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Boron isotope composition of geothermal fluids and borate minerals from salar deposits (central Andes/NW Argentina)

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Abstract

We have measured the boron concentration and isotope composition of regionally expansive borate deposits and geothermal fluids from the Cenozoic geothermal system of the Argentine Puna Plateau in the central Andes. The borate minerals borax, colemanite, hydroboracite, inderite, inyoite, kernite, teruggite, tinalconite, and ulexite span a wide range of $\delta^{11}\text{B}$ values from -29.5 to -0.3% , whereas fluids cover a range from -18.3 to 0.7% . The data from recent coexisting borate minerals and fluids allow for the calculation of the isotope composition of the ancient mineralizing fluids and thus for the constraint of the isotope composition of the source rocks sampled by the fluids. The boron isotope composition of ancient mineralizing fluids appears uniform throughout the section of precipitates at a given locality and similar to values obtained from recent thermal fluids. These findings support models that suggest uniform and stable climatic, magmatic, and tectonic conditions during the past 8 million years in this part of the central Andes. Boron in fluids is derived from different sources, depending on the drainage system and local country rocks. One significant boron source is the Paleozoic basement, which has a whole-rock isotopic composition of $\delta^{11}\text{B} = -8.9 \pm 2.2\%$ (1 SD); another important boron contribution comes from Neogene-Pleistocene ignimbrites ($\delta^{11}\text{B} = -3.8 \pm 2.8\%$, 1 SD). Cenozoic andesites and Mesozoic limestones ($\delta^{11}\text{B} \leq +8\%$) provide a potential third boron source.

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1. Introduction

The central Andes host the biggest South American borate deposits, and the Argentine Puna Plateau is one of the most important borate-producing regions of the world (Alonso and Viramonte, 1990). Boron is mainly concentrated in Cenozoic borate deposits but is also a common element in the fluids of active thermal springs and in most Andean rock units. Therefore, the Puna Plateau geothermal system offers excellent opportunities to investigate time-dependent changes in the boron isotope composition of rocks, minerals, and fluids from the Paleozoic basement to

recent deposits and thereby to understand the genesis of the borate deposits.

Previous investigations have shown the suitability of using B-isotope studies of borate minerals to recalculate the B-isotope composition of the mineralizing fluid to trace the origin of boron in geothermal systems (Swihart et al., 1986; Oi et al., 1989; Palmer and Helvacı, 1995). These studies conclude that boron isotope characteristics in borate minerals and solutions are affected by (1) the boron coordination in the crystal lattice of the mineral, (2) the boron isotope composition of the source, (3) the amount of precipitated boron-bearing minerals, and (4) the degree of isotope fractionation. The latter is mainly controlled by B speciation (tetrahedral or trigonal) of the phases, with ^{11}B concentrated in trigonal species. The degree of isotope fractionation is also controlled by the pH and temperature conditions of the mineralizing fluid (Kakihana et al., 1977; Palmer et al., 1992). Furthermore, studies of subaerial

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geothermal fields indicate that thermal waters often have $\delta^{11}\text{B}$ values similar to those of the adjacent rocks, suggesting leaching of boron from these local rocks or the local hydrologic reservoir (Musashi et al., 1988; Palmer and Sturchio, 1990; Leeman et al., 1992). Even at high temperatures, isotope fractionation between vapor and fluid does not change the $\delta^{11}\text{B}$ values of the fluid significantly. Studies of vapor/liquid systems have shown that the effect of this fractionation is less than 3‰ (Kanzaki et al., 1979; Nomura et al., 1982). Therefore, the boron isotope ratio of thermal waters can identify different source rocks in a geothermal system.

We document the B-isotope composition of Quaternary and Recent borate deposits, their associated fluids, and the dominant borate minerals from vertical profiles through the Neogene borate deposits of the Argentine Puna Plateau. In turn, we can compare borate deposits on both a regional and a temporal scale, as well as correlate ancient and modern deposits. The major aims of this study are to (1) examine the origin and geochemical evolution of regionally extensive borate deposits and thermal fluids, (2) investigate the interaction between the host rock and fluids as recorded by evaporite deposits, and (3) compare empirically deduced fractionation factors with theoretical ones.

2. Geological setting

2.1. Geological environment

Tertiary and Quaternary borate deposits of economic interest are concentrated in the Puna region of the Altiplano-Puna Plateau. This high plateau, with a base elevation of ~4 km, was formed in a compressional orogene during the late Cenozoic and is situated between the Western Cordillera with its active volcanic arc and the fold-and-thrust belt of the Eastern Cordillera (Fig. 1). It is characterized by back-arc magmatism, crustal thickness caused mainly by shortening of the Pre-Mesozoic crust, and internally drained basins filled by active nonmarine sedimentation during the Neogene (Isacks, 1988; Allmendinger et al., 1997; Lamb and Hoke, 1997).

In the Puna, internal drainage and accumulation of evaporitic strata started at approximately 15 Ma (Alonso et al., 1984; Vandervoort et al., 1995) as a response to Miocene subsidence, with the development of intramontane basins and evaporitic climatic conditions (Allmendinger et al., 1997). Deposition of borates started about 8 Ma ago and is thought to be linked to volcanic activity that generated closed drainage basins (Viramonte et al., 1984; Alonso et al., 1991). In the magmatic arc of the Altiplano-Puna region (Central Volcanic Zone), volcanic activity has been continuous since 20 Ma into the Quaternary and has produced stratovolcanic complexes and large-volume dacitic-rhyolitic ignimbrite eruptions (de Silva, 1989; Coira et al., 1993).

2.2. Neogene borate deposits

Tertiary sediments hosting evaporitic deposits are exposed across the Puna area, and additional evaporitic units are assumed to occur beneath the salars and volcanic deposits (Alonso et al., 1991). Known borate deposits extend as a chain along the eastern Puna, restricted to the area of Salar del Hombre Muerto and Salar de Pastos Grandes in southern Puna and Salar de Cauchari in the northern part (Fig. 1). These continental borate deposits are part of the late Miocene Sijes Formation, composed of various evaporitic and clastic units. Fig. 2 shows the detailed stratigraphy of the Miocene rock units (Alonso and González-Barry, 1982; Alonso, 1987; Alonso et al., 1988; Alonso and Viramonte, 1990; Alonso et al., 1991; Helvaci and Alonso, 2000).

One of the world's largest borax deposits appears in the northwest of Salar del Hombre Muerto at Tincalayu (Fig. 1). The depositional features seem related to a small, closed lake environment, fed by thermal springs carrying the borate-bearing solution. This deposit contains a 30-m thick, massive borate body, which lies concordantly between the salt rock at the base and the overlying silt and sandstones (Fig. 2). Due to compaction and deformation, many of the primary structures have disappeared, and diagenetic structures and minerals have formed. The borate body is mainly composed of borax with minor kernite, with rare and unique borate minerals, such as ameghinite and rivadavite (Alonso, 1986, 1999; Alonso and Helvaci, 1988).

