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Groundwater flow in a closed basin with a saline shallow lake in a volcanic area: Laguna Tuyajto, northern Chilean Altiplano of the Andes

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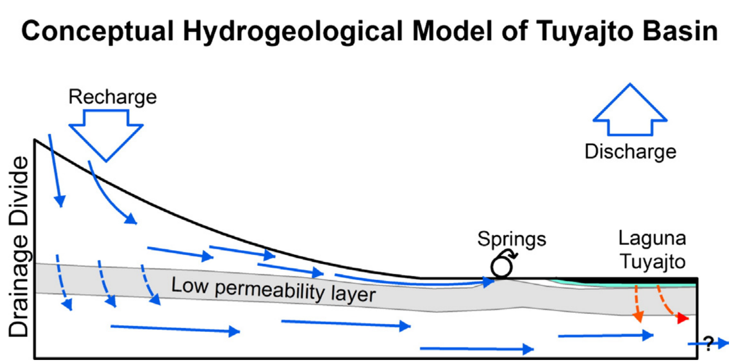
HIGHLIGHTS

- Recent volcanism formations play a key role in producing recharge.
- Groundwater can flow across local interbasin boundaries.
- The origin and concentration of ions dissolved in spring waters are mostly the dissolution of buried evaporitic deposits.
- The stable isotopic content of water from the springs shows that recharge originates mainly from snow.

GRAPHICAL ABSTRACT



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ABSTRACT

Laguna Tuyajto is a small, shallow saline water lake in the Andean Altiplano of northern Chile. In the eastern side it is fed by springs that discharge groundwater of the nearby volcanic aquifers. The area is arid: rainfall does not exceed 200 mm/year in the rainiest parts. The stable isotopic content of spring water shows that the recharge is originated mainly from winter rain, snow melt, and to a lesser extent from some short and intense sporadic rainfall events. Most of the spring water outflowing in the northern side of Laguna Tuyajto is recharged in the Tuyajto volcano. Most of the spring water in the eastern side and groundwater are recharged at higher elevations, in the rims of the nearby endorheic basins of Pampa Colorada and Pampa Las Tecas to the East. The presence of tritium in some deep wells in Pampa Colorada and Pampa Las Tecas indicates recent recharge. Gas emission in recent volcanoes increase the sulfate content of atmospheric deposition and this is reflected in local groundwater. The chemical composition and concentration of spring waters are the result of meteoric water evapo-concentration, water–rock interaction, and mainly the dissolution of old and buried evaporitic deposits. Groundwater flow is mostly shallow due to a low permeability ignimbrite layer of regional extent, which also hinders brine spreading below and around the lake. High deep temperatures near the recent Tuyajto volcano explain

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the high dissolved silica contents and the δ^{18}O shift to heavier values found in some of the spring waters. Laguna Tuyajto is a terminal lake where salts cumulate, mostly halite, but some brine transfer to the Salar de Aguas Calientes-3 cannot be excluded. The hydrogeological behavior of Laguna Tuyajto constitutes a model to understand the functioning of many other similar basins in other areas in the Andean Altiplano.

1. Introduction

Research in closed basins in arid and semiarid zones around the world has been mainly motivated by the great biodiversity that develops in this type of environments (Warren, 1999; Yechieli and Wood, 2002; Harper et al., 2003; Rodríguez-Rodríguez et al., 2006; Nield et al., 2008) and the ecological services they provide to mankind. Many of these closed basins contain salt flats or saline water bodies in their lowest areas. They hold unique ecological systems (Hammer, 1986; Comín and Alonso, 1988; Haukos and Smith, 1994) and minerals of interest that are closely associated with saline lakes and playa lakes. Understanding the role of the hydrological and hydrogeological processes is essential to assess the degree of fragility of these ecosystems (Williams, 2002; Montalván et al., 2014) and to set the actions and regulations to protect their services in spite of the pressure to develop groundwater resources in them or in their surroundings.

Most of the research developed in these basins focused primarily on the ecology, biodiversity, limnology, and open water chemistry of the natural environment. On the other hand, research on the hydrological and hydrogeological aspects in the source of the water feeding and outflowing into the playa lakes and surroundings is less frequent because of the poor water quality found in these hydrological systems (Lines, 1979). Most of the researches on the hydrogeology of saline lakes and playa lakes have been carried out in large basins such as the Great Basin in western United States (Duffy and Al-Hassan, 1988; Fan et al., 1997) and in central Australia (Jacobson, 1988; Jacobson et al., 1991; Tweed et al., 2011). Hydrogeological research has also been carried out in the small saline and evaporite-rich closed basins of Los Monegros (Berga, 1993; García-Vera, 1996; Samper-Calvete and García-Vera, 1998; Castañeda and García-Vera, 2008), Chiprana Lake (Berga et al., 1994; Valero-Garcés et al., 2000), and Gallocanta Lake (Luzón et al., 2007), in north-eastern Spain, and in Fuente de Piedra Lagoon (Montalván et al., 2014) and other areas (Rodríguez-Rodríguez et al., 2006) in south-eastern Spain. Results from these studies cannot be applied directly to the Central Andean Altiplano due to the arid to hyper-arid conditions existing there, the important and recent volcanic activity, the associated land changes due to accumulation of volcanic deposits, and the existence of buried saline deposits.

In the arid Central Andes of Chile there are important closed basins in which the central depression is occupied by saline lakes, salt crusts, and playa lakes (Risacher et al., 2003). Most of these basins are in an active volcanic environment at altitudes exceeding 4000 m (Table 1). Recently, hydrogeological research has greatly increased in these areas with very scarce water resources as a result of the increasing water demand to supply growing urban centers, irrigated agriculture, some incipient touristic activity and different industrial activities like mining, which is a national priority interest, and also some planned geothermal energy developments (Johnson et al., 2010). The mining companies have produced numerous reports to try to solve their needs, but most of them are not available to the public, they have a very local and focused point of view, or environmental aspects are ignored or lessened. However, ecological impact studies sent to the public authorities to try to get groundwater exploitation permissions and concessions are public and some of them contain valuable information that has not been fully used to get a deeper understanding of the local and regional hydrogeology.

In 2003, study efforts were launched and centered in the Laguna Tuyajto basin. This is a topographically closed (endorheic) basin of the Chilean Central Andes with a variable saline lake (Laguna Tuyajto). New data acquisition was focused on the assessment of the water balance of this shallow lake through hydrological, hydrogeological, hydrochemical and isotopic techniques. This data is limited due to economic restrictions and to the notable difficulties to access and move through the area. In parallel, an extensive exploration campaign of water resources, supported by boreholes, was carried out by Water Management Consultants (WMC, 2006). Nevertheless, these data have not been used together yet in a research that involves the entire functioning of the basin.

The main objective of this research, which is going on currently, is to understand the surface water–groundwater interaction in a closed basin of the volcanic Central Andes, using the Tuyajto basin case study. To achieve this aim it is necessary to develop a conceptual hydrogeological model to explain the major processes in this type of basins. For this, chemical and isotopic data from spring, rain and groundwater are used. In addition, information from observation wells are used to know the soil physical properties and groundwater flow. Extrapolation and modification of the conceptual model here developed could help to understand the origin of groundwater recharge, interbasin transfer and solute transport in areas where both groundwater functioning and mass transport are still poorly know.

2. The studied area

2.1. Background of Laguna Tuyajto

The Tuyajto basin, containing Laguna Tuyajto, is an endorheic basin located in the Andean Altiplano of the Antofagasta Region (Fig. 1a). To the West, the Tuyajto basin is bordered by the Salar de Aguas

Table 1
Characteristics of Tuyajto basin and the neighboring basins. See Fig. 1 for location and the emplacement of the salt deposits at the lowest areas. (1) Aguas Calientes-2 includes Pampa de Puntas Negras. Playa lakes are ephemeral ones with infiltration that prevents permanent salt accumulation.

Basin	Surface (km^2)	Maximum altitude (m)	Minimum altitude (m)	Situation relative to Tuyajto basin	Comments
Tuyajto	249	5852	4040		Shallow saline lake. 3 km^2
Pampa Colorada	58	5269	4266	NE	No saline lake; no salt
Pampa Las Tecas	109	5685	4195	E	No saline lake; no salt
Laco	271	5852	4237	E. E of Pampa Colorada and Pampa Las Tecas basins	Playa lake. 16.2 km^2
Aguas Calientes-3	476	5910	3938	W	Playa lake. 46 km^2
Aguas Calientes-2	1168	6046	4200	N	Playa lake. 134 km^2
Miscanti Lake	303	5910	4120	NW	Shallow lake. 13.4 km^2

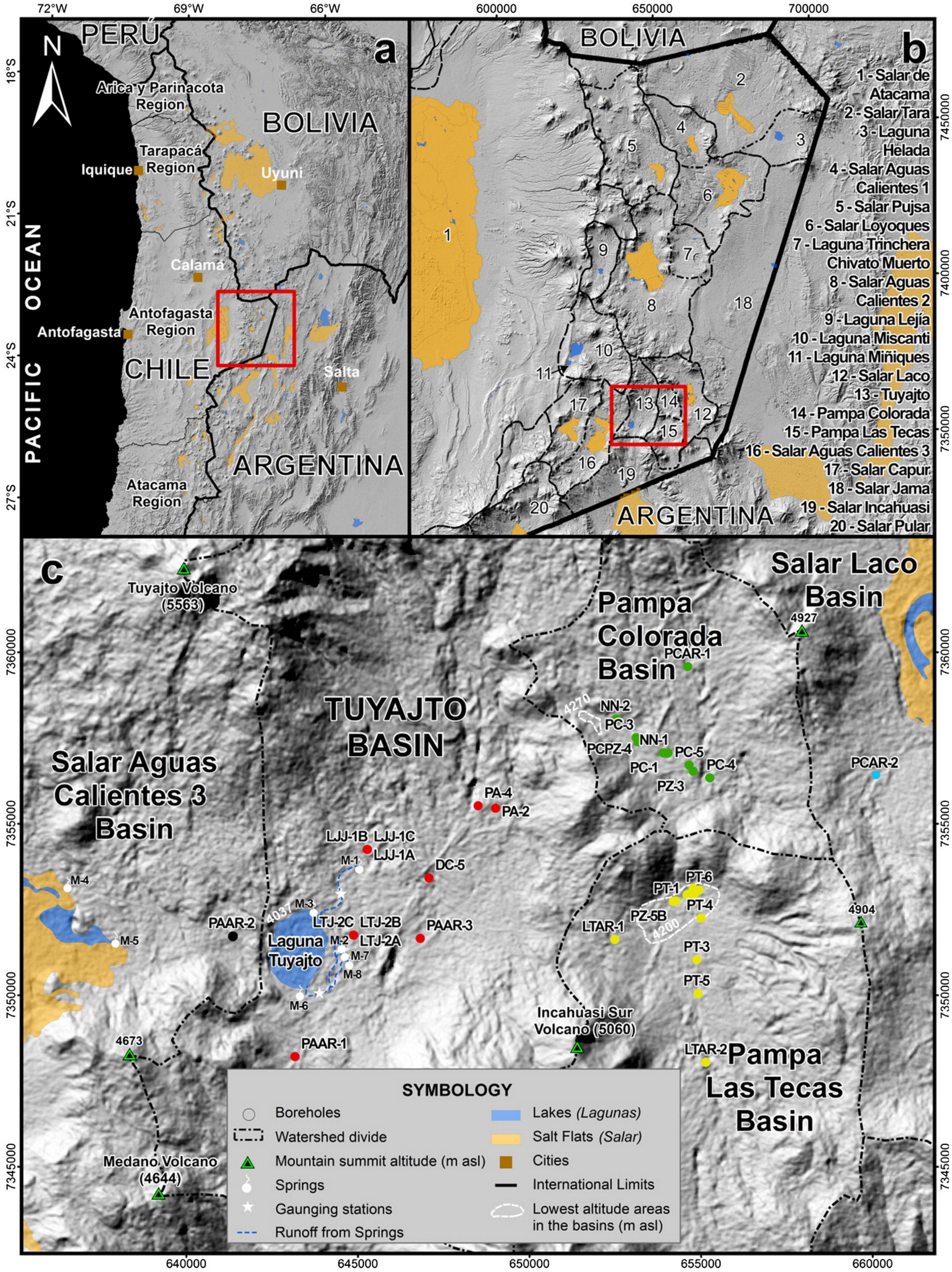

Fig. 1. Location map of the study area. Panel a shows the location of significant basins with salt flats or lakes in arid-semiarid conditions of Central Andes. The numbers in the panel b correspond to the main areas in the vicinity of the studied area (DGA, 1987 and Risacher et al., 1999). Panel c shows the location of the springs and boreholes in Tuyajto, Salar de Aguas Calientes-3, Pampa Las Tecas, Pampa Colorada and Salar Laco basins. The white dots correspond to the springs and the colored dots to the boreholes: red in Tuyajto Basin; green in Pampa Colorada Basin; black in Salar Aguas Calientes-3 Basin; sky-blue in Salar Laco Basin and yellow in Pampa Las Tecas Basin. Figures b and c are projected on WGS-84 UTM (19°S) local coordinates. (For interpretation of the references to color in this figure legend, the reader is referred to the online version of this chapter.)

Calientes-3 basin (at a lower elevation) and to the East by the Pampa Colorada and Pampa Las Tecas basins (at a higher elevation) and these last two by the El Laco basin at the easternmost part (Fig. 1b).

An important feature of the whole area is its arid climate. In the Tuyajto basin, the average precipitation varies between 150 and 200 mm/year (DGA, 2014). The average environmental air temperature is 1 °C and the average potential evaporation is about 1500 mm/year (Risacher et al., 1999).

Laguna Tuyajto is a shallow saline open water body located in the lower part of the Tuyajto basin (4010 m asl). It has not surface outflow and it has a variable salinity, up to salt saturation. Its current maximum water depth is 0.6 m; the average water depth is 0.35 m and the maximum surface area is 2.7 km^2 out of a basin area of about 249 km^2. Laguna Tuyajto receives water from 6 main springs located in the northern and eastern part of the lake and from diffuse discharge in the eastern part.

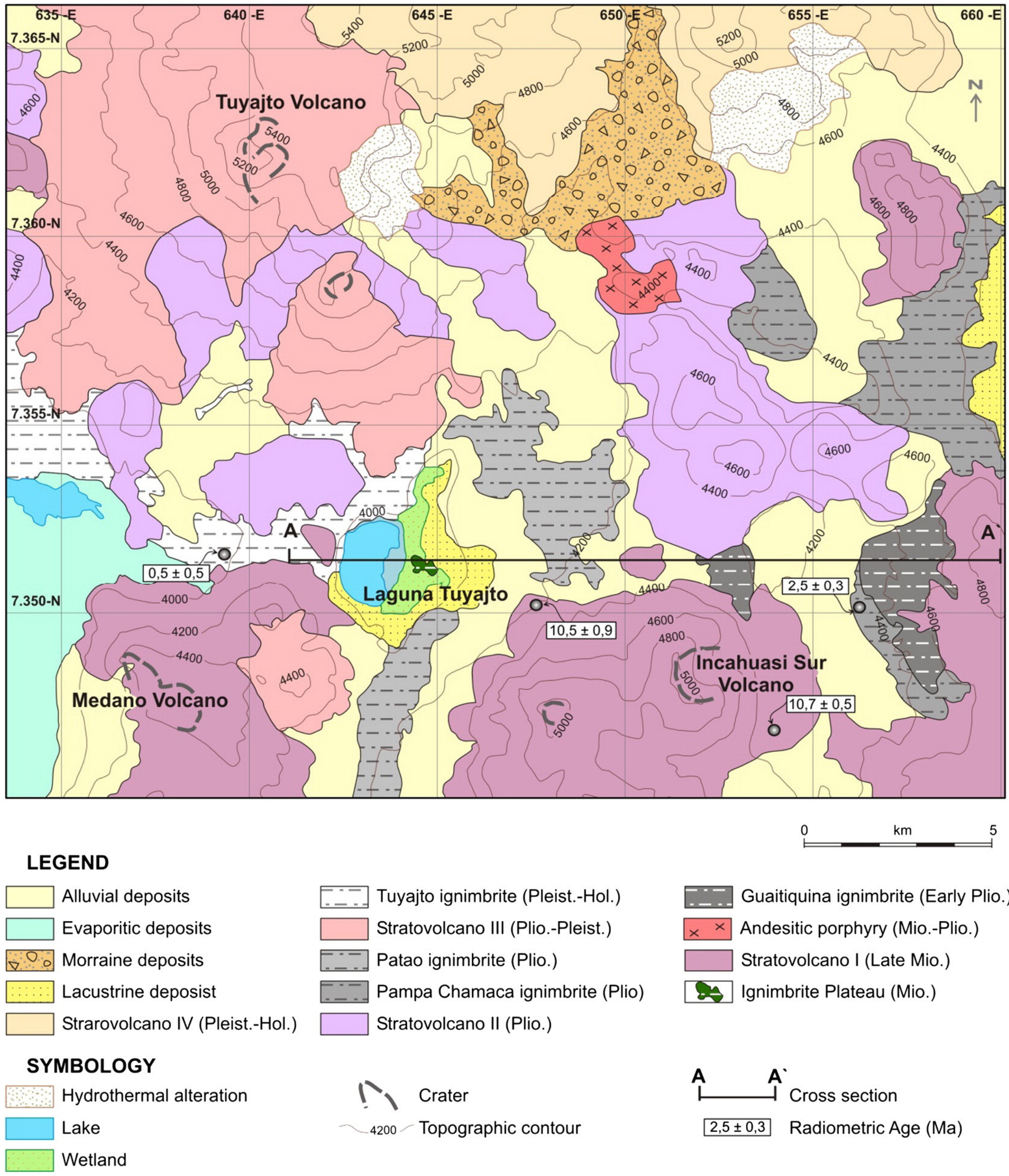

Fig. 2. Geological map of the study area (modified from Ramírez and Gardeweg, 1982). Line A–A′ is the location of the cross-section in Fig. 11. The regional ignimbrite layer (Ignimbrite Plateau) only shows up in a small patch near Laguna Tuyajto but has large outcrops outside the represented area.

The sensitivity of this hydrological lake system is reflected on the significant seasonal variation of its water surface area. In autumn and winter months, the water surface area of the lake reaches the maximum of 2.7 km^2. However, during the summer months it reduces to 1.7 km^2 (Fig. S1 in the Supplementary material), and in some dry years it was close to be dry. The important seasonal variation of the water surface area is basically due to a) the gentle land surface slope from the lake shore toward the center, which implies large surface variations of the lake water level, b) the seasonal variations in spring flow, and c) the seasonal variation of the water evaporation rate, which during the winter months can be reduced to almost zero when the lake surface is frozen. Salt efflorescence, mainly halite and gypsum, are exposed on the margins of the lake in periods of more intense evaporation, when the water surface area is small.

2.2. Geological and hydrogeological setting

In the Chilean Altiplano, the majority of the well-preserved volcanoes are emplaced on a large ignimbrite plateau of regional extent which may be up to tens of meters thick (Francis and Baker, 1978; Mardones, 1977; De Silva, 1989; De Silva and Francis, 1991; Stern et al., 2007). This ignimbrite erupted in the late Miocene and is considered part of the cover of a big volcanic caldera in the Central Andes named La Pacana Caldera (Baker, 1981; Ramírez and Gardeweg, 1982; Lindsaya et al., 2001; Self et al., 2008). The numerous volcanic edifices around have ages ranging from the late Miocene to the Holocene. Some of these volcanoes exceed 5300 m of elevation, while the flats and gentle elevations around and among them do not exceed 4000 to 4300 m.

The geology of the studied area (Fig. 2) is dominated by volcanic flows, tuffs, and breccia, ranging from the Miocene to the Holocene (Stoertz and Ericksen, 1974; Mahlburg et al., 2010). The part of the ignimbrite plateau here considered is in an intra-caldera position (Lindsaya et al., 2001). In the eastern part of the studied area, the boreholes drilled in the basins of Pampa Colorada and Pampa Las Tecas attained this regional ignimbrite flows, thus pointing to their relatively shallow depth.

Among the most important stratovolcanoes are the Incahuasi Sur and Médano, of Upper Miocene age, located in the southern part of the studied area. The Tuyajto volcano, of Pliocene-Pleistocene age, is located just to the North of Laguna Tuyajto. Other existing ignimbrite formations are associated to recent volcanism, like the Guaiquitina ignimbrite (Upper Miocene) and the Pampa Chacana Ignimbrite (Late Pliocene). The Tuyajto ignimbrite (Pleistocene–Holocene) is one of the youngest ignimbrites in the area (Ramírez and Gardeweg, 1982), cropping out in the western part of Laguna Tuyajto.

Recent groundwater exploration in the area was performed by Water Management Consulting (WMC, 2006) in the Altiplano of the Antofagasta Region. The calculated transmissivity values range from about 3 to 1000 m^2/d (Table S1 in the Supplementary material). The highest values are found in boreholes located in the central part of the basins of Pampa Colorada and Pampa Las Tecas. These values are attributed to the existence of unconsolidated alluvial fans with interbedded volcanic flows. Risacher and Fritz, (2009) suggest two origins of the salts dissolved in groundwater: weathering of Andean volcanic rocks and dissolution of evaporite units like halite or gypsum.

3. Materials and methods

3.1. Water sampling

To extend and complete existing chemical data, systematic water sampling and chemical analysis of the springs that outflow in the boundaries of Tuyajto and Aguas Calientes-3 lakes were performed for the hydrogeochemical and isotopic study of groundwater. It included in-situ measurement of temperature, pH and electrical conductivity. A total of 14 rainfall and groundwater samples were analyzed for major ions. Anions were analyzed by ion chromatography (Cl, Br), absorption spectrometry (SO_4, NO_3) and acid titration (HCO_3), and cations by atomic absorption spectrometry. The results have been combined with chemical and water isotopic analyses obtained by WMC (2006) in water samples from boreholes located in the Tuyajto basin and in the neighboring basins to the East. Standard methods were applied in the certified laboratory at the Universidad Católica del Norte. Analytical error is typically less than 10%.

