferos y rocas de aplicación de la región NOA. *Anales XX. Subsecretaría de Minería*. Ministerio de Economía, Buenos Aires, 1-196.
- SUNDER, M.S. 1980. Geochemistry of the Sarıkaya borate deposits (Kirka-Eskişehir). *Bulletin of the Geological Society of Turkey* **2**, 19-34.
- SURDAM, R.C. & PARKER, B.R. 1972. Authigenic aluminosilicate minerals in the tuffaceous rocks of the Green River Formation, Wyoming. *Geological Society of America Bulletin* **83**, 689-700.
- SUREDA, R., GALLISKI, M., ARGANARAZ, P. & DAROCA, J. 1986. Aspectos metalogenéticos del noroeste argentino (provincias de Salta y Jujuy). *Capricornio* **1**, 39-96.
- STRECKEISEN, A. 1976. To each plutonic rock its proper name. *Earth Science Reviews* **12**, 1-33.
- VANDERVOORT, D.S., JORDAN, T.E., ZEITLER, P.K. & ALONSO, R.N. 1995. Chronology of internal drainage development and uplift, southern Puna plateau, Argentine Central Andes. *Geology* **23**, 145-148.
- VIRAMONTE, J.G., GALLISKI, M.A., ARANÁ, V., GARCIA, L. & MARTIN-ESCORZA, C. 1984. El finivulcanismo básico de la depresión de Arizaro, provincia de Salta, IX Congress. *Geologica Argentina* **3**, 234-253.