The borate deposit of Loma Blanca occurs in northern Puna, southwest of the volcano Coranzulí (Fig. 1). The borate body (30 m), formed from hot spring water in a shallow basin between volcanic events, has been relatively unaffected by deformation, and the mineral deposits have preserved their original primary features (Alonso, 1999). The main borate mineral is borax with minor ulexite and inyoite deposited in a well-defined vertical sequence and interlayered with clastic and pyroclastic rocks (Fig. 2). Teruggite, colemanite, and tincalconite occur less frequently (Alonso, 1987; Alonso et al., 1988; Alonso and Viramonte, 1990).

The Sijes deposit, which contains the largest of the hydroboracite reserves, is located east of Salar de Pastos Grandes (Fig. 1) and is composed of two formations (Pozuelos and Sijes) with volcanoclastic and evaporitic sequences of nearly 2000 m (Fig. 2). The borate deposits are located discontinuously along a belt representing a chain of small, permanent lakes from which the borate deposits originated. The formations are faulted and folded but still contain largely intact borate beds. The Sijes Formation contains the two main borate-bearing members—Monte Amarillo and Monte Verde—with beds of hydroboracite and colemanite as the major minerals alternating with clastic and pyroclastic strata. The minor minerals include borax, inyoite, and ulexite (Alonso, 1986, 1992, 1999).

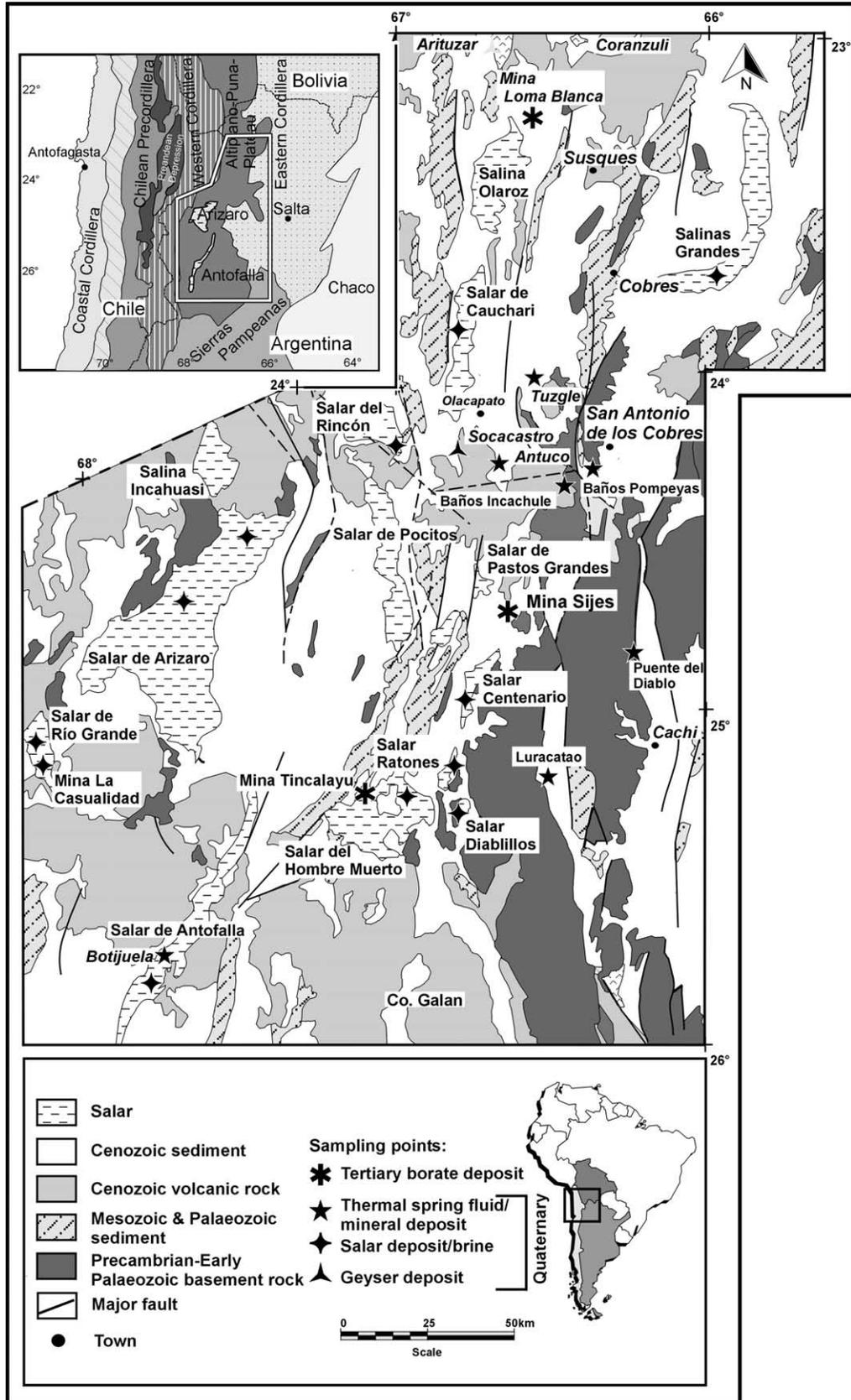


Fig. 1. Simplified geological map of the Puna Plateau in the central Andes (23–26°S) showing the location of the investigated boron-bearing deposits and sample area for fluids. Sketch in the upper left shows the morphostructural units and outline of the study area. Base map from Hoja Geológica San Antonio de los Cobres (Blasco et al., 1996) and Geological Map of the Central Andes (Reutter et al., 1994).

