

# On the origin of La Puna Borates

## Sobre el origen de los boratos de La Puna

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### RESUMEN

Se analiza la fenomenología que llevó a la formación de importantes depósitos de boratos cenozoicos en la Puna argentina. En esa región se conocen yacimientos miocenos y cuaternarios. Los depósitos miocenos corresponden a una tipología de evaporitas interestratificadas en sedimentitas de cuencas lacustres de ambiente semiárido. Durante el cuaternario se formaron depósitos a partir de fuentes termales, y en los actuales salares. Se realiza un análisis histórico de las ideas genéticas de diferentes autores. Se discute el origen "primario" versus "secundario" de los principales boratos terciarios y las teorías "lixiviacionista" versus "termalista" para los boratos de salares. En base a las observaciones de campo y trabajos actuales se elabora un modelo sintético que contempla la concurrencia de volcanismo, clima semiárido, fuentes termales y cuencas cerradas como parámetros mayores en la generación de estas sales exógenas.

*Palabras clave:* Génesis de los Boratos. Evaporitas. La Puna. Andes. Argentina.

### ABSTRACT

This paper analyses the formation of Cenozoic borates in the Argentine Puna. Various interpretations of the genesis of borates are examined; first, those recorded in primary sources dating from the last century to the present day, and second via data collected in the field. Theories propounding a primary or secondary origin of the Tertiary borates, as well as those that suggest a leaching or thermal origin of playa-lake borates, are discussed.

*Key words:* Borate genesis. Evaporites. La Puna. Andes. Argentina.

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### INTRODUCTION

The origin of the borate deposits in Argentina has been the subject of study since the end of the last century (Becerra, 1887; Brackebusch, 1893). Various theories

have been postulated to explain the occurrence of playa-lake deposits and the subsequent formation of Neogene borate deposits. Alonso (1986) postulated that the origin of the ulexite (with minor borax) of the Puna salars (salt flats) lay in thermal springs, whereas others have linked

them to the lixiviation processes of the existing rocks. Alonso (1986) suggested a primary rather than a secondary origin for the borates of the Neogene deposits of tinalconite, colemanite and hydroboracite, and noted some minor diagenetic transformations. Recent papers (Smith and Medrano, 1996; Garrett, 1998) trace the discussion concerning the origins of the world's borate deposits. Thus today we can differentiate between two schools of thought; that of the "North-American school", represented mainly by Bob Kistler, Siegfried Muessig and George Smith, which claims a secondary origin for the Tertiary borates, and the "Turkish-Argentine school", represented by Cahit Helvacı, Federico Orti-Cabo and Ricardo Alonso, which claims a primary origin. Both sides of the argument were widely discussed during the IESCA meetings (Izmir, 1990 and Golluck, 1995 in Turkey), GSA meetings (San Diego, California, USA, 1991) and other geological forums.

#### EVOLUTION AND ANALYSIS OF IDEAS CONCERNING GENESIS

The first discussion of the origins of the Puna borates was undertaken by Becerra (1887, p. 24) who interpreted the borate deposits of the Cauchari salar as having been formed by the waters of the "Tocomar, Olacapato, and Cata" Rivers. He speculated that the Puna salars' feed waters infiltrated the Cordillera Oriental to emerge as spring waters. He seems not to have considered evaporation, and despite mentioning the borate springs of Antuco and Blanca Lila he did not describe any relationship with hot springs. He was the first to consider the idea of leaching, that is the generation of evaporites by the direct deposition of stream waters into basins.

Brackebusch (1893), in discussing borate deposits, refers to boronatrocalcite as a "soft mud which accumulates in small ponds, drying in the air and forming a white crystalline mass". He does not venture an opinion as to how the boron was introduced to the ponds, but he is explicit about the mechanism of evaporation.

Ambrosetti (1900, p. 110-112) wrote a highly interesting and thoughtful study in which he related the genesis of the borates and caliches along the edge of the Cauchari salar (specifically the "Siberia" concession) to the presence of extinct geysers. However, he partially misinterpreted the mechanisms of deposition when he remarked that "In addition to the spreading (sic) of borate produced by the eruptions one has to keep in mind the mechanical transport of the substance (...) the "*papas*"

(potatoes) are pieces which have been rounded, transported, and deposited there along the pathways produced by rain." As is evident, he believed geysers had an ejection mechanism identical to that of volcanoes, and therefore he postulated that the borate had been violently expelled to various distances where it accumulated. He also concluded that the "*papas*" (local name for mineral aggregates of nodular structure), formed of ulexite, had been mechanically rounded. This, however, is refuted by abundant evidence in the salar profiles, certifying that the so-called potatoes have grown in a muddy-sand to muddy-clay, permeable and porous medium by a process of nucleation and slow growth through incorporation of boron-rich solutions. Moreover, in all cases the potatoes have a higher content of boric anhydride and a lower content of sodium chloride than either massive ulexite or their muddy environment, which shows that they cannot have developed from the latter.

Reichert (1907, p. 10-11) differentiated for the first time the forms of occurrence of ulexite as stratified or bar and nodular or potatoes ("*barra*" and "*papas*"). In line with the previous author he believed that the "*papas*" were secondary. He argued that the deposits had formed in the salars on the arrival of water heated in the vicinity of the volcanoes. This water, he believed, carried dissolved subterranean rock salt deposits with a high borate content. However, this theory does not solve the basic problem as it is dependent upon subterranean deposits (the existence of which were assumed without any specific evidence), though it does not explain how the borate formed in them. It is interesting to note how the ideas concerning the role of hot water in the formation of borate gather strength by direct analogy with the geothermal fields of Larderello (Italy).

Barnabé (1915, p. 18-26) gave extensive consideration to the genesis of the borates in the Puna. He described for the first time the borate geysers of the Coranzuli district (Jujuy). As for borates in the salars, however, he wrote at some length about the geyser deposits on the skirts of volcanoes. In some cases he considered the borate salars to be formed from the weathering of the geyser deposits washed downstream to the salt pans, and in other cases he referred to the borate salars as having formed "in situ". He maintained that the red clays and salts of the salars derived from the destruction of the superstructure of volcanoes, but he also erroneously considered the granites of Macón and Arita (Salta) to be volcanic. He believed that borates were always associated with red clays (though evidence to the contrary exists at Turi Lari, Lina Lari, etc.). Nevertheless, he always strove

to give a coherent interpretation of the deposits formation considering different points of view. Above all, he favored the ideas of leaching and the mechanical destruction of the borates followed by downstream transport. Thus he claimed that the difference between potatoes and bars of ulexite was due to differences in the permeability of the ground in which they are found.

Catalano (1927, p. 20-22) interpreted the various salts present in the Puna salars as having derived from volcanism, in a hot spring model. He carried out extensive chemical analyses to show how the boric acid in the thermal waters reacted to form borates.

Ahlfeld (1948, p. 273) considered that the ulexite beds of the Coyahuaima hot spring were deposited in a doughy state, in a similar way to mud flows. He associated the thermal waters with acid volcanism and used the presence of antimony in the ulexite to support his interpretation. He maintained that the genesis of borates was more closely related to sources of hot water than solfataras.

Muessig and Allen (1957a, p. 435-436) analyzed the Tincalayu deposit, interpreting the borates as an ancient salar deposit in which euhedral crystals grown in a muddy matrix had been recrystallized into a massive body as a consequence of tectonic forces. Muessig (1966, p. 158), after studying playa deposits, came to the conclusion that the majority of them were caused by local thermal springs, contrary to various authors who believed they resulted from the leaching of surrounding rocks.

Aristarain and Erd (1971, p. 195) concluded that the calcium borates of the Puna, such as the inyoite at Sijes, Tincalayu, and Loma Blanca, had a primary origin, whilst also interpreting the kurnakovite of Tincalayu as having a primary origin.

Alonso and Gutiérrez (1984) interpreted the ulexite of the salars as "in situ" deposits derived from hot springs following the fractures that bound the depressions. They discuss a zonation of structural characteristics of the ulexite, which vary with the distance from the source.

Rusansky (1985) examined the Tertiary borates of the Sijes Formation in the Santa Rosa deposit. He sustains that the hydroboracite has a mixed origin, being primary in some cases and secondary in others. He interpreted the boron as being a product of hot springs of unknown origin.

Alonso (1986), and Alonso and Viramonte (1993) examined all the known borate deposits of the Puna and pre-

sented a model of formation for both Tertiary and Quaternary occurrences. Alonso et al. (1989; 1991; 1992), and Vandervoort et al. (1993; 1995) discuss the chronology of the borate formation in the Argentina Puna.

## GEOLOGICAL SETTING

The boron-bearing region is located in the Altiplano/Puna plateau, which is approximately 2,000 km long, 300 km wide with an average elevation of 3,700m (Fig. 1), controlling the geomorphology of the central Andes (Isacks, 1988). The plateau overlies a 30° east-dipping segment of the Nazca plate; North and South of the plateau the subducted plate dips subhorizontally and no internally drained plateau has been described (Jordan et al., 1983; Isacks, 1988). A volcanic arc forms the western margin of the Puna/Altiplano. East of the volcanic arc, local volcanic edifices are present within the plateau. The volcanic arc and eastern volcanic centers have been active from Miocene times to the present day (Jordan and Gardeweg, 1989) and they are the origin of boron fluids. Uplift of the plateau is the combined result of late Tertiary crustal shortening and magmatic addition (Isacks, 1988).

The climate of the Puna varies from semiarid on the eastern border to arid along the western volcanic arc. The volcanic arc marks the limits of the Puna hydrologic basin to the west and a tectonic highland area to the east (Eastern Cordillera). In the southern Puna, combinations of east-trending volcanic chains and north trending, reverse fault-bounded structural blocks bound several hydrologic sub-basins (Alonso, 1986; 1991; Vandervoort, 1993). Extensive salars cover the basin floors; these are surrounded by expansive alluvial systems. Thick (up to 5 km) sections of Neogene strata are present within the modern depositional base (Jordan and Alonso, 1987; Alonso et al., 1991); these levels contain evaporites (mainly halite, gypsum and borates) and alluvial clastic material with fewer tuffaceous deposits (Alonso, 1986). Exposed Neogene strata are present in reverse fault-bounded slices along salar margins or as intrabasin uplifts within salars (Vandervoort, 1993).