Rainwater samples were collected in three open pots to obtain bulk (wet and dry) atmospheric deposition. To avoid evaporation during the time between sample collections, a liquid paraffin-oil layer was placed in the pots. The collectors were located in the Salar de Aguas Calientes-3 (3900 m asl), Laguna Tuyajto (4040 m asl) and Pampa Colorada (4426 m asl). The cumulative rain samples correspond to January, March and May 2004, and December–January 2005. A total of 10 rainfall samples were obtained and analyzed for major ions and stable water isotopes. Also, six samples of snow were taken at altitudes between 3850 and 4500 m to determine $\delta^{18}O$ and δ^2H. They correspond to two stormy events in July and August 2004.

A total of 27 water samples for $\delta^{18}O$ and δ^2H analyses were recovered: 8 of snow, 10 of rain, 8 of springs, and 1 of Laguna Tuyajto, plus 31 $\delta^{18}O$ and δ^2H analyses in boreholes in Pampa Colorada and Pampa Las Tecas. All $\delta^{18}O$ and δ^2H analyses were performed in the Environmental Isotope Laboratory of the Chilean Nuclear Energy Commission. The measurement error for $\delta^{18}O$ is ± 0.05‰ and ± 1‰ for δ^2H. All values are relative to the V-SMOW standard (Clark and Fritz, 1997).

3.2. Spring flow

In this research, spring flows were gauged monthly during one year period to estimate their discharge, in Station A, downstream of spring M-1, and in Station B that receives the combined discharges of M-2, M-6, M-7 and M-8 springs. Fig. 1c shows the location of the gauging points and Table 2 shows the results. As spring M-3 is sporadic, gauging was only performed in four of the sampling months. Stream gauging was carried out with a flow meter in different sections of the channels after reconstructing the geometry of the sections used to measure water velocities as a means to capture the changes in the channel as a result of erosion and vegetation growth.

3.3. Water level in Laguna Tuyajto and estimation of evaporation

A pressure transducer was installed in the deepest part of Laguna Tuyajto to get a continuous water level record in the shallow lake. To prevent wind disturbance in the measured levels, the sensor was installed inside a PVC tube open at the bottom and strongly anchored at the base. During July and August 2004 it was not possible to get data due to technical difficulties; however, three manual measurements were done.

For the determination of evaporation in the lake, it was used a Type A evaporation tank that exists at the nearby Incaliri station site, located 4100 m to the North of the studied area, close to the El Tatio geyser site. The open water evaporation could be estimated following the procedure of Peña (1986), after introducing corrections to take into account the high salinity of lake water.

4. Results and discussion

4.1. Water balance of Laguna Tuyajto

Laguna Tuyajto has no surface outflow. Most water inflow comes from the four main springs in the north and east of the lake. These springs flow several hundred meters before reaching the lake (Fig. 1). The higher discharges were measured in the M-1 spring, in the northern part of Laguna Tuyajto (Table 2). Water from M-2, M-7 and M-8 springs merge into a single stream that runs along the eastern edge of the lake toward the southern part of Laguna Tuyajto, incorporating spring M-6 as well as some diffuse flow from the eastern boundary, and the total flow is gauged before entering Laguna Tuyajto (Table 2). These springs altogether discharge between 74 and 245 L/s, variable during the year. The total water contribution during 2004 was 4.4 hm^3. The lake also receives small, non-quantified water outflows from other sporadic springs as well as diffuse groundwater discharging into the wetlands (*bofedales*) in the northern and eastern parts of the lake.

Table 2
Flow rates of Laguna Tuyajto springs. Station A measures spring M-1 and station B measures the joint flow of springs M-2, M-6–M-7 and M-8. nf = no flow.

Gauging points	Date of measurement during year 2004. Discharge in L/s.											Total in hm^3
	28-January	06-March	04-April	06-May	20-June	11-July	07-August	12-Septem.	16-October	14-Novem.	19-Decem.	
Station A	39	41	19.8	88.3	57.2	34	43.1	39	64.3	63.1	65.4	1.3
Station B	50.8	90.9	54.4	155.7	162.3	183	159.9	122	89.9	133.8	64.3	3.1
Spring 3	nf	nf	nf	1.1	0.9	1.2	1.5	nf	nf	nf	nf	0.01
Total	89.8	131.9	74.2	245.1	220.4	218.2	204.5	161	154.2	196.9	129.7	4.4

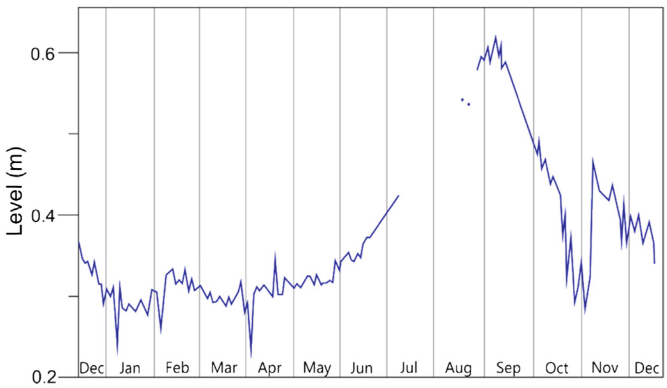

Fig. 3. Daily water level fluctuations in Laguna Tuyajto between December 15, 2003 and December 19, 2004. The blue dots correspond to manually measured data in the period of instrumentation failure. Levels are relative to the local altitudinal reference.

The water level changes in the lake allow the evaluation of the effect of spring inflow and the fluctuations due to evaporation (Fig. 3). The sustained lake level decline recorded between December 2003 and January 2004 is consistent with the measured low spring flow in late January 2004 (90 L/s) and with the higher rate of evaporation in those months. The slight level increase recorded in February and mid-March 2004 is consistent with a small inflow increase in early March (132 L/s) and with the rainfall events recorded in February. Subsequently, an upward level trend was observed from late April to September 2004, up to 62 cm water depth in the lake. The water inflow tended to decrease in September, which could be explained by the reduced evaporation rate in the austral winter months. The low temperatures in some days of June, July and August partially froze the lake surface. Finally, from September to December 2004, a steady decline in water levels in the lake was observed and it only changed in late October and early November, when a significant level increase was registered, consistent with a significant increase in water inflow to the lake, especially from spring M-1 (Station A; Table 2).

Considering the surface area of Laguna Tuyajto in different months, the yearly volume of water evaporating from the lake is about 3.1 hm^3/yr. (Table S2 in the Supplementary material). This is less than the 4.4 hm^3 of the measured inflow to the lake during 2004. The difference can be explained by the uncertainty of the calculated values, but some underground water transfer to the Salar de Aguas Calientes-3 is possible.

4.2. Groundwater flow

The patterns of groundwater flow and the hydraulic gradients of the Tuyajto area can be inferred from the groundwater level contours shown in Fig. 4. The piezometric map shows that groundwater flow may occur from the basins of Pampa Las Tecas and Pampa Colorada toward the Laguna Tuyajto basin, with a general East to West direction, feeding the springs at the eastern side of Laguna Tuyajto. In general, the hydraulic gradients are relatively low in the topographic depressions filled by volcano-sedimentary materials, but they increase when groundwater flows through the altered volcanic rocks that are generally found at the low elevation rim areas, which often follow volcanic lineation. This flow behavior may be explained by the existence of top permeable deposits from young volcanoes. The geological investigation did not found dykes and significant shallow alteration zones in the low areas and gentle topographic elevations. From the observations herein, it seems that gaps in the low permeability rocks in the boundary areas are filled with recent permeable volcanic-derived sediments, providing hydraulic connection (thus groundwater flow) between these units. Therefore, it can be assumed that some of the topographically closed (endorheic) basins, including Miscanti and Miñique lakes to the North, could be hydraulically interconnected through the subsurface

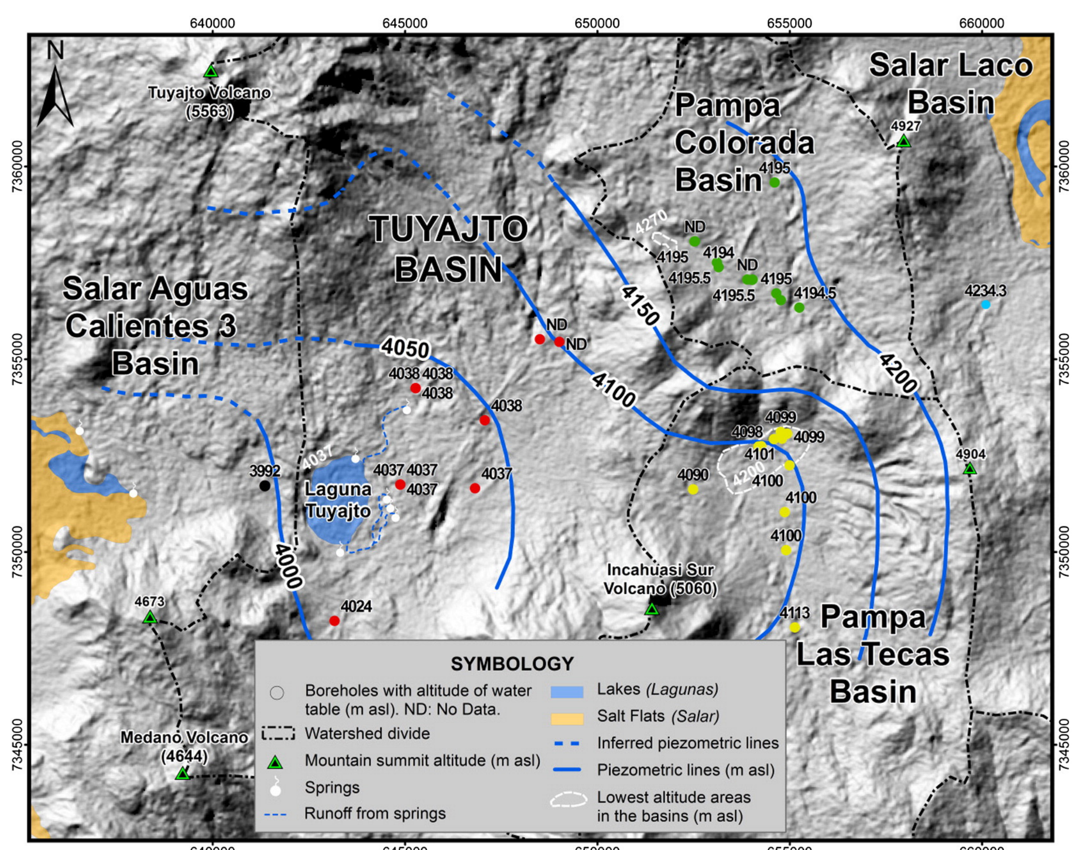

Fig. 4. Piezometric map of the study area. Groundwater flows from recharge areas in the high parts to the depressed zones (NE to SW).

in these areas. The occurrence of groundwater flow among closed basins in volcanic terrains in the Altiplano of northern Chile have been already demonstrated, such as the basins of the Salar de Michincha and Salar de Coposa, located 350 km north of Lake Tuyajto (Montgomery et al., 2003). This may also explain why the higher elevation endorheic basins around Laguna Tuyajto do not contain active saline bodies, even with the relatively small altitude differences between them, of the order of 100 m. The recharge produced in the volcanoes seems to be affected by the mixing in springs and long-screened wells of recharge water produced along the slope at the foothill springs, with a radial divergent flow pattern (Custodio, 2010). It makes the outflowing water or the water pumped from deeply penetrating wells less saline and isotopically lighter than locally recharged waters.