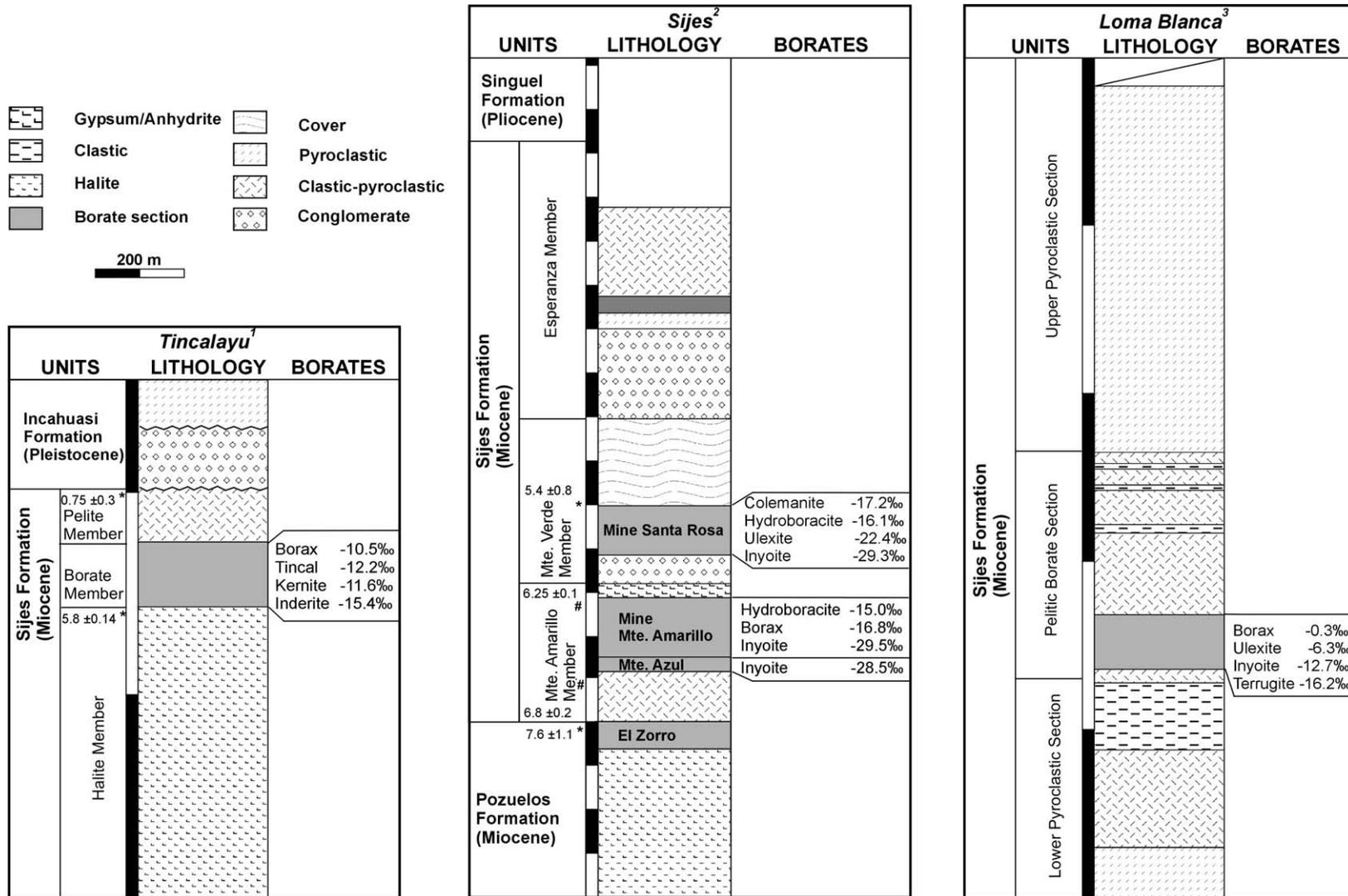


Fig. 2. Sketch of the stratigraphy of Neogene borate deposits and results of boron isotope ratio determination of mineral separates ($\delta^{11}\text{B}$ in ‰). Modified after Alonso and González-Barry (1982)¹, Alonso (1992)², and Chavez (1989)³; note different scales for the three columns. # is K/Ar ages (Alonso, 1986); * is fission-track ages (zircon in pyroclastic rocks; Alonso et al., 1988, 1991).

2.3. Quaternary borates in salars, thermal springs and geysers

Borate deposits in Recent salars are restricted to the eastern part of the Puna. Borates are rare or absent in the typical salar deposits in western Puna (Salar de Arizaro, Salar de Río Grande, and Salar de Antofalla), which usually consist of Na–Ca-sulphates or Na–Ca-carbonates and chlorides. Cenozoic volcanic rocks and Tertiary sediments surround these salars. The separation between the two types of salar deposits coincides with the N–S-trending Early Paleozoic sediment belt and the boundary of ignimbrite outcrops (Fig. 1; Alonso and Viramonte, 1990).

In eastern Puna, the geological setting of the borate-bearing salars is variable. Salars Ratonos, Centenario, and Diablillos are surrounded by magmatic and metamorphic Precambrian-Paleozoic basement. Basement rocks, Cenozoic volcanic rocks, and Ordovician and Tertiary sediments bound Salar del Hombre Muerto. Salars Pocitos, Pastos Grandes, Cauchari, and Rincón lie within Ordovician and Tertiary sediments and Cenozoic volcanic rocks (Fig. 1); Salars Pastos Grandes and Hombre Muerto are also located close to the Neogene borate deposits. The dominant borate mineral in all eastern salars is ulexite, with minor borax or tinalconite formed by the evaporation of boron-bearing thermal fluids. The maximum thickness of the borate layers is approximately 1.5 m (average 0.3 m). Ulexite occurs in massive beds or as nodules distributed within the sediment. Borax occurs in euhedral crystals grown in a muddy matrix. Other commonly associated evaporite minerals include carbonate, gypsum, and halite. The evaporitic mineral deposits originated from ancient thermal springs located along fractures in the rim of the salt pans (Alonso and Gutierrez, 1984).

Borate deposits of ulexite from Antuco, Arituzar, and Socacastro (Fig. 1), which are directly related to geysers and hot springs, represent special forms of boron concentrations in the Puna region. Ulexite is interlayered with travertine and deposited as a cone or platform around the thermal vent. The accompanying minerals are tinalconite, pinnoite, inderite, halite, and gypsum. These thermal springs are exhausted, with the exception of the spring at Antuco, where active borate mineralization can be observed (Alonso and Gutierrez, 1984; Alonso and Viramonte, 1985).

Tuzgle, Baños de Pompeya, Baños Incachule, Puente del Diablo, Luracatao, and Botijuela are active thermal springs (Fig. 1) related to volcanic activity. The fluids are heated to 160 °C in their reservoir and then cooled to intermediate surface temperatures of ≥ 30 °C. Similar active hot springs are located in the Altiplano-Puna volcanic complex of the western Puna Plateau in northern Chile. The springs from Tuyaito, Sico, Aguas Calientes, and the geyser field of El Tatio have been included for comparison (see Schmitt et al., 2002). The deposits consist mainly of halite (Alonso and Viramonte, 1985).

3. Sampling and analytical methods

All sample localities are shown in Fig. 1. Typical borate minerals were collected in outcrops and open cuts from the main Neogene borate units of Loma Blanca, Sijes, and Tincalayu (Fig. 2). Special care was taken to sample only major borate minerals (borax, ulexite, inyoite, colemanite, hydroboracite) of primary origin. The samples were collected from largely intact borate beds of primary origin, which display well-preserved original and finely detailed sedimentary features. The borate crystals did not contain any evidence of secondary alteration, recrystallization, or pseudomorphs and were not collected out of segregation veins or impregnates. Secondary minerals were only collected for minor borate minerals, in the form of tinalconite as the dehydration product of 'dry air'-exposed borax crystal and kernite as the diagenetic product of borax at the base of the borate body in Tincalayu. Other possible secondary minerals were inderite and terrugite, which probably formed as alteration products of the primary borate minerals in Tincalayu and Loma Blanca, respectively. A sample description is given in Appendix A.

