Origin of waters from small springs located at the northern coast of Chile, in the vicinity of Antofagasta

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ABSTRACT. The origin of waters from small springs located at the hyper-arid northern coast of Chile, in the vicinity of Antofagasta, is discussed after hydrogeochemical and isotopic studies and supported by groundwater flow hydrodynamic considerations. Spring water is brackish to saline, with electrical conductivity ranging from 2 to 25 mS/cm. Chemical and water isotope data (^{18}O and ^2H) show that the rainfall events that produced part of the recharge could correspond to wetter conditions than at present. Their origin could be related to the emplacement of warm sea currents facing the coast of northern Chile, possibly associated to incursions of El Niño Southern Oscillation (ENSO). Radiocarbon dating and preliminary groundwater hydraulic calculations indicate that these spring waters could be remnants of a more significant recharge in the Cordillera de la Costa than that produced today during the less arid period about 5,000 to 3,000 years ago. The exception is Las Vertientes spring which is the only one that receives water transferred from the Central Depression. The springs are the visible discharge of a regional groundwater body in the very low permeability Cordillera de la Costa, whose hydraulic conductivity decreases downward and flow is dominantly though fissures and storage in the low porosity rock matrix.

Keywords: Cordillera de la Costa, Antofagasta, Spring, Groundwater, Stable isotopes, Radiocarbon, Arid climate, Recharge.

RESUMEN. Origen de las aguas de pequeños manantiales de la costa del norte de Chile, en las cercanías de Antofagasta. Se discute el origen de las aguas que surgen en pequeños manantiales localizados en la costa hiperárida del norte de Chile a partir de un estudio hidrogeoquímico e isotópico, apoyado en consideraciones hidrodinámicas del flujo del agua subterránea. Las aguas de los manantiales son salobres a salinas, con valores de la conductividad eléctrica que varían entre 2 y 25 mS/cm. El estudio de la composición química e isotópica (^{18}O y ^2H) de las aguas revela que las precipitaciones que produjeron la recarga se registraron en condiciones más húmedas que en la actualidad. Su origen estaría relacionado con el emplazamiento de corrientes marinas cálidas frente a las costas del norte de Chile, posiblemente asociadas a la incursión de El Niño-Oscilación del Sur (ENOS). Las dataciones con radiocarbono y los cálculos hidráulicos preliminares indican que las aguas que afloran en estos manantiales pueden corresponder a remanentes de una recarga más significativa ocurrida en un período menos árido que el actual alrededor de 5.000 a 3.000 años atrás, si bien también hay evidencia de alguna recarga reciente en situaciones locales. La única excepción corresponde a las aguas del manantial de Las Vertientes, que recibe contribución de aguas subterráneas de la depresión Central. Los manantiales son la descarga visible de un cuerpo general de agua subterránea en los materiales muy poco permeables de la Cordillera de la Costa, cuya conductividad hidráulica decrece en profundidad y donde el flujo se produce dominantemente por fisuras y el almacenamiento, en una matriz de baja porosidad.

Palabras clave: Cordillera de la Costa, Antofagasta, Manantiales, Aguas subterráneas, Isótopos estables, Radiocarbono, Clima árido, Recarga.

1. Introduction

Along the coastline of northern Chile, in the Atacama Desert, an extensive mountain range called Cordillera de la Costa (coastal range) exists. It is one of the driest regions of the world, containing areas whose average annual precipitation in many cases is less than 1 mm, which means long periods of extreme aridity and occasional rainfall events widely separated in time. On the western slope of the Cordillera de la Costa some low discharge springs can be recognized. The numerous archaeological sites located in the vicinity of these springs show they are permanent ones (Núñez and Varela, 1968). The small flow is the result of current or past groundwater recharge despite the extreme aridity. The research carried out is to identify the conditions of such recharge.

Spring water is of the sodium-chloride type, being the sulfate the second anion in importance. Water composition has some similarity to seawater, which is due to atmospheric deposition being dominated by marine aerosol and the high salinity to intense concentration by evapotranspiration (evapoconcentration) of precipitation. Soluble salts deposited in the soil are dissolved and transferred to aquifer recharge when some of rare significant precipitations occur.

2. Location and climate

The Cordillera de la Costa corresponds to an extensive mountain range that stretches along the coastline of northern Chile. Its width is between 15 and 50 km and reaches an average altitude of 1,600 m (Fig. 1). In general, the altitude of the Cordillera de la Costa increases from north to south and reaches the highest elevations, approximately 2,800 m a.s.l. (above sea level), at the latitude of Paposo. In some parts, this mountain range rises abruptly from sea level, forming a cliff that can reach up to 1,000 m a.s.l. Its eastern boundary is smooth and slopes gently toward the Central Depression, although in some places topographic breaks separate these two geomorphological units, which could correspond to faults (Chong, 1991). The Central Depression extends to the Pre-cordillera (fore range) and the Altiplano (highlands of the Andes), with elevations above 4,000 m.

The six springs and the water well studied are located on the western slope of the Cordillera de la Costa (Fig. 1) and are far apart from each other. The physical characteristics of each one of these springs and the water well are presented in table 1, plus the rock types that dominate in the respective assumed recharge area. Permanent springs yield a few m³/day, except Las Vertientes spring, which yield two orders of magnitude more water. All of them are known since the old times.

The extreme dryness of the Cordillera de la Costa and the Central Depression owes its origin to permanent anticyclone conditions off the coast of northern Chile and the cold Humboldt ocean current (Klohn, 1972; Rutllant, 1985). On the other hand, the Andes range is an impressive mountain barrier preventing the arrival of moisture coming from the Atlantic Ocean through the Amazon Basin. Some of this moisture reaches the western slope of the Andes in the summer months, in the so-called 'Invierno Altiplánico' (highlands winter), but not the Central Depression.

The Cordillera de la Costa has an extremely arid climate. Average rainfall is between 0.5 and 8 mm/yr (Table 2), without any precipitation for 4 or 5 consecutive years and only some sporadic short storms. Temperatures at the coast are mild and stable most of the year due to the smoothing effect of the sea. Monthly mean values range between 13.5°C and 20.1°C in the city of Antofagasta (DGA, 1987).