## THE TERTIARY BORATE DEPOSITS

### Genesis of Tincalayu borax deposit

Among the few studies that refer to the origin and evolution of the Tincalayu deposit (see location in Figs. 1,2), the contributions of Muessig and Allen (1957a,b)

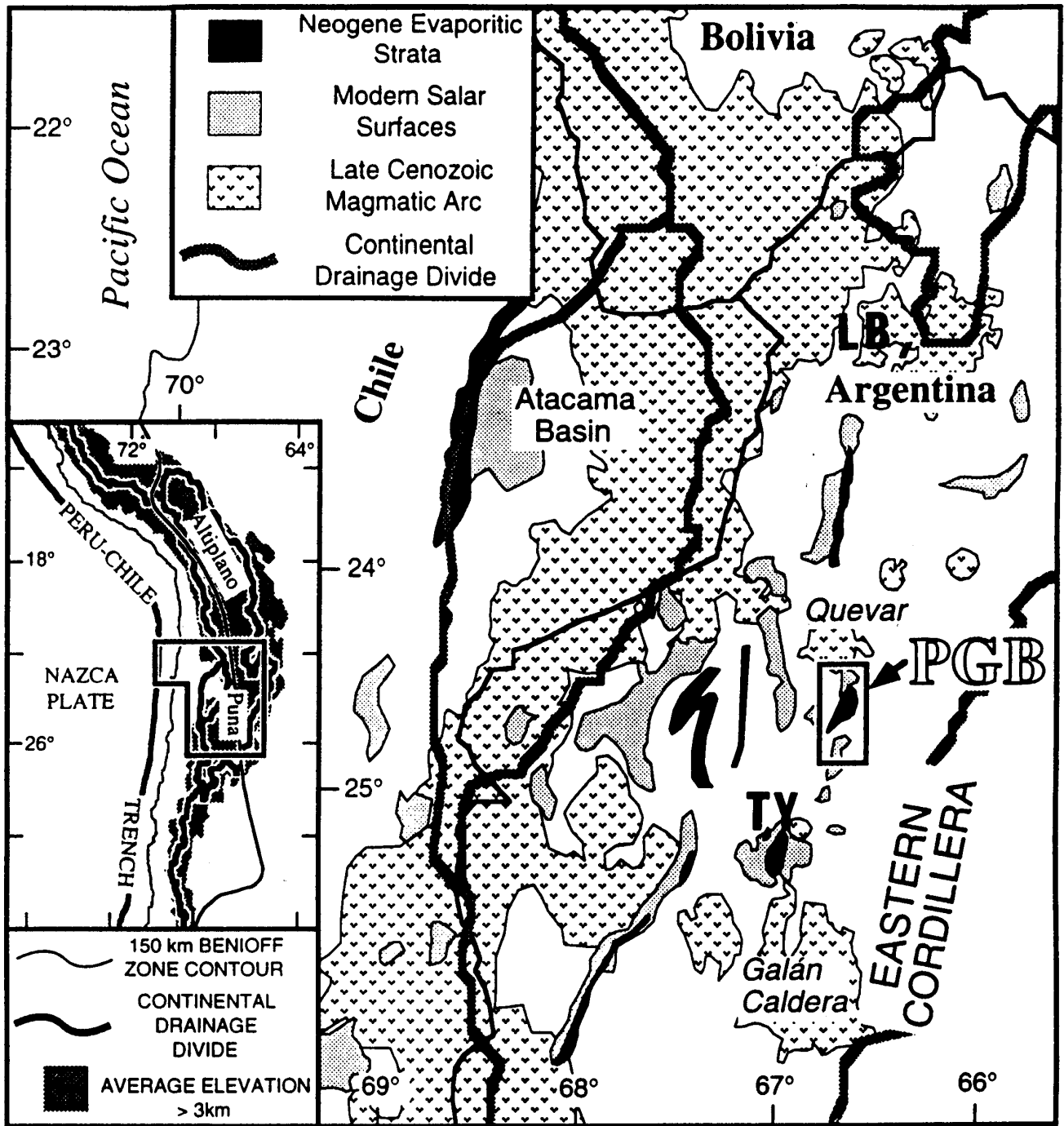


Figure 1. Map showing location of the Puna region in the Central Andes. Location of the main Tertiary borate deposits: LB) Loma Blanca; PGB) Pastos Grandes basin; TY) Tincalayau; The Salars are closed basins with saline-crust floors (modified from Vandervoort et al., 1995).

Figura 1. Situación de La Puna respecto a los Andes Centrales. Situación de los principales depósitos boratíferos terciarios: LB) Loma Blanca; PGB) Pastos Grandes basin; TY) Tincalayau; Los Salares corresponden a cuencas cerradas con desarrollo de costras salinas (modificado de Vandervoort et al., 1995).

and Hurlbut, et al. (1973) are noteworthy. Their mineralogy (see Table 1, for chemical composition of the mineral species) was given particular attention by Aristarain and Hurlbut (1967a,b; Hurlbut and Aristarain, 1967a,b; Hurlbut et al., 1973; Hurlbut and Erd, 1974).

Other contributions were made by Alonso (1986, 1991), Alonso and González Barry (1989), Alonso and Ruiz (1997). The geological history in evidence at the deposit begins with a thick succession of halite (Fig. 3). A 145-meter deep borehole drilled into the salt beds did not reach the base level (Alonso et al., 1984,a). At the time of the formation of the salt body, it can be inferred that a closed basin occupied by a salar embraced at least the area of the present Tincalayu Peninsula, as the mass of rock salt has been found in drill holes throughout the peninsula. The total area actually covered by the salar is not known. It is possible that the Gallego Range formed the western shore of the depression. Hot water with a high content of sodium chloride, associated with the thermal activity of the regional volcanism, flowed into the basin where great supersaturating and/or evaporation formed the halite beds. This is in direct analogy with present day salars where thick sections of rock salt are exposed, at least partially related to recent intense saline thermal activity. A current example is the salar of Antofalla, the central-western edge of which is being fed sodium chloride waters from hot springs, which evaporate to form thick halite crusts. The stratigraphic succession of halite beds with only small amounts of terrigenous material indicates a lack of sediment feed during deposition, while the presence of abundant tuffaceous layers gives evidence of periodic ash falls deriving from the regional volcanism.

The few localized and disseminated occurrences of borax within the salt indicate that the thermal activity also contributed some borate-bearing solutions to the hydrologic system. The transformation of the salt body into borate is a transitional process, reflected in a persistent sedimentary rhythm, and represented by the evaporitic beds changing from chlorides to borates. Ash is the principal interlayered material, with smaller amounts of terrigenous sediments. A volcanic center was emplaced coevally along the eastern flank of the depression. This provided some olivine basalt for andesite flows, the folded and eroded remnants of which are found intercalated within a lithologic unit, the Sijes Formation. These flows are fundamental to our understanding of the genesis of the deposit.

Although the existence of regional volcanism is well established, no evidence has been found to date for local

volcanism. As will be seen on comparing the Tincalayu deposit with its analogue at Kramer (USA), the main difference between them lies in the substrate below the borate zone. At Tincalayu, this is constituted by a body of rock salt while at Kramer it is a basalt flow. This latter evidence shows that there are basalt flows synchronous with the borax deposit at Tincalayu. However, it is not known how the form of the Tincalayu paleosalar evolved into that existent at the time of deposition of the borate-bearing beds. It is assumed here that this would have involved a reduction in size and that at the same time a small lake of saline water formed in the interior part of the basin.

Certain characteristics of the deposit such as the massive borate beds, the shape of the deposit, and the green coloration, which indicates a strongly reduced medium, show this. The lake would have received the hot borate waters directly into its interior where cooling would cause the chemical precipitation of borax, which was then gradually covered by new borate beds and ash. Further evidence for this assumption is found in the subsidence of the lake bed which led to the formation of the substantial thickness of mineral found in the deposit. There were also inflows of meteoric and subterranean waters charged with other elements. Gypsum with some ulexite was deposited along the eastern border of the lake, probably due to a variation in solubility. Because of a lack of drill holes in the borax-gypsum transition zone it is not possible to determine whether this is a facies change within the same body or if there existed a pair of parallel lakes, one of which deposited borax and the other gypsum.

Excellent examples of extinct thermal springs at numerous borate salars of the central Andes that feed directly to the central part of their depressions may be found. Among them, the present day case of the Laguna Salinas (Peru) allows us to extrapolate this situation back in time to explain the Tincalayu deposits. Nevertheless certain questions deserve careful treatment within the framework of the present argument. All the present day borax deposits known in the Puna are composed of euhedral crystals of various sizes growing within a muddy matrix. Thus, for example, Turi Lari exhibits a deposit of perfectly euhedral borax crystals no more than 2 cm long included in a green plastic clayey matrix. An almost identical example from the Miocene is provided by the Loma Blanca borax deposit.

Within the Cauchari salar, large borax crystals reaching a maximum size of up to 30 cm appear at the Inundada mine. Borax beds of this type have not been previously reported. A similar scheme, though less deformed than

Mineral	Structural formula	B <sub>2</sub> O <sub>3</sub> content (wt %)
<b>Boric Acid</b>		
Sassolite	B(OH) <sub>3</sub>	56.4
<b>Borates</b>		
Borax	Na <sub>2</sub> [B <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub> ]·8H <sub>2</sub> O	36.5
Tincalconite	Na <sub>2</sub> [B <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub> ]·3H <sub>2</sub> O	47.8
Kernite	Na <sub>2</sub> [B <sub>4</sub> O <sub>6</sub> (OH) <sub>2</sub> ]·3H <sub>2</sub> O	51.0
Ulexite	NaCa[B <sub>5</sub> O <sub>6</sub> (OH) <sub>6</sub> ]·5H <sub>2</sub> O	43.0
Probertite	NaCa[B <sub>5</sub> O <sub>7</sub> (OH) <sub>4</sub> ]·3H <sub>2</sub> O	49.6
Priceite	Ca <sub>4</sub> B <sub>10</sub> O <sub>19</sub> ·7H <sub>2</sub> O (?)	49.8
Inyoite	Ca[B <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> ]·4H <sub>2</sub> O	37.6
Meyerhofferite	Ca[B <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> ]·H <sub>2</sub> O	46.7
Colemanite	Ca[B <sub>3</sub> O <sub>4</sub> (OH) <sub>3</sub> ]·H <sub>2</sub> O	50.8
Hydroboracite	CaMg[B <sub>3</sub> O <sub>4</sub> (OH) <sub>3</sub> ] <sub>2</sub> ·3H <sub>2</sub> O	50.5
Inderborite	CaMg[B <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> ] <sub>2</sub> ·6H <sub>2</sub> O	41.5
Kurnakovite	Mg[B <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> ]·5H <sub>2</sub> O	37.3
Inderite	Mg[B <sub>3</sub> O <sub>3</sub> (OH) <sub>5</sub> ]·5H <sub>2</sub> O	37.3
Szabelyite	Mg <sub>2</sub> (OH)[B <sub>2</sub> O <sub>4</sub> (OH)]	41.4
Pinnoite	Mg[B <sub>2</sub> O(OH) <sub>6</sub> ]	42.5
Kaliborite	HKMg <sub>2</sub> [B <sub>6</sub> O <sub>8</sub> (OH) <sub>5</sub> ] <sub>2</sub> ·4H <sub>2</sub> O	58.3
Suanite	Mg <sub>2</sub> [B <sub>2</sub> O <sub>5</sub> ]	46.3
Kotoite	Mg <sub>3</sub> [BO <sub>3</sub> ] <sub>2</sub>	36.5
Tunellite	Sr[B <sub>6</sub> O <sub>9</sub> (OH) <sub>2</sub> ]·3H <sub>2</sub> O	52.9
Veatchite	Sr <sub>2</sub> [B <sub>5</sub> O <sub>8</sub> (OH) <sub>2</sub> ]·B(OH) <sub>3</sub> ·H <sub>2</sub> O	58.6
Vonsenite	(Fe <sup>2+</sup> , Mg) <sub>2</sub> Fe <sup>3+</sup> O <sub>2</sub> [BO <sub>3</sub> ]	13.5
Ludwigite	(Mg, Fe <sup>2+</sup> ) <sub>2</sub> Fe <sup>3+</sup> O <sub>2</sub> [BO <sub>3</sub> ]	17.8
<b>Borates with halogens</b>		
Boracite	Mg <sub>3</sub> Cl[B <sub>7</sub> O <sub>13</sub> ]	62.2
Fluoborite	Mg <sub>3</sub> (F,OH) <sub>3</sub> [BO <sub>3</sub> ]	18.7
<b>Borates with arsenate or phosphate</b>		
Lüneburgite	Mg <sub>3</sub> [PO <sub>4</sub> ] <sub>2</sub> [B <sub>2</sub> O(OH) <sub>4</sub> ]·6H <sub>2</sub> O	14.6
Teruggite	Ca <sub>4</sub> Mg[AsB <sub>6</sub> O <sub>11</sub> (OH) <sub>6</sub> ] <sub>2</sub> ·14H <sub>2</sub> O	33.8
Cahnite	Ca <sub>2</sub> [AsO <sub>4</sub> ][B(OH) <sub>4</sub> ]	11.7
<b>Silicoborates</b>		
Howlite	Ca <sub>2</sub> [B <sub>3</sub> O <sub>4</sub> (OH) <sub>2</sub> SiB <sub>2</sub> O <sub>5</sub> (OH) <sub>3</sub> ]	44.5
<b>Borosilicates</b>		
Scarlesite	Na[BSi <sub>2</sub> O <sub>5</sub> (OH) <sub>2</sub> ]	17.1
Danburite	Ca[BSiO <sub>4</sub> ] <sub>2</sub>	28.3
Datolite	Ca <sub>4</sub> [B <sub>4</sub> (SiO <sub>4</sub> ) <sub>4</sub> (OH) <sub>4</sub> ]	21.8

Table 1. Common Boron minerals (Erd, 1980; Smith and Medrano, 1996).