The samples of Quaternary ulexite from the salars are exclusively from the upper 30 cm of the deposits. Samples are white and needle-like fibrous aggregates, concentrated in nodular structures. Accompanying minerals include gypsum and calcite, with minor amounts of inyoite and borax. Halite samples were taken from fine-grained to skeletal-shaped crystals from the surface exposures at the salars and spring deposits, which were directly connected to the boron-bearing brines of the salars and the fluids of the thermal springs. The ulexite minerals from the geyser deposits originated from the thermal vent and consisted of fine fibrous concretions. The thermal water samples were collected from the thermal spring vents, whereas the brine samples, supplied by superficial meteoric water, came from water ponds inside the salars. These solutions were filtered without additional purification and then used for boron isotope and concentration analysis. The temperature and pH values for the different solutions were measured with a thermometer and potentiometer, respectively.

Several samples of borate minerals were intergrown with other evaporitic and clay minerals. To verify the chemical composition and purity of the analyzed material, minerals were separated under a binocular microscope and assessed by X-ray diffraction. Approximately 1 g of each cleaned borate and halite sample was powdered and dissolved in 1 M HCl. Boron concentrations of the minerals and fluids were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a VARIAN Liberty 200 instrument at Geo-ForschungsZentrum, Potsdam. The analytical uncertainty for the boron determination was less than 5% (1 RSD). Boron isotope analysis was performed on a static multi-collector VG SECTOR 54-30 mass spectrometer with

negative polarity (N-TIMS) at GeoForschungsZentrum, Potsdam, using the method described by Kasemann et al. (2001). Boron isotope ratios were determined conventionally in relation to the NIST SRM 951 boric acid reference material. The average $^{11}\text{B}/^{10}\text{B}$ ratio for the reference material NIST SRM 951 was 4.0158 ± 0.0019 ($1\sigma\text{SD}$). The uncertainty for the isotope ratio of the minerals and fluids was 1‰, calculated as two standard deviations of the mean ($2\sigma_{\text{mean}}$).

4. Results

4.1. Neogene borates

The $\delta^{11}\text{B}$ values of borate minerals in the Neogene deposits range from -29.5% in inyoite to -0.3% in borax. The differences in $\delta^{11}\text{B}$ values between the same minerals from different deposits display a similarly broad range: from -22.4% in a sample of ulexite from Sijes and from $-6.30/00$ in a sample of ulexite from Loma Blanca. In contrast, the same borate minerals from different members (e.g. inyoite from Sijes) or layers (e.g. borax from Tincalayu) from the same deposit have similar $\delta^{11}\text{B}$ values (Table 1).

With the exception of Sijes, the boron isotope values of the borate minerals within single deposits vary systematically according to the coordination of boron in the crystal lattice. Borate minerals with more trigonal coordinated boron sites display higher concentrations of ^{11}B . For example, in Loma Blanca, borax gives the highest $\delta^{11}\text{B}$ values, followed by ulexite and inyoite (Table 1).

4.2. Quaternary deposits

In eastern Puna, the $\delta^{11}\text{B}$ values of Quaternary ulexite salar deposits range from -23.2 to -14.2% . Quaternary ulexite deposits from geysers and thermal springs in the same region yield a comparable range in $\delta^{11}\text{B}$ values (-22.1 to -15.4%) (Table 2). Currently formed ulexite ($\delta^{11}\text{B} = -22.1\%$) was found at the Antuco thermal spring. The $\delta^{11}\text{B}$ values of fluids from active thermal springs in eastern Puna vary from -15.3 to -10.4% , with boron concentrations in the fluids ranging from 41 to $570 \text{ mg l}^{-1}\text{B}$. One water sample from inside Salar Salinas Grandes shows a boron isotope composition and concentration of -18.3% and $647 \text{ mg l}^{-1}\text{B}$, respectively. The measured pH values for the thermal fluids range 7.9–8.7, with an average of 8.3 (Table 2). The temperatures of the thermal spring fluids at the well range 30–60 °C (Ferretti and Alonso, 1993). Except for Antuco, the thermal springs built up mainly travertine and halite deposits, with high boron concentrations of up to 1200 mg kg^{-1} and B-isotope values from -16.4 to -5.2% (Table 2). The boron-bearing minerals were precipitated at an average fluid temperature of 10 °C.

In western Puna, halite of the salar deposits displays a more variable range of $\delta^{11}\text{B}$ values (-14.6 to $+5.2\%$) and great variation in boron concentrations of 20–921 mg kg^{-1} (Table 2). The $\delta^{11}\text{B}$ values of the associated brines and thermal spring fluid from Botijuela are less variable and range from -6.6 to -3.7% and to $+0.7\%$, respectively, with boron concentrations ranging 22–171 mg kg^{-1} . The pH values of the salar solutions range 7.1–8.0, with

Table 1
Boron isotope composition, structural formula and boron coordination of Neogene borate minerals of the central Andes

Location	Mineral	Structural formula	B-coordination	$\delta^{11}\text{B}$ (‰) ^a	Calculated fluid $\delta^{11}\text{B}$ (‰)
TINCALAYU	Borax	$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-10.5	~ -11
	Borax	$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-9.9	
	Borax	$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-9.7	
	Tincalconite ^{2°}	$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-12.2	
	Kernite ^{2°}	$\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2] \cdot 3\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-11.6	
	Inderite ^{2°}	$\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_3] \cdot 5\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-15.4	
LOMA BLANCA	Borax	$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-0.3	~ ± 0
	Ulexite	$\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$	$2\text{B}^{(3)}; 3\text{B}^{(4)}$	-6.3	
	Inyoite	$\text{Ca}[\text{B}_3\text{O}_3(\text{OH})_3] \cdot 4\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-12.7	
	Terrugite ^{2°}	$\text{Ca}_4\text{Mg}[\text{AsB}_6\text{O}_{11}(\text{OH})_6] \cdot 14\text{H}_2\text{O}$	$4\text{B}^{(3)}; 8\text{B}^{(4)}$	-16.2	
SIJES Monte Verde Member	Colemanite	$\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-17.2	~ ± 0
SIJES Monte Verde Member	Hydroboracite	$\text{CaMg}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot 3\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-16.1	
	Ulexite	$\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$	$2\text{B}^{(3)}; 3\text{B}^{(4)}$	-22.4	~ -13
	Inyoite	$\text{Ca}[\text{B}_3\text{O}_3(\text{OH})_3] \cdot 4\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-29.3	
SIJES Monte Verde Member	Hydroboracite	$\text{CaMg}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot 3\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-15	~ ± 0
	Borax	$\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$	$1\text{B}^{(3)}; 1\text{B}^{(4)}$	-16.8	~ -13
	Inyoite	$\text{Ca}[\text{B}_3\text{O}_3(\text{OH})_3] \cdot 4\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-29.5	
	Inyoite	$\text{Ca}[\text{B}_3\text{O}_3(\text{OH})_3] \cdot 4\text{H}_2\text{O}$	$1\text{B}^{(3)}; 2\text{B}^{(4)}$	-28.5	~ -13

A correlated sample description appears in Appendix A.

^a Uncertainty is 1‰ given as $2\sigma_{\text{mean}}$. ^{2°} minerals assumed to be secondary phases.

Table 2
Results of boron isotope composition of Quaternary borate minerals, halite, and fluids from Puna Plateau

Location	Sample	Mineral	$\delta^{11}\text{B}$ (‰) ^a	B (mg kg ⁻¹)	Fluid _{measured}			Fluid _{calculated}
					$\delta^{11}\text{B}$ (‰) ^a	B (mg l ⁻¹)	pH	$\delta^{11}\text{B}$ (‰)
<i>Salar</i>								
<i>Eastern Puna</i>								
Salar de Cauchari	S7/79U	Ulexite	-23.2					-13.5
Salar de Cauchari	S7/798B	Borax	-18.0					
Salar del Rincón	S1/91	Ulexite	-19.1					-9.4
Salar de Pocitos	S1/89	Ulexite	-16.7					-7.1
Salar de Centenario	S1/15	Ulexite	-20.2					-10.5
Salar Ratonés	S1/19	Ulexite	-19.5					-9.8
Salar Diablillos	S1/21	Ulexite	-14.2					-4.6
Salar del Hombre Muerto	S1/49	Ulexite	-15.7					-6.1
Salinas Grandes	S7/99	Halite	-14.5	108	-18.3	647	7.1	
<i>Western Puna</i>								
Salar de Arizaro (NE)	S7/71	Halite	-10.7	847	-6.6	39	7.4	
Salar de Arizaro (SW)	S7/73	Halite	-14.6	20	-4.6	22	7.2	
Salar de Río Grande (N)	S7/66	Halite	-14.2	921	-3.7	23	8.0	
Salar de Río Grande (S)	S7/68	Halite	-2.0	89	-4.9	138	7.4	
Salar de Antofalla	S1/81	Halite	+1.2	68				
Salar de Antofalla	S1/82	Halite	+5.2	62				
<i>Thermal spring</i>								
<i>Eastern Puna</i>								
Arituzar ^b	S1/82	Ulexite	-19.2					-9.6
Socacastro ^b	S1/83	Ulexite	-15.4					-5.8
Tuzgle	S7/60				-13.2	41	8.2	
Antuco	S1/92	Ulexite	-22.1		-12.5	570	7.9	
Baños Pompeya	S6/95				-12.1	56	8.7	
Baños Incachule	S7/37	Halite	-16.4	0.5% m/m	-15.3	26	8.5	
Puente del Diabolo	S7/21	Halite	-5.2	1% m/m	-13.1	138	8.1	
Luracatao	S7/8	Halite	-6.2	12% m/m	-10.4	230	8.1	
<i>Western Puna</i>								
Botijuela	S6/80				+0.7	171	7.1	
El Tatio ^c	S6/96				-4.6	128	7.2	
Aguas Calientes ^c	S6/104				+2.9	23	7.8	
Sico ^c	S6/102				-2.7	12	8.1	
Tuyaito ^c	S6/103				+5.7	315	7.6	

^a Uncertainty is 10/00 given as $2\sigma_{\text{mean}}$.

^b Fossil geysers.

^c Northern Chile, Calama (Schmitt et al., 2002).

an average of 7.4 (Table 2). The average temperature of the salar brines is 10 °C.

5. Discussion

5.1. Fractionation factors and fluid calculation

Experimental isotope fractionation factors for different borate minerals are lacking. Calculations of the difference between the bond strength of ¹¹B and ¹⁰B with oxygen (Kakihana and Kotaka, 1977; Kakihana et al., 1977) yield differences in the isotope fractionation factor of 2‰ for borax and ulexite ($\alpha_{(\text{borax/ulexite})} = 1.002$) and 1.3‰ for ulexite and inyoite ($\alpha_{(\text{ulexite/inyoite})} = 1.0013$), respectively assuming that all borate minerals precipitated in equilibrium

at 25 °C (Oi et al., 1989). However, these values are much lower than the observed fractionation factors of coexisting borate minerals from Cenozoic Puna deposits. The isotope fractionation factor between borax and ulexite in Loma Blanca and Salar de Cauchari varies between 1.0056 and 1.006. At Loma Blanca and Sijes, the $\alpha_{(\text{ulexite/inyoite})}$ values are 1.0064 and 1.007, respectively. The variation of isotope ratios of borate minerals ($\alpha_{(\text{borax/ulexite})} = 1.0042$, $\alpha_{(\text{ulexite/inyoite})} = 1.006$ and 1.0085) from Turkey and the United States (Oi et al., 1989; Palmer and Helvacı, 1995, 1997) is consistent with these results.

Possible explanations for the differences between the calculated and observed isotope fractionation factors include different temperatures and compositional conditions in experimental and natural systems. The differences cannot be explained by temperature control alone, because

calculated fractionation factors differ by less than 1‰ for temperature changes between 0 and 25 °C (Oi et al., 1989). Therefore, compositional differences of the boron-bearing fluids, which may include variations in pH and major element composition or a change in the boron isotope composition of the natural fluid during crystallization (Oi et al., 1989; Palmer and Helvacı, 1995), are the most likely causes. The most significant factor is the change in pH during the formation of different Na–Ca-borates (Christ et al., 1967). A decrease in $\delta^{11}\text{B}$ values from Na- through Na–Ca- to Ca-borates from the same locality could be due to Ca-borates precipitating at a lower pH than Na-borates (Oi et al., 1989; Palmer and Helvacı, 1995, 1997). Minerals with identical boron coordinations and Na–Ca-ratios, such as colemanite, hydroboracite, and inyoite, show similar boron isotope values. However, the pH of the fluid not only controls the isotope composition and order of crystallization, but also the absolute and relative amounts of the precipitating phases. For example, the Rayleigh fractionation model of Palmer and Helvacı (1995) suggests that the initial pH of the fluid is responsible for the type of dominantly crystallizing borate. Pure Na-borates are the dominant minerals precipitated from a fluid at a higher pH, rather than Na–Ca-borates or Ca-borates.

On the basis of these considerations, Oi et al. (1989) and Palmer and Helvacı (1995) calculate the influence of fluid pH on the $\delta^{11}\text{B}$ values of the borate minerals. These calculations are based on assumptions about fluid compositions, not measured compositions. To constrain the $\delta^{11}\text{B}$ values and the pH of the fossil thermal fluids in the Puna Plateau localities, we use the chemical properties and empirical fractionation factor of the modern geothermal system in Antuco and the model calculations mentioned previously. Although there is no proof that the composition of the active thermal springs is equivalent to the fluids of Neogene time, it is a reasonable assumption because of their similar environmental and geological conditions.

By analogy with the Antuco thermal spring system, a boron solution that precipitates mainly ulexite has a pH of 7.9 at 10 °C. A comparison of the $\delta^{11}\text{B}$ values of the presently forming ulexite (–22.1‰) and the solution (–12.5‰, Table 2) results in an empirical fractionation factor of $\alpha_{(\text{solution/ulexite})} = 1.0096$ (pH 7.9, 10 °C). Although this factor is identical to the isotope fractionation factor of ulexite in a solution of 1.0095, Oi et al. (1989) mention a higher pH of 8.6 for ulexite precipitation.

Typical pH or $\delta^{11}\text{B}$ values of a boron solution for borax or inyoite precipitation has not been reported for the Puna geothermal system, and thus, no empirical fractionation factor can be calculated. However, compared with ulexite, borax must have formed under more alkaline and inyoite under more acidic conditions. Oi et al. (1989) and Palmer and Helvacı (1995) suggest typical borax precipitation conditions occurred at a pH of approximately 8.8, where the mol fraction of $\text{B}(\text{OH})_3/\text{B}(\text{OH})_4^-$ species in the solution is identical to the B-coordination ratio ($1\text{B}^{[3]}:1\text{B}^{[4]}$) in

the Na-borates and no isotope fractionation between the solution and borax ($\alpha_{(\text{solution/borax})} = 1$) occurs. To calculate the $\delta^{11}\text{B}$ value of a fluid in equilibrium with the coexisting Na/Ca-borate, such as ulexite, we conclude that

$$\begin{aligned} &({}^{11}\text{B}/{}^{10}\text{B})_{\text{solution}_{\text{calculated}}} \\ &= ({}^{11}\text{B}/{}^{10}\text{B})_{\text{ulexite}_{\text{measured}}} \times \alpha_{(\text{solution/ulexite})}, \end{aligned} \quad (1)$$

using the empirical fractionation factor from Antuco ($\alpha_{(\text{solution/ulexite})}$). To provide a useful approximation of the isotope composition in Ca-borate-producing fluids, we assume

$$\begin{aligned} &({}^{11}\text{B}/{}^{10}\text{B})_{\text{solution}_{\text{calculated}}} \\ &= ({}^{11}\text{B}/{}^{10}\text{B})_{\text{Ca-borate}_{\text{measured}}} \times \alpha_{(\text{solution/ulexite})} \\ &\quad \times \alpha_{(\text{ulexite/Ca-borate})}, \end{aligned} \quad (2)$$

using the empirical fractionation factor from Sijes and Loma Blanca ($\alpha_{(\text{ulexite/inyoite})}$).

5.2. Quaternary borate minerals

We assume the physicochemical conditions for Quaternary ulexite deposits in the salars, from geysers and thermal springs to be identical to those of the Antuco deposits. From the isotope fractionation factor $\alpha_{(\text{solution/ulexite})} = 1.0096$, we calculate that the $\delta^{11}\text{B}$ values for the boron-rich fluids range from –13.5 to –4.6‰. The actual present day composition of the active thermal spring fluids from this area is generally within this range (–15.3 to –10.4‰) but restricted to the more negative $\delta^{11}\text{B}$ values.

The Quaternary halite deposits from the Puna Plateau display a wide range in boron isotope values from –16.4 to +5.2‰, comparable to the overall isotope range of the related thermal spring waters and brines of the salars (–18.3 to +0.7‰). However, neither a systematic correlation nor a constant isotope fractionation factor between the B-isotope composition of the halite deposits and their connected brines and fluids was observed. Halite normally contains little boron in crystal; the high boron contents (up to 1200 mg kg^{–1}) therefore may suggest that most of the boron comes from fluid inclusions, a finding that further explains the lack of correlation between halite and the brines and fluids.

5.3. Neogene borate minerals

Neogene deposits from Sijes, Tincalayu, and Loma Blanca differ significantly in their borate mineralogy. In Tincalayu and Loma Blanca, the major minerals are Na-borate, whereas in Sijes, they are Ca-borate (Alonso, 1986; Chavez, 1989). As previously discussed, we assume that these differences are related to the distinct chemical compositions and pH of the thermal fluids or brines in the basins. In Loma Blanca and Tincalayu, with Na-borate

borax as the main mineral, a thermal fluid enriched in Na with a higher pH and possibly higher $\delta^{11}\text{B}$ values than in Sijes would be predicted, whereas the Ca-borates inyoite and colemanite in Sijes point to a more acidic, Ca-rich fluid. The hydroboracite deposits at Sijes are special, in that comparable occurrences of hydroboracite are usually restricted to marine borate deposits.

In Tincalayu, Na-borates with the same boron coordination have similar $\delta^{11}\text{B}$ values (Table 1): borax as the main mineral, tincalconite as the dehydration product of borax, and the diagenetic product kernite. Because tincalconite and kernite show $\delta^{11}\text{B}$ values identical to the primary mineral borax, no loss of boron during together with isotope fractionation from the system is supposed. As discussed for Na-borate-dominated deposits, the likely pH of 8.8 for the mineralizing fluid points to a fractionation factor of $\alpha_{(\text{solution}/\text{borax})} = 1$. In this case, the estimated $\delta^{11}\text{B}$ value for the mineralizing fluid in Tincalayu is approximately -11% , similar to the average $\delta^{11}\text{B}$ value for the primary Na-borate borax (Table 1).

In Loma Blanca, the $\delta^{11}\text{B}$ values of Na-, Na-Ca-, Ca-, and Ca-Mg-borate (Table 1) are inconsistent with coeval precipitation from a common fluid. We suggest successive precipitation of these primary minerals at different times, as supported by the vertical borate mineral zonation up section. As in Tincalayu, the main mineral in Loma Blanca is borax, and again, a pH of 8.8 for the mineralizing fluid, which favors borax precipitation, is most likely with no isotope fractionation between the solution and borax ($\alpha_{(\text{solution}/\text{borax})} = 1$). Accordingly, a $\delta^{11}\text{B}$ value similar to borax of $\pm 0\%$ (Table 1) for the mineralizing fluid of the main borate deposit is estimated.

The borate deposits in Sijes are more complicated. Two different groups of borate assemblages are observed in the borate units on the basis of the isotope values and the boron coordination of the minerals. The first group of coexisting primary borax, ulexite, and inyoite is characterized by a steady succession of decreasing $\delta^{11}\text{B}$ values from Na- to Ca-borates. The second group is represented by primary hydroboracite and colemanite with a higher $\delta^{11}\text{B}$ value (-17.2%) than inyoite ($\sim -29\%$). Note that both Ca-borates (colemanite and inyoite) have the same $\text{B}^{[3]}/\text{B}^{[4]}$ ratio. If they formed as an equilibrium paragenesis, identical $\delta^{11}\text{B}$ values would be expected (Oi et al., 1989). The different B-isotope composition for the Ca-borate samples therefore might suggest that either inyoite or colemanite is an alteration product. This indication can be disproven for the inyoite samples because of their clear primary origin and the steady $\delta^{11}\text{B}$ succession from borax to inyoite. Because alteration from inyoite to colemanite in equilibrium should have no effect on $\delta^{11}\text{B}$, the higher values for colemanite must be explained by boron loss during dehydration, with a fluid of high pH (≥ 9) or substantial input of boron with heavier $\delta^{11}\text{B}$ values. However, the colemanite samples are of primary origin, and the difference in Ca-borate isotope composition is therefore best explained by a change

in B-isotope composition of the mineralizing fluid, which could have happened in two different ways. In each depositional sequence, the sampled borax, ulexite, and inyoite precipitated first, followed by colemanite and hydroboracite. Because the first period of mineral formation decreases the amount of boron in the fluid, the $\delta^{11}\text{B}$ value of the remaining fluid increases. If, after the formation of inyoite, hydroboracite and colemanite were formed, high B-isotope compositions are likely. Alternatively, a periodic water flow with different B-isotope composition might have led to the independent formation of hydroboracite and inyoite sequences. In each case, mineralizing fluids favored precipitation of Ca-borate and/or Ca-Mg-borate, and therefore, a lower pH at Sijes than at Tincalayu and Loma Blanca is indicated. However, because the empirical isotope fractionation factor of Ca-borate and mineralizing fluid in the Puna is unknown, Eq. (2), with empirical data from Antuco ($\alpha_{(\text{solution}/\text{ulexite})} = 1.0096$), is adopted for the calculations. For the borax, ulexite, and inyoite group, we calculate a $\delta^{11}\text{B}$ value of approximately -13% . In contrast, a heavier fluid of $\pm 0\%$ is calculated for the colemanite and hydroboracite precipitation.

5.4. Boron sources and provenance of the solutions

Previously, boron in the geothermal system of the Argentine Puna Plateau was assumed to have derived from weathering and leaching of volcanic rocks and fresh volcanic ashes without significant contribution from the basement (Alonso and Gutierrez, 1984; Alonso and Viramonte, 1985; Alonso et al., 1991). Because thermal waters often have $\delta^{11}\text{B}$ values similar to the local rocks in the geothermal system (Musashi et al., 1988), the boron isotope composition of the measured water samples and the calculated values can be used to identify the source rocks from which B was leached.

Ion probe (SIMS) and TIMS studies of well-characterized, representative, Precambrian-Cenozoic rock suites provide strong constraints on the boron distribution of the upper continental crust in the central Andes. Paleozoic metamorphic and magmatic basement rocks reveal an average $\delta^{11}\text{B}$ value of $-8.9 \pm 2.2\%$ (1 SD) with a boron concentration of approximately $43 \text{ mg kg}^{-1} \text{ B}$ (Kasemann et al., 2000). Boron isotope analyses of Mesozoic sedimentary rocks with up to $60 \text{ mg kg}^{-1} \text{ B}$ from the central Andes show a wide range in $\delta^{11}\text{B}$ values. For Jurassic limestones, the values range from -11.5 to -10.3% , compared with -7.3 to $+8\%$ for Cretaceous sediments (Yacorite and El Molino Formations; Fiedler, 2001; Kasemann, unpublished data). The $\delta^{11}\text{B}$ data from the Cenozoic igneous systems yield values of approximately $-3.8 \pm 2.8\%$ (1 SD) for the Neogene ignimbrites with a boron concentration of $10\text{--}40 \text{ mg kg}^{-1} \text{ B}$. A $\delta^{11}\text{B}$ value $\geq 0\%$ and up to $+6\%$ can be predicted for andesitic-dacitic volcanic rocks and slab-derived melts of the central Andean arc (Schmitt et al., 2002), respectively.

The calculated mineralizing fluids of the Neogene Tincalayu (-11%) and Sijes (-13% , first group) borate deposits, as well as of most Quaternary ulexite deposits, show similar negative boron isotope values (-13.5 to -9.4%). These isotope values are similar to those of the surrounding Paleozoic basement ($-8.9 \pm 2.2\%$), which highlights its significance as the main source of boron for this part of the geothermal system. However, the slightly lighter calculated isotope values from the fossil geyser Socacastro and Salars Pocitos, Hombre Muerto, and Diablillos (-7.1 to -4.6%) may reflect an additional, lighter boron source from adjacent Cenozoic volcanic rocks ($-3.8 \pm 2.8\%$). The exceptionally high $\delta^{11}\text{B}$ value calculated for the Neogene fluid from Loma Blanca ($\pm 0\%$), as well as for the recent fluid system at Botijuela ($+0.7\%$), suggests another, more positive $\delta^{11}\text{B}$ boron source. Potential source rocks of positive $\delta^{11}\text{B}$ values are marine limestones of Mesozoic age in the Puna Plateau, which seem spatially correlated with the high $\delta^{11}\text{B}$ values (Alonso et al., 1984). Other possible sources of boron are andesitic-dacitic volcanic rocks of the Cenozoic magmatic arc, which formed at the same time as the borates.

The measured active thermal spring fluids and recent salar brines show the same range in their boron isotope values as those from the calculated fluids for the Neogene borate deposits (-18.3 to $+0.7\%$). They also show a similar trend in the general boron isotope distribution, from more negative values in eastern Puna to more positive values in western Puna. This isotope pattern continues in thermal water located in the Altiplano-Puna volcanic complex of western Puna in northern Chile, with $\delta^{11}\text{B}$ values from -4.6 to $+5.7\%$ (Schmitt et al., 2002). These samples include hydrothermal fluid from the Tatio geyser field and waters from salars related to hot spring systems (Aguas Calientes, Sico, Tujaito). The $\delta^{11}\text{B}$ values of the fluids in western Puna overlap with the values of Neogene-Pleistocene ignimbrites; in eastern Puna, the values are similar to those of the local Paleozoic basement. This difference suggests that boron is leached from regional source rocks—in this case, Paleozoic basement and Neogene ignimbrites—and that the borate deposits were formed by mixing waters from different sources, depending on the drainage system. An additional contribution of boron from the Neogene borates to the Quaternary fluid by remobilization also is postulated, especially for Salar de Pastos Grandes and Salar del Hombre Muerto (Alonso and Gutierrez, 1984), though it cannot be documented isotopically. In the case of Salar de Cauchari, thermal waters from the Antuco spring, as suggested by Viramonte et al. (1984), likely contributed, in that the estimated -13% $\delta^{11}\text{B}$ value for the fluid that formed the borax and ulexite deposit is similar to that of the Antuco spring (-12.5%).

In the preceding discussion, we have assumed that the high $\delta^{11}\text{B}$ value of the hydroboracite/colemanite section in Sijes, and consequently that of the calculated B-bearing fluids (second group, $\pm 0\%$), can be explained in different

ways. A change in B-isotope composition of the fluid due to previous mineral formation is supported by variations in the rate of water supply. Increasing evaporation evident in both sections (Alonso, 1992) indicates a large amount of boron precipitated from the solution. However, facies associations imply an environment fed by a permanent stream of water, and there is no evidence for a linked depositional and evolutionary sequence of the two investigated borate sections. The investigated borate sections are separated by clastic sediments, and the borate minerals from the first section (borax, ulexite, and inyoite) are interbedded with sandy and silty sediments, whereas the hydroboracite/colemanite mineralization, for example, is interbedded mainly with tuff and sulphates (Alonso, 1999; Orti and Alonso, 2000). This finding suggests that the inyoite (first group) and colemanite (second group) sections were formed separately of water from different sources, depending on the drainage system. Whereas we assume that the boron in the main mineralizing fluid of the first borate group in Sijes is sourced from the local Paleozoic basement, for the second group in Sijes, the assumed boron isotope composition of the mineralizing fluid is similar to that of Botijuela and Loma Blanca, which indicates a positive boron source such as the volcanic rocks of the Cenozoic magmatic arc. A possible volcanic source for these fluids is also supported by the primary origin of the Ca–Mg-borate hydroboracite. Analytical studies and field data from Alonso (1999) and Orti and Alonso (2000) imply that magnesium was associated with boron in the hot mineralizing fluids of volcanogenic origin.

The observations of an east–west distribution in the boron isotope composition of ancient and modern mineralizing fluids in the Puna Plateau correspond with the conspicuous feature that divides the Puna Plateau into two regions of Quaternary evaporite deposits (see Section 2). A fault system and Early Palaeozoic sedimentary belt (Fig. 1) mark the boundary both between these regions and of ignimbrite outcrop (Schmitt et al., 2002). High boron concentrations are found in the fluids and salar deposits in eastern Puna, whereas western Puna is characterized by lower boron amounts but higher quantities of sulphates. The high boron contents and lower isotope composition in the east appear to have resulted from leaching boron from the Paleozoic country rocks (and possibly from the Tertiary borate strata), whereas lower boron concentrations and higher isotope data correlate with ignimbrite outcrops (Schmitt et al., 2002).

6. Summary and conclusions

Calculated $\delta^{11}\text{B}$ values of -13 and -11% for the main mineralizing fluids in Sijes and Tincalayu, respectively, indicate a similar isotope composition for the boron source. In Sijes, a second boron rich fluid with a high $\delta^{11}\text{B}$ of $\pm 00/00$ of different origin and with a high $\delta^{11}\text{B}$ of $\pm 0\%$ is found. In Loma Blanca, the calculated value for

the main mineralizing fluid is $\pm 0\%$, which reflects a similarly high $\delta^{11}\text{B}$ ($\geq 0\%$) source material as that for the second fluid at Sijes. The $\delta^{11}\text{B}$ values of the calculated associated fluids of the Quaternary ulexite deposits and the active thermal springs show they have the same wide isotope range (-13.5 to -4.6% and -15.3 to $+0.7\%$, respectively) as the Neogene deposits, which indicates sampling of the same boron sources.

The significant isotope variations of the borates and, especially, the fluids in Puna Plateau reflect boron sources with different isotope signatures. A major source of boron is the leaching of the Paleozoic metamorphic and magmatic basement with variable but clearly negative isotope values ($-8.9 \pm 2.2\%$, 1 SD). Another important source of boron is Neogene-Pleistocene ignimbrites ($\delta^{11}\text{B} = -3.8 \pm 2.8\%$, 1 SD), whose isotope composition overlaps that of basement rocks but is more positive. Potential rocks for a third boron source include Cenozoic andesites and Mesozoic limestones with positive $\delta^{11}\text{B}$ values of up to $+8\%$.

Borate deposits in Puna Plateau show a rough east–west distribution in their boron concentrations and isotope composition, with higher values observed in eastern Puna. This east–west pattern implies boron contributions from different source rocks, according to the location of the thermal springs/borate deposits and their surrounding rocks.

This pattern correlates with the boundary of ignimbrite outcrops, which suggests that leaching of boron and borate deposition is controlled by hydrothermal systems in local country rocks. Also, the boron isotope values appear to reflect variations in the isotope composition of the source rocks, rather than being the result of secondary processes such as phase separation or precipitation of secondary minerals.

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Appendix A

Neogene borate deposits

Location	Mineral	Sample	Description
Tincalayú	Borax	S7/106B	Well-preserved, colorless, euhedral borax crystals (~ 5 cm in diameter) from a massive primary borax layer in the middle of the main borate body
	Borax	S7/105	Band (3 cm) of small borax crystals from the top of the massive borax bed
	Borax	S7/103	Thin band of small (< 2 cm), euhedral borax crystals from the top of the borate body
	Tincalconite	S7/106T	Cryptocrystalline alteration product from the dehydrated part of a borax crystal
	Kernite	S7/104	Sample from the base of the main borate body. Crystals up to 10 cm in length, colorless, euhedral, and grown above a layer of lumpy to fibrous crystal aggregates. Probably formed during diagenesis from recrystallization of bedded borax
Loma Blanca	Inderite	97/7	Samples from above the borate body intercalated in cavities in calcareous schist and slate. Crystals are subhedral, colorless to pale red, up to 2 cm in length, and possibly secondary in origin
	Borax	97/3	Band of small euhedral (< 3 cm) borax crystals from the center of main borax body
	Ulexite	97/4	Massive aggregates of fine-grained ulexite irregularly intercalated with tuffaceous material from above the borax body
	Inyoite	97/5	Layer of large (2 cm) nodules of subhedral tabular and colorless inyoite crystals above the ulexite.
Sijes: Mte. Verde	Teruggite	97/6	Fine needles (< 0.5 mm) of white teruggite concentrated in massive nodules that seem to replace borax
	Colemanite	S7/44	Bed of primary, concentric-fibrous nodules of colorless, translucent, euhedral (< 1 cm) crystals interfingering with silty sediment and sulphates from the upper part of the colemanite unite

(continued on next page)

Appendix A (continued)

Location	Mineral	Sample	Description
Sijes: Mte. Amarillo	Hydroboracite	S1/2	Layer of close-grained crystals intercalated with anhydrite and tuffites from the middle of the colemanite unit
	Ulexite	S7/45	Aggregates of needles and fibers surrounded by clastic material from the base of the colemanite unit
	Inyoite	S1/3	Tabular and colorless crystals, mainly disseminated in gypsum, from the base of the colemanite unit
	Hydroboracite	S7/41	Synsedimentary bed of fibrous to coarse-grained nodules of white crystals intercalated with clastic material from the top of the hydroboracite unit
	Borax	S7/107	Large (5 cm) euhedral crystals with intensive red color interlayered in the inyoite unit
	Inyoite	S7/43	Bed of primary spherular inyoite from the middle of the inyoite unit.
	Inyoite	S7/44	Band of clear, translucent, prismatic (< 1 cm) crystals as nodules interfingering with rock salt from beneath the inyoite unit

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