

Geochemical survey of thermal springs from the Atacama region, northern Chile

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ABSTRACT

This work presents the chemical and isotopic ($\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$) composition of five thermal areas from the Atacama region (northern Chile), namely Laguna Verde, Juncalito, Termas de Rio Negro, Panteón de Aliste, and Salar de Piedra Parada. The chemical and isotopic (^3He , ^4He , $\delta^{13}\text{C-CO}_2$, and $\delta^{13}\text{C-CH}_4$) composition of gases bubbling from Juncalito is also reported. This work aims to (i) constrain the origin and physicochemical processes controlling the chemical and isotopic composition of bubbling gases and (ii) estimate the equilibrium temperatures of hydrothermal reservoirs. The thermal springs are fed by meteoric waters whose chemistry, during the underground circulation, is mainly controlled by water-rock interaction involving volcanic rocks and volcano-sedimentary sequences. Notable Li, B, and As enrichments are recognized, likely related to the leaching of hydrothermally altered andesitic to rhyolitic rocks and the presence of sedimentary sequences, distinctly below the Claudio Gay Cordillera. The $^3\text{He}/^4\text{He}$ ratios ($\sim 1.4\text{--}1.5\text{ Ra}$), within the range of the typical values for low-temperature hydrothermal gases from the Central Volcanic Zone, likely represent a mixture of an atmospheric endmember mixed with a differentiated cooling magma residing within the crust for a long time. The $\delta^{13}\text{C-CO}_2$ values suggest a dominant crustal CO_2 source with a minor (1 %) mantle contribution. Chalcedony geothermometer provides reservoir temperatures up to 91 and 88 °C in Termas de Rio Negro and Laguna Verde, respectively. Further geophysical and geostructural investigations are recommended to constrain the source of heat in the Laguna Verde area, especially considering the presence of the quiescently degassing Ojos del Salado volcano.

1. Introduction

A significant geothermal potential related to Cenozoic volcanism has been recognized in several areas of the Central Volcanic Zone (CVZ), including El Tatio, Pampa Apacheta, Puchuldiza, Surire in northern Chile (Urzuza et al., 2002; Tassi et al., 2010) (Fig. 1), and up to sixty isolated thermal springs scattered in Chile, Bolivia, and Argentina (Risacher et al., 2011; Veloso et al., 2020). Close to the Laguna Verde

(LV) lake in the Atacama region, up to twenty thermal springs with temperatures up to 47 °C have been reported to occur. These thermal manifestations are possibly related to the Holocene volcanic activity of the quiescently degassing Ojos del Salado volcano, located 25 km to the southwest (Alam and Muñoz, 2024). Preliminary geothermometric estimations suggest reservoir temperatures up to 140 °C in LV (Alam and Muñoz, 2024). Additionally, two thermal areas were also recognized in the east margin of the Claudio Gay Cordillera (CGC), namely Termas de

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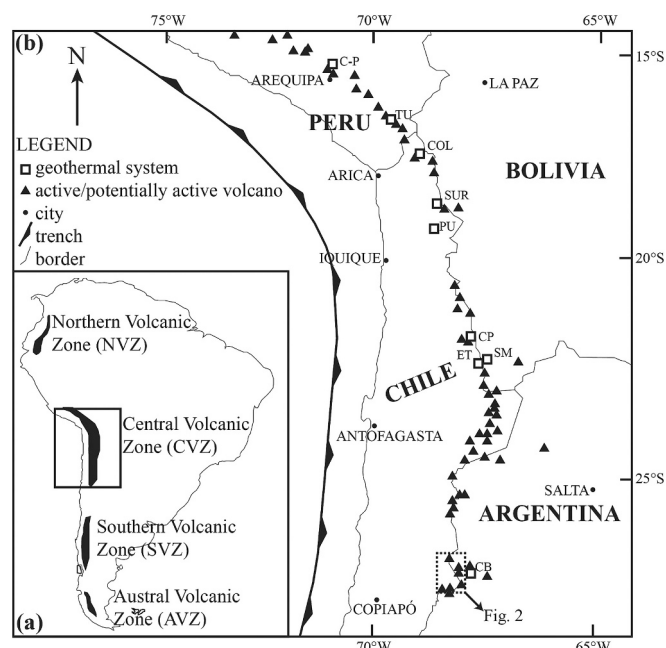


Fig. 1. (a) Location map of the Central Volcanic Zone (CVZ) of the Andes in South America. (b) detailed view of the CVZ with active and potentially active volcanic systems (triangles) and main geothermal areas (open squares). The dotted frame shows the study area presented in Fig. 2. C-P: Chivay-Pinchollo; TU: Tutupaca, Ancocollo, and other neighboring thermal areas (Vilcapona et al., 2022); COL: Colpitas (Inostroza et al., 2020); SUR: Surire; PU: Puchuliza; CP: Cerro Pabellon; ET: El Tatío (Tassi et al., 2010); SM: Sol de Mañana (Pereyra-Quiroga et al., 2023); CB: Cerro Blanco (Chiodi et al., 2019). The list of active and potentially active volcanoes is extracted from Aguilera et al. (2022).

Rio Negro (TRN) and Juncalito (JUN), where conductive zones were detected, and reservoir temperatures were estimated at 140–160 °C (Mayorga, 2011; Lira et al., 2011; García and Díaz, 2016).

Northern Chile and the Altiplano-Puna area contain volcanic emissions and thermal waters with anomalously high concentrations of As, Li, B, Cd, Sb, and Cu than other active volcanic zones within the Andean, Central American, or Lesser Antilles volcanic arcs (Tapia et al., 2019, 2021; Morales-Simfors et al., 2020; Inostroza et al., 2024). This phenomenon is closely linked to hydrothermal fluid circulation in porphyry and epithermal ore deposits, as well as volcanic activity in the presence of a thickened continental crust (Tapia et al., 2021; Murray et al., 2023; Inostroza et al., 2024). Despite some elements such as Li, Cu, and Mo correspond to strategic minerals and a pillar in the Chilean economy, others such as As, which exhibit a significant geochemical anomaly in northern Chile (Romero et al., 2003; Capaccioni et al., 2009; Tapia et al., 2021), are regarded as polluting elements impacting drinkable water, agriculture, and livestock of exposed communities.

This work presents and discusses the compositional and isotopic features of thermal fluids from LV, TRN, and JUN, as well as of springs from two areas, Salar de Piedra Parada (SPP) and Panteón de Aliste (PA), which have been poorly investigated. This work provides valuable information for the first time for JUN bubbling gases, besides trace element contents from thermal springs located in an area with natural anomalies of B, As, and other elements. The main aims are to (i) investigate the origin and evolution of thermal fluids, (ii) better constrain reservoir temperatures using silica and cation geothermometers, and (iii) determine the mechanisms regulating B and As anomalies characterizing these areas.

2. Geological setting

The study area (68.4–68.9° W; 26.3–26.9° S) pertains to the southern end of the CVZ of the Andes, a volcanically active zone including south Peru, west Bolivia, northwest Argentina, and northern Chile volcanoes (Fig. 1a), where a temperate and cold arid climate occurs (Köppen-Geiger classification; Peel et al., 2007). Being located 160 km northeast of Copiapó city (Fig. 1b), the study area lies within the La Puna, a high-altitude flat area with more than fifteen summits above 6000 m asl (Fig. 2) and endorheic basins hosting salt flats (i.e., Pedernales or Maricunga) and saline lakes (i.e., Santa Rosa, Negro Francisco). This area is overwhelmed by the Ojos del Salado volcano, the highest active volcano on Earth's surface (6893 m asl) with persistent fumarolic emissions, which lies at the southernmost end of the CVZ, delimiting a break in the volcanism to the south, attributed to the occurrence of flat slab segment between 28 and 33°S (Barazangi and Isacks, 1976; Stern, 2004).

The CGC is a north-south volcanic chain (Fig. 2) formed by volcanic structures such as Cerros Nevados de Juncalito (Lower Miocene andesitic lava flows and rhyodacitic lava domes), Cerro del Agua, and Agua de la Falda volcanoes (Middle Miocene andesitic to dacitic lava flows), built over an Oligocene to Lower Miocene basement formed by volcano-sedimentary rocks such as Estratos de Río Juncalito and the Sierra de Aliste sequence (Clavero et al., 2012). Following volcanic activity in the CGC area, the volcanic front shifted eastward during the Upper Miocene (9–5 Ma), reaching the current position and bringing the CGC to its present proximal forearc position (Mpodozis and Clavero, 2002; Clavero et al., 2012). Such activity built the Wheelwright, LV, and Mulas Muertas volcanoes. At ~5 Ma, an eruption that produced the Wheelwright ignimbrite of dacitic composition, mainly distributed northwest of the Wheelwright caldera (Clavero et al., 2012), occurred. Overlying the Wheelwright ignimbrite, volcanic activity was related to andesitic to dacitic lava flows emitted from Peñas Blancas, Ermitaño, and Cerro el Toro volcanoes (5–4 Ma), whose position was controlled by annular fractures of the Wheelwright caldera (Clavero et al., 2012). The LV ignimbrite (3–5 Ma; González-Ferrán et al., 1985; Mpodozis, 1995; Mpodozis et al., 1996), which corresponds to pyroclastic density currents of rhyolitic composition, covered the current position of the LV lake and depressions of the Wheelwright and Laguna Escondida calderas. During the Upper Pliocene (4–3 Ma), andesitic volcanic edifices were randomly distributed in the area, being Kunstmann, Negro Grande, and Rio Negro volcanoes the most prominent ones, located to the north of the LV lake (Clavero et al., 2012). The last vestiges of volcanic activity correspond to massive volcanic edifices composed of mostly dacitic lava flows, besides fallout and current density flows spread on the north, east, and south of LV lake (Clavero et al., 2012). The major volcanic structures that emerged during this period (from 2 to <1 Ma) are the Sierra Nevada and Falso Azufre Volcanic Complexes, along with the Incahuasi, Fraile, Tres Cruces, and Ojos del Salado volcanoes (Baker et al., 1987; Gardeweg et al., 1997; Clavero et al., 2012).