Tabla 1. Minerales boratíferos usuales (Erd, 1980; Smith and Medrano, 1996).

Tincalayu, is the Kramer deposit, which shows rhythmic bedding of euhedral borax crystals and green clays. Basing their analysis on the Kramer deposit, Message and Allen (1957a) interpreted Tincalayu as a salar deposit formed originally by crystals growing in a muddy matrix, which was later transformed from loose crystals to massive beds by the great pressure exerted on it during deformation. They believe this occurred where the deposit suffered maximum deformation and where metamorphic borax minerals such as kernite and ezcurrite are found. In peripheral zones, separate crystals are found in the matrix. This interpretation though can be questioned for various reasons. In the first place, the presence of discrete crystals within the matrix in areas away from the main deposit can be explained normally by the growth of crystals in a lacustrine playa. At the same time in the main deposit there are primary beds that have preserved small crystals of borax grown in matrix, with massive borax beds both within and on top of them. From our point of view, such transformations may occur but massive borax beds are not always necessarily secondary features.

The massive primary beds could be chemical deposits formed directly on the bottom of a small lake, of unknown depth, by a rain of fine crystals produced by boron supersaturating in the water as a result of the constant input from borate springs either around or within the lake. Although it has been observed that modern hot springs provide the feed for borate deposits, this assumption can be projected backward in time and applied to explain deposits formed at an earlier time. However, the assumed geological framework of the Tincalayu deposits has no equivalent in the present day. No data exist about lakes in which borax is being deposited. Yet, the Tincalayu deposit features seem to be related to a lake depositional environment.

The transition between the borax rock-body and its overlying sediments is smooth. There is a change of color from green to dark brown and compact clay beds appear which enclose abundant primary ulexite, either in thin massive beds, as rhythmic bedding, or as "*papas*". The lithology indicates a change in environment from that of a lake to a playa, similar in this respect to the modern salars. There was more calcium in the borate-bearing water causing the precipitation of ulexite rather than borax, though perhaps the thermal feed water changed to calcium borates. Before the sedimentation of the Pelitic Member at the top of the borax member had terminated, two beds of crystals were formed; one contains kurnakovite and the other contains inyoite. At the same time, the borax body buried at depth was beginning the process of

compaction and the elimination of interstitial water. Thus, some of the original structures began to be obliterated and diagenetic structures and textures appeared. The importance of the Pelitic Member lies in its role as a caprock, covering and preserving the borax deposit. The Pelitic Member was contemporary to the major compressive events at Tincalayu basin. This deformation caused the complete disappearance of a large number of primary structures. At that time, several diagenetic minerals appeared, probably derived from borax, such as kernite and ezcurrite. The compressive shortening caused slip planes and bedding separation in which ground water deposited recrystallized borax. Some of this mineral was brecciated within or between fracture planes. The ground water may have given rise to some of the mineral species that are present through the incorporation of new elements. The mineral assemblage at the Tincalayu deposit (borax, tincalconite, kernite, ulexite, ezcurrite, ameghinite, rivadavite, aristarainite, macallisterite, inderite, kurnakovite, inyoite, ginorite, strontiumginorite, probertite and searlesite) can only be explained by the operation of several combined processes including diagenesis, deformation, circulating ground water and local thermal springs.

### **Genesis of Loma Blanca borax deposit**

Loma Blanca deposit (Figs. 1,2) is a relatively simple deposit (Fig. 3) with only gentle structural deformation (Alonso et al., 1988a,b), despite being a million years older than Tincalayu (6.99 Ma). The nature of the borax at Loma Blanca does not greatly differ from Turi Lari and Lina Lari salars. Deposits are characterized by evaporite crystals grown with regular form and no preferred orientation into green tuffaceous clays. Some meters below the borax there is a thin bed of primary spherular colemanite (interfingering with primary inyoite). Three layers of primary inyoite cap the borax, which might be comparable to the inyoite level lying above the borax body at Tincalayu.

Ignimbrites and numerous levels of wavy pyroclastics (L.U. 1 and 2 on the columnar section, "lower pyroclastic section" of Alonso, 1986) accumulated in a shallow basin within an area of intense, explosive volcanism. Afterwards, deposition of claystones and tuffs in a low energy environment occurred. These volcanoclastics were derived from the weathering of the regional ignimbrites. During this period of absence of explosive volcanism, hot springs formed and discharged into the basin. These hot waters originally contained calcium borate and formed the first level of colemanite. The water chemistry changed until

## TERTIARY BORATE DEPOSITS

- A: Tincalayu
- B: Sijes
- C: Loma Blanca

## PLAYA-LAKE DEPOSITS

1. Hombre Muerto
2. Diablillos
3. Ratones
4. Centenario
5. Pozuelos
6. Pastos Grandes
7. Acazoque
8. Rincón
9. Cauchari.
10. Salinas Grandes
11. Guayatayoc
12. Olaroz
13. Lago Mucar
14. Xilón
15. Jama
16. Celti
17. Turi Lauri
18. Vilama
19. Lina Lari

## GEYSER AND HOT SPRING DEPOSITS

- a. Coyahuaima
- b. Cañuelas
- c. Volcancito
- d. San Marcos
- e. Daniel
- f. Arituzar
- g. Ojo de agua
- h. El Toro
- i. Lari
- j. Los Bayos
- k. Tropapete
- l. Adriana
- m. Antuco
- n. Socacastro
- o. Blanca Lila
- p. Oire

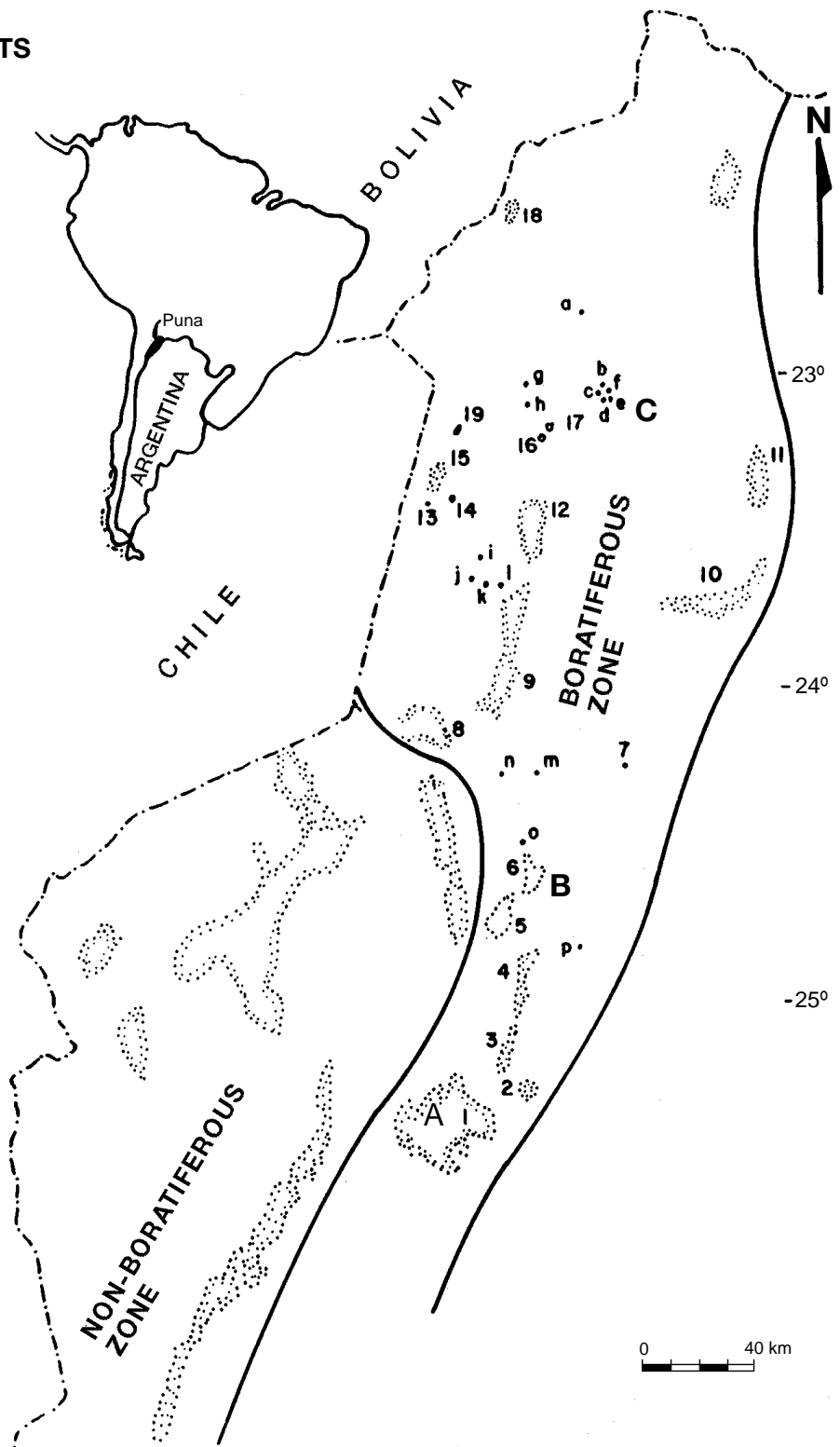


Figure 2. Location of different types of Borate deposits in the Argentine Puna.

Figura 2. Localización de los diferentes tipos de depósitos boratíferos en la Puna argentina.



the precipitation of sodium borate and the emplacement of borax deposits.

The relationship with hot springs is suggested not only by boron but also by the presence of other ions such as arsenic and antimony. The last two elements form an uncommon "geochemical pair" having anomalous values usually found at several borate paleo-hot-springs analyzed in the Puna. Inoyite evaporite crystals were developed at a later date within a muddy environment. Afterwards, only travertines contaminated with terrigenous material were deposited and this constituted the top of the "pelitic-borate section". This was overlain by pyroclastics as a result of the reactivation of explosive volcanism, culminating in the thick ignimbrites of the Coranzuli and Coyahuaima calderas.

Tectonic movements since the deposition of the Sijes Formation have produced only gentle warping and fracturing, tilting the beds towards the east. The borax body was preserved and fossilized by the enclosing plastic, impermeable clay levels. Nevertheless erosion has exposed some of the mineralization to weathering. Due to its instability, the borax was rapidly altered and gave way to an ulexite crust with minor amounts of teruggite (Aristarain and Hurlbut, 1960). Borax was only preserved below the phreatic zone, remaining unknown and unappreciated by the early miners. In the zone of capillary action and aeration, borax transforms slowly into ulexite, the latter forming as white needles within the borax crystals until the crystals have completely regrown into pseudomorphs. Inoyite also alters to ulexite, albeit to a lesser extent. The colemanite remains in its original state. The results of this study show that the Loma Blanca deposit provides an excellent control on the mechanism of borate genesis.