The groundwater flow in the Tuyajto volcano may be closely related to the geological structure of the volcanic edifice. No high elevation springs are found in it. This fact points to the absence of permanent perched aquifers sustained by very low permeability levels interbedded in the volcanic structure. Groundwater flow coming from the Tuyajto volcano discharges through the foothill springs at the northern part of Laguna Tuyajto, forced by the low permeability ignimbrites below. This does not exclude the possible existence of a low permeability volcanic core of thermally and chemically altered rock and intrusive bodies, as observations indicate the presence of an upper layer of permeable volcanic rocks that allow recharge transfer to the lower areas.

4.3. Origin of groundwater and its chemical composition

Most groundwater in the studied area is brackish to saline. Rain, spring and groundwater chemistry data are given in Tables S3 and S4 in the Supplementary material.

The chemical composition of groundwater is spatially characterized by the use of modified Stiff diagrams (Fig. 5). Borehole groundwater and spring water are of the sodium chloride type, sulfate being often the second major anion present. Spring waters of the eastern edge of Laguna Tuyajto have a similar salinity and hydrochemical signature as waters from wells in the neighboring basins of Pampa Colorada and Pampa Las Tecas. Spring waters from the Salar de Aguas Calientes-3 and from the north of Laguna Tuyajto (M-1) have lower but still moderate salinity levels. Laguna Tuyajto water exhibits a much greater salinity than groundwater sampled around the lagoon.

Low salinity groundwater is only present in four wells. First in Pampa Las Tecas and in El Laco, trending to moderately saline groundwater, and also in some wells in Pampa Colorada and Pampa Las Tecas and at the springs at the foot of the Tuyajto volcano. These four wells are near the lower slopes of the high, recent volcanoes. However, some of these boreholes show a marked salinity increase with depth. Only the borehole in El Laco has low salinity all along its depth.

The rCl vs. rNa (r means that the concentration is in meq/L) plot of Fig. 6a shows that Na is positively correlated with Cl for relatively low and moderate salinity waters (Fig. 6a). The small Na deficit, especially for relatively high salinity waters, tends to disappear for very high salinity.

The plot of rCl/rBr vs. Cl (Fig. 6b), which includes three rain water samples from Salar de Atacama (to the West of the studied area, Fig. 1b), shows a clear trend, increasing from the marine ratio to about 655 to values of about 10,000, which is characteristic of brines derived from halite dissolution (Custodio and Herrera, 2000; Alcalá and Custodio, 2008a,b). In the inserted rBr/rCl versus 1/rCl plot, binary mixtures plot along a straight line, which shows that both mixtures between saline water and rainfall and brackish water and brines are

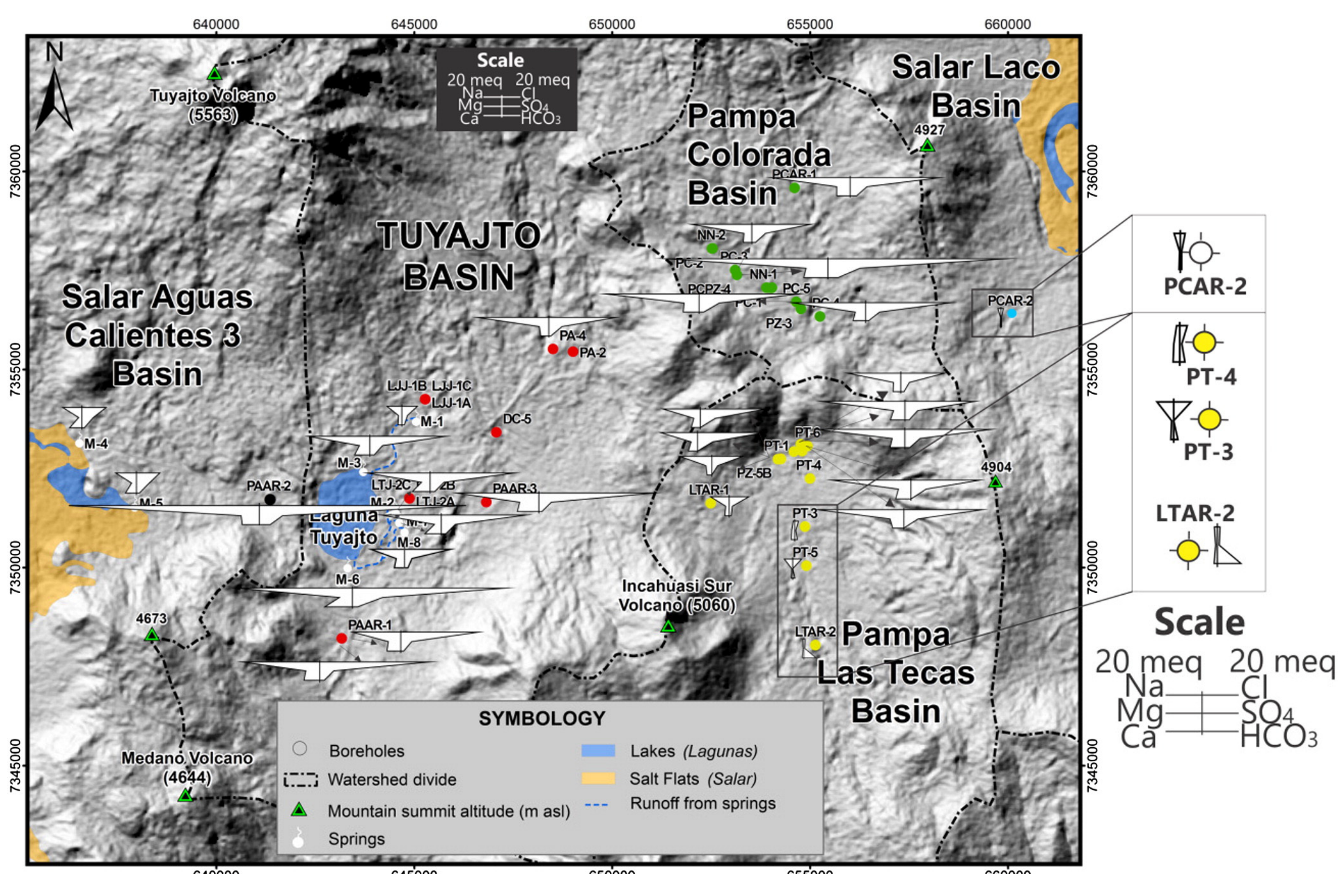

Fig. 5. Modified Stiff diagrams of spring water in Tuyajto lagoon and Salar de Aguas Calientes and groundwater from boreholes on Pampa Colorada, Pampa Las Tecas and Laguna Tuyajto basins. Water from Laguna Tuyajto is not shown due to its very high salinity. The two samples with low salinity are encircled and reproduced at an extended scale out of the map.

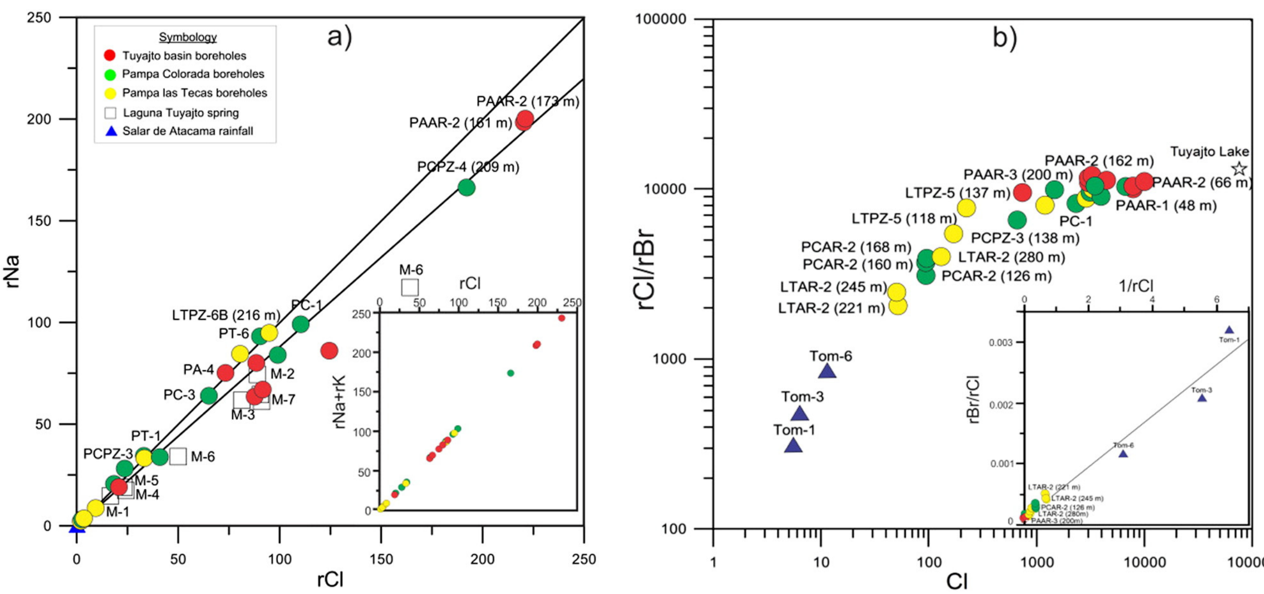

Fig. 6. a) Plot of rNa vs. rCl (r = meq/L) of waters from springs in Laguna Tuyajto and from the boreholes in Tuyajto basin, Pampa Las Tecas and Pampa Colorada. Some samples present a Na deficit relative to Cl higher than the 0.88 ratio in average oceanic water; the inset considers rNa + rK. b) Plot of rCl/rBr; the inset is the plot of rBr/rCl vs 1/rCl; it shows a binary mixing of two end members: a highly concentrated brine and local rainfall, here represented by samples taken near the Salar de Atacama.

possible. Unfortunately no data for low groundwater salinity water is available to check such conditions.

Most waters have a SO_4 excess over Cl relative to the marine water composition ($rSO_4/rCl = 0.09$), as shown by the rSO_4/rCl ratio vs. Cl (Fig. 7a), which is generally between 0.2 and 0.5. The values increase in the area closer to the Tuyajto volcano. The very high salinity waters have an rSO_4/rCl ratio of 0.1 to 0.2.

The rCa and rMg are lower than rNa. This fact points to chemical weathering of plagioclase minerals of local rocks in approximately similar rCa and rMg for most waters, except for part of the springs at the foot of the Tuyajto volcano, for which rCa doubles rMg.

The ratio rNa/rK is rather low for saline waters (Fig. 7b), less than 30, dominantly in the range 10–15, and trending toward 11 at high salinity conditions. The springs have low values while in Laguna Tuyajto it is close to 30.

The bicarbonate ion concentration increases with Cl content (Fig. 7c), attaining about 500 mg/L at very high salinity, with the exception of three low salinity wells in Pampa Las Tecas, where it increases to around 800 mg/L HCO_3. In Laguna Tuyajto the value is close to 400 mg/L.

Spring and well groundwater have relatively high concentrations of SiO_2, above 50 mg/L for moderate to intense rock silicate minerals weathering at low temperature and up to 170 mg/L in waters that have been subjected to high temperature. The spread is large (Fig. 7d).

Groundwater in Laguna Tuyajto area derives from rain and snow precipitation. This precipitation is acidic and has low salinity, with Cl concentrations ranging from 4 to 8 mg/L, an rSO_4/rCl ratio of about 0.2, and HCO_3 of 300 to 800 mg/L. The cation content shows a variable dissolution of atmospheric salts and dust, which could include wind-borne soil particles, precipitated salts on the soil, saline efflorescence, salt flat particles, and atmospheric salts, such as sulfate and remnants of marine salt. The contribution of marine airborne salts is expected to be very small due to the long distance to the up-wind coastal areas, which are across the continent from the Atlantic side.

Rainfall chemical composition at the Salar de Atacama is assumed similar to local precipitation in the study area but it is expected to be slightly greater in SO_4 concentration due to environmental gypsum deflated in the periphery areas of the large salt flat (*salar*). A further local source of atmospheric sulfate comes from the oxidation in the atmosphere of sulfur compounds contained in the emanated gases from cooling deep volcanic chambers and intrusions (i.e. mostly SO_2). In fact, the recent Tuyajto volcano has a fumarolic patch. This is consistent with the hydrogeochemical model proposed by Risacher et al. (2003) for the low salinity springs around other salt flats of the Chilean Altiplano and with unpublished observations recorded for parts of southern Peru. Sulfate contents are within the expected range for non-industrial environments located far from the sea coast. The limited data on $\delta^{34}S$ of sulfate dissolved in the spring waters are within the expected ranges for the conditions noted above.

Rainfall and snow-melt infiltrate through the bare rock in the volcanic high areas and through the poorly developed soil with sparse vegetation in the flat areas (*pampas*). Consequently, the CO_2 partial pressure in the unsaturated zone gas can be expected to be close or slightly higher than in the atmosphere. Thus, infiltrated water has a low capacity to alter the rock minerals and is subjected to significant evapo-concentration due to climatic aridity, except for concentrated recharge from some part of the snow-melt water. The CO_2 partial pressure in the unsaturated zone gas can be locally high in the vegetation-rich patches of the wetlands (bofedales) in the low areas and valley bottoms, although they are scarce in the studied area.

The fresher groundwater is probably recharged in the high areas of the volcanoes. However, most groundwater has higher salinity which suggests that there is likely another source of chloride source within the region. Intense evaporation in open surface bodies does not seem probable due to the lack of a large isotopic fractionation, except for Laguna Tuyajto itself. The most likely possibility is the progressive dissolution of salt bodies buried below recent sediments and lava flows, such as remnants of old salt flats, affected by land elevation changes due to local volcanism-associated tectonics.

Groundwater of moderate to high salinity is common fact in arid areas when recharge is produced in high water capacity soils and where evaporation rates are high (Custodio, 1992; Herrera and Custodio, 2003,2014a); however, this does not seem to be the case in Tuyajto. In fact, the rCl/rBr ratio increases with salinity toward the halite value, which points to its dissolution. The halite incorporation effect is already visible for the moderate salinity groundwater. Unfortunately, there is no data available of the low salinity groundwater. The more dilute rain waters exhibit rCl/rBr values between 300 and 500, similar to those found in continental arid zones (Davis et al. 1985; Custodio and Herrera, 2000; Alcalá and Custodio, 2008a,b). A similar phenomenon has been recognized in the spring waters located in the eastern part of

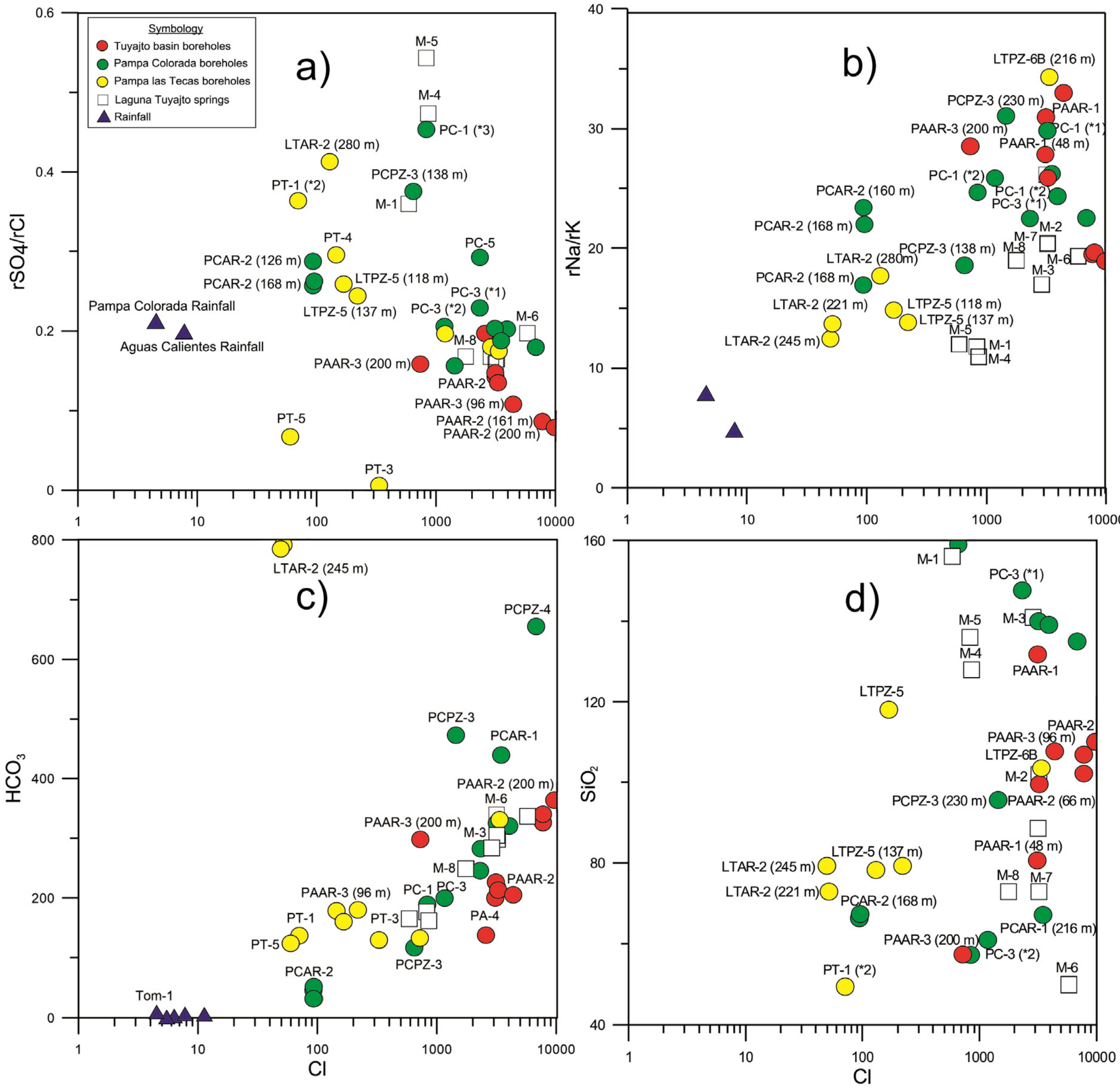

Fig. 7. a) Plot of rSO_4/rCl (r = meq/L) vs. Cl (mg/L) in rain, spring and borehole waters. b) Plot of rNa vs. rCl (r = meq/L) of waters from springs in Laguna Tuyajto and from the boreholes; some samples present a Na deficit relative to Cl, higher than the 0.88 ratio in average oceanic water. c) Plot of HCO_3 vs. Cl, both in mg/L. d) Plot of SiO_2 vs. Cl in spring and borehole waters, both in mg/L.

the Salar de Atacama, where the highest concentrations of sodium and chloride have been attributed to halite dissolution (Alonso and Risacher, 1996; Carmona et al., 2000).

The trend of increasing rSO_4/rCl in the water samples closer to the Tuyajto volcano can be explained by the above commented sulfur-rich gas emanations, which contribute to the higher relative S concentrations. This effect seems to decrease with distance to Tuyajto volcano as the other volcanoes are older and probably related to lower or negligible associated degassing rates. The rSO_4/rCl ratio is higher for moderate salinity groundwater when compared to higher salinity groundwater, thus pointing to the evapo-concentration effect, which is progressively obscured by halite dissolution as salinity increases, whereby the high salinity groundwater shows a much lower ratio. It is assumed that halite deposits do not contain a significant proportion of associated gypsum and other sulfate minerals.

The behavior of HCO_3 seems to be consistent with the process of salinization, from relatively small values for low salinity water up to about 300 to 500 mg/L HCO_3 for saline and highly saline groundwater. The important decrease in HCO_3 activity due to the increasing ionic strength may play a role. However, moderate salinity samples from two wells in Pampa Las Tecas have a very high HCO_3 content (i.e. 800 mg/L). This may be the result of the incorporation of deep volcanic CO_2 from the degassing chambers and its reaction with the rock to yield HCO_3. This means that, even if an important part of volcanic gas is vented to the atmosphere through the high volcanic edifices, a part may be transferred to groundwater in the depressions, directly or by lateral discharge of groundwater in the volcanic cores. This process has been well-documented in the islands of Tenerife and Gran Canaria (SPA-15, 1975; Custodio, 2004; 2007; Marrero Díaz, 2010). It should be noted, however, that in the studied area ^{13}C data were unavailable to further investigate and confirm such processes. The maximum concentration found seems to be close to CO_2 saturation at local atmospheric pressure.

The dominant local rock is of andesitic composition. When porphyritic, it contains sodic plagioclase (andesine), variable amounts of biotite, hornblende and pyroxene, and Ca-rich plagioclases and Mg-rich minerals. Rock weathering yields Ca, Mg, Na, and possibly K, according to rock chemical composition. This is spatially variable and it depends on the specific location where the weathering is produced. The plot of Mg vs. Ca gives an rMg/rCa ratio about 1 (not shown). However, some of the spring waters present a ratio of about 0.5 but without a clear spatial distribution. This may be due to variable rock chemistry and also to some $CaCO_3$ precipitation. The process of rock dissolution can be seen in the displacement from the 1/1 slope line in the rNa vs. rCl plot. The relatively low rNa/rK ratio (relative high proportion of K) in most groundwater samples may be due to the dissolution of K-rich minerals, but this has not been studied. The fact that the high salinity waters tend to exhibit a rNa/rK ratio of approximately 10 cannot be explained by the simple dissolution of halite. The mixing with K-rich deep brines cannot be excluded, but no data supports this. Ion exchange may play a role in the slowly renovating deep parts of the aquifer system.

While in many volcanic areas there is a clear excess of Na relative to Cl in groundwater, especially in basaltic rocks, most spring and well water located in the northern part of the studied area show a moderate sodium deficit relative to chloride which does not disappears when rNa + rK is considered. This is also observed in other areas, as in the geothermal field of El Tatio, not far away from the area considered here, wherein chloride-rich well waters have an rNa/rCl ratio of about 0.9 and between 0.84 and 1.1 in the hot springs (Giggenbach, 1978). Recent research in this geothermal field indicates that the highest chloride contents in the thermal waters may be due to HCl contribution from degassing of the magma chamber (Cortecci et al., 2005), although in the Tuyajto area this is probably a minor contribution, both from the atmosphere and directly to the saturated zone. The dominant salinization process is primarily due to halite dissolution processes from buried saline deposits.

4.4. Stable isotopes

The stable isotope characterization of groundwater ($\delta^{18}O$ and δ^2H) was performed in samples from the springs that outflow in Laguna Tuyajto boundaries and in the neighboring basin of Salar de Aguas Calientes-3. Rain, snow, spring, and groundwater isotopic data are given in Tables S5 and S6 in the Supplementary Material.

Due to the scarce rainfall events recorded in northern Chile and the small amount of rain produced in each one, it is very difficult to characterize the stable isotopic composition of precipitation and define the deuterium excess ($d = \delta^2H - 8\delta^{18}O$ ‰) of the local meteoric line relative to the global meteoric line ($\delta^2H = 8\delta^{18}O + 10$‰). The local meteoric line obtained by Chaffaut (1998) in the Salar de Quisquiro, located to the North of the studied area, has d = 15.3‰. The rainfall and snow samples of the studied area plot in-between these two lines (Fig. 8). Results are also very close to those of other rain samples obtained close to 4000 m asl in northern Chile (Aravena et al., 1999; Herrera et al., 2006). A base value of −11 to −10.5‰ $\delta^{18}O$ in the Tuyajto area can be compared with the range −14 to −13‰ in the Collacagua basin (Acosta and Custodio, 2008; Acosta et al., 2013) and with about −13‰ in Pampa Lirima (Achurra et al., 2011), both in the Tarapacá Region, to the North of the studied area, at an altitude of about 500 m higher than in Tuyajto.

The isotopic composition of local snow varies according to the altitude at which the samples were obtained. Most of them are isotopically lighter than the rainfall samples collected in the same place (Fig. 8). They do not show a significant isotopic deviation (i.e. fractionation) due to snow sublimation. The isotopic composition of snow samples from about 4400 m asl and spring water are similar (Fig. 8). Only a sample of rain collected in March 2004 in Pampa Colorada (4426 m asl), corresponding to a very intense precipitation event, approaches the isotopic composition of spring water. This indicates that aquifer recharge likely has a significant component of winter rainfall, meltwater infiltration in the highest parts of the area associated with the most intense rainfall events. This holds for rainwater samples obtained between the years 2004 and 2005. The spring discharge being the result of recharge under past wetter conditions is unlikely considering the relatively small groundwater turnover time in the studied area, as discussed later in more detail.

Springs located in the northern part of Laguna Tuyajto and Aguas Calientes-3, which outflow at the southern slope of the 5482 m asl Tuyajto volcano, have an isotopic composition very close to that of meteoric water (Fig. 8). Recharge likely comes from snowfall melting at high elevation areas.

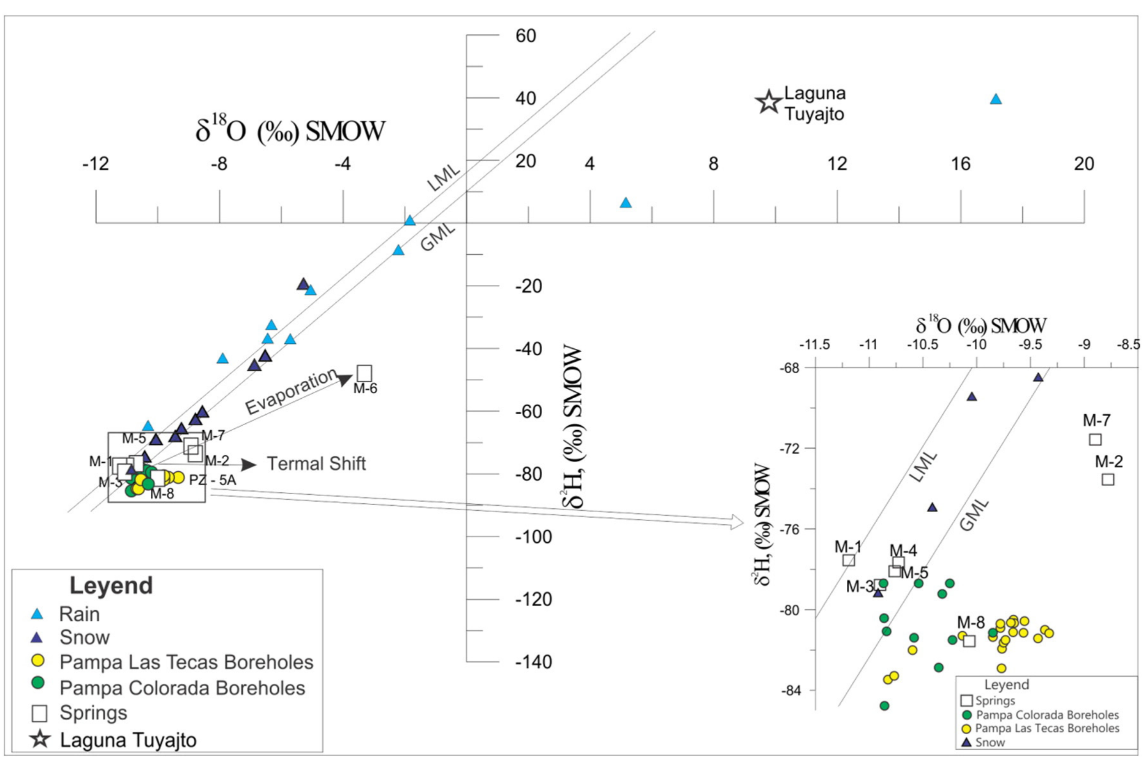

Fig. 8. Plot of $\delta^{18}O$ and δ^2H isotopic composition of precipitation in the study area, spring water, and water from the boreholes. LML: Local meteoric line. GML: Global meteoric line. The LML is parallel to the GML but with a deuterium excess of 15,7‰ instead of 10‰.

Springs M-2, M-7 and M-8 and the boreholes located in Pampa Colorada and Pampa Las Tecas have isotopic compositions with a clear shift toward more enriched $\delta^{18}O$ values with respect to the isotopic content of meteoric water. This suggests that the original recharged meteoric water is being affected by high temperature isotopic exchange with local rocks. However, these springs have lower temperatures than springs at the southern slopes of the Tuyajto volcano. Spring M-6, at the southern edge of the lake, shows isotopic fractionation by evaporation that can be explained by sampling almost still water in a small pond.

The hypothesis of isotopic exchange under hydrothermal conditions is a plausible one considering the volcanic environment where the aquifer is located and the existence of hot springs in the vicinity of Laguna Tuyajto. The volcanic environment, with meteoric waters infiltrating at different altitudes, produces variations in recharge water isotopic content (Giggenbach, 1992; Risacher et al., 2003; Cortecci et al., 2005; Custodio, 2010). The low δ^2H values of some groundwater samples could be explained by the light isotopic composition of the original meteoric water, which may reflect that the snowfall event occurred at high elevation.

The $\delta^{34}S$ in sulfate dissolved in the spring waters have been measured. No other data is available nor is the $\delta^{18}O$ content of sulfate known. The $\delta^{34}S$ values vary between 3.3 and 6.2‰ CDT.

4.5. Relationship between altitude and $\delta^{18}O$ and δ^2H

The water isotopic content is plotted against sample elevation (Fig. 9a). The $\delta^{18}O$ of snow samples vs. altitude fits a linear altitudinal gradient of −0.34‰ per 100 m, with a correlation coefficient of 0.67 (neglecting sample M6 due to potential evaporative effects). This altitudinal gradient is in the upper range of what is commonly obtained in other parts of the world (Plata, 1994; Lambán et al., 2015), although it is smaller than some of the $\delta^{18}O$ altitudinal gradients obtained in northern Chile that vary between −0.76 and −1.0‰ per 100 m (Aravena et al., 1999; Herrera et al., 2006). The $\delta^{18}O$ isotopic gradient determined in the Collacagua area is about −0.4‰ per 100 m (Acosta et al., 2013) and −0.7‰ per 100 m for Pampa Lirima (Achurra et al., 2011), both in the Altiplano of the Tarapacá Region to the North of the area considered herein. However, these high values should be considered with caution as they may represent the effect of variable sources of atmospheric vapor.

Fig. 9 shows that the waters from springs M-2, M-6 and M-7 and most of the groundwater samples from Pampa Colorada and Pampa Las Tecas plot on the $\delta^{18}O$ altitudinal regression, consistent with recharge at that corresponding elevation. However, this result is erroneous due to the thermal $\delta^{18}O$ shift. The shift does not affect the δ^2H altitudinal gradient −2.7 δ^2H‰/100 m ($r = 0.74$) (Fig. 9b). This trend corresponds to the −0.34‰/100 m for $\delta^{18}O$. Now, all springs, excluding the M-6 spring, are below the δ^2H altitudinal line. This fact points to aquifer recharge being produced between 4100 and 4600 m asl for confined flow conditions in between. Under the case of unconfined conditions and increasing recharge with altitude, a greater elevation of the upper unit boundary is needed to produce the observed results. The lack of further data precludes a detailed analysis. These altitudes are only found outside the boundaries of the Laguna Tuyajto basin, at the rims of the neighboring basins of Pampa Colorada and Pampa Las Tecas, to the East.

The spatial distribution of springs located in the northern part of Laguna Tuyajto and the springs of Aguas Calientes-3 suggests that groundwater feeding these springs is most likely recharged in the Tuyajto volcano (<4600 m asl) as the surface area of this volcano above that altitude is only a few km^2.

4.6. Characterization of groundwater recharge

Spring flow shows that recharge is rather important in spite of the aridity and is also observed in other areas of the Altiplano (Herrera et al., 2006). For an expected recharge area of 400 to 600 km^2 and a spring discharge of 3 hm^3/year (1 hm^3 = 1 million m^3 = 1 cubic hectometer), the average recharge can be crudely estimated as 5 to 7.5 mm/year, which is about 2 to 4% of average rainfall. This may be much greater in topographic high areas to negligible in depressions (basins).

Using data from the area close to the Salar de Atacama, the chloride concentration in precipitation water is estimated to be about 5 mg/L. This yields a chloride deposition rate of about 0.5 to 1 g m^{-2} year^{-1} as a reasonable estimate. This is compatible with estimates in similar

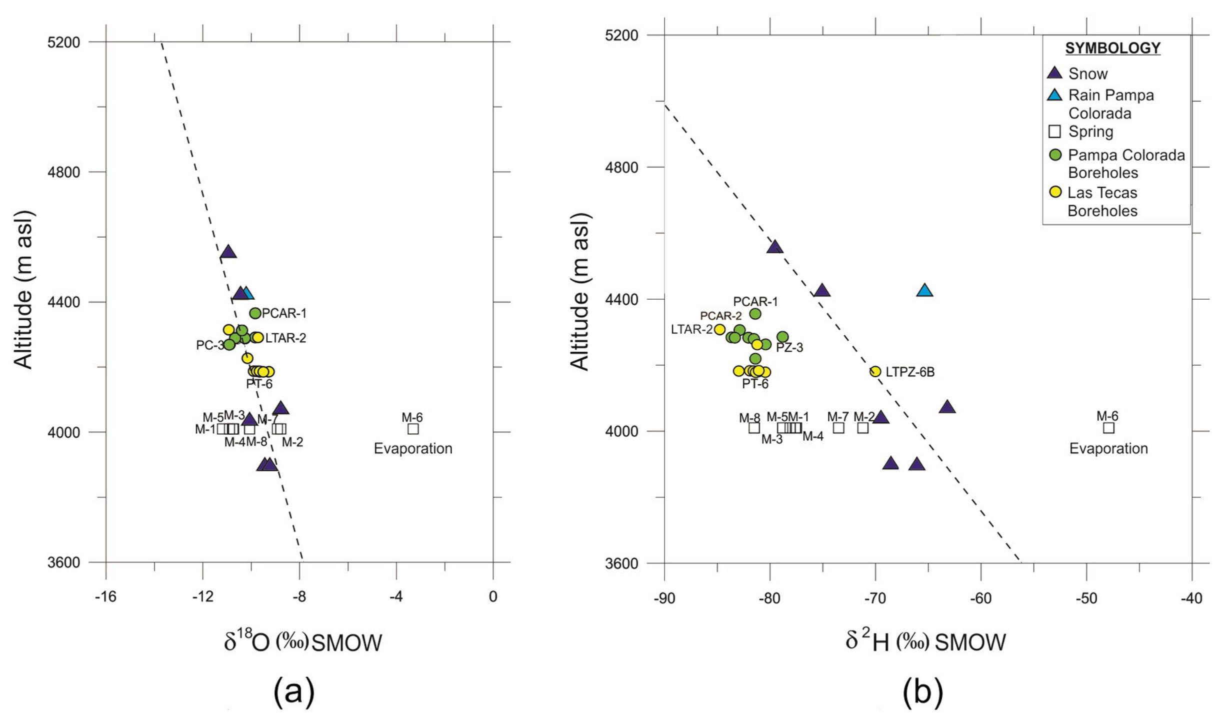

Fig. 9. Relationship of snowy precipitation and rain isotopic content vs altitude for: a) $\delta^{18}O$ and b) δ^2H.

arid areas, such as Fuerteventura Island (Herrera and Custodio, 2014a, b), the south-western Iberian Peninsula (Alcalá and Custodio, 2008a,b, 2014; Alcalá et al., 2011) and in others areas mentioned in these last papers. This is a relatively high value considering the transcontinental origin of the precipitation, which comes from the Atlantic Ocean through the South-American Continent. However, these values are consistent with a local saline environment due to the wind effect on the saline deposits existing on the land surface of the area. As mentioned previously, the possible local contribution of Cl to the atmosphere by volcanic emanations is presumably small, as commented before. Bulk atmospheric deposition samplers are being installed to try to apply the atmospheric chloride balance method, but results are not yet available.

The notable recharge in this arid environment is likely due to snow-melt and occasional intense rainfall on bare rock and to low water retention in the upper soil, preferentially at the higher areas and less clearly in the sediment-filled depressions. Using satellite images, Ammann et al. (2001) estimated an average of 8 major snowfall events in winter within this part of the Altiplano. However, in other parts of the Altiplano the main rainfall events take place in the austral summer, between December and March (Bolivian winter). In Laguna Tuyajto area the main rainfall events occur in the austral winter months (DGA, 2014). The $\delta^{18}O$ and $\delta^{2}H$ in precipitation and groundwater samples from studied area show that winter snow-melt water has an important role in aquifer recharge (Fig. 8).

The WMC (2006) report contributes 9 tritium measurements in water samples from Pampa Colorada and Pampa Las Tecas boreholes. Most results show tritium concentrations below the laboratory measurement threshold of about 0.8 TU (tritium units). Thus, it can be assumed that at least a large fraction of sampled groundwater was recharged before the 1960s, except in borehole PC-3 of the Pampa Colorada basin (1.5 $\pm$ 0.6 TU, a significant fraction of thermonuclear tritium) and perhaps in boreholes LTPZ-6B (0.85 $\pm$ 0.5 TU) and LTAR-2 (0.95 $\pm$ 0.6 TU) of the Pampa Las Tecas basin. The tritium values from rainfall collected by Aravena et al. (1999) in the Altiplano to the North of the studied area, range from 3 to 10 TU in 1994–1995. The current average tritium content is stable and presumably about 5 TU.

The transit time of water through an unsaturated zone of 10 to 100 m in young volcanic rocks containing an estimated 5% humidity in volume is on the order of several decades. Thus, a significant decay of infiltrated tritium during percolation through the vadose zone can be expected, which may explain the low or non-measurable tritium content observed in groundwater and springs. This does not exclude current recharge, as pointed out by the samples showing measurable tritium. But most samples are a mixture of relatively long transit time (high residence time) groundwater. The measurable tritium concentrations may correspond to snow-melt increased recharge in high areas when these are not far away from the springs.

The estimated recharge rate in a 100 m thick saturated zone result in an average renewal time of approximately 1000 years, so most deep samples should be tritium-free. Only some samples taken close to the water table and in springs drain shallow groundwater bodies that may contain a significant proportion of tritium.

4.7. Groundwater temperature

The water temperature in boreholes in the Pampa Colorada basin and springs located in the north edge of Laguna Tuyajto is above 20 °C and, in some cases close to 40 °C in depth. These temperatures are generally higher than that in the boreholes located in the southern part of the studied area, while in the southern basin of Pampa Las Tecas the temperature is generally between 10 and 20 °C. The average air temperature in the area is 1 °C and the upper soil is expected to have an average temperature a few degrees higher due to the low albedo of bare soil and rock exposures. The expected temperatures at the land surface were obtained by extrapolating the temperature logs of the boreholes and the temperatures of deep groundwater based on consideration of the global average thermal vertical gradient are well above actual temperatures (Table S7 in the Supplementary materials). This indicate that an increased thermal flow due to local volcanism and magmatism, which is common along the Andes.

The wells and springs with higher temperatures are located close to the Tuyajto volcano (M-1 and M-3), a likely result of its recent magmatic activity. A crude estimation of the original temperature can be obtained by means of ad hoc geothermometers. For such interpretations it is assumed: a) chemical and isotopic equilibrium at high temperature with existing minerals, b) rapid ascent of water to the surface so cooling has no time to significantly change the chemical and isotopic composition of deep water when water cools, and c) mixing with other waters is not occurring (Custodio and Llamas, 1983). These conditions must be checked and validated in each case. Halite dissolution in water further complicates the use of cation-based geothermometers (Giggenbach, 1988). Such conditions should be noted.

The SiO_2 content measured in spring waters is between 128 and 156 mg/L. The quartz geothermometer (Fournier, 1981) allow estimating temperatures of 151 to 163 °C assuming no vapor loss, and 145 to 155 °C assuming the maximum vapor loss that can occur through boiling. Evaporation is not pointed out by the water isotopic signatures (Fig. 8). The results depend on the actual presence and equilibrium with quartz and lack dilution with other groundwater and are consistent with the $\delta^{18}O$ shift in some water samples due to isotopic water–rock exchange at high temperature.

The spring waters that outflow into the eastern edge of Laguna Tuyajto do not show clear hydrothermal effects, except spring M-8, but they have at greater $\delta^{18}O$ shift to heavier isotopic contents. This water–rock isotopic exchange may be occurring away from the discharge area, with cooling along the flow path but without significant modification of the thermal footprint. The $\delta^{2}H$ content indicates that the recharge areas of groundwater that outflow in these springs are at high altitudes, beyond the boundaries of the Laguna Tuyajto basin.

Water from boreholes located in Pampa Colorada and Pampa Las Tecas also show water–rock isotopic exchange at high temperature. The above comments apply. In any case, the heat source seems to be located away from the hot manifestations.

There is no clear correlation between SiO_2 and HCO_3 content (plot not shown), which indicates that diverse processes act together. The

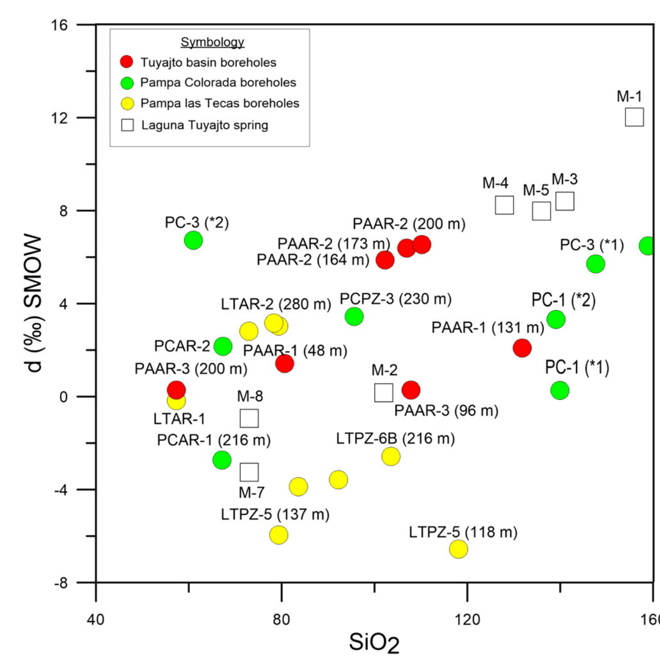

Fig. 10. Plot of d (excess deuterium, $d = \delta^{2}H - 8\delta^{18}O$ ‰) vs. SiO_2. Data from Laguna Tuyajto have been excluded due to affected by an intense evaporation effect.

plot of d (excess deuterium) versus SiO_2 (Fig. 10) shows a trend to an inverse lineal relationship, which confirms the $\delta^{18}O$ shift. Deviations can be due to other concurrent processes and incomplete equilibrium. Some outliers could correspond to fast flow but with intense rock weathering by acidic water, unstable high silica concentration, or evaporation.

4.8. Relation between Laguna Tuyajto brine and the groundwater system

The brine in Laguna Tuyajto is close to saturation to saturated with respect to halite. In a thick aquifer, driven by density buoyancy forces, this brine would flow downwards and spread below the fresher groundwater body around (Duffy and Al-Hassan, 1988; Fan et al., 1997; Warren 1999). This is a common situation in many similar saline groundwater regions. The water isotopic composition of the fresher groundwater displaced by the brine generally shows the effects of evaporative fractionation (Kohfahl et al., 2008). However, in Laguna Tuyajto, the low permeability ignimbrite found at the bottom of the shallow lake impacts groundwater discharge and seems to act as a barrier that prevents or makes brine convection difficult (Fig. 11). The spring water that outflows around Laguna Tuyajto generally exhibits lake surface water characteristics that are subjected to evaporation, converted into brine, and finally into salt deposits with negligible or minimal vertical brine infiltration. Well water surrounding Laguna Tuyajto, in spite of its high salinity, does not show significant $\delta^{18}O$ and δ^2H isotope fractionation due to evaporation. Therefore, the brine present in Laguna Tuyajto may be considered as a body of water that is half-isolated from the regional groundwater flow system and that potentially receives inflow from below. Observations show that the brine has spread laterally only to a small extent into the shallow formations around the lake. Fig. 12 compares schematically the conceptual model proposed here with the classical model of Duffy and Al-Hassan (1988) in which free convection occurs in the sediments under a saline lake.