The primary structural domain in the study area consists of north-south high-angle reverse faults forming the CGC, caused by extensive regional deformation likely between 20 and 19 Ma (Mpodozis and Clavero, 2002; Clavero et al., 2012). To the east of the CGC, post-Upper Miocene volcanoes have craters and emission points arranged along northwest-southeast, northeast-southwest, and east-west lineaments. This suggests that the pre-volcanic basement contains structures that allow magma to ascend to the surface (Clavero et al., 2012).

Surficial hydrothermal manifestations (Fig. 2) originate from TRN, JUN, and LV (Risacher et al., 2011; Navarrete, 2012), while PA and SPP consist of warm springs. A brief description of each sampling site, with geological information from Clavero et al. (2012) and Naranjo et al. (2016), is here reported:

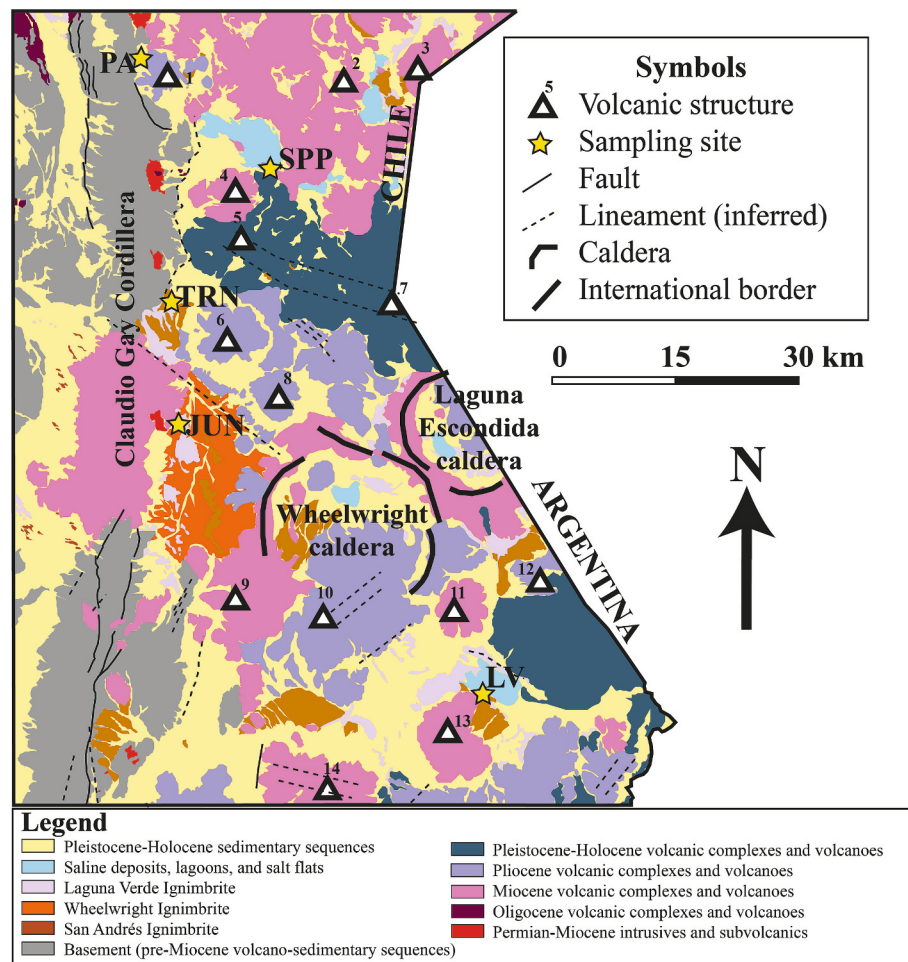


Fig. 2. Map of the study area (68.2–68.9° W; 26.3–26.9° S) showing the Claudio Gay Cordillera (CGC) and relevant volcanic structures. Yellow stars are the sampling sites such as Panteón de Aliste (PA), Salar de Piedra Parada (SPP), Termas de Río Negro (TRN), Juncalito (JUN), and Laguna Verde (LV). White triangles with volcano names are: (1) Panteón de Aliste, (2) Lagunas Bravas, (3) Tridente, (4) Piedra Parada, (5) Azufrera de los Cuyanos Volcanic Complex, (6) Río Negro, (7) Sierra Nevada, (8) Negro Grande, (9) Pircas de Indios, (10) Peñas Blancas, (11) Laguna Verde, (12) Kunsmann, (13) Mulas Muertas, (14) Barrancas Blancas. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.1. Panteon de Aliste (PA)

Warm spring emerging in the Estratos Quebrada Aliste (Upper Miocene) unit, consisting of sandstones, breccias, and scoriaceous pyroclastic flow deposits, on the northwest flank of the Panteón de Aliste volcano (Fig. 2). The permanent water flow from the spring develops wetlands with abundant native flora and fauna (Villa, 2015).

2.2. Salar de Piedra Parada (SPP)

Springs emerging in the south margin of the Piedra Parada salt flat, on the northeast flank of the Piedra Parada volcano (Fig. 2), at the geological contact between andesitic lava flows and evaporitic deposits. The springs feed small streams that infiltrate beneath the salt crust. These waters have a sodium-chloride composition and temperatures from 12 to 16 °C (Risacher et al., 1999).

2.3. Termas de Río Negro (TRN)

Hot springs emerging at the base of the Río Negro Creek and on the LV ignimbrite at the northwest flank of the Río Negro volcano (Fig. 2). The thermal area includes a ~ 7 m diameter bubbling pool and small pools, while other springs emerge throughout the Río Negro Creek. Risacher et al. (2011) state that circumneutral waters of TRN emerge at 40.2 °C and have a sodium-chloride composition.

2.4. Juncalito (JUN)

Hot springs with bubbling gases occurring at the base of a valley carved on the Wheelwright ignimbrite. There is a central pool of 3 m in diameter with persistent gas bubbling and small bubbling gas emissions. The thermal springs create a small stream that flows into the Juncalito River. JUN waters have neutral to slightly acidic pH, temperatures up to 54 °C, and a sodium-chloride/sulfate composition (Navarrete, 2012).

2.5. Laguna Verde (LV)

Up to twenty thermal springs occurring at the LV lake's southwest border, emerging from small fissures within the LV ignimbrite. Some pools have a diameter of 2 m, with temperatures up to 47 °C, pH of ~7.5, and a sodium-chloride composition (Risacher et al., 2011; Alam and Muñoz, 2024). This area is highlighted because of high As concentrations, up to 23 times over the international guidelines for drinkable water (i.e., 0.01 ppm), besides high B and Li contents (Risacher et al., 1999; Alam and Muñoz, 2024).

2.6. Other relevant thermal areas

The Ojos del Salado volcano, located 26 km south of LV Lake, shows permanent fumarolic emissions near its summit. Fumarolic activity melts ice and snow, forming a rivulet with acid water (pH 2.1; Aszalós

et al., 2020) that flows downslope for about 100 m, culminating in a lake of approximately 350 m² at an elevation of around 6500 m asl.

Different hydrothermal manifestations have been reported to occur at the Cerro Blanco (CB) caldera, 70 km east of LV, where the principal manifestations are CB fumaroles, El Médano springs, and Los Hornitos bubbling pools (Chiodi et al., 2019). CB fumarolic gases reach outlet gas temperatures of up to 93.7 °C and are dominated by CO₂ and non-negligible H₂S contents (Chiodi et al., 2019). Bubbling pools reach up to 67 °C and have circumneutral sodium-chloride/bicarbonate waters, while the gas phase is dominated by CO₂ with significant contents of N₂ (Chiodi et al., 2019). In this area, preliminary estimations based on the chalcedony, K–Mg, and Li–Mg geothermometers suggest reservoir equilibrium temperatures up to 135 °C (Chiodi et al., 2019).

3. Methods

3.1. Water sampling

Samples for the analysis of the main anions were collected and stored in 50 mL polyurethane flasks. Samples for the analysis of the main cations were filtered (0.45 µm) and acidified (Suprapur® HCl 1 vol%) in the field. Samples for silica determination were filtered (0.45 µm) and diluted (1:10) to prevent silica precipitation. Samples for the analysis of trace elements were filtered (0.45 µm) and acidified (1 vol% of Suprapur® HNO₃). The analyses of oxygen and hydrogen stable isotopes (δ¹⁸O–H₂O and δD–H₂O, respectively) were carried out on samples collected in 12 mL glass flasks equipped with a rubber pierceable septum after filtering at 0.45 µm.