Despite being older than the other Tertiary deposits, Loma Blanca has been preserved by: a) a shallow basin of deposition (less than 500 meters of accumulated material), b) rapid pre- and post-borate sedimentation, derived from waves of pyroclastic debris, and c) gentle see-sawing and warping of the enclosing sediments. The above factors allowed the borate deposit to form during a quiescent period between two explosive volcanic events, under shallow overburden and it has been relatively unaffected by deformation. As a result, the borates, especially borax and inoyite, seem to have preserved their original primary features. The presence of colemanite supports a previous hypothesis concerning the generation of borates generation at Sijes Formation located in the Pastos Grandes salar. This material, at least in its spherulitic form, is primary and demonstrates that the Miocene was a unique pe-

riod of borate generation, producing for instance hydroboracite, which is no longer being formed.

### **Genesis of Monte Amarillo hydroboracite deposit**

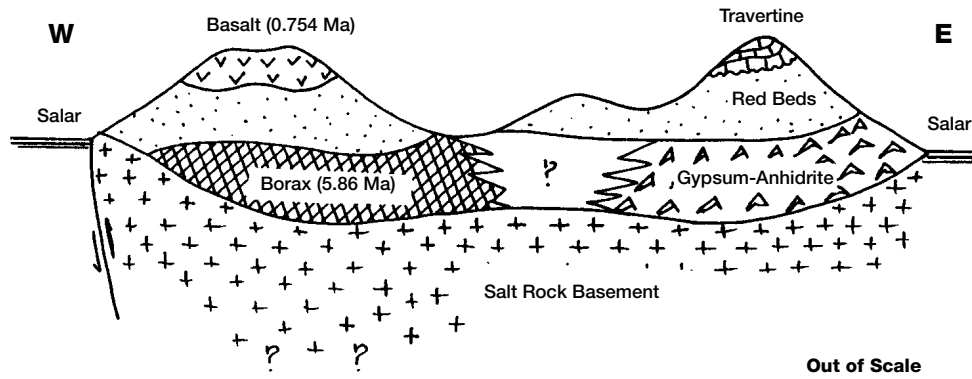
Few genetic studies have been conducted on borates and most of these deal with borax, which is the principal mineral of the largest mining deposits. There is no comparable information on hydroboracite, due in large part to the lack of major deposits in other parts of the world. The deposits in the Sijes Formation (Pastos Grandes basin, Fig. 1) have been little studied. There is sufficient evidence to indicate an origin for the borates in an arid climate with active volcanism, in closed continental basins with permanent shallow lakes or salars, during Monte Amarillo time, i.e., early sedimentation of the Sijes Formation. (Fig. 3). Evidence includes the evaporite/non-evaporite pairs, tuffs, bird tracks, rain drop marks, and desiccation cracks. An analysis of the relations of the lateral faces shows the approximate dimensions of the different superposed lake levels, which formed bodies of evaporation extending 2 to 3 kilometers N-S.

The horizontal extension cannot be completely reconstructed as the beds have been eroded to the west and buried to the east. However, from previous data it is possible to partially reconstruct the Monte Amarillo paleosalar. If we analyze the lithofacies present, then between the tuff, gypsum/anhydrite, and sediment beds the interfingering hydroboracite mineralization seems to be a syndepositional bedding. This disposition is anomalous respect to modern salars where no primary hydroboracite is known to occur. An exception might be the Chilean nitrate salars where hydroboracite has been mentioned as occurring in amounts qualifying it as a mineralogical curiosity (Chong, 1984).

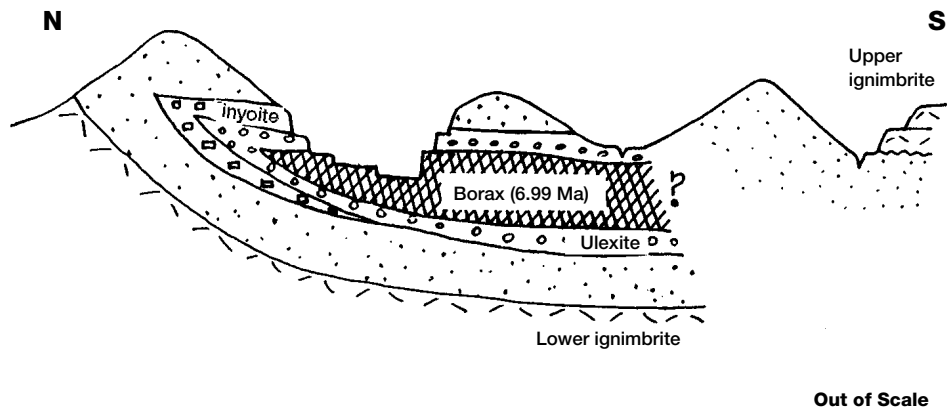
Hydroboracite has been found worldwide in marine contexts both as an apparent primary mineral (Stassfurt, Germany) and as a secondary weathering product of other borates in the caprock of a salt dome (Inder, USSR, Barker and Lefond, 1985).

At the present salars, the absence of hydroboracite deposits is noticeable, supporting the hypothesis that the mineral is not of primary origin. This consideration implies that the hydroboracite beds in the Sijes Formation were formed by the postdepositional transformation of pre-existing borates. Accepting this idea, several different circumstances of formation might be considered. The hydroboracite might have originated as a highly hydrated calcium borate that lost water on burial and gained mag-

## TINCALAYU MINE



## LOMA BLANCA MINE



## PASTOS GRANDES BASIN

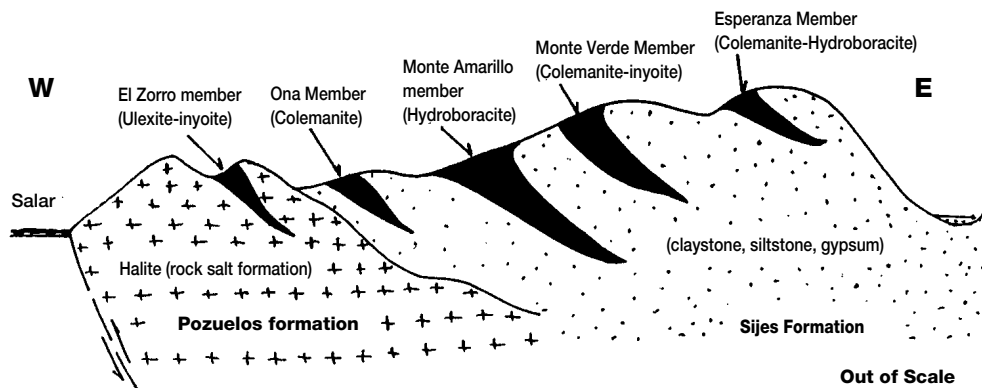


Figure 3. Borate facies in the main Tertiary borate deposits. Idealized diagrams (not to scale).

Figura 3. Facies de boratos en los principales depósitos boratíferos terciarios. Esquemas conceptuales sin escala.

nesium ions from its medium. It may also have formed as a calcium-magnesium borate in a high state of hydration that only required a loss of water to convert to hydroboracite. A phenomenon such as this, though without the addition of ions, has been suggested for the formation of colemanite (Foshag, 1921; Kistler and Smith, 1983; Helvacı, 1984a). However, if hydroboracite is examined, the classic empty spaces found within colemanite are not observed. Taking into consideration the different forms in which hydroboracite occurs, we have to accept that in certain cases the mineral is indeed secondary, for instance the fractures within massive beds of hydroboracite that have been filled with the same mineral. The hydroboracite has evidently dissolved and recrystallized within the fissures as segregation veins. It is noteworthy, that in the few places where hydroboracite veins have been found, they occur only within hydroboracite beds. Nowhere do they penetrate into the enclosing rock material. In some locations the hydroboracite impregnates pyroclastic, gypsiferous, or clastic beds, replacing the original material. Only a few remnants of the original material can be found. This process may occur during early diagenesis, or be produced by strongly boron- and magnesium-rich groundwater.

The widespread intercalation of clay beds might act as impermeable barriers preventing this process. Exposed to the atmosphere for long periods of time, hydroboracite may slowly dissolve, giving ulexite as a final product. Ulexite is the most stable borate mineral under external conditions which is the reason for its widespread occurrence as a secondary mineral, both within the borate beds and in the host rocks where it is found as disseminations or as small veins.

Although hydroboracite has been previously interpreted as having a secondary origin (Muessig, 1959), hydroboracite at Monte Amarillo is considered to be primary. Six findings support this argument. First, the geometric arrangements with the host rocks are in accordance with the regional structure. Second, the lateral facies arrangements are different in lake and beach environments (Alonso, 1987). Third, the presence of alternating hydroboracite, tuff and anhydrite rhythmic bedding suggests a normal depositional sequence. Fourth, the constant presence of interclasts and paraclasts of hydroboracite demonstrate that the "hydroboracitic mud" was dried, cracked, eroded and finally transported towards the center of the sedimentary basin. The original material must have been hydroboracite, otherwise, it would be difficult to explain a complete hydroboracite replacement of the transported clasts found along the sedimentary succession.

Supporting this argument, the presence of hydroboracite clasts syngenetic breccia in a small gully at Monte Amarillo is noticeable. Fifth, syngenetic structures (wavy bedding, bird tracks, and desiccation cracks) are preserved within hydroboracite levels. Sixth, continuous lateral facies from hydroboracite to gypsum suggest a common evaporitic origin.

An appropriate genetic model for the Sijes Formation might envisage a string of shallow lakes within a semi-arid continental environment of playas and alluvial plains marked by regional explosive volcanism and a high degree of tectonic stability. The mineralizing solutions were channeled along fracture zones, either on the sides or in the interior of the present basin during Sijes time, and emptied into the lakes forming hydroboracite and gypsum-anhydrite by supersaturating and chemical precipitation. The lakes expanded and contracted from time to time, their beds building up through continued sedimentation, and were periodically subjected to volcanic ash falls. One difficulty with the proposed genesis is the fact that the hydroboracite contains around 10% magnesium oxide, an anomaly that requires explanation. Magnesium is a common element in marine environments, where it sometimes forms minerals of economic value (among them magnesium borates, such as in Stassfurt, Germany), but generally occurs in lower proportions in continental environments.

Analytical studies conducted on stream waters, brines of salars, and modern hot springs have shown that the magnesium values are too low to allow for the formation of magnesium minerals. The same problem occurs when the magnesium is consumed, extracted from the clays by the "borate liquor". If the clays were capable of releasing trapped cations, this would leave unexplained the presence of non-magnesium-bearing borates at other stratigraphic levels with identical properties. Therefore, here we postulate that the magnesium was associated with the boron, derived in its turn from the boron-magnesian thermal waters that were characteristic of a certain stage in the volcanic, tectonic, and geothermal evolution of the region. Thus the hot mineralized waters moved through the interrelated fracture system mixing with meteoric water and with any additions from active magmatic chambers, venting on the surface along the length of the zone and feeding minerals to the local closed hydrological system. This is supported by the discovery of geysers and extinct boron-magnesian thermal springs in Socacastro Canyon (the Quevar transverse volcanic chain) immediately to the north of the present day Pastos Grandes depression (Alonso, 1986; Ruiz et al., 1994). A chemical analysis of

the evaporitic material present showed 18.72% magnesium. Mineralogical analyses proved the presence of the borate mineral pinnoite [ $\text{Mg}(\text{BO}_2)_2 \cdot 3\text{H}_2\text{O}$ ].

It would be safe to assume, therefore, that thermal springs of this type could have been active during the time of deposition of the Monte Amarillo Member. It is interesting to reflect on the curious correspondence that exists between the calcium borates (inoyite-colemanite) and calcium-magnesium borates (hydroboracite) on the one hand, with calcium carbonates (limestones) and calcium-magnesium carbonates (dolomites) on the other. When the geochemical environment is saturated in boron ions, the calcium and magnesium present join with the boric anhydride to form borates, hindering the formation of limestone and dolomite. Another characteristic of the Sijes Formation is the absence of beds of halite. These features suggest that the environmental conditions for the borate precipitation at Sijes Formation differ markedly from those prevailing today.

### **Genesis of Monte verde Colemanite-Inoyite deposit**

The genetic framework given for the underlying Monte Amarillo borate member is generally valid for the Monte Verde Member, but there are major differences in the dominant modes of mineralization. For instance, above the interval represented by Lithologic Units 99 to 110 (Alonso, 1986) borate mineralization begins anew at Monte Verde, although the center of deposition is displaced a few hundred meters to the south. Hydroboracite, which was the principal mineral in the underlying member, is subordinated while inoyite, which was found only in thin beds below is a major mineral in the Monte Verde Member (Fig. 3). The principal difference between the two units is the dominance of colemanite at Monte Verde whereas it was absent from Monte Amarillo. Other significant changes from the lower member are the absence of anhydrite beds and the substantial reduction in the amount of tuff in favor of sandy and silty sediments. The question of genesis revolves around colemanite. This mineral is known to form numerous deposits in Death Valley (USA) and in Anatolia (Turkey), where it is 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), as it has also been in the salars of Argentina (Buttgenbach, 1901; Catalano, 1926) and Bolivia (Avila, 1969), although in the latter two cases subsequent studies have failed to confirm its presence. This is one of the reasons why numerous au-

thors tend to favor a secondary origin for colemanite (Foshag, 1921; Muessig, 1959; Inan, et al., 1973; Kistler and Smith, 1975). Indeed the major deposits in the U.S.A. and Turkey show characteristics suggesting secondary deposition from postdepositional transformations. Nevertheless, Helvacı and Firman (1976) and Helvacı, (1977; 1978; 1984a,b) claim that at least part of the colemanite at Emet (Turkey) is of primary origin. In this study, we base our considerations regarding genesis on evidence from the field.

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: a) the colemanite beds interfinger regularly with the beds of sediments and other evaporites, maintaining contacts that are flat, sharp and laterally regular and continuous. Colemanite beds penetrating under- or overlying beds are not observed (transgressive phenomena are very common within a given colemanite bed, but not between such beds), b) the presence of massive colemanite beds interbedded with sediments or with other evaporites, all within a larger colemanite unit, and c) the presence of nodules and spherules of colemanite grown within the sediments which locally show ovoid deformation due to lithostatic pressure. Given this evidence, it would seem necessary to accept that at least some of the colemanite is of primary origin - beneath the water-sediment interface in the case of the nodules, and at the interface in the case of the crystalline massive beds.

Given the sedimentary characteristics of the Monte Verde section (large amounts of greenish colored clay, scarcity of sedimentary features such as desiccation cracks, raindrop marks, bird tracks, paraclastics, etc.), the colemanite rich-beds are interpreted as having been deposited in deeper water than the borate beds of Monte Amarillo. Similarly, the colemanite level discovered in the Loma Blanca mine some meters below the borax is considered here to be of primary origin. This supports the idea that the Miocene environment of the Puna was appropriate to the formation of certain borates such as hydroboracite and colemanite, though these are not found in recent deposits. Other colemanite ores exhibit features that are typical of a secondary origin. For instance transgressive veins and stringers, colemanite crystals within geodes and druses or colemanite spherules with hollow cores.

Nevertheless the question remains as to whether the pre-existing borate from which the colemanite formed was itself colemanite. In this case the secondary mineral

was formed by simple diagenetic recrystallization. The colemanite spherules with hollow cores suggest a dewatering process. Additional characteristics are ambiguous as to their origin. Large colemanite deposits in southwestern United States show abundant evidence of their secondary origin by transformation of pre-existing borates such as ulexite, inyoite, or meyerhofferite (Rogers, 1919). One such expression are 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 (Noble, 1923; 1926), both in the USA and in Turkey.

However, there is also evidence in both regions indicating a primary origin. The author 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 the colemanite. In some cases the colemanite has undergone little change since its original deposition, as at "Aniversary", "Lila - C", "Gerstley", and "Cerro Blanco" in Death Valley, Ca. Elsewhere, transformations can be seen which were favored in part by more intense tectonic development (Ryan District, USA). As for other major borate mineral, inyoite, although it may not be an easy genetic problem to resolve due to the large amounts involved, at least it has the advantage of having already been described as a primary mineral (Muessig, 1958b; Aristarain and Erd, 1971; Alonso, 1986).

Several alternatives might be considered for the formation of colemanite as a secondary mineral by the transformation of a pre-existing borate: a) Colemanite derived from ulexite. This occurs frequently in deposits in the USA but there is no evidence for this at Monte Verde where interstratified ulexite is notably absent and the mineral is found only as an alteration product in the surface weathering zone. Thus neither relicts nor pseudomorphic replacements of this mineral are found, although it occurs in thick primary beds in other parts of the Sijes Formation (Santa Rosa, Sorpresa, and other mines). It must also be considered that for ulexite to totally replace 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, though it is not possible to tell whether they are due to dehydration or to leaching of soluble material. There are other similar beds that are massive, compact and lack such openings. The loss of sodium does not solely involve a reduction in mass by the mineral in transfor-

mation, but also a transfer of sodium to the surrounding medium. However, there are no indications that this might have occurred. b) Colemanite derived from inyoite. This is also common in some North American and 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 colemanite 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, though it has been noted at the level of a mineralogical curiosity (Aristarain, in Rusanisky, 1985).

It is also difficult to explain the coexistence of both minerals in numerous places, some of which are within series of alternating facies changes. The genesis of the other borate present, hydroboracite was dealt with at length in the section on Monte Amarillo, where it was concluded to have been fundamentally of primary origin. In the present case there seem to be two alternatives: first, when hydroboracite forms independent beds or when it is observed in a facial relationship with inyoite, gypsum, or colemanite; second, by transformation from colemanite, which requires only the substitution of magnesium for calcium and the addition of water (Helvacı and Firman, 1976). A few small diffuse patches of hydroboracite within colemanite may have had this secondary origin. An additional factor, which aids in this analysis, is the gypsum beds. These show the stratification and structures of a normal evaporitic deposit, formed at ambient temperature and pressure in a body of water enriched in calcium sulfate. Gypsum beds are found in some localities alternatively intercalated between beds of colemanite and in others in a lateral facies relationship with borates. Lithologic Unit 118 (Alonso, 1986) is a gypsum bed between beds of colemanite and composed of gypsum rosettes within a gypsiferous clay, exactly the same example as found in present salars.

The preservation of the original features in this bed is a clear indication of the lack of any major epigenetic transformations. In line with the above discussion, the conclusion of this section is that the borate beds of the Monte Verde Member are substantially of primary origin, with only minor changes having occurred after deposition. Thus, either the geothermal systems which were active during the deposition of Monte Amarillo reactivated during Monte Verde deposition or new systems formed over a wide area which produced and carried borate-rich solutions into the nearby closed basins. The new borate

solutions can be differentiated from the preceding ones by their calcium content, indicating a significant geochemical transformation. These solutions poured into and crystallized within a perennial shallow lake. Due both to supersaturation in boric anhydride and the environmental 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 diagenetic and post-diagenetic changes consisting of dehydration and dissolution, with the conjugate formation of internal openings which developed into the classic geodes and druses (Alonso, 1992).

### Genesis of Esperanza Colemanite deposit

The position of the borate section at Esperanza (Fig. 3) indicates that the center of deposition moved towards the north relative to the underlying members. As noted above, the center of deposition shifted towards the south between the Monte Amarillo and Monte Verde members. The decenter migration provides evidence for the differential deformation of the underlying basement during deposition of the Sijes Formation. From the lithologic analysis (Alonso, 1986) it is apparent that as sedimentation of the Esperanza Member began the nearby positive areas were upraised and their accumulated detritic material was carried into the basin of sedimentation. This is shown by the conglomerates, which comprise Lithologic Units 160 to 171 which exhibit paleocurrents from the east. Following this there was a stage of reactivated explosive volcanism (L.U. 172 to 178); pumice fragments up to 3 cm across in some of the layers demonstrate the violence of this event. 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 problem of colemanite genesis has already been examined in the section on Monte Verde, so this discussion will be confined to a few points here. The characteristics of colemanite that show it to be a primary mineral, as described previously, may be best expressed in this deposit as those mineralized sediments that have been little deformed. The mineral appears either as massive beds within the brown or greenish mudstones, or as spherule growths. Some of the spherules show flattening due to the weight of the overlying sediments, becoming oval shaped with their long axis parallel to the stratification. The

spherules form either in isolation or in groups of greater or lesser density. This shows that the spherules grew from distinct centers of crystallization and that 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 cottonball ("*papas*") of ulexite in the present day salars. In this regard the author has had the opportunity to observe potatoes of colemanite in equivalent positions in edges or playa facies of the Gerstley borate deposit near Shoshone, California. Lithologic Unit 184 is a special case within this deposit, being composed principally of hydroboracite, with very scarce inyoite, and crossed by thick veins of colemanite.

This unit lies along the faulting which is parallel to the strike of the structure. A possible explanation for its unique composition and structure is that the relatively competent bed of hydroboracite was weakened along the fracture system, with fluid mobilization of the borate, which recrystallized as colemanite in the interior of the bed. Except for this possible case of secondary colemanite, in the rest of the deposit the mineral is of primary origin. The composition of the Esperanza Member again exhibits the prevalence of the calcium borate which dominated the geochemical system during the Monte Verde deposition, with a reduction in number and thickness of the mineralized layers (González Barry and Alonso, 1987).

### BORATES IN GEYSERS AND HOT SPRINGS

We refer here to those geysers and hot springs that discharge their borate-bearing waters in areas away from the salars or depressions (see location in Figure 2). These are the sources found in the mountains surrounding the saline depressions. They seem to form a distinct category within the Central Andean Borate Province of South America (Alonso and Viramonte, 1985b) and are among the most spectacular examples known in the world (Muessig, 1966). The differentiation between geyser and hot spring is made exclusively on the basis of the shape of the deposit formed at the vent - "cones" in the case of geysers and "shelves" in that of hot springs. The geysers, then, are the vents which have built their own cone-like structure composed principally of travertine and later borate material with lesser amounts of limonite, manganese oxides, halite clays, sodium carbonate, gypsum, etc. Because of their unique form they resemble volcanoes with "cones", "craters", "chimneys", "secondary vents", and "flows". The structures were built up by the intermittent violent

expulsion of gases and strongly mineralized waters. At present most of the geysers of the Puna region are either extinct or show only minor residual activity such as venting of CO<sub>2</sub> or H<sub>2</sub>S or the slow leakage of cold saline water.