Condensing fog in the winter months, known locally as Camanchaca, is a common fact. It consists on thin, small clouds trapped against the Cordillera de la Costa at the coastal side. Sometimes this fog produces local small drizzle and horizontal rain when droplets are intercepted by vegetation, especially when the system is altered by the spread towards the north of cold fronts coming from the south (Ogaz and Fuenzalida, 1981; Houston, 2006). In the most favorable areas for fog condensation, further south of the area here considered, the total distributed contribution does not exceed 10 mm/yr (Román, 1999). Isotopic studies of rainfall in the central-northern Chile indicate that this type of precipitation does not produce significant recharge increase to aquifers (Aravena *et al*., 1989; Squeo *et al*., 2006), but it favors the existence of vegetation. Similar situations are found in Perú (Jiménez *et al.*, 2012) and in the Canary Islands, especially in Tenerife (Braojos, 2011; Santana, 1987). The wet air, when climbing above 500 m partially condense in the soil surface, allowing a limited development of some species of cacti and small shrubs in the highest parts of the Cordillera de la Costa (Ramírez, 1982). The greater penetration of the Camanchaca occurs in the
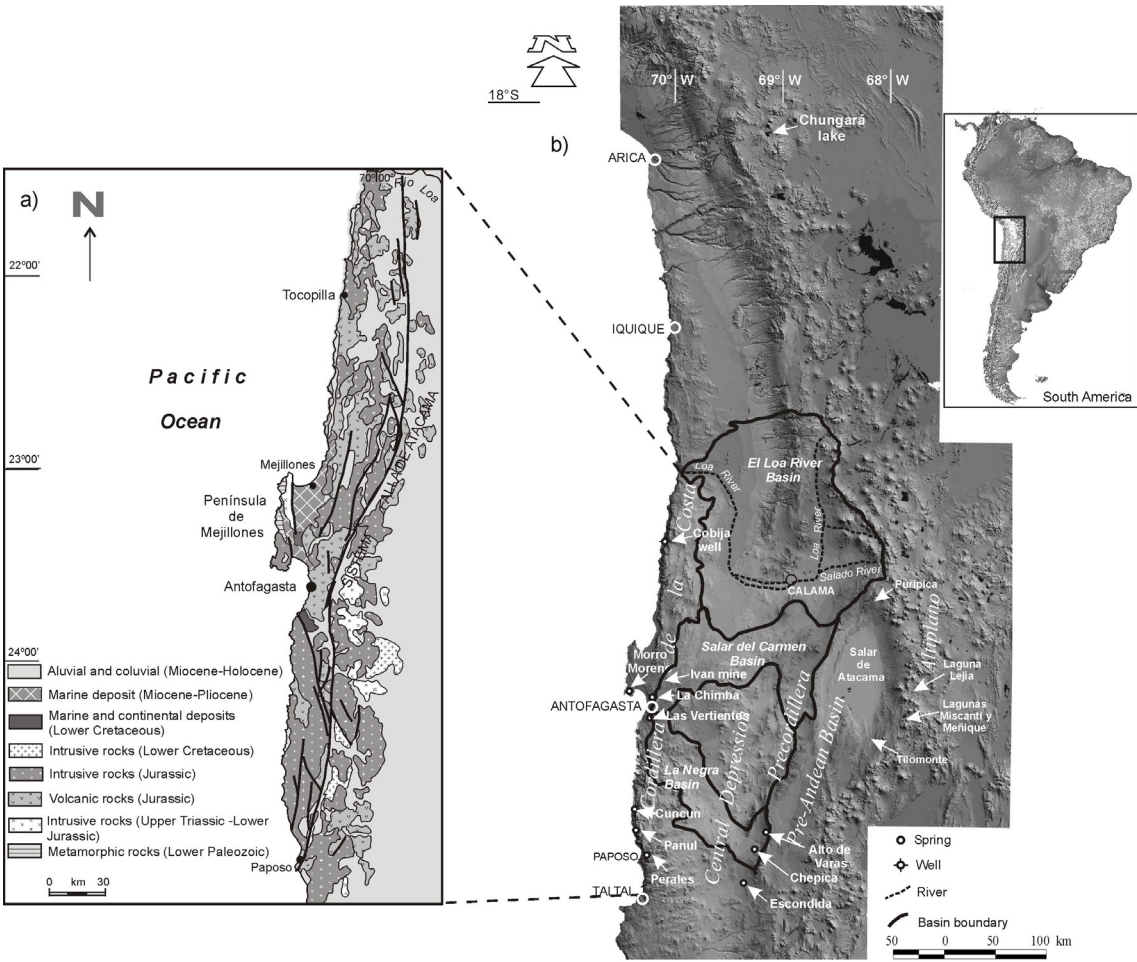
FIG. 1. Location map. **A.** Geologic map of the Cordillera de la Costa in the Antofagasta Region; **B.** Elevation digital model of northern Chile showing the springs in the Cordillera de la Costa and location of the main geographic points mentioned in the text.

TABLE 1. LOCATION AND MAIN CHARACTERISTICS OF COASTAL SPRINGS.

Name	UTM		Elevation m a.s.l.	Distance from the coast m	Discharge m³/day	Lithology
	N	E				
Cobija well	7,513,608	3,72,177	21	100	-	Andesite
Morro Moreno spring	7,398,012	3,38,621	22	12	7	Gabbro
La Chimba spring	7,396,287	361,268	450	3,700	19	Andesite
Las Vertientes spring	7,378,137	357,724	154	1,000	216	Debris flow and andesite
Cuncun spring	7,281,691	341,980	12	20	13	Granodiorite
Panul spring	7,258,933	345,728	370	2,800	14	Granodiorite
Perales spring	7,231,045	353,426	389	2,000	19	Diorite

TABLE 2. AVERAGE ANNUAL RAINFALL OF COASTAL CITIES OF NORTHERN CHILE*

Station	Lat. S	Rainfall (mm/year)
Arica	18.5	0.5
Iquique	20.8	0.6
Tocopilla	22.0	2.0
Antofagasta	23.5	1.7
Taltal	24.4	8.0
Chañaral	26.2	12.0
Caldera	27.0	27.0
La Serena	29.9	78.0

* Quezada *et al*., 2010.

breached coastal areas of the Loa River mouth and Quebrada La Negra (Ramírez, 1982). Hyper-arid conditions fully shows up in the Central Depression, where there is no influence of low fog and almost total absence of rainfall. The dryness and high thermal variability prevent the development of any kind of vegetation (Quade *et al.*, 2007; Cereceda *et al*., 2008).