Water temperature, pH, and electrical conductivity were measured in situ using a multiparametric instrument (Hanna Instruments HI991301), except for waters having temperatures >50 °C, which were measured using a thermocouple (Hanna Instruments HI935002 and HI766CL).

3.2. Bubbling gases sampling

Gases from bubbling pools were collected using a plastic funnel and a silicone tube. Bubbling gases were collected in 60 mL pre-evacuated glass ampoules filled with 0.15 M Cd(OH) and 4 M NaOH suspension, according to the procedure described by Montegrossi et al. (2001) and Vaselli et al. (2006). Additionally, 60 mL pre-evacuated and empty ampoules were used to analyze noble gases. The carbon isotopic composition (δ¹³C) in CH₄ and CO₂ was analyzed in samples stored in the 12 mL glass vials equipped with a rubber pierceable septum.

3.3. Analytical procedures

Chemical analyses of water samples were carried out at the Laboratory of Fluid Geochemistry at the University of Florence (UNIFI), Italy. Anions and cations were analyzed by Ion Chromatography (IC; Metrohm IC models 761 and 861, respectively), while the HCO₃[–] and CO₃^{2–} contents were determined via Acidimetric Titration (AT) (Metrohm Basic Titrino). The concentrations of minor and trace elements (Si, Al, Sb, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ba, Pb, As, Rb, and Sr) were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES Perkin Elmer, Optima 8000). The analytical error for IC and AT analyses was <5 %, while ICP-OES analyses had an error of <10 %.

The δ¹⁸O–H₂O and δD–H₂O values were determined at the Laboratory of Stable Isotopes Geochemistry at UNIFI by Cavity-Ring Down Spectroscopy (CRDS) using a Picarro L2130i instrument calibrated using IAEA international standards. Measurement precisions, also based on the repeated analysis of in-house standards, were ± 0.67 ‰ for δD and ± 0.09 ‰ for δ¹⁸O. The analytical errors were ± 0.34 ‰ for δD and ± 0.055 ‰ for δ¹⁸O.

Gases were analyzed at the Laboratory of Fluid Geochemistry (UNIFI). Inorganic and organic species in the headspace of the glass

ampoule were analyzed by Gas Chromatography (GC) using three instruments: Shimadzu 15 A, Shimadzu 14, and Thermo Focus. The analytical error of the GC analysis was <10 %. Liquid and solid phases of the suspension were separated by centrifugation: the liquid phase was analyzed by AT (Basic Titrino) to determine CO₂ as CO₃^{2–} and by IC (Metrohm 761) for SO₂, HCl, and HF as SO₄^{2–}, Cl[–], and F[–], respectively. Cadmium sulfide in the separated solid phase, produced by the combination of Cd and H₂S during the gas sampling, was oxidized to SO₄^{2–} using H₂O₂ and analyzed by IC (Metrohm 761) (Montegrossi et al., 2001).

The carbon isotopic composition (δ¹³C = ((¹³C/¹²C)_{sample} / (¹³C/¹²C)_{standard}) - 1) of CO₂ and CH₄ (δ¹³C–CO₂ and δ¹³C–CH₄, respectively, expressed in ‰ vs. V-PDB) was analyzed at the Laboratory of Stable Isotopes Geochemistry (UNIFI) by CDRS using a Picarro G2201-i. The precision was 0.16 ‰ for δ¹³C–CO₂ and 1.15 ‰ for δ¹³C–CH₄.

The ³He/⁴He and ⁴He/²⁰Ne ratios were determined at the Noble Gas Isotope Laboratory of the Istituto Nazionale di Geofisica e Vulcanologia (INGV), Palermo, Italy. Helium isotopes were measured using a Helix SFT (GVI) mass spectrometer, while ²⁰Ne was measured using a Helix MC plus (Thermo). The ³He/⁴He ratios were reported as R/R_a, where R is the ³He/⁴He measured in the sample normalized to the same ratio in the atmosphere (R_a = 1.39 × 10^{–6}; Mamyurin and Tolstikhin, 1984). The sample injection, purification, and standard procedures followed the internal protocols described by Rizzo et al. (2015, 2019). The analytical error was <1 %. The ³He/⁴He ratios were corrected for atmospheric contamination based on the ⁴He/²⁰Ne measured in each sample and are reported as R_c/R_a as follows:

$$R_c/R_a = ((R/R_a) - r) / (1 - r)$$

where $r = ({}^4\text{He}/{}^{20}\text{Ne})_{\text{air}} / ({}^4\text{He}/{}^{20}\text{Ne})_{\text{meas}}$; $({}^4\text{He}/{}^{20}\text{Ne})_{\text{air}} = 0.318$ (Ozima and Podosek, 1983) and $({}^4\text{He}/{}^{20}\text{Ne})_{\text{meas}}$ is the ⁴He/²⁰Ne measured in the sample.

4. Results

Water and gas samples were collected in January 2020. Tables 1 and 2 present the location, physical parameters, and chemical composition of major compounds and trace elements, as well as the δ¹⁸O–H₂O, δD–H₂O, δ¹³C–CO₂, δ¹³C–CH₄, R/R_a, R_c/R_a, and ⁴He/²⁰Ne values.

4.1. Chemical and isotopic composition of waters

Outlet temperatures of the thermal springs ranged from 14.0 to 53.3 °C (Table 1), with minimum and maximum temperatures measured at the LV springs. LV, TRN, PA, and SPP had a circumneutral pH, while JUN showed a slightly acidic pH (5.69 to 5.84). Springs at LV (>11 mS/cm) and SPP (15 mS/cm) had relatively high conductivity values, while those of the other sites ranged from 2.2 to 6.9 mS/cm.

Chloride concentrations ranged from 304 to 5020 mg/L, with the highest in LV and SPP and the lowest in JUN. Sulfate ranged from 343 to 2122 mg/L, with minimum and maximum concentrations at LV. Bicarbonate showed the highest concentrations (278–565 mg/L) at PA and JUN. Fluorine concentrations were < 5 mg/L, except for the SPP (19 mg/L). Bromine concentrations ranged from 0.29 to 4 mg/L, with maximum values in SPP. Sodium concentrations ranged from 350 to 3616 mg/L, while those of potassium were from 28 to 247 mg/L, with the highest values for LV and SPP and the lowest in JUN and TRN. Calcium ranged from 38 to 425 mg/L, showing the highest concentrations in PA, SPP, TRN, and occasionally at JUN. Magnesium concentrations were in a wide range (7.1 to 219 mg/L), with the highest values in SPP and two LV samples (Table 1). The highest Li concentrations, up to 15.8 mg/L, were measured in LV and SPP, while those of PA, TRN, and JUN were < 7.1 mg/L. Boron concentrations ranged from 0.6 to 13.5 mg/L, with the highest values in SPP and some LV and JUN samples.

Table 1
Major and trace element concentration for Atacama thermal springs. The sampling date, coordinates (UTM WGS 84), and physical and chemical parameters are shown. Isotopic composition for oxygen and deuterium are expressed in ‰ vs. V-SMOW. NA: not applicable or not determined.

Cod	Site	Date	dd-mm-yy	North	East	Altitude	Temperature	pH	Conductivity	CO ₃ ²⁻	HCO ₃ ⁻	F ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	NH ₄ ⁺	Li ⁺	B	SiO ₂	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Sb	Ba	Pb	δ ¹⁸ O		
				m	m	m asl	°C		mS/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	‰
LV-01	Laguna Verde	18-01-2020	7025624	551018	4324	53.3	7.27	>20	NA	257	4.9	3649	2.5	5.9	1641	109	123	3058	247	NA	15.8	4.5	67	442	19	12	316	0.35	44.0	29	195	1162	289	1164	4.4	93	12	NA	NA		
LV-02	Laguna Verde	18-01-2020	7025599	551099	4223	41.3	7.24	6.0	NA	228	1.5	1257	0.91	5.0	631	46	14	1147	89	6.3	2.4	2.5	68	233	19	81	192	0.26	12.0	14	202	978	193	648	2.5	79	91	-9.8	-76.0		
LV-03	Laguna Verde	18-01-2020	7028789	548293	4334	14.0	8.18	3.0	NA	93	0.87	482	0.41	7.2	343	38	8.0	399	43	1.2	1.2	1.2	33	217	23	3.6	134	0.12	8.9	8.5	207	1412	70	2357	0.31	84	3.5	-12.9	-94.5		
LV-04	Laguna Verde	18-01-2020	7026368	549947	4333	25.2	7.64	6.9	NA	156	1.2	1648	1.3	4.6	666	55	34	1335	87	6.8	4.1	3.8	42	478	37	185	388	0.45	16.0	31	543	1787	143	1315	3.4	81	15	NA	NA		
LV-05	Laguna Verde	18-01-2020	7026363	549971	4328	26.6	7.33	1.1	NA	166	5.0	5020	3.5	5.7	2122	113	126	3616	241	15	8.4	13.5	43	462	42	99	436	0.49	14.0	42	356	2831	486	2574	2.1	109	12	NA	NA		
PA-01	Pantoon de Aliste	19-01-2020	7095363	512860	4088	22.5	6.46	5.1	NA	565	1.1	969	1.5	5.9	666	277	67	692	53	NA	3.1	6.1	48	869	9.8	44	248	0.33	7.33	23	195	2242	756	3397	1.5	123	4.7	-11.8	-92.4		
PA-02	Pantoon de Aliste	19-01-2020	7095321	512788	4088	21.2	6.47	4.9	NA	512	0.91	824	1.2	5.8	615	263	34	669	56	NA	4.4	3.9	48	1247	18	180	353	0.70	15.8	34	617	1530	490	2284	4.3	202	11	NA	NA		
SPP-01	Salár Piedra Parada	19-01-2020	7082829	528217	4130	22.8	7.34	1.5	NA	87	19	4352	4.0	6.7	2407	485	219	2638	201	NA	9.0	8.7	34	753	7.3	22	975	0.23	6.0	23	1154	858	476	5718	1.3	99	2.8	NA	NA		
TRN-01	Termas Río Negro	19-01-2020	7067710	518004	4115	40.7	7.27	3.1	NA	57	3.3	715	1.7	5.1	379	154	7.1	423	45	1.2	1.6	0.7	64	413	3.0	9	73	0.32	8.8	10	199	339	63	755	1.3	154	3.0	-8.6	-75.0		
TRN-02	Termas Río Negro	19-01-2020	7067660	517972	4097	40.0	7.07	4.2	NA	63	2.7	958	1.3	4.1	535	242	18	506	71	NA	3.0	2.5	72	860	15	141	301	0.35	13.3	25	1428	1430	174	2994	1.8	278	6.0	NA	NA		
TRN-03	Termas Río Negro	19-01-2020	7067150	517410	4034	30.6	7.02	NA	NA	69	2.2	1396	1.1	3.9	578	223	51	797	78	NA	3.1	2.9	69	1342	7.3	34	438	0.50	4.5	43	1130	965	188	2441	2.9	213	10	NA	NA		
TRN-04	Termas Río Negro	19-01-2020	7067314	517209	4029	34.9	7.50	3.4	NA	61	2.6	832	1.7	5.8	542	205	26	478	68	5.5	1.4	1.8	65	915	8.7	14	313	0.26	5.7	18	506	725	181	1800	1.3	234	3.7	NA	NA		
JUN-01	Juncalito	20-01-2020	7055469	518378	4156	32.4	5.69	5.7	NA	439	3.1	1011	1.2	0.40	1503	400	69	800	50	NA	7.1	9.9	32	547	14	1861	3300	0.30	7.4	89	187	2660	265	3428	0.77	84	2.8	-8.8	-79.0		
JUN-02	Juncalito	20-01-2020	7055433	518357	4161	32.3	5.84	2.9	NA	394	0.94	419	0.57	0.45	406	82	21	464	34	2.2	5.9	5.2	28	402	13	328	1174	0.33	5.7	33	325	1785	132	882	0.53	122	1.7	NA	NA		
JUN-03	Juncalito	20-01-2020	7055446	518348	4155	32.1	5.69	4.0	NA	357	4.3	524	0.44	1.8	1461	425	70	548	60	NA	4.7	5.8	33	541	14	38	509	0.38	20.3	106	612	813	28	559	1.3	145	5.5	-9.3	-81.0		
JUN-04	Juncalito	20-01-2020	7055435	518321	4159	24.7	5.75	2.2	NA	278	1.1	304	0.29	0.36	367	97	21	350	28	5.9	4.0	3.9	303	6.4	207	906	0.94	3.9	15	164	900	114	775	3.1	99	1.2	NA	NA			

Table 2
Chemical (expressed in mmol/mol) and isotopic composition of Juncalito bubbling gases. The isotopic composition of CO₂ and CH₄ are expressed in ‰ vs. V-PDB, whereas R/Ra and Rc/Ra correspond to uncorrected and corrected helium ratios, respectively. M, L, and S represent mantle, and organic-rich sediments, respectively, determined using the procedure of Sano and Marty (1995). NA: not applicable or not determined. Bdl: below the detection limit.

Location	CO ₂	H ₂ S	N ₂	Ar	O ₂	H ₂	CO	He	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₄ H ₆	CH ₄ /(C ₂ H ₆ + C ₃ H ₈)	δ ¹³ C- CO ₂	δ ¹³ C- CH ₄	R/ Ra	Rc/ Ra	⁴ He/ ²⁰ Ne	M	L	S	
JUN-1	934	bdl	63	1.60	0.95	bdl	bdl	0.0009	0.03	0.00031	0.000081	0.000022	0.00011	79.28	-11.5	-36.3	1.37	1.57	0.9	0.96	%	60.67	38.37
JUN-2	947	bdl	51	1.20	0.51	bdl	bdl	0.0007	0.03	0.00022	0.000064	0.000016	0.00016	98.59	-12.9	-39.1	NA	NA	NA	NA	NA	NA	NA
JUN-3	899	bdl	97	2.40	1.10	bdl	bdl	0.0015	0.05	0.00045	0.000088	0.000071	0.00019	83.64	-10.7	-34.4	1.51	1.72	1.1	1.03	%	63.88	35.09
JUN-4	954	bdl	44	1.10	0.88	bdl	bdl	0.0009	0.056	0.00063	0.000120	0.000051	0.00013	74.67	-11.6	-32.2	NA	NA	NA	NA	NA	NA	NA

Strontium showed the highest concentrations from 559 to 5718 $\mu\text{g/L}$, followed by As, with concentrations ranging from 339 to 2831 $\mu\text{g/L}$. In general terms, most of the sites showed concentrations $>1000 \mu\text{g/L}$ for Sr and As. Iron, Al, and Zn concentrations ranged from 73 to 1428, whereas Rb, Mn, and Ba were 28–756, 3.6–1861, and 79–278 $\mu\text{g/L}$, respectively. Copper, Cd, and Ni concentrations were $<113 \mu\text{g/L}$, while Pb, Sb, and Co concentrations were generally $<10 \mu\text{g/L}$.

The $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ values were in a narrow range, from -12.9 to -8.6 ‰ and from -94.5 to -75 ‰ vs. V-SMOW, respectively (Table 1).

4.2. Chemical and isotopic composition of bubbling gases

Bubbling gases were CO_2 -rich (899–954 mmol/mol) and showed significant concentrations of N_2 (44–97 mmol/mol) and minor concentrations of O_2 (<1.1 mmol/mol). Methane concentrations were 0.028–0.056 mmol/mol, whereas those of Ar and He were 1.1–2.4 and 0.0007–0.0015 mmol/mol, respectively. Light hydrocarbons concentrations were <0.00063 mmol/mol (Table 2).

The $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$ values ranged from -12.9 to -10.7 and -39.1 to -32.2 vs. V-PDB, respectively (Table 2). The helium ratios from JUN samples were 1.37 and 1.51 Ra (Table 2).

5. Discussion

5.1. Chemical and isotopic composition of waters

The $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ values of the thermal waters suggest that they originated by meteoric water likely infiltrating between 4000 and 4500 m asl according to the trend of the altitudinal $\delta^{18}\text{O-H}_2\text{O}$ gradient of -3.1 ‰/km (Urrutia et al., 2022; Fig. 3). These waters were affected by (i) isotope fractionation due to evaporation and/or (ii) mixing with magmatic/andesitic water (Taran et al., 1989; Giggenbach, 1992) (Fig. 3). However, the lack of a significant correlation between Cl^- concentrations and $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ values (Fig. 4) suggests that a magmatic water contribution is unlikely.

Most thermal waters had a $\text{Cl}^-(\text{SO}_4^{2-})\text{-Na}^+$ composition (Fig. 5, Table 1), which is typical of springs located in volcanic environments and suggesting a contribution from a hydrothermal system located at

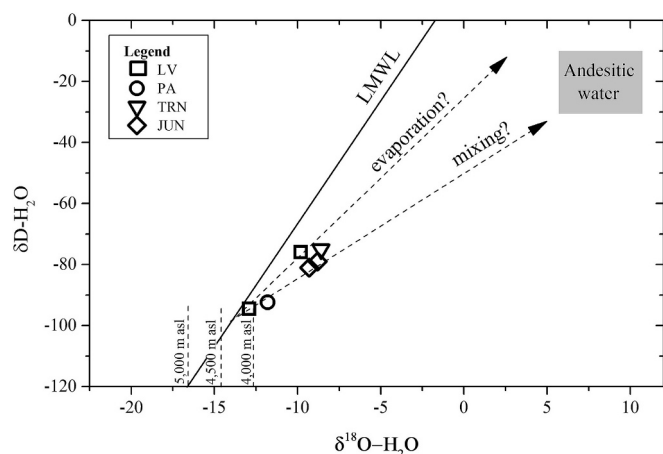


Fig. 3. $\delta^{18}\text{O-H}_2\text{O}$ vs. $\delta\text{D-H}_2\text{O}$ binary diagram (expressed in ‰ vs. V-SMOW) for thermal springs from the Atacama region. The Local Meteoric Water Line (LMWL) from Boschetti et al. (2019), is reported. The evaporation line for the southern part of the Altiplano-Puna area ($\delta\text{D} = 5.2 \cdot \delta^{18}\text{O} - 25.4$) from Valdivieso et al. (2022), where groundwaters and surface waters approach into similar values, is also reported. The grey box represents the field of andesitic waters (Taran et al., 1989; Giggenbach, 1992). Dotted lines in the $\delta^{18}\text{O-H}_2\text{O}$ axis show the oxygen isotope variation with altitude in the Altiplano area, extracted from Urrutia et al. (2022).

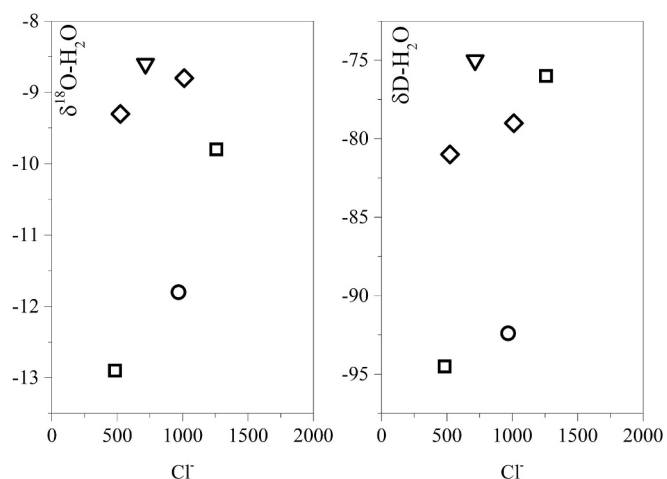


Fig. 4. Cl^- versus $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ binary diagrams for thermal springs from the Atacama region. Chlorine concentrations are in mg/L, $\delta^{18}\text{O-H}_2\text{O}$ and $\delta\text{D-H}_2\text{O}$ values are in ‰ vs. V-SMOW. Symbols as Fig. 3.

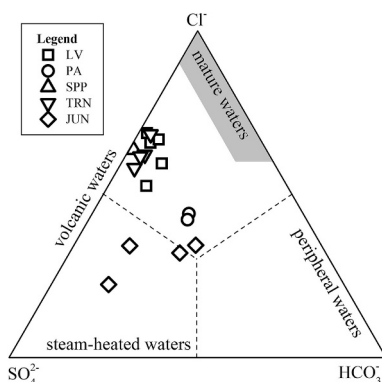


Fig. 5. HCO_3^- - Cl^- - SO_4^{2-} ternary diagram for thermal springs from the Atacama region.

depth (Giggenbach, 1991; Nicholson, 1993); a magmatic source could be discarded, given that $\delta\text{D-H}_2\text{O}$ and $\delta^{18}\text{O-H}_2\text{O}$ values show a predominantly meteoric source of waters (Fig. 2 and Fig. 3). JUN waters had SO_4^{2-} as dominant anions (Fig. 5), possibly due to (i) interaction with hydrothermally altered rocks and/or (ii) dissolution of H_2S -rich vapors. The first hypothesis is supported by the occurrence of a hydrothermally altered porphyry intrusion and a dacitic lava dome on the southeast flank of the Agua de la Falda volcano immediately to the west of the bubbling pools (Clavero et al., 2012). On the other hand, interaction with hydrothermal gases, typically rich in CO_2 and H_2S , is indicated by the relatively low pH and high HCO_3^- contents of these waters (Table 1). The PA water shows a relatively higher HCO_3^- concentration and is relatively poor in Cl^- . This suggests that this site represents a distal discharge relative to the main hydrothermal system (Giggenbach, 1991), consistent with the peripheral position of this emergence (Fig. 2).

TRN and SPP samples fall along the Na/Cl molar ratio of 1 (Fig. 6a), while low salinity waters at PA and JUN appear with molar ratios slightly above unity. Then, LV presented higher Na/Cl than the stoichiometric ratio expected for typical geothermal brines (Giggenbach, 1997). Given Cl^- is characterized by a conservative behavior in hydrothermal solutions, higher Na/Cl ratios are explained by water-rock interaction including Na-silicates within hydrothermal aquifers, especially in the case of LV, and to a lesser extent in PA and JUN sites.

Thermal spring from the Atacama region appears to follow two geochemical trends, namely trend A and trend B (Fig. 6). Low and high salinity samples from TRN, SPP, and, to a lesser extent, LV, follow trend

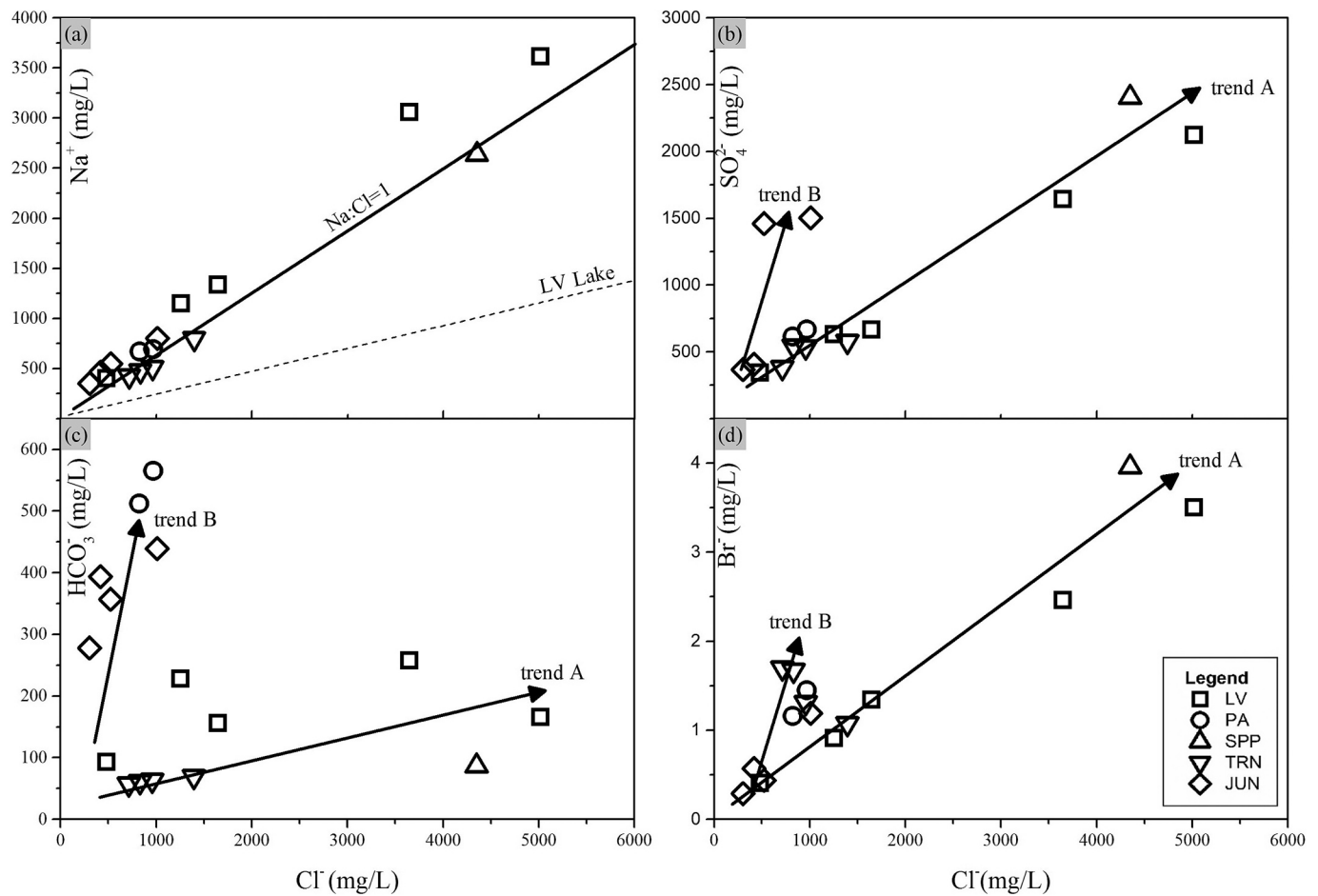


Fig. 6. Cl^- vs. Na^+ , SO_4^{2-} , HCO_3^- , and Br^- binary diagrams (in mg/L) for thermal springs of the Atacama region. Dashed line in a) shows mixing lines considering the Na^+ and Cl^- composition of the LV lake (data extracted from Alam and Muñoz, 2024), while the solid line depicts the Na/Cl molar ratio = 1. Trends A and B were constructed based on apparent data tendencies observed in binary diagrams.