There is only one present example of an active geyser field, that of the Rosario River geyser (non-borate) near the town of Coyahuaima. A single vent shoots a thin, continuous flow of hot water to a height of 1.5 meters. Within the area, other vents have a large strong flow but their openings are under water and they present a turbulent bubbling activity. There are historical records (early in this century) of activity at many geysers that are now extinct. The largest example of present-day geyser activity in the Andean region is at El Tatio thermal spring field in the Puna region of Chile. Hot water vents with relatively quiescent activity are here categorized as hot springs. The surface flows of such vents may be rapid, slow, or variable depending on the steepness of the slope. The surface structure depends substantially on the mineral content of the solutions and may consist of travertine or borate-bearing material in the shape of shelves, fans, walls, slopes, etc. At present, Antuco is the only example of a borate-bearing hot spring where ulexite is being deposited. All the rest are either extinct or show only a residual venting of gases or cold saline water. There are few references in the literature dealing with borate-bearing geysers or hot springs. Among the principal contributions are those of Ambrosetti (1901), Barnabé (1915), Catalano (1926; 1930; 1964), Ahlfeld (1948), Muessig (1966), Alonso and Gutierrez (1984), and Alonso and Viramonte (1985a; 1986). The latter works constitute a comprehensive description of both borate and non-borate geysers and hot springs in the Puna region of Argentina.

## BORATES IN SALARS

Borate salars constitute the largest Quaternary Argentine borate deposits (Fig. 2). Many of the salars of the Puna region of Argentina exhibit bedded borate within their sedimentary fill. These are principally those located along the eastern border of the southern Puna and the majority of those in the northern Puna. There are some very large salars, such as Arizaro, Pocitos, and Antofalla, that are practically devoid of borates. Ulexite is the predominant mineral and it occurs in two main forms, known as "potato" and "bar" ("*papas*" and "*barra*") (Reichert, 1907; Alonso, 1995). Potatoes are nodules grown in a sandy muddy environment which vary in size from 1-2 cm up to 20-25 cm, with most of them in the 5-10 cm

range. These nodules are very pure ulexite, with a white interior, from which derives their nickname in English, "cotton balls" (Alonso, 1995). The "bars", "benches", or "slabs" ("*barras*", "*bancos*", and "*planchas*") are blanket-like beds of hard ulexite (Alonso, 1995). Potatoes are preferred to bars due to their higher boric anhydride and lower sodium chloride content.

In some salars, borax (or "*incal*") is also found (Muessig, 1958a; Alonso, 1986; 1987), either as disseminated specks (Diablillos, Centenario) or as small deposits of economic interest (Turi Lari, Cauchari, Rincón). It occurs as euhedral to subhedral crystals, in some places transparent and in others carrying the color of its entraining gangue material (pink, green, or brown). The crystals typically have inclusions, corroded faces, and locally exhibit "sand clock" forms. The crystal size varies from a few millimeters up to 20-30 cm, like those found occasionally in the Inundada mine (Cauchari salar). Other borate minerals such as hydroboracite, colemanite, boracite, have been mentioned as occurring in the salars of the Puna but subsequent investigations have failed to confirm this (Catalano, 1926; 1964a; Buttgenbach, 1901). The borate generally lies at or near the surface of the salars and is covered by a thin saline efflorescence or a mixture of muddy clay and salts. The borate-bearing beds vary from a few centimeters in thickness up to 2 meters (Cauchari salar). The substrate underlying these beds is quite variable, locally consisting of terrigenous material, evaporites, travertine (Igarzábal, 1979; 1984; Igarzábal and Poppi, 1980). In numerous places the water table is exposed, coincidentally with a bed of black, fetid clay of high organic content.

The lack of deep drill holes in the salars precludes an understanding of their borate content at depth. The areal distribution of the borates is irregular and is related to the location of the hot springs from which they are derived. In many places the remains of ancient hot spring deposits can still be seen (Diablillos, Ratones, Centenario, Cauchari), while elsewhere they have been destroyed by erosion or buried under subsequent sedimentation. The genesis of borates in the salars is directly related to the supply of hot borate-bearing water from vents at the margins and/or interior of the depressions (Alonso and Gutiérrez, 1984; Alonso, 1988). These waters rose via the fracture planes that structurally control the depressions during periods of relaxation, or within extensional sections, in the generally compressive regional tectonics. Most of the literature published on the borates of the Puna refers to the borates in the salars. This constitutes a large bibliography, both published and unpublished. Among the

principal contributions are Brackebusch (1893), Ambrosetti (1900), Buttgenbach (1901), Reichert (1907), Barnabé (1915), Catalano (1926; 1927; 1964a,b,c,d), Muessig (1966), Aristarain et al. (1977), Alonso and Gutiérrez (1984), Alonso (1986; 1987; 1988; 1991), Alonso and Viramonte (1990).

## CONSIDERATIONS REGARDING GENESIS

As has been demonstrated for the previously described borate deposits, it is possible on the basis of field observations to begin to understand their genesis. An analysis of the concepts put forth by various authors contributes to a more solid basis to this understanding (Aristarain and Hurlbut, 1972; Alonso and Viramonte, 1993; Kistler and Helvacı, 1994; Smith and Medrano, 1996; Garrett, 1998).

The Argentine Puna is an excellent laboratory for the study of phenomena which work together in the formation of borate deposits (Fig. 1). Thus the metallogenetic heritage from the Miocene onward is related to the preservation of a geologic framework with interrelated parameters, such as closed basins, active volcanism, hot springs and an arid climate.

Analysis of the Puna Holocene borate occurrences reveals two main types of deposit; first, the borate beds which are an integral part of the fill material of the present depressions (salars, salt pans, and playa lakes) and second, the borate beds deposited directly from geysers or hot springs outside of the depressions. In the first case, the borates in the depressions are linked to the output of the hot spring borate-bearing waters, which ascended along the fracture planes that bound the sedimentary depressions. The mechanism by which the water rose is controlled by local extensional phenomena within a regionally compressive tectonic framework. In some cases this mechanism is favored by the set of tensions produced between fractures of Andean orientation (approximately N-S) and the transverse fracture system (approximately WNW-ESE) which controls the basement of the Puna. The borate spring at Oire is evidence of this: It comes to the surface through a fracture system in the crystalline basement as described above. In other cases the aqueous fluids took advantage of listric fracture planes associated with overriding plates, or rose directly along extensional relaxation faults.

It is noticeable that in most cases the fractures, through which the hot borate-bearing waters rose, were aligned

along the flanks of the salars. Thus, for example the fracture that was a borate conduit for the Ratones and Centenario salars lay along their east sides while that of the Cauchari salar was on the west side. Both fractures had hot springs along them, which deposited mainly ulexite, showing similar zonation. Nevertheless, they differ substantially in that the fracture of the Cauchari salar lies on its active piedmont side, in the sandy zone of the alluvial cones, while the Ratones-Centenario fracture is on the morphologically passive side where the sedimentation is pelitic-evaporitic. Therefore the borates along the east side of the Cauchari salar are incorporated in a sandy matrix and those of Ratones-Centenario grow in pelitic-saline levels. This difference has important economic implications.

The present author holds that thermal waters are the direct and main source of the borate, as was suggested in the earliest studies (Ambrosetti, 1901) and by successive authors (Catalano, 1927; Muessig, 1966; Aristarain and Hurlbut, 1972; Alonso and Gutiérrez, 1984; Alonso, 1986). Leaching of the surrounding rocks as a contributing factor is valid only on a very small scale as in the case of the Sijes Formation of the Pastos Grandes salar and of the Tincalayu deposit on the peninsula of the same name. Evidence against leaching in other salars includes: a) absence of borate occurrences within the geological setting (Diablillos salar), b) salars with identical geological setting, a short distance apart, one containing borates and the other not (Rincón and Pocitos salars), c) absence of a developed drainage network, d) concentration of borate in a context opposite to the regional slope (Cauchari) and e) boron structural traps (Ratones salar).

This last point may be analyzed to serve as an example. In the Ratones salar there is an island-mountain with an embayment on its east flank. The regional slope inclines from west to east. If leaching played an important role, any borate deposited would be found on the western side of the island-mountain. However the borate is within the eastern embayment, where the obliterated remains of the hot spring that deposited the mineral are also found. The example of borate beds deposited opposite the regional slope and the embaying of borate in the Diablillos salar provide evidence (for those salars in this situation) against their origin by concentration and later deposition from an ancient evaporating lake.

Another point to keep in mind is that this also controls the distribution of borate once the waters have come to the surface. The mineralized waters arrive hot, and with a high gas content. On coming into contact with the atmosphere they experience rapid cooling and loss of gases. The boron



acid reacts with the cations present to produce borates. When the boron-rich water flows out onto a relatively dry site, a massive deposit is formed near the vent. In contrast, if they flow out into a shallow body of water, either perennial or ephemeral, the borate-bearing solution is diluted in the water. There might then occur either of two situations depending on the size and nature of the body of water. If it is an ephemeral body of water, a thin crust of mineral will form on its floor on drying - the larger the body of water, the thinner the crust. If a permanent body of water exists, chemical precipitation could begin when the water reaches supersaturation, and a deposit would be formed on the bottom. Like ephemeral lakes, the thickness of the deposit is an inverse function of water volume. In some salars such as Hombre Muerto and Pozuelos, thin beds of ulexite are found which were produced by dilution of hot spring waters in the lake. The same situation applies to the rhythmic bedding containing ulexite in the Pleistocene terraces of the Pastos Grandes salar.

The Surire salar (Chile) is an example of the formation of borate in a perennial lake, within a salar, with active hot springs. Ulexite is being formed by supersaturation of the lake waters (Chong, G., pers. comm.).

The other occurrence of Quaternary borates is linked with thermal springs in the areas surrounding the salars. The numerous examples which occur in the Argentine Puna, and which seem to be unique in the central Andes region (Ahlfeld, 1948), may be the most spectacular examples in the world (Muessig, 1966). Several examples exhibit borates deposited directly on the travertine structure or in the area immediately around it. The Antuco borate area is an interesting example of borate deposition from thermal waters evaporating on the alluvial plain at the mouth of the ravine, in addition to hot borate springs related with "in situ" deposits. This generates a deposit of ulexite, though within the gravels. This has been an object of great interest since the time when the older deposits began to be explored in a search for low energy facies. The presence of this ulexite in fluvial facies might also explain certain interesting colemanite deposits in the United States, which occur partly in conglomerates (Gerstley, USA). Another fact to note is that no actual examples have been found of borate geysers or springs in Tertiary rocks. Many remnants of thermal travertine structures occur in the upper Tertiary but with no associated borate deposits (Farallon Catal Island, Cerros de Cauchari). Perhaps the only example worth mentioning would be the travertine of the Sijes Formation, located some 200 meters north of the encampment of the same name, which grades laterally into an ulexite facies.

Geysers and hot springs normally occur in areas of structural weakness where the Tertiary rock cover is minimal. With the exception of Antuco whose flows surface in volcanic rock, the rest of those in the Argentine Puna either take advantage of fault zones (Toro, Oire, Ojo de Agua) and/or the unconformity between the Ordovician rocks and the pre-Miocene Tertiary rocks (San Marcos, Volcancitos, Blanca Lila). Neither group of rocks [Ordovician and pre-Miocene Tertiary] contains borate deposits because the boron was largely derived from endogenous gases, which were mobilized by volcanic magma and injected into the local hydrologic circuits. This also includes the thermal waters, which found their way upward through the Tertiary rocks of the Tincalayu borate deposit during the Pleistocene, but did not form a borate deposit on the surface. This evidence should be kept in mind when prospecting for hidden borate masses, since the existence of a borate spring at the surface does not necessarily indicate the presence of underlying mineralization.

At the present time the majority of borate geysers and springs are either dead or give off only a small amount of carbon dioxide and/or hydrogen sulfide gas along with cold ferruginous brines. The only active borate spring is Antuco. The relationship that exists between water temperature and boron content demonstrates that the most enriched waters are only lukewarm (Argañaraz and Nadir, 1973). Barker and Barker (1985) in complete agreement with the latter obtained the data given by these two authors by analysing 34 hot springs in the southwestern United States.

Analysis of the structure of a borate geyser or spring shows that in every case they are built on travertine cones or platforms, respectively. Only one borate geyser (Adriana) has a structure built up of limonitic mud and thin beds of ulexite. The presence of an initial travertine structure indicates that the source water did not reach a high enough temperature to deposit silica. As the temperature declined to lukewarm, the deposition of borate began. From then on, there was a system of travertine "flows" overlain by a similar structure of borates. In a few cases (San Marcos, Arituzar) there is an interlayering of borate and travertine, suggesting temperature fluctuations.

According to chemical analyses (Alonso, unpublished) of travertine and borates of several geysers and springs (San Marcos, Arituzar, Volcancito and Socacastro) anomalies occur in the content of antimony and arsenic. Another type of Quaternary borate deposit seems to

Mineral Name \ Epoch	Borax (Na)	Kernite (Na)	Ulexite (Ca-Na)	Colemanite (Ca)	Hydroboracite (Ca-Mg)	Inyoite (Ca)	Inderite (Mg)	Pinnoite (Mg)
Holocene	█		█			█	█	█
Pleistocene			█			█		
Pliocene			█	█	█	█		
Miocene	█	█	█	█	█	█	█	

Figure 4. Boron minerals and period of generation.

Figura 4. Minerales de Boro y época de formación.

be clearly related by mechanical concentration of colemanite and hydroboracite, produced by the downstream transport and deposition in alluvial cones, from weathering and erosion of mineralized stratiform blankets.

The category of exogenous deposits treated as Quaternary may be partially and tentatively classified as buried exogenous deposits in Mio-Pliocene beds. As was seen in discussing the deposits and occurrences of Tincalayu, Pastos Grandes, and Loma Blanca, a special geologic situation was found to exist in each case, though all of them form part of the same regional framework. The presence after the Quiche Phase of active bimodal volcanism, hydrological closed basins, and a relatively hot, dry climate created the conditions necessary for the generation of boron enrichments thousands of times greater than its "clarke" (Barker and Barker, 1985).

Analysis of the facies arrangement suggests that the Puna borate formations are very simple. Ancient saline lakes, perennial or ephemeral, which were in some places isolated as at Tincalayu and Loma Blanca, can be recognized. Other interconnected deposits can be identified at the Sijes District. In all the related cases, the relationship

with volcanism is clear, as much for the presence of synchronous volcanic structures in the regional context as for volcanic ash beds that accompany, and sometimes cover the borate deposits.

Although boron-rich hot springs are universally accepted as the origin of borate concentrations (Aristarain and Hurlbut, 1972; Barker and Lefond, 1985), the relationship between hot springs and buried deposits is not always clear. In some places a facies change is encountered between the borate beds and the thermal travertine deposits (Southern parts of the Santa Rosa mine). In other cases there is either no travertine deposit or it is hidden and has not been detected. Nevertheless, the presence of similar concentrations of arsenic, antimony, and lithium both in modern hot springs and in buried deposits favors a common origin model (Viramonte et al., 1984).

The mechanisms of deposition of the borates are the same as those that control the other evaporites in the Puna, that is, chemical-evaporitic precipitation from a supersaturated solution within a shallow, relatively small body of water. The borate may grow either at the water-

sediment interface or within the lake muds by the growth of evaporite crystals from nucleation centers within a boron-rich medium. The thickness and quality of the borate deposit formed depends on various factors, among them the amount of boron in the hot springs as well as the size, variability, duration, degree of subsidence, and rate of sedimentation of the lakes. In some deposits (Sijes) it is possible to distinguish an evaporitic zonation between the gypsum and the borates. The gypsum is found around the periphery of the playas or lake bodies while the borate is displaced toward the center. The theoretical zonation by solubilities seems only partially to control the situation. At Tincalayu there is a salt-gypsum-borate interrelationship and carbonates are absent. At Loma Blanca there is more borate and carbonates, but salt and gypsum are absent. At Sijes the facies relations are between gypsum and borates, carbonates being restricted and salt absent. Salt, however, is predominant in the Pozuelos Formation underlying the borate succession.

The evolution of a borate-depositing event is controlled by two parameters, which may act independently or in conjunction. These are namely the life span of the lake body and the duration of the geothermal system. Thus it may happen that the lake dries up and the springs deposit boron in a dry environment, building nearby deposits. Or the lake may endure but due to a lack of minerals from the springs it deposits only clay beds. It follows then that the maximum development of borate deposits comes about when relatively small, shallow desert lakes and their conjugate geothermal springs have concurrent lifetimes.

#### DEPOSITIONAL ENVIRONMENT OF BORATE OCCURRENCE

A careful analysis of both the current and older exogenous borate occurrences in the Argentine Puna quickly reveals their differences. Only two species of borates are well represented in both Tertiary and Quaternary deposits: ulexite and borax. There are no major differences between the ulexite of Tincalayu and of some parts of Sijes on the one hand and that of present day salars on the other. Neither is the borax of Loma Blanca different from that of the Turi Lari and Lina Lari salars. Inyoite, however, which occurs in appreciable amounts in the three principal Tertiary deposits (Tincalayu, Sijes, and Loma Blanca) and also in the Pleistocene terraces of the Pastos Grandes salar is practically absent in modern salars (Fig. 4). To date only two small occurrences are known in South America, one in

Laguna Salinas, Peru (Muessig, 1958b) and the other in a tiny lake in the Puna near Coyambuyo volcano (Alonso, 1986; Helvaci and Alonso, 1994). Inderite occurs in Tincalayu and the Socacastro geyser (Fig. 4). Pinnoite occurs in the Socacastro geyser (Fig. 4).

All of the currently depositing borax occurrences in the Puna are evaporite crystals growing in red mud (Cauchari, Rincón, Centenario areas) or in green mud (Turi Lari, Lina Lari areas) in salars or small ephemeral lakes (Fig. 5). The Tincalayu mine is different, having a body of massive borax at its center and evaporite crystals toward its periphery. This would indicate a permanent lake body in which euhedral crystals grew in the playas and with a rain of fine crystals forming chemical beds on the bottom. Appreciable quantities of kernite also occur at Tincalayu, a mineral which has only been found in Tertiary rocks. This species has been interpreted as a metamorphic transformation of borax. Nevertheless it is interesting to note that in a drill hole which cut the borax and the underlying rock salt basement, borax and kernite were observed to coexist as isolated and independent inclusions in various sections of the cuttings (Alonso and Robertson, 1991;1992).

Likewise, other mineral species such as hydroboracite and colemanite are restricted to Tertiary environments. Their absence in modern salars has caused many authors (Gale, 1913; Foshag, 1921; Muessig, 1959; Kistler and Smith, 1975; 1983) to believe that these were secondary borate minerals produced by postgenetic phenomena. This point of view is strengthened by laboratory experiments carried out by Christ, et al. (1967), Inan, et al. (1973), and reviews in Grew and Anovitz, eds. (1996) and Garrett, (1998). Nevertheless, the weight of direct field evidence inclines toward a primary origin with minor, subsequent transformations.

Thus, for example, Loma Blanca consists of largely intact beds (that is, with little or no deformation) of tincal, ulexite, and inyoite that are identical in nature to those which occur in modern salars. The minimal deformation and thinness of the cover overlying the borate (because the basin of deposition underwent little subsidence) give the impression that the borate beds are primary. Between these beds there lies a 20-cm thick layer of colemanite. Within this context there is no evidence to suggest that this mineral might be secondary. The same situation occurs with the beds of colemanite, hydroboracite, and inyoite in the type section of the Sijes Formation. If we analyze any of the borate levels, for example those composed of alternating inyoite-hydroboracite-tuff, and

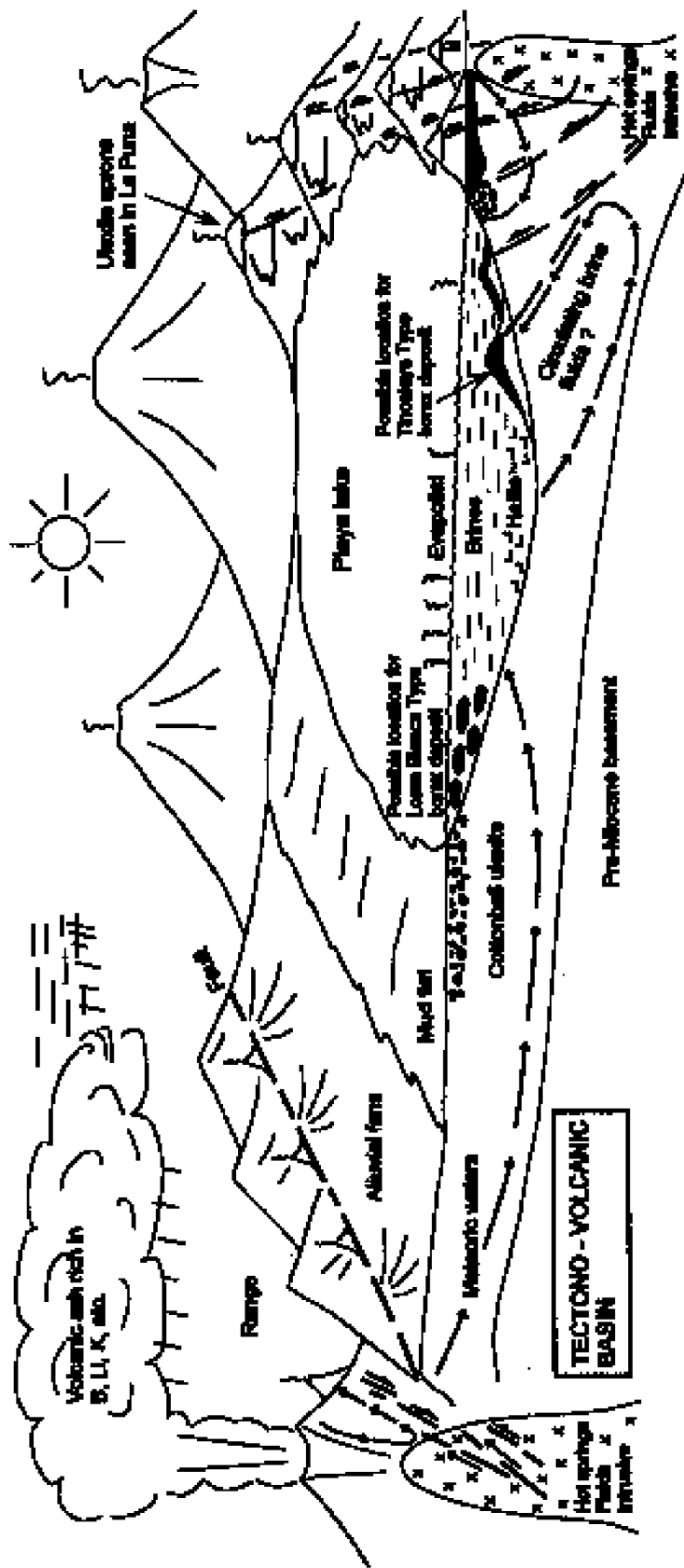


Figure 5. Cartoon of generalized model for the origin of the Tertiary and Quaternary Borate deposits in the volcano-tectonic basins of La Puna high plateau, Central Andes.  
 Figura 5. Esquema de modelo conceptual idealizado del origen de los depósitos terciarios y cuaternarios de boratos, en las cuencas tectono-volcánicas de la alta meseta de la Puna, Andes Centrales.

accept that the inyoite is primary, there is then no reason to believe the hydroboracite to be secondary. The same thing occurs in the case of colemanite beds. To this we can add the rest of the line of arguments given in Alonso (1986) as well as recent unpublished petrographic analysis, and incorporate such field observations as the absence of brecciation and/or deformation of the enclosing strata. This would indicate that there was no substantial volumetric change and an absence of ion mobility and cation replacement during lithification that would be registered in the surrounding rocks.

From this analysis it may be assessed that the great majority of the borates of the Puna are of primary origin, with little post genetic modification. The question then becomes, why are certain borate minerals not being formed presently? The response might be that they in fact do occur. From this derives a philosophical disquisition tied to the Principle of Uniformitarianism. James Hutton, one of the fathers of geology, developed the concept of uniformitarianism to assert that the geologic processes that operated in the past are the same as those at work today. This we now know to be only partially true, as the study of geology itself has demonstrated to us. As Harrington (1973) has pointed out, "...Uniformitarianism is not a scientific principle but a supposition, a presumption, a postulate that is not necessarily correct, on which has been constructed the body of belief of geology, the latter being no more valid than the postulate on which it is founded." The case of the borates shows that approximately the same geologic parameters, which existed during the Miocene, hold true today. Nevertheless, the results in some cases are substantially different. The fact that borate minerals, which formed in the past, are not now forming may be linked to factors that have escaped our notice. It is known, for example, that volcanism reached its greatest intensity during the Miocene and decreased slowly after that and that at the present time there are abundant sodium sulfate beds forming, and on a smaller scale sodium carbonates, which have not been found in older deposits. It should also be pointed out in this regard that there are no continental exogenous borate deposits known in the world older than Miocene.

Finally, chemical experimental data have helped substantially in solving geologic problems. Nevertheless, the complex results achieved in the laboratory (removed from the geologic non-temporal framework governed by infinite non-quantifiable variables) should in no way be allowed to serve as an obstacle, subordinating simpler and more elemental geologic field observations.

## CONCLUSIONS

1. All of the deposits and occurrences of exogenous borates in Argentina are restricted to the Puna Geologic Province (Turner, 1972) - specifically to the Northern Puna and the eastern border of the Southern Puna (Alonso, et al., 1984). The borate deposits of the Argentine Puna constitute the greatest known reserves in South America, as well as in the Southern Hemisphere, and the third largest in the world, after those of Turkey and the United States of America. The hydroboracite concentrations of the Sijes District form the greatest reserves of this mineral known in the world.
2. The borate-bearing section of Tincalayu mine represents a lake. In this depositional environment boron concentration progressively increases until it reaches a state of continuous precipitation within a framework of interrelated chemical-evaporitic mechanisms. The generation of the deposit was directly related to the evolution of a geothermal system linked to the interparoxysmic development of the Ratones volcano complex.
3. The largest borate deposits of the Argentine Puna occur in the Sijes District. The deposits, composed mainly of hydroboracite and colemanite, with smaller amounts of ulexite and inyoite, are located discontinuously along a 30-km-long belt oriented approximately NNE-SSW. At least 10 large deposits each 1-4 km long and smaller related occurrences are found along the length of this belt and represented a chain of small lake-salars at the time of the deposition of the Sijes Formation. A vertical analysis of the borate succession near the middle of the deposit distinguished three members, in ascending stratigraphic order: Monte Amarillo Member, Monte Verde Member, and Esperanza Member (Fig. 4). These demonstrate an evolution of the borates from hydroboracite (Monte Amarillo), to colemanite-inyoite (Monte Verde), and finally to colemanite (Esperanza). The lateral facies relations show, in many cases, a change to gypsum/anhydrite, then to clastics, or sometimes directly to clastics. The vertical and lateral development of the borate-bearing zones indicates the existence of three stages in the evolution of the lake body: 1. Initial restricted; 2. Maximum expansion; and 3. Retraction. This allows each deposit, viewed in a three dimensional scheme, to acquire the form of a biconvex lens. An internal analysis of a deposit recognizes an alternating rhythmic order formed by the pair levels of borate/non-bo-

rate, the latter represented by clastics or tuffs in beds averaging about 1/2 meter in thickness. For its part, the evolution of the deposits with time shows a progressive displacement of the lacustrine centers of deposition, which themselves are an excellent indicator of the degree of substratal mobility of the basin during the upper Miocene. The discovery of an abundance of bird tracks in the clay beds associated with the borate levels in the Sijes District constitutes a very good bathymetric indicator positively identifying a shallow water environment at the time of borate deposition. This author also identified similar fossil bird tracks in deposits in the United States, indicating a comparable bathymetric situation.

4. Loma Blanca (the fourth largest borax deposit in the world) has only recently been discovered (1982) and its potential size is still largely unknown due to a lack of drill holes. Its lithology is basically a volcanoclastic succession lying on an ignimbritic flow, with an interval of lacustrine sediments dated at 6.9my enclosing a borate section composed mainly of borax and inyoite. The areal extent of the lacustrine sediments and the presence of "Boron" type rhythmic bedding indicate excellent prospects for the development of the deposit at depth.
5. Several locations with borate geysers and/or springs, formed during the Holocene, have been recognized in the vicinity of salars. A few of them are known from the literature (Coyahuaima, Antuco, Volcancito), many others have been mentioned previously by the author of this work (Alonso and Viramonte, 1985a), and others are presented for the first time here (Ojo de Agua, Calichar, Daniel). The distinction between geysers and springs is made on the basis of a wide range of morphologic criteria. Geysers are those thermal deposits which have formed a cone-shaped structure, and springs are those which have built only a platform or shelf structure. A thermal borate locality might consist of an isolated geyser and/or hot spring (Tropapete geyser and Lari hot spring) or a group of geysers and/or hot springs (San Marcos, Blanca Lila). Thus one name might indicate a single borate vent (Oire) or a large number of vents (Antuzar, with 8 geysers and hot springs). Most of the vents are extinct or give off only gas and/or cold saline water. The only active unit is Antuco. The basement under the sources lies mainly along zones of weakness (faults and/or unconformities) between Ordovician and pre-Miocene Tertiary rocks (San Marcos, Arituzar, Blanca Lila, Socacastro), or sometimes directly above the Ordovician base-

ment (Ojo de Agua, Toro). In some cases their waters flow out onto alluvium (Tropapete, Adriana, Lari). Two unique examples are Antuco, with volcanic basement rocks, and Oire, which flows out onto granitic rocks of the Oire Formation.

6. The main borate bodies of the Quaternary are the salar deposits. A large number of the salars in the Puna have borate deposits or occurrences, principally those of the Northern Puna and the east side of the Southern Puna. The predominant mineral is ulexite, which occurs in two main varieties known by the miners as "papas" and "barra" ("potatoes" and "bars"). The potatoes are nodules grown within the muddy matrix, mainly mud-clay to mud-sand. They have a thin clastic crust and a clean, white interior. The bars consist of massive bedded ulexite. The potatoes are preferred to bars due to their higher boric anhydride and lower chloride content. The average grade of boric anhydride varies around  $28 \pm 2$  % for most of the ulexite. Impurities common in both varieties of borate are clastic material, chlorides, and sulfates. The mineral varies in thickness from thin beds to 1.5-meter benches. Another borate found in the salars is borax, or tincal. It occurs as evapocrystals grown in green or reddish clayey material. All of the borate of the salars is found in near-surface fill, either on the surface or buried up to 1.5 meters deep. It is not possible to know whether there is only one episode of borate occurrence or whether there are others at depth, due to a lack of drill holes. The few boreholes existing in the Cauchari, Rincón, and Diablillos salars have not shown the presence of deep borates. In many salars there is a distant relationship between the borate beds and the thermal springs. The borate-bearing springs are aligned over fractures located along the edge or crossing the depressions. All the borate hot springs or geysers observed at the salars are extinct.
7. A fundamental model for the formation of borate deposits established in this paper is related to three dominant factors: 1. Active volcanism (expressed by hot springs with borate-bearing water); 2. Closed basins; and 3. Arid to semiarid climate.
8. All the borate deposits of the Puna are interpreted as being directly or indirectly related to thermal springs. This relationship is unmistakable at the borate geysers and springs in the area surrounding the salars. It is also clearly expressed in some salars (Diablillos, Ratonos, Cauchari), but all evidence has been obliterated in others. In the buried and deformed Tertiary deposits

there is little direct evidence demonstrating a relationship with thermal springs. Nevertheless, there is some indirect evidence to affirm this mode of origin.

9. The thickness and grade of borate deposits is directly related to the ionic concentration of the thermal waters, and their dilution is a function of the size of the lake body to which they are transported. Thus small amounts of boron diluted in a large lake have little chance of forming an economic deposit. The opposite of this process is therefore the most appropriate.
10. Volcanism seems to be the only absolutely indispensable condition for the generation of borates in the Puna. Thus, for example, all the deposits seem to have formed following the emplacement of volcanic chains. In the red beds, which preceded the volcanism, no evidence of borates has been found. Likewise, the deposits are all invariably related to effusive material (cinders, tuffs) which would indicate their direct affiliation.
11. Closed basins containing small, shallow lakes are necessary for the formation of significant deposits. Nevertheless, one type of deposit in the Puna, those related to borate geysers and springs outside the salars, do not need this condition.
12. An arid to semiarid climate, which is the present dominant climate in the Puna, is important for the mechanism of evaporation which aids the process of supersaturation and precipitation of the mineralized solutions. In this sense it is interesting to note that in the extreme north of the Northern Puna there are neither borate deposits, nor other evaporites, in the Tertiary despite the existence of appropriate conditions. The discovery of fossil vegetable remains indicating a more humid climate for this region (Alonso, et al., 1985) may provide an explanation for the absence of such deposits.
13. Borate geysers and hot springs are at present exclusive to the Argentine Puna. They vary in their geologic framework, type of basement, structure and deposited materials. The Tincalayu and Loma Blanca borate deposits are comparable to those at Boron, California, but only those that are predominantly composed of sodium borates. The same relationship exists with Kirka in Turkey. Likewise a similar situation prevails at the Sijes District, Death Valley (USA), and Bigadic-Emet-Kestelek (Turkey). Beyond this, it is necessary to be careful in applying these conditions to prospecting because they are appropriate only within a de-

finied context. In many cases what may be valid in one region may not be significant in others.

14. The temporal distribution of borates in the Argentine Puna covers the Miocene-Holocene time period. Among the common borate minerals found, some occur in all borate-forming periods (ulexite and inyoite); others are restricted to the Mio-Pliocene (hydroboracite, colemanite), one mineral is restricted to the Miocene (Kernite), and only borax is associated with the Miocene and Holocene. At present, the fact that certain minerals are found only in the Tertiary has caused some authors to suspect that they are secondary minerals. Nevertheless, as we have discussed considered at length above, not enough evidence has been found to support this reasoning. On the contrary, the evidence so far points towards a main, primary origin for the minerals examined.
15. The temporal permanence of the borates and related evaporites from the Miocene to the Present are suggested by the conspicuous presence of similar bird tracks and plant associations. These paleogeographic characteristics are determined on the basis of a comparative analysis of modern bird tracks with those discovered in the Pliocene and Miocene rocks of the Puna region. This observation concerning an inherited environment not only constitutes another useful guide for prospecting but also permits, with some degree of certainty, the direct association of the present characteristics of borate genesis with those prevailing in the past.

#### ACKNOWLEDGMENTS

I would like to thank two anonymous referees and Mack Taylor, Don Robertson, Teresa Jordan, Guillermo Chong-Díaz, José Viramonte, Cahit Helvacı, Don Garrett, Federico Orti Cabo, Lorenzo Aristarain, Bob Kistler, Ricardo Sureda, Teresita Ruiz, Rina Eiguez, Alicia Quiroga, Mario Pepi, José Salfity, José González, Alberto Taco, César González-Barry for long term cooperation. Financial support for this work was provided by CONICET and CIUNSa (Grants 509 and 551).

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