Laguna Tuyajto has been assumed to be a terminal lake of a topographically closed flow system where contributed salts cumulate in the salt flat. There is no information of the salt thickness actually deposited, but it is probably small as the regional ignimbrite formation is at shallow depth and even outcrops in a patch. The boundary of Laguna Tuyajto facing the Salar de Aguas Calientes-3 seems to be a barrier comprised of recent ignimbrites. However, the Salar de Aguas Calientes-3 is about 90 m lower than Laguna Tuyajto, so some outflow from the Tuyajto basin may be hydraulically possible if the boundary formations have some degree of permeability. The accumulation of salt deposits in Laguna Tuyajto indicates that this water transfer should be relatively small. This small transfer may be produced through the boundary materials or the regional ignimbrite layer below. This water transfer (or dilution) process would tend to affect mostly the denser terminal brines after halite deposition. However, it should be noted that these inferences or hypotheses are speculative and there is no data to support or reject what has been said.

5. Conclusions

Despite the limited and difficult accessibility of the area and the limited available data (especially time series), a consistent hydrogeological conceptual model was developed to describe groundwater flow, salinity distribution and water chemical composition in an arid high altitude volcanic setting. This was done by different methods, including hydrometric observations and hydrochemical and water isotope composition from a number of field monitoring campaigns.

Despite of local aridity recharge is possible, mostly in the highest areas especially where snow exists seasonally and some winter storms occur. Recent volcanism and the associated formations play a key role in producing recharge.

The studied area may be described as part of a kind of “water tower” that is slightly elevated with respect to the surrounding areas, which discharge locally, mostly through the basins of Tuyajto and Salar de Aguas Calientes-3. Local discharge is favored by the existence of a regional Miocene ignimbrite formation related to a mayor volcanic caldera which acts as a lower boundary. Existing data does not provide enough information of the hydrogeologic system of other potentially permeable formations below the ignimbrite layer. However, the transfer of water to such units below and outside the area may not be quantitatively significant. The existence of small deep groundwater flow could be a way to transfer brines and terminal brines to the much lower areas around the basin.

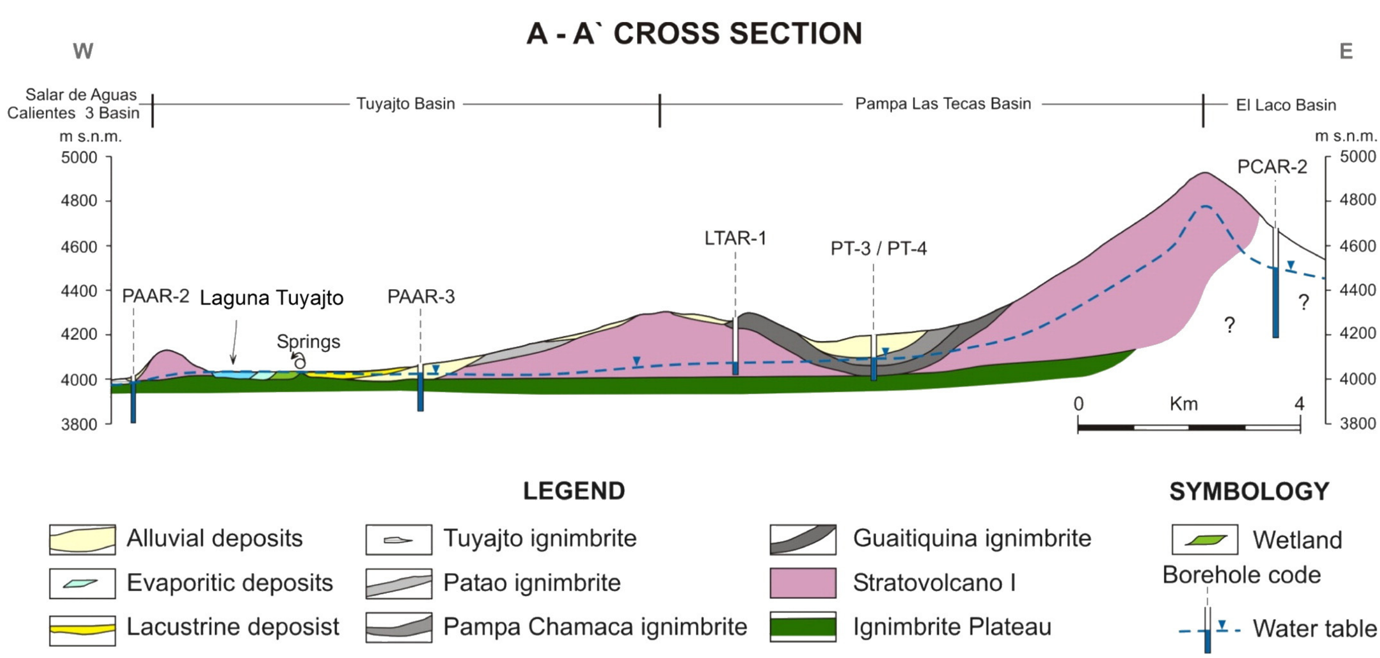

Fig. 11. Geological cross-section through line A–A′ in Fig. 2. Data come from field campaigns, regional geological letters, and descriptions of wells done by CME. In the PCAR-2 borehole zone the groundwater level is projected and the geology is unknown. The thickness of the ignimbrite forming the ignimbrite plateau is not known and presumably highly variable as it filled previous land surface irregularities.

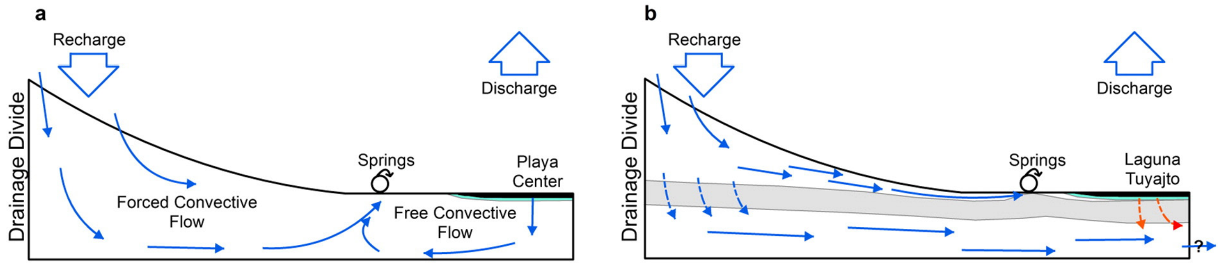

Fig. 12. Comparison of groundwater flow conceptual model in closed desert basin with a thick flow space below by (a) Duffy and Al-Hassan (1988) and (b) after this research, when a low permeability layer (the regional ignimbrites) is emplaced in a shallow position.

Groundwater can flow across local inter-basin boundaries, whereby heat/chemical altered rocks and dyke injected volcanics are consistent with recent volcanic and volcanoclastic deposits responsible for the current topography and concomitant tectonic activity. Evidence of such local water transfer processes are denoted by the water isotopic composition signatures.

Local tectonic disturbances associated with volcanic activity likely play a significant role in the detailed configuration of the basins and some-related lineal shapes. The existence of warm and potentially hot groundwater shows that some deep groundwater flow is possible across relatively low permeability formations. This elevated thermal gradient is most likely associated with recent volcanism of the Tuyajto volcanic system. The chemical and isotopic composition of the spring water of the basins of Laguna Tuyajto, Pampa Colorada, and Pampa Las Tecas is primarily controlled by the dissolution of evaporite minerals. The dissolution of halite and sulfate-bearing minerals associated with ancient salt deposits deposited under past land and climate conditions may have been later covered by later volcanic flows and sediments. For example, only a few boreholes yield relatively low salinity water that could be associated to current recharge in the volcanoes.

Volcanic gases are mostly vented through the volcanoes and contribute to a relative sulfate increase in rainfall chemical composition around the recent Tuyajto volcano, which is reflected in groundwater chemical composition. The volcanic CO_2 is mostly vented to the atmosphere, though two wells close to the Tuyajto volcano are directly affected and exhibit relatively high HCO_3 concentrations. The predominantly andesitic rock composition does not produce a sodium excess, but tends to play a role in the higher dissolved Ca and Mg concentrations with less abundant Na, and a relatively large K contents relative to Na. The deficit of sodium relative to chloride in Laguna Tuyajto springs may be related to the dissolution of rock minerals, enhanced by volcanic CO_2 contribution. The deep thermal anomaly is reflected in a ^{18}O shift to heavier $\delta^{18}O$ values due to exchange with the rock and this trend is consistent with increasing SiO_2 contents, although there are exceptions due to lack of chemical and isotopic equilibrium or preferential silica dissolution enhanced by volcanic CO_2 under low temperature in the underground environment.

Many of the boreholes show increasing salinity with depth and in some cases there is a sharp interface separating less saline water from highly saline water, although this could be due to head changes along the borehole. The existence of brine at the bottom of the aquifer system seems a common condition. The origin of this brine is not clear due to insufficient data, but it may be related to past conditions supporting a larger closed water system producing downward-convected brines and/or produced from the dissolution of buried salt deposits. To some extent, these brines are incorporated to the active groundwater flow.

The fate of evaporation brines in Laguna Tuyajto is not clear. It can be assumed that they are locally evaporated, increasing the mass of halite salts deposited since the current landscape was established after the effusions of the Tuyajto volcano. However, some small underground transfer to the Salar de Aguas Calientes-3 basin could be possible, especially for the terminal evaporation brines.

The above conclusions refer to the Tuyajto area, where available data, even if incomplete and poorly distributed, allows the characterization of the major hydrogeological, hydrogeochemical and geothermal conditions, and the knowledge of inter-basin relationships. This can be used to understand other common situations in the Andean Altiplano and in other areas under similar climatic and geological–volcanological conditions, such as those existing in the arid part of the African Rift whereby data is more limited and the conceptual groundwater functioning models are not well-defined or understood. The results and methods employed from this study are important for elucidating and constraining the hydrologic/hydrogeologic processes (i.e. flow) occurring across boundaries of topographically closed (endorheic) basins within active volcanic and tectonic regions. Basins can be isolated or not (as is the often non-documented experience in other areas of the Andean Altiplano), depending on local geology of recent deposits and volcanic effusions. Therefore, careful characterization and the design of well-conceived hydrochemical and isotopic studies are required to try to solve these situations when groundwater development and protection plans are planned. This study shows that recharge is important in these arid areas under the specific conditions that have been identified, but it can be negligible under other conditions. The salinization produced by buried salt deposits is a fact that has been pointed out in other areas, but there are not published reports. The results of this study are relevant for explaining and locating the presence and accumulation of some commercially important solutes and salts in low elevation salt-flats (*salares*) and brine lakes such as those in the Atacama region.

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