A, showing relatively good correlation among Cl^- , Na^+ , SO_4^{2-} , Br^- , and HCO_3^- concentrations, resembling the dilution of a geothermal end-member with negligible Cl^- contribution from other sources. In contrast,

JUN (trend 2; Fig. 6b) appears to receive SO_4^{2-} from different sources, likely related to the leaching of hydrothermally altered volcanic rocks and/or H_2S dissolution in the aquifer, as mentioned above. At the same

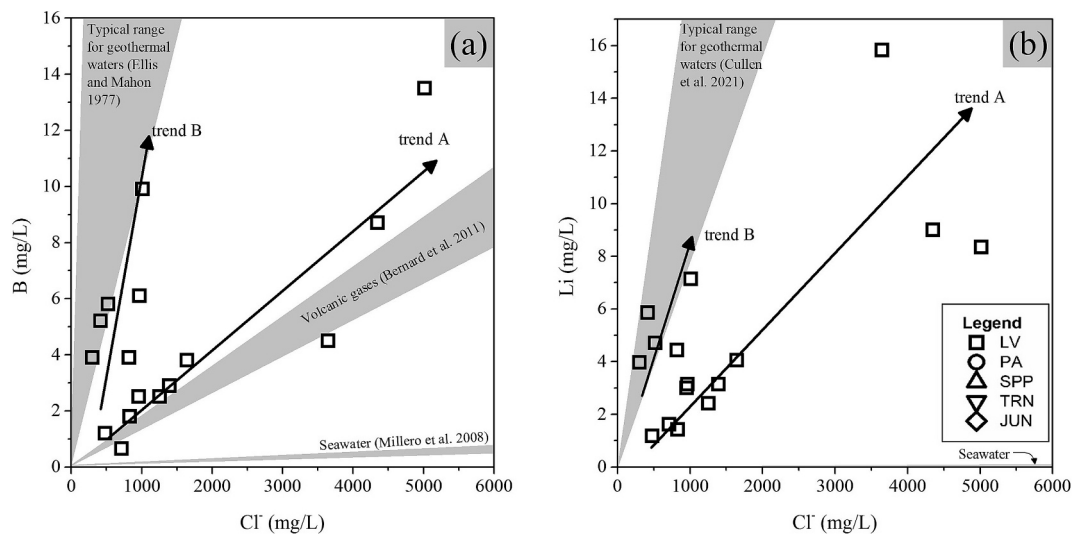


Fig. 7. Cl^- vs. B and Li binary diagrams for thermal spring from the Atacama region. The grey area shows the typical Cl/B ratios for geothermal waters (10–100; Ellis and Mahon, 1977), seawater ($\sim 10,000$; Millero et al., 2008), and volcano degassing (550–750; Bernard et al., 2011). The grey area shows typical Cl/Li ratios for geothermal waters (50–125; e.g., Cullen et al., 2021) and seawater ($\sim 1 \times 10^7$; Schroeder, 1978; Millero et al., 2008). Trends A and B were constructed based on apparent data tendency observed in binary diagrams.

time, JUN and PA springs present a bicarbonate excess (Fig. 6c), which may be ascribed to the dissolution of geogenic CO_2 remainder beneath the CGC, in agreement with the occurrence of bicarbonate waters at these sites. Variation in Br and Cl contents would reflect halite precipitation/dissolution processes involving brines in sedimentary basins (Martini et al., 1998; Siemann and Schramm, 2000). Higher Br/Cl ratios in the samples located in trend B may suggest halite precipitation, which also agree with low Na^+ and Cl^- contents in PA and TRN springs. Though, halite has not been reported previously at these springs.

A relatively good correlation among Cl, B, and Li (trend A; Fig. 7) indicates that such concentrations would be related to mixing hot and cold waters in the upflow zone. The Cl/B ratios for Atacama thermal springs are within the range of 77 and 1100 (Fig. 7a), higher than those typical of geothermal waters (10–100; Ellis and Mahon, 1977). Formation of B-bearing secondary minerals or high Cl/B steam feeding such springs (Arnórsson and Andrésdóttir, 1995) may explain this geochemical feature at LV, TRN, and SPP sites (trend A; Fig. 7a). High Cl/B ratios at LV springs correspond to some extent with the Cl/B ratios of the LV lake (224–537; Alam and Muñoz, 2024) suggesting the LV spring's influence on the chemistry of the LV lake. Conversely, JUN springs follow trend B with Cl/B ratios of 77–102 (Fig. 7a). Higher B concentrations relative to Cl could be ascribed to (i) absorption of deeper gaseous B into shallow water levels or (ii) the influence of volcano-sedimentary horizons containing organic matter (Giggenbach, 1995), such as the lacustrine facies of the Estratos de Rio Juncalito sequence (e.g., Clavero et al., 2012). The relatively low temperature of JUN springs makes the first hypothesis unlikely. Alternatively, B may derive from volcano-sedimentary layers forming the basement of the CGC, a process likely facilitated by the increased thermal gradient due to north-south faults allowing the passage of deep hydrothermal fluids. A similar process is believed to be for PA springs, whose chemistry would also be influenced by volcano-sedimentary rocks forming the basement of the CGC.

Trend B in Fig. 7b shows a Li enrichment in JUN springs, and to a lesser extent in PA ones. High Li contents are frequently related to the leaching of rhyolitic volcanic products in the presence of heated aqueous solutions (Nicholson, 1993). JUN and PA are placed in the CGC, which volcano-sedimentary successions include pyroclastic tuffs and breccias, and porphyry bodies of rhyolitic composition, such as those found in La Tabla (Carboniferous-Permian) and Pantanoso (Permian) Formations (Naranjo et al., 2016; Clavero et al., 2012). Therefore, it is believed that water-rock interaction in a reservoir containing these rhyolitic products may be responsible for high Li contents, and then lower Cl/Li ratios found in JUN and PA springs (Fig. 7b).

5.2. Origin of bubbling gases

The N_2/Ar and N_2/He ratios indicate a predominant meteoric origin of JUN gases (ASW; N_2/Ar ratios of 38, Giggenbach, 1992), consistent with the composition of Los Hornitos and El Médano (Chiodi et al., 2019), two thermal areas within the CB caldera (Fig. 8). Although a predominant meteoric origin, a minimal extra-atmospheric source of He is observed in these samples, given the higher $^4\text{He}/^{20}\text{Ne}$ ratio (~ 1) compared to the same ratio in the air ($^4\text{He}/^{20}\text{Ne} = 0.27$; Pinti et al., 2019). Moreover, $^3\text{He}/^4\text{He}$ ratios of 1.37 and 1.51 Ra (Table 2) reflect a dominant atmospheric end-member mixed with a small fraction of mantle-derived and crustal helium, which are expected to have 1 Ra, 8 ± 1 Ra, and 0.02 Ra, respectively (Oxburgh et al., 1986; Graham, 2002). This can be observed in a classical $^4\text{He}/^{20}\text{Ne}$ vs. R/Ra plot (Fig. 9), where JUN bubbling gases well approach the air end-member. A $^3\text{He}/^4\text{He}$ signature of ~ 1.5 Ra is much lower than expected in active volcanoes of the CVZ (> 7 Ra; Robidoux et al., 2020), but it is relatively close to the signature found at CB caldera (1.1 and 2.1 Ra; Chiodi et al., 2019) and in low-temperature fluids from the CVZ (Fig. 9; Robidoux et al., 2020; Lages et al., 2021; Barry et al., 2022, 2025). A faint magmatic signal from JUN and other low-temperature springs in the CVZ is likely

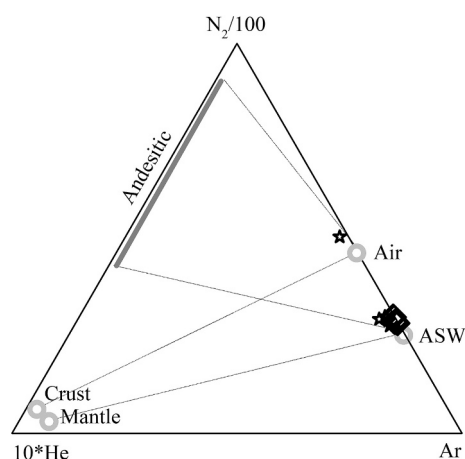


Fig. 8. Ar- $\text{N}_2/100$ - 10He ternary diagram (Giggenbach and Matsuo, 1991; Giggenbach, 1996) for JUN bubbling gases. The andesitic field, the air, crust, mantle, and ASW (Air-saturated water at 20 °C) endmembers are reported (Giggenbach, 1996). Stars are CB fumarolic gases, Los Hornitos bubbling gases, and El Médano springs (Chiodi et al., 2019).

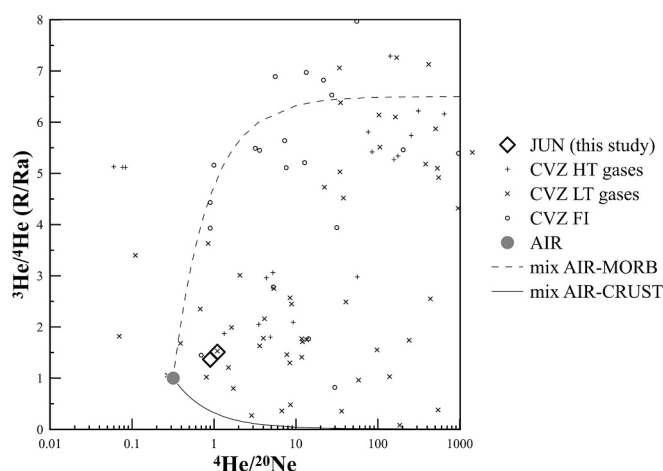


Fig. 9. $^4\text{He}/^{20}\text{Ne}$ vs. R/Ra binary diagram for JUN bubbling gases (open rhombuses) compared to literature data from the CVZ by Lages et al. (2021) and references therein. Mantle: R/Ra of 8 ± 1 (Graham, 2002) and $^4\text{He}/^{20}\text{Ne}$ of 1000 (Sano and Wakita, 1985); crust: R/Ra of 0.02 (Oxburgh et al., 1986) and $^4\text{He}/^{20}\text{Ne}$ of 1000 (Sano and Wakita, 1985); and Air: R/Ra = 1 (atmospheric) and $^4\text{He}/^{20}\text{Ne}$ of 0.270. The solid and dashed lines represent hypothetical mixing between air-crust and air-MORB end members (e.g., Pinti et al., 2019), respectively. +: high-temperature (HT) gases; x: low-temperature (LT) gases; °: fluid inclusions (FI).

produced by a thick continental crust (~ 70 km thick; Heit et al., 2014) with U- and Th-rich rocks and prolonged residence times of melts within the crust (Sano and Fischer, 2013).

The $\delta^{13}\text{C}\text{-CO}_2$ values of the JUN gases (-12.9 to -10.7 ‰ vs. V-PDB) are slightly lighter than typical mantle-derived gases (-6.5 ± 2.5 ‰ vs. V-PDB; Sano and Marty, 1995), suggesting a possible mixing between deep magmatic and shallow biogenic CO_2 , the latter incorporated from organic-rich sediments such as those of the Estratos de Rio Juncalito sequence. However, a ^{12}C enrichment may be due to secondary processes such as calcite precipitation or multi-step CO_2 dissolution within the conduits feeding thermal springs (Venturi et al., 2017), masking the original isotopic signature. Although calcite precipitation is likely to occur within hydrothermal systems (Chiodini et al., 2015; Güleç and Hilton, 2016), no surficial evidence of calcite or presence of Ca-Al-silicates, which can be converted into calcite through the reaction

with deep CO₂ (Giggenbach, 1984), have been reported in the JUN area.

Therefore, excluding the significant influence of secondary processes on the $\delta^{13}\text{C}$ -CO₂ values, the relative CO₂ contributions of crustal, i.e. carbonate-rich sediments (L), and organic-rich sediments within the crust (S), and mantle (M) sources was computed according to the approach proposed by Sano and Marty (1995) using the following equations:

$$(\delta^{13}\text{C}-\text{CO}_2)_{\text{meas}} = M(\delta^{13}\text{C}-\text{CO}_2)_{\text{MORB}} + L(\delta^{13}\text{C}-\text{CO}_2)_{\text{Lim}} + S(\delta^{13}\text{C}-\text{CO}_2)_{\text{Sed}} \quad (1)$$

$$1/(\text{CO}_2/{}^3\text{He})_{\text{meas}} = M/(\text{CO}_2/{}^3\text{He})_{\text{MORB}} + L/(\text{CO}_2/{}^3\text{He})_{\text{Lim}} + S/(\text{CO}_2/{}^3\text{He})_{\text{Sed}} \quad (2)$$

$$M + L + S = 1 \quad (3)$$

subscripts *meas*, *MORB*, *Lim*, and *Sed* refer to the values measured in the sample and proxies to the mantle, limestones, and sediments (organic-rich sediments), respectively. Endmembers are: $(\delta^{13}\text{C}-\text{CO}_2)_{\text{MORB}} = -6.5\text{‰}$, $(\delta^{13}\text{C}-\text{CO}_2)_{\text{Lim}} = 0\text{‰}$, $(\delta^{13}\text{C}-\text{CO}_2)_{\text{Sed}} = -30\text{‰}$, $(\text{CO}_2/{}^3\text{He})_{\text{MORB}} = 1.5 \times 10^9$, $(\text{CO}_2/{}^3\text{He})_{\text{Lim}} = 1 \times 10^{13}$, and $(\text{CO}_2/{}^3\text{He})_{\text{Sed}} = 1 \times 10^{13}$. M, L, and S contributions (Table 2, Fig. 10) indicate that only ~1 % of carbon comes from the M component. In comparison, ~99 % of carbon is derived from crustal sources, where L is the principal carbon source, with ~62 % on average, followed by the S component (~37 %). The CO₂/{}³He versus $\delta^{13}\text{C}$ -CO₂ diagram (Fig. 10) indicates that JUN gases have comparable mantle contributions to those found in other geothermal areas in northern Chile, such as Puchuldiza, El Tatio, Surire, and Colpitas.

The JUN gases show $\delta^{13}\text{C}$ -CH₄ and CH₄/(C₂H₆ + C₃H₈) ratios (Table 2) consistent with a thermogenic source (Bernard et al., 1977; Schoell, 1980; Whiticar, 1999). Then, CH₄ was likely produced at depth within volcano-sedimentary sequences of Estratos de Rio Juncalito or Estratos de Huidobro.

5.3. Geothermometry

Deep reservoir temperatures are usually estimated based on the

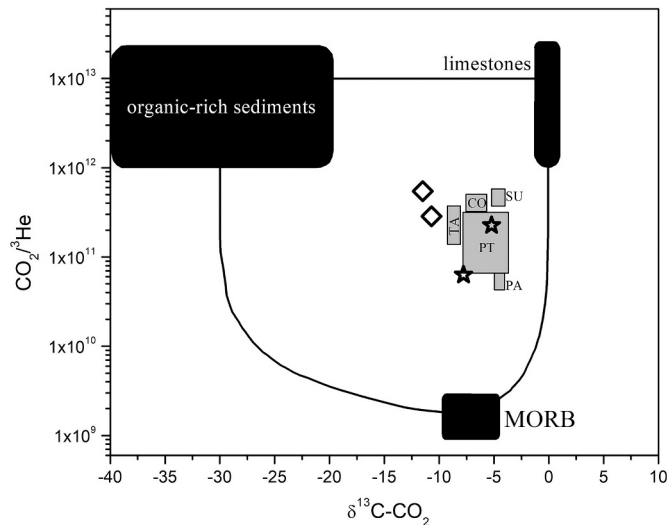


Fig. 10. $\delta^{13}\text{C}$ -CO₂ vs. CO₂/{}³He binary diagram (Sano and Marty, 1995) for JUN bubbling gases in comparison to CB (stars; Chiodi et al., 2019), Colpitas (CO; Inostroza et al., 2020), Tatio, Puchuldiza-Tuja, Pampa Apacheta, and Surire (TA, PT, PA, and SU, respectively; Tassie et al., 2010) geothermal areas. Black areas depict expected $\delta^{13}\text{C}$ -CO₂ values and CO₂/{}³He compositions for MORB, limestones, and organic-rich sediments endmembers (Sano and Marty, 1995).

chemistry of discharged thermal fluids considering (i) the solubility of silica in waters and/or (ii) the attainment of chemical equilibrium among cations in water-rock interactions. Chalcedony geothermometer (e.g., Arnórsson et al., 1983) retrieved estimated temperatures <55 °C for JUN and SPP, between 71 and 72 °C for PA, between 85 and 91 °C in TRN, and 88 °C in the hottest sites at LV springs. However, these temperatures must be considered as minimum values since they may be affected by dilution and silica precipitation within hydrothermal conduits. These results at TRN are inconsistent with those of 140–160 °C provided by Mayorga (2011) using silica geothermometers. According to the Mg-Na-K system (Giggenbach, 1988), most Atacama waters are immature (Fig. 11). Therefore, a temperature estimation using Na/K and Mg/K geothermometer cannot provide reliable results (Romano and Liotta, 2020).

5.4. Trace elements

To discriminate the trace element enrichment of Atacama thermal springs, it is proposed the use of enrichment factors (EF; Duce et al., 1975; Mroz and Zoller, 1975; Zoller et al., 1983), which can be calculated as follows: $EF = (X/Y)_s / (X/Y)_r$, where X and Y are the elements of interest and reference, respectively, and subscripts *s* and *r* represent their concentrations in the spring water and the reference material, respectively. Given the unavailability of this data for local rocks, the reference data adopted for this study is the average upper crustal composition by Rudnick and Gao (2014). The chosen reference element was Co, which was selected in previous works in volcanic-hydrothermal environments due to its low concentrations in both host rocks and hydrothermal emissions and low mobility in hydrothermal solutions (Kaasalainen et al., 2015).

Li, B, and As show EF_{Co} values of $\sim 1 \times 10^4$ (Table 3), indicating significantly higher enrichment than Sr, Zn, Sb, Rb, and Cu in Atacama thermal springs (Fig. 12). Conversely, Pb, Ni, Ba, Cr, and Co appeared less enriched. In general terms, elements moderately to poorly enriched in thermal waters show low mobility within the hydrothermal system, and they were probably scavenged into secondary sulfide or oxide minerals (Kaasalainen et al., 2015). Conversely, enriched elements were stable and highly mobile at the pH, temperature, and pressure conditions within the hydrothermal reservoir, as in the case of Li, B, and As.

The high EF for Li and B may be ascribed to the interaction of the circulating fluids within the silicic basement and the influence of B-rich volcano-sedimentary sequences, respectively, as reported for the basement of the CGC. A further contribution of these elements due to the devolatilization of B- and Li-bearing slab components (Leeman and Sisson, 1996) is to be considered insignificant, given the poor mantle-

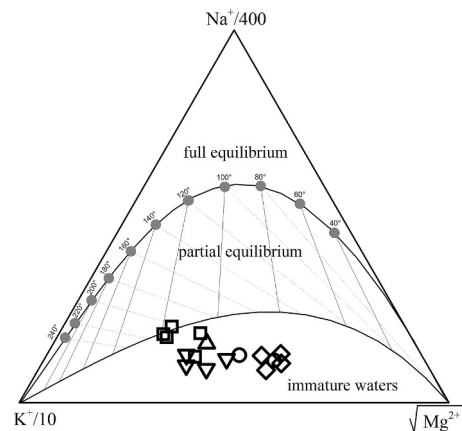


Fig. 11. $\sqrt{\text{Mg}^{2+}}\text{-Na}^+/400\text{-K}^+/10$ ternary diagram (Giggenbach, 1988) for thermal springs of the Atacama region. Symbols as Fig. 3. Equilibrium temperatures in Celsius degrees.

Table 3
Average Co-normalized enrichment factors for LV, PA, SPP, TRN, and JUN.

Cod	LV		PA		SPP		TRN		JUN	
Site	average	±	average	±	average	±	average	±	average	±
Li	14,871	5121	6504	894	32,807	0	5226	537	12,052	3022
B	13,935	3222	12,164	4580	39,175	0	5566	1035	14,004	6411
As	20,613	5057	16,082	5786	13,677	0	8876	1989	15,800	5648
Sr	364	158	364	132	1368	0	307	62	224	118
Zn	258	49	190	27	1318	0	573	157	219	67
Sb	317	69	229	29	252	0	218	11	118	15
Rb	143	21	306	114	434	0	91	19	77	34
Cu	45	3	37	5	62	0	39	6	107	37
Pb	32	2	15	0	13	0	15	2	8	2
Ni	23	6	8	0	10	0	9	2	9	3
Ba	9	2	9	1	12	0	18	3	8	2
Cr	18	4	5	0	6	0	5	1	6	1
Co	1	0	1	0	1	0	1	0	1	0

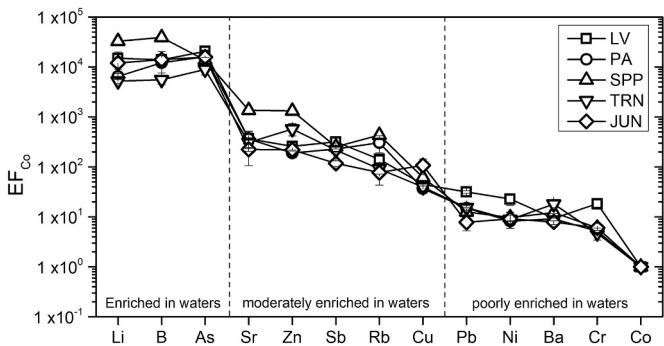


Fig. 12. Average Enrichment Factors relative to Co (EF_{Co}) for thermal springs in the Atacama region. Dashed lines are situated when higher slopes are observed and separate elements enriched, moderately enriched, and poorly enriched in Atacama thermal springs.

related contribution to the chemistry of the discharged fluid (e.g., Fig. 9, Fig. 10). Consequently, the relatively high B and Li concentrations and high EF may indicate water-rock interaction processes within an upper continental crust with superior Li and B concentrations and circulation of B-rich volcanic fluids (Inostroza et al., 2021, 2024).

A remarkably high concentration of As is a distinctive characteristic of thermal springs from the Altiplano-Puna region (Capaccioni et al., 2009; Alsina et al., 2014; Tapia et al., 2018, 2021; Murray et al., 2023). The enrichment of As is relatively well correlated ($R > 0.79$) with B and

Li (Fig. 13). Despite the controversial magmatic or cortical origin of As in hydrothermal systems of the CVZ, a positive correlation among As, B, and Li, suggests a common source, as reported by Tapia et al. (2021). While spring with the highest As concentrations such as PA, LV, and JUN, would involve fluid circulation within areas affected by hydrothermal alteration (e.g., Murray et al., 2023): For example, hydrothermal alteration at Agua de la Falda volcano would increase As concentrations in JUN springs, while the active hydrothermal system at Ojos del Salado volcano (Alam and Muñoz, 2024) could be linked to high As contents in LV.

Regarding the chemical elements moderately to poorly enriched in thermal springs, Zn-, Pb-, Cu-sulfides, and Cr-oxides have been predicted to be saturated in hydrothermal solutions (Kaasalainen et al., 2015), while Sr and Ba may be incorporated into alteration minerals replacing Ca, such as calcite, epidote, or anhydrite (Kaasalainen et al., 2015). Consequently, solution saturation and incorporation into secondary minerals would be responsible for weakened EFs of moderately and poorly enriched elements in the thermal waters of the Atacama region.

6. Conclusions

The southern part of the CVZ presents various hydrothermal manifestations in the forearc position near the CGC (SPP, PA, JUN, and TRN) and in the main volcanic arc (LV). These springs are primarily fed by meteoric waters infiltrating at altitudes likely >5000 m asl. Hydrothermal springs represent a mixture of cold and hot chlorine waters with moderate water rock interaction, but enough to remove a fraction of

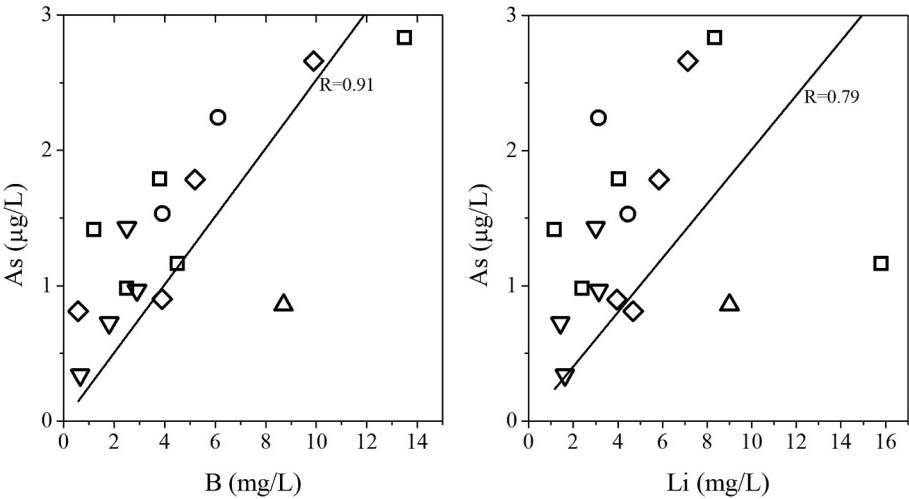


Fig. 13. B vs. As and Li vs. As binary diagrams for thermal waters of the Atacama region. The solid lines represent the linear fit between element concentrations (Table 2), and R represents Pearson's correlation coefficient. Symbols as Fig. 3.

temperature-dependent compounds from host rocks, like Na^+ , SiO_2 , B, and Li. Interestingly, JUN and PA springs show increased Li/Cl and B/Cl ratios compared to other sites of this study, attributed to the leaching of volcano-sedimentary and rhyolitic volcanic rocks forming the basement of the CGC. Thermal springs from the Atacama region are enriched in B, Li, and As, relative to average upper crustal values. Primarily, the enrichment of B and As can be attributed to the heat transport in the crust. However, fluid circulation in a thickened continental crust with an increased geogenic content of As, B, and Li may also impact such higher enrichments in Atacama thermal springs. On the other side, elements such as Zn, Cu, Pb, Sr, and Ba are less mobile and tend to be incorporated into alteration or secondary minerals.

JUN bubbling gases' chemical and isotopic composition demonstrate a minimal mantle contribution (1 %). At the same time, the $\delta^{13}\text{C}\text{-CO}_2$ values seem controlled by local lithologies constituted by volcano-sedimentary sequences.

The immaturity of the thermal springs leads to cation geothermometers not providing reliable reservoir temperatures. However, chalcedony geothermometer appears with more reliable reservoir temperatures of $\sim 90^\circ\text{C}$ in TRN and LV. These temperatures contrast with those of $140\text{--}160^\circ\text{C}$ determined by previous works. The geothermal potential is modest in LV, TRN, and other sites in this study. However, applying geophysical and geochemical techniques is recommended to better constrain the heat source in the LV area, which is probably the active Ojos del Salado volcano.

CRedit authorship contribution statement

Manuel Inostroza: Writing – review & editing, Writing – original draft, Validation, Methodology, Data curation, Conceptualization. **Yazmin Godoy:** Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **María Donoso-Peña:** Writing – original draft, Methodology, Funding acquisition. **Franco Tassi:** Writing – review & editing, Validation, Methodology, Formal analysis. **Felipe Aguilera:** Supervision, Methodology, Investigation, Conceptualization. **Francesco Capecchiacci:** Writing – review & editing, Methodology, Formal analysis. **Andrea Luca Rizzo:** Writing – review & editing, Formal analysis.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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