The study area extends between the mouth of the Loa River at the north and the town of Paposo in the south. In this area there are not ravines connecting hydrologically the coastline with the inner basins of the Central Depression (Fig. 1). Although La Negra basin (different from the La Negra Quebrada mentioned above) almost comes across the Cordillera de la Costa in a pass about 15-20 m high, their altitude is above current overflow threshold of the basin, so that upstream water contributions end in the Salar del Carmen endorheic area.

Up to now groundwater discharges from basins located east of the Cordillera de la Costa have not been identified, but as discussed below, Las Vertientes spring receives recharge generated at the Pre-cordillera. While the structural domain of the Cordillera de la Costa is defined by the mainly oriented north-south Atacama Fault system, there are other structures with north-west and north-east orientation associated with this fault system capable of producing discontinuities in the rock mass.

3. Geological setting

The geologic units of the Cordillera de la Costa are mainly andesitic volcanic rocks of the La Negra

Formation (García, 1967) and intrusive rocks of Jurassic age (Fig. 1A). The lavas of the La Negra Formation form a monoclinal sequence that dip west and can reach up to 7,000 m thick (González and Niemeyer, 2005) and correspond to the vestiges of intense volcanic activity in an ancient magmatic arc (Boric *et al.*, 1990; Quezada *et al.*, 2010). They consist of andesitic lavas, andesite-basalts and basalt breccia with interbedded volcanic tuffs and sandstones (Boric *et al.*, 1990). These rocks have a massive appearance and in many cases it is difficult to recognize the different lava flows. These units are cut by dikes of basaltic, andesitic and dacitic composition. These formations can be considered very low permeability rocks.

The intrusive rocks recognized in the Cordillera de la Costa are mainly gabbros, diorites, granodiorites and tonalities, and granites with a lesser extent. They are dominantly of Jurassic age, but also some intrusive Triassic and Cretaceous bodies exist. Contacts between the units correspond to intrusion boundaries and faults. In some cases the intrusive bodies of the Middle-Upper Jurassic include vein deposits of copper, gold and silver (Boric *et al.*, 1990).

The main structural system that controls the Cordillera de la Costa corresponds to the Atacama System Fault, about north-south oriented, and the associated faults. The movement of this fault system was mainly vertical during the Cenozoic (Armijo and Thiele, 1990; Scheuber and Andriessen, 1990; Riquelme *et al.*, 2003).

On the western slope of the Cordillera de la Costa, large alluvial fans descend from the east toward the coast. They could have some potential hydrogeological interest. The alluvial deposits of these fans are interbedded with eolian deposits and in many cases they are completely covered by eolian silica sands. In the Cordillera de la Costa some small inner basins are also found, which can hold small aquifers, but the hydrogeological explorations made in some of them have not yielded good results. Only a small basin located north of the Antofagasta city in the past was exploited for water supply of Mine Ivan, but it was abandoned due to the small yield and poor water quality.

4. Climatic history during the late Pleistocene-Holocene in the Antofagasta Region

Several sedimentological, archaeological and limnological studies made in the Atacama Desert

provide a background on past climate during the late Pleistocene-Holocene. Also the paleoclimate research conducted in the Antofagasta Region shows differences between the Altiplano and the coastal and Pre-Andean areas during the Pleistocene-Holocene.

Most of these studies show that during the Last Glacial Maximum (16,000 yr B.P.) arid conditions dominated in the Altiplano (Geych *et al.*, 1999; Latorre *et al.*, 2002; Núñez *et al.*, 2002), with a rainier period when it ended, between 14,000 and 9,000 yr B.P. Indeed, radiocarbon dating indicates that most lakes of the Altiplano began to expand in the period about 14,000-12,000 yr B.P., reaching its highest levels between 10,800-9,200 yr B.P. (Geych *et al.*, 1999; Grosjean *et al.*, 2001; Rech *et al.*, 2002; Maldonado and Rozas, 2008). The maximum extent of the lakes was attained 9,200 yr B.P. and then a water level decline began until many of them disappeared or its surface was significantly reduced about 8,400-8,000 yr B.P. (Geych *et al.*, 1999). The sedimentological records and paleohydrological studies conducted in Lejia lake, in the Western Corillera, show that in the time of its maximum extension the water level was 25 m above current level and rainfall was around 500 mm/yr, higher than the current 200 mm/yr (Núñez and Grosjean, 1994). The lowest rainfall in the Altiplano at the end of the early Holocene coincides with a significant reduction of the Altiplano lakes extent (Núñez *et al.*, 1997, 2002; Grosjean *et al.*, 2001; Tapia *et al.*, 2003). This decreased rainfall affected the most sensitive ecological systems, such as wetlands, and had a significant impact on the development of indigenous populations, which remained only in those areas where water sources had some stability, as at Puripica and Loa rivers (Lynch and Stevenson, 1992; Grosjean *et al.*, 1997).

Data on the paleoclimatic history of the coastal and Pre-Andean zones in the Region of Antofagasta are scarce. Paleohydrological studies correspond to the study of paleo-wetlands (Rech *et al.*, 2002). Two periods of increased groundwater discharge are identified: a first period from 12,800 and 8,100 yr B.P., recorded only in the eastern part of the Salar de Atacama (in Tilomonte), and a second period of increased activity from 7,400 and 3,000 yr B.P. recorded in the Tilomonte area, Loa river, Salado River, and Quebrada Puripica.

Deposits between the two periods are not preserved. The mentioned study also shows that groundwater levels declined significantly between 3,000 and 800 yr B.P.

On the coastal edge of the Antofagasta Region, the more accurate information about rainfall during the Pleistocene-Holocene corresponds to stratigraphic and chrono-stratigraphic studies conducted in alluvial fans. From radiocarbon dating of seashells located at the base of a sequence of debris-flows above eolian deposits show that the end of the great drought occurred about 5,450 yr B.P. (Vargas *et al.,* 2006). The correlation of the eolian deposits located at the base of these alluvial deposits with eolian deposits found in the archaeological site Chimba-13, in Quebrada Las Conchas, Cordillera de la Costa, limits the period of drought between 10,280 and 5,453 yr B.P. [10]Be ages of the skin of quartz clasts exposed on the surface of alluvial fans hung by faults in the northern part of the Mejillones Peninsula show that the last time water flowed in these alluvial fans occurred approximately 14,000 yr B.P. (Cortés *et al.*, 2012). Therefore, the period of great drought in coastal northern Chile probably spread between 14,000 and 5,400 yr B.P., followed by a semi-arid period, and again by hyper-arid conditions lasting until present.

The start of the period of drought in the Altiplano does not match the period in which the archaeological site Chimba-13 (near the Chimba spring) was abandoned by their inhabitants, about 9,150 years ago, but it is quite close to the beginning of water level decline in the Altiplano lakes 9,200 years ago (Geych *et al.*, 1999). Radiocarbon dating indicates that settlement in this place occurred between 10,280 and 9,150 yr B.P. (Llagostera *et al.*, 1997).

5. Sampling and analytical methodology

The springs of the coastal edge of Antofagasta Region have been sampled directly from the fractures through which water outflows. Water temperature, pH, electrical conductivity, and other chemical determinations were determined in the field. Two field campaigns were conducted, in June 2005 and July 2006 respectively. In the first campaign only complete chemical analyses were performed. After looking at the first results, in the second sampling only selected springs were considered for complete chemical and isotopic (^{18}O, ^{2}H, and ^{3}H in water, ^{13}C and ^{14}C in the DIC (dissolved inorganic carbon, and

^{34}S and ^{18}O in dissolved sulfate) analysis. Three water samples from springs at the headwaters of the La Negra basin, in the Pre-Andean area of the Antofagasta Region were also analyzed to compare the results.

Water samples for chemical analysis were filtered (0.45 mm) in the field at the time of sampling and stored in 1,000 mL double stopper polyethylene bottles, without air bubbles and protected from light. The anions were determined by absorption spectrophotometry (Cl, SO_4, NO_3) and titration (HCO_3), and cations by atomic absorption and plasma emission spectrometry; SiO_2 content were determined by molecular absorption photometry. The ion balance of most samples is less than 5%.

All chemical determinations were made at the Water and Riles Area Analysis of the DICTUC. The ^{18}O and ^{2}H analyses were performed at the Environmental Isotope Laboratory of the Chilean Nuclear Energy Commission (CCHEN), the ^{34}S and ^{18}O of dissolved sulfate in the laboratories of the Scientific-Technical Services of the University of Barcelona, and the tritium in the laboratories of the CEDEX in Madrid. In all cases standard techniques and common procedures were used. Due to the large amount of dissolved sulfate and the low dissolved inorganic carbon concentrations in water, the ^{14}C (and also the ^{13}C) content was determined by accelerator mass spectrometry (AMS) in the Beta Analytic laboratories in the United States. Isotopic ratios are reported referred to the usual standards, V-SMOW for δ^2H and δ^{18}O, V-PDB for δ^{13}C, and CDT for δ^{34}S.

6. Results

6.1. Spring water hydrogeochemistry

The major chemical components and some ion ratios from the analyses of waters from the July 2006 field campaign have been used for the hydrogeochemical characterization of the coastal springs to identify the origin of the salinity.

The waters of the coastal springs are brackish to saline, with electrical conductivity values between 2 and 25 mS/cm and temperatures between 18 and 23°C (Table 3). The chemical composition corresponds to the sodium chloride type, being sulfate the second anion, and mimics seawater. This is attributable to dry and wet atmospheric deposition dominated by marine aerosol. The precipitation, which besides dissolve salts in the top soil from previous dry deposition and evaporated precipitation, suffers intense evapoconcentration. Thus, when some recharge is produced it is highly saline. Similar conditions, although under not so extreme arid conditions, are found in the eastern Islands and southern coastal areas of The Canaries (Custodio 1990, 1992; Herrera and Custodio, 2002, 2004). As there is no long-term accumulation of soluble salts in the Cordillera de la Costa topsoil, except for some calcium carbonate and perhaps some gypsum in some cases, dry and wet deposition contributed salts are dissolved and passed to the aquifer when occasional significant precipitation events produce some recharge (Fig. 2). The Camanchaca could play

TABLE 3. ANALYTICAL DATA IN mg/L. THE PREFIX ´r´ IN THE RATIOS MEANS THAT CONCENTRATIONS ARE IN meq/L. EC IS ELECTRICAL CONDUCTIVITY AT 20°C IN mS/cm.

| Sample	T (°C)	EC	pH	Na	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	NO$_3$	SiO$_2$	Br	rCl/rBr	rNa/rCl	rSO$_4$/rCl
Cobija	21.3	6.1	7.75	1,007	45	212	87	1,600	645	133	12	18.1	5	721	0.97	0.30
Morro Moreno	21.6	8.65	8.13	1,175	52	180	220	2,500	380	89	20	18.9	8	704	0.73	0.11
La Chimba	17.6	25.3	7.28	4,950	100	647	394	9,200	1,440	78	18	18.7	25	829	0.83	0.12
Las Vertientes	19	24.0	7.31	3,100	60	1,015	176	6,200	1,640	42	210	23	2	6,984	0.77	0.20
Cuncun	23.2	16.96	8.2	2,758	60	707	352	5,850	760	30	37	21.7	16	823	0.73	0.10
Panul	13.5	2.0	8.73	133	7	126	38	360	122	81	60	16	1	811	0.57	0.25
Perales	18	6.2	7.71	1,018	26	185	129	1,820	420	180	9	14.8	6	683	0.86	0.17
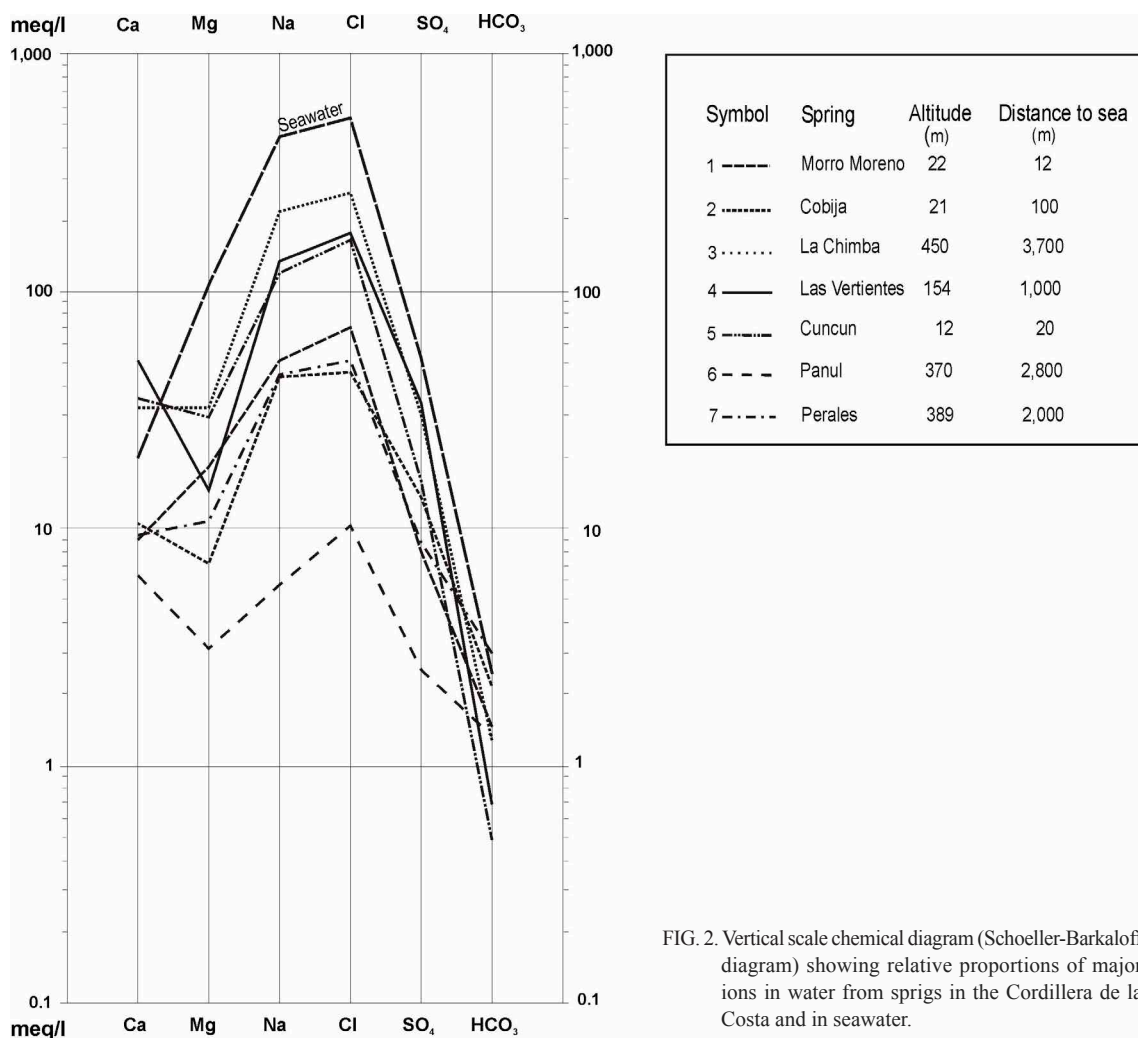
FIG. 2. Vertical scale chemical diagram (Schoeller-Barkaloff diagram) showing relative proportions of major ions in water from sprigs in the Cordillera de la Costa and in seawater.

a role in the mobilization of marine aerosol from the air because it can incorporate large suspended particles, thus allowing their penetration inland (Berger and Cooke, 1997). As the Camanchaca is generally produced between 300 and 1,000 m a.s.l., it is expected than most marine salt deposition occurs at these altitudes (Cereceda *et al.*, 2008). Near the coastline and below 800 m, gypsum is found in the material cementing the sediments of old alluvial deposits and occasional 2 to 5 mm isolated gypsum crystals (Rech *et al.*, 2003). Calcium carbonate has often been recognized cementing alluvial ancient deposits, usually below 900 m (Quade *et al.*, 2007).

The Panul spring, in Paposo area, escapes from the general trend of high salinity coastal springs,

as it has a lower mineralization, albeit it shows similar ionic ratios. At this spring location local orographic precipitation is produced, resulting in a less dry environment.

In order to assess the origin of the dissolved ions in spring waters, the theoretical contribution of seawater calculated from the chloride content, assuming that all chloride is of marine origin, is subtracted from the actual chemical composition of spring water. This difference is given as D in table 4. The most important results are:

1. Almost systematic Na+K deficit, except for the Cobija well water, with an equivalent excess of Ca+Mg, especially of Ca (it shows up because Ca concentrations are lower). This can be attributed

TABLA 4. CONCENTRATIONS IN meq/L.

Sample	rNa	rK	rCa	rMg	rCl	rSO$_4$	rHCO$_3$	rNO$_3$	Δ rNa	Δ rK	Δ rCa	Δ rMg	Δ rSO$_4$	Δ rHCO$_3$
P. Cobija	43.8	1.1	10.6	7.2	45.1	13.4	2.2	0.2	4.9	1.0	8.9	–1.8	8.7	2.0
M. Morro Moreno	51.1	1.3	9.0	18.3	70.4	7.9	1.5	0.3	–9.6	–1.3	6.7	4.3	0.6	1.2
M. La Chimba	215.2	2.6	32.3	32.8	259.1	30.0	1.3	0.3	–8.3	–2.1	22.6	–18.8	3.2	0.2
M. Las Vertientes	134.8	1.5	50.7	14.7	174.6	34.2	0.7	3.4	–16.2	–1.7	44.1	–20.1	16.2	0.0
M. Cuncun	119.9	1.5	35.3	29.3	164.8	15.8	0.5	0.6	–22.3	–1.5	23.1	2.5	–1.2	–0.2
M. Panul	5.8	0.2	6.3	3.2	10.1	2.5	1.3	1.0	–5.2	0.0	5.9	1.2	1.5	1.2
M. Perales	44.3	0.7	9.2	10.7	51.3	2.7	2.9	0.1	0.0	–0.2	8.8	0.5	3.4	2.7
Sea	459.0	9.7	20.0	106.0	532.0	55.0	2.3	0.0	-	-	-	-	-	-

M= spring; **P**= well. An average composition of seawater is included (Custodio and Llamas, 1983; sec 10, Annex 1). Δ is the result of substracting from theactual concentration the contribution of diluted seawater calculated after the cl content of the water.

to the chemical alteration of atmospheric dust and rock by precipitation water, with possible neoformation of clay minerals in arid environment, preferably illite, which retains part of the cations. Excess Ca increases with greater salinity.

2. Mg deficit only in La Chimba and Las Vertientes springs. Since these springs are the only ones with water flowing through andesitic lavas, the deficit could be explained as a result of weathering of ferro-magnesian minerals in the matrix of these rocks.

3. Moderate SO$_4$ excess, explainable by the incorporation of airborne natural volatile sulfur compounds. The effect is larger the lower the marine contribution is. The significant SO$_4$ excess in Las Vertientes spring could due to the dissolution of gypsum in the Central Depression.

4. Low to moderate HCO$_3$ content, which is controlled by the partial pressure of CO$_2$ in the soil, the possible contribution of wind-transported biogenic carbonate particles from the coast (the area has eolian deposits and prevailing winds from the coast), and rock-water reactions.

5. Relatively high NO$_3$ concentration despite the absence of significant human activities. This is common in arid areas and it is due to mineralization of atmospheric input of nitrogen compounds when soil activity is low or nil, and high evapoconcentration. Transport of nitrate-laden inland dust from the Central Depression, where the largest nitrate deposits of the world exist, is also possible. Spring waters have relatively low concentrations of SiO$_2$, between 15 and 23 mg/L, indicating scarce to moderate water interaction with the dominating rock silicate minerals due to low water aggressiveness due to the low CO$_2$ partial pressure in the soil, besides the weathering characteristics of existing rocks.

Accurate determinations of bromide and chloride were made to ensure the precision of the rCl/rBr ratio. Results in table 3 show a small rCl/rBr dispersion and values that in most cases are higher than 655, the value of seawater (Custodio and Herrera, 2000; Alcalá, 2005; Alcalá and Custodio, 2012). This can be explained by the possible incorporation of almost Br-free halite formed in the coastal marine environment by partial evaporation of sea water droplets produced and transported by the wind, but this is a poorly known and documented phenomenon. The contribution of halite particles carried by the wind from inland salt lakes is also possible, although unlikely. The largest value of the rCl/rBr ratio corresponds to Las Vertientes spring, which clearly escapes the general trend of the other coastal springs and in this case points to some possible halite dissolution in the Central Depression.

Apart of the Las Vertientes spring, the more saline waters are from La Chimba and Cuncun springs. Since the rCl/rBr value of these springs do not reveal dissolution of evaporate salts, the high salinity of

the La Chimba spring can be explained by a greater effect of climatic aridity and for Cuncun spring by a higher deposition of marine aerosol because of its closeness to the coastline.

Las Vertientes spring is also characterized by high nitrate concentrations (220 mg/L), significantly higher than in the other springs. This can be explained by nitrate-rich evaporite salts in La Negra basin (Pueyo *et al*., 1998). In general, groundwater of the Central Depression is characterized by a high natural content in NO_3. Up to 15 g/L of NO_3 have been found in groundwater in the Salar de Pintados (Risacher *et al*., 1999), in Pampa del Tamarugal, north of the study area. Thus, high salinity, high rCl/rBr, and high nitrate content in Las Vertientes spring shows that its water is affected by evaporite salts dissolution and therefore it can be considered that at least part of the water of this spring comes from groundwater in the Central Depression.

Mineral saturation indices have been calculated using the computer code PHREEQC (Pankhurst, 1995). Most of the waters are undersaturated with respect to gypsum (except for Las Vertientes spring, which is close to saturation), supersaturated with respect to dolomite, and approximately in equilibrium with respect to calcite (Table 5), which possibly has limited the Ca content by calcite precipitation, as has being commented before. All water samples are undersaturated with respect amorphous silica. Calculated partial CO_2 pressures (PCO_2) vary between $10^{-2.6}$ and $10^{-4.0}$, which are low and in some cases very close to that in the atmosphere ($PCO_2=10^{-3.4}$, currently). The small PCO_2 in the soil gas, even taking into account the possible decrease by rock-water reaction in a closed system, suggests low soil CO_2 of organic origin as a result of the sparse vegetation present in the Cordillera de la Costa, so that a significant part of the CO_2 can be of atmospheric origin.

6.2. ^{34}S and ^{18}O of dissolved sulfate in spring water

The isotopic results for dissolved sulfate are depicted in figure 3. Current seawater δ^{34}S is 21‰ CDT (Claypool *et al*., 1980; Fritz and Fontes, 1986) and 20‰ in sulfate precipitated from it. δ^{34}S in spring water vary between 7.7 and 18.1‰ CDT (Table 6). The greater the chloride content the more the δ^{34}S values tend to that of seawater, pointing to the marine origin of sulfate (Fig. 3A). The lower δ^{34}S values correspond to Panul and Las Vertientes springs, with respective values of 7.7 and 8.4‰. The light contribution can be explained by the addition of isotopically light (δ^{34}S between 7 and 16‰) gaseous atmospheric S, which is relatively more important the lower the salinity is The δ^{34}S in the spring waters are very close to the values measured by Rech *et al*. (2003) in sulfate-containing soils in the Cordillera de la Costa, +16.6‰ to +18.3‰, whose origin is attributed to atmospheric aerosol deposition on the ground. The alignement of points in figure 3A, except for Las Vertientes spring, is apparent since the Cl scale is logarithmic, but points to a non-marine S contribution of about 7 to 8%. Also dissolved sulfate δ^{34}S becomes heavier with increasing sulfate concentration (Fig. 3B), except for Las Vertientes spring, and point to the same non-marine value of δ^{34}S. The increase in sulfate content is due to higher marine sulfate contribution.

TABLE 5. CALCULATED LOGARITHMIC SATURATION INDICES AND EQUILIBRIUM CO_2 PARTIAL PRESSURE (ATMOSPHERES) FROM ANALYTICAL DATA.

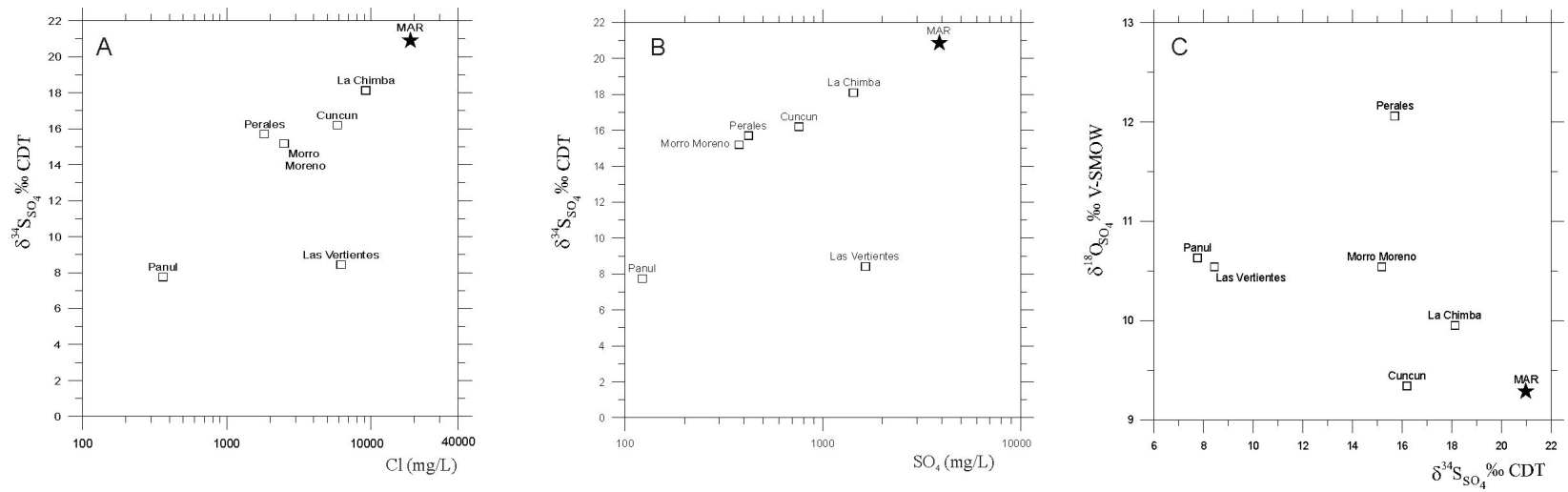| Spring	Calcite	Dolomite	Gypsum	SiO_2(a)	Quartz	$logPCO_2$
Las Vertientes	-0.15	-0.67	-0.13	-0.62	0.69	-2.88
Cuncun	0.47	0.98	-0.58	-0.7	0.58	-3.96
Morro Moreno	0.45	1.31	-1.19	-0.76	0.53	-3.33
La Chimba	-0.15	-0.25	-0.43	-0.68	0.64	-2.6
Cobija well	0.35	0.62	-0.82	-0.77	0.52	-2.74
Panul	0.93	1.53	-1.41	-0.79	0.56	-3.99
Perales	0.01	1.2	-1.74	-1.91	-0.59	-2.75

SiO_2(a) = Amorphous Silica.

FIG. 3. Sulfate and dissolved sulfate isotopes in waters from springs in the Cordillera de la Costa. **A.** $\delta^{34}S_{SO_4}$ *versus* Cl; **B.** $\delta^{34}S_{SO_4}$ *versus* SO_4; and **C.** $\delta^{34}S_{SO_4}$ *versus* $\delta^{18}O_{SO_4}$.

TABLE 6. ISOTOPIC COMPOSITION OF WATERS AND SOLUTES (IN δ‰ RESPECT TO THE STANDARD) OF CORDILLERA DE LA COSTA SPRINGS.

Sample	$\delta^{18}O$(‰) V-SMOW	$\delta^{2}H$(‰) V-SMOW	d(‰)	^3H (TU)	$\delta^{34}S(SO_4)$ (‰) CDT	$\delta^{18}O(SO_4)$ V-SMOW	$\delta^{13}C$(‰) V-PDB	^{14}C (pmC)
La Chimba	-0.09	-3.2	-2.48	0.27±0.2	18.13	9.95	-21.1	65
Morro Moreno	-0.85	3.3	10.10	-	15.18	10.54	-12.5	55
Cuncun	0.18	-0.4	-1.84	0.17±0.2	16.2	9.34	-14.8	65
Las Vertientes	-2.22	-33.6	-15.84	-	8.44	10.54	-21.6	74
Los Perales	-2.2	-10.0	7.60	0.05±0.2	15.71	12.06	-13.6	70
Panul	-1.71	-1.8	11.88	0.88±0.2	7.76	10.63	-	-

D: deuterium excess = $8\delta^{18}o$-$\delta^{2}h$ (‰). **TU**: tritium units (10^{-18} ^3h/^1h). **pmC**: percent modern carbon.

The relatively $\delta^{34}S$ light value of Las Vertientes spring agrees with that of soil sulfate in inland basins, between 5 and 8‰ and whose origin is attributed to atmospheric dust inputs that have accumulated for millennia in the desert (Rech *et al.*, 2003; Michalski *et al.*, 2004; Ewing *et al.*, 2006, 2008). The low $\delta^{34}S$ value of Panul spring (+7.7‰) approaches the non-marine atmospheric value and shows a small marine influence. Sulfate reduction is neither expected nor shown due to the oxidizing environment.

The $\delta^{18}O$ of sulfate dissolved in modern ocean water is around 9.6‰ (Clark and Fritz, 1997). In spring waters it varies between 7.8‰ and 12.1‰. Samples with high $\delta^{18}O_{SO_4}$ generally have small dissolved sulfate contents and tend to the value of $\delta^{18}O_{SO_4}$ of seawater when sulfate increases. Although it is difficult to establish confidently the origin of the more enriched values of $\delta^{18}O_{SO_4}$, they are close to what is expected for the non-marine S in the atmosphere.

Comparing the values of $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate (Fig. 3c), despite the large scatter it is observed that there is a mixture of two end members, one atmospheric non-marine sulfate of poorly defined low $\delta^{34}S$ values and high $\delta^{18}O$ values, with marine sulfate. Las Vertientes spring has a $\delta^{34}S$ isotopic composition typical of the sedimentary gypsum observed in Pre-Andean basins. Many isotopic determinations done in continental sedimentary formations of the Salar de Atacama basin have sulfate that vary from 6‰ to 9‰ for $\delta^{34}S$, and 13‰ to 18‰ for $\delta^{18}O$ (Carmona *et al.*, 2000; Cortecci *et al.*, 2005). In Panul spring a greater non-marine atmospheric effect associated with its location in an area less influenced by the Camanchaca is possible.

6.3. Stable isotopes of water

Due to the scarce rainfall recorded in the northern coast of Chile and the small amount of rain produced in each event, it is very difficult to characterize the stable isotopic composition of precipitation and define a local meteoric line. Figure 4 shows $\delta^{18}O$ and δ^2H data from coastal springs, the world mean meteoric water line ($\delta^2H=8\delta^{18}O+10$‰), and three water samples from the Pre-cordillera of the Antofagasta Region, corresponding to Alto de Varas, Chépica and Escondida springs, the first two located at the headwaters of the La Negra basin (Fig. 1), as well as springs of

Salar de Atacama and Chungará lake area (north of the study area). In the area of Collacagua-Salar de Huasco-Pica at the latitude of Iquique (Region I of Tarapacá, to the north of Antofagasta), average $\delta^{18}O$ and δ^2H values in the Altiplano are -15‰ and -110‰, respectively, similar to those of the Chungará lake, and in the intermediate area of Pampa del Tamarugal from -7‰ to -55‰ (Acosta *et al.*, 2013), similar to those of Salar de Atacama.

Table 6 shows the stable isotope data of spring waters. They range from +0.2‰ to -2.2‰ for $\delta^{18}O$ and +3.3‰ to -33‰ for δ^2H, while the isotopic composition of the waters of the Pre-cordillera are isotopically lighter, ranging from -3.1‰ to -4.2‰ for $\delta^{18}O$ and about -34‰ for δ^2H.

As shown in figure 4, the water of the Las Vertientes spring is isotopically lighter than the other coastal springs, despite a remarkable evaporation effect (deuterium excess of -15.6‰). Considering an evaporation line slope of 4 to 5 in a plot of δ^2H versus $\delta^{18}O$, Las Vertientes spring extrapolates to a possible initial water that resembles the isotopic composition of spring waters sampled in the Pre-cordillera, specifically in the headwaters of La Negra basin, in the Central Depression, whose western boundary is close to a local coastal gully where Las Vertientes spring is located (Fig. 1). Therefore it is assumed that the water of Las Vertientes spring may correspond to groundwater recharge in the headwaters of the La Negra basin. Not so the waters of the other coastal springs whose waters correspond to recharge produced at the Cordillera de la Costa.

The more lighter isotopic composition of spring from headwaters of La Negra basin (Alto de Varas, Chépica and Escondida springs) may have been originated from a mixture of air masses coming from Amazon Basin and vapor produced in the Pacific Ocean. However a major contribution of vapor from the Pacific Ocean cannot be ruled out because the isotopic composition of these springs is very close to that of precipitation in the city of La Serena, albeit this last hypothesis is unlikely because of the barrier effect of the Cordillera de la Costa, which would prevent the entry of air masses coming from the coast.

Coastal spring waters are isotopically heavier, generally plot close to the seawater point, and differ significantly from the isotopic composition of the lighter rainfall recorded in the Cordillera and Pre-cordillera of northern Chile. These coastal springs
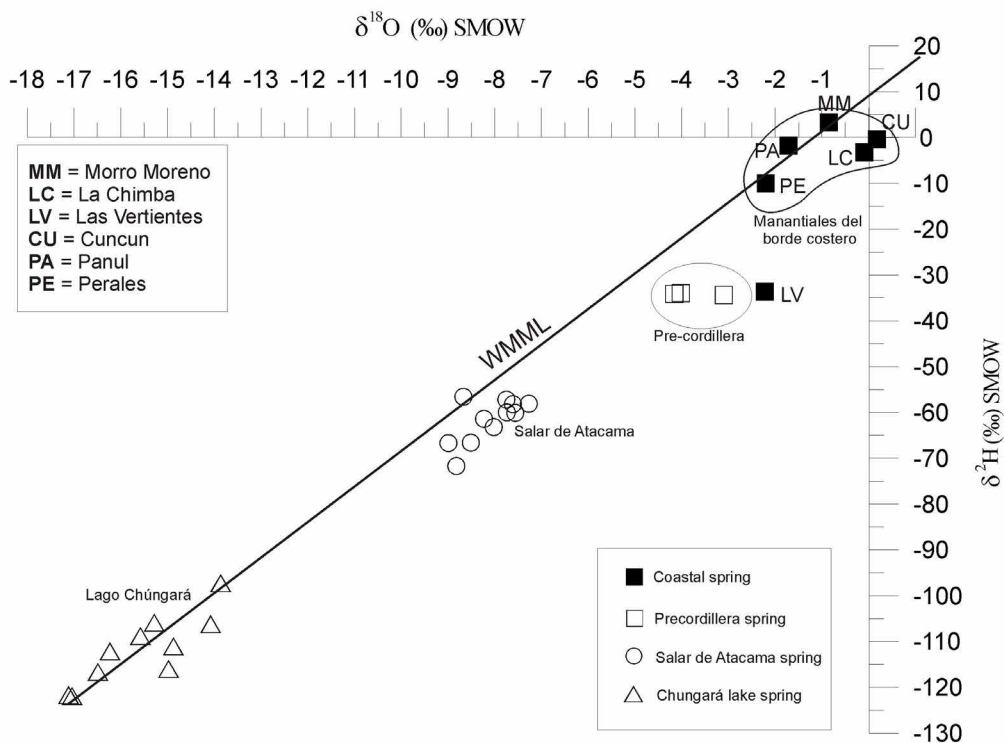
FIG. 4. δ¹⁸O y δ²H of springs from Cordillera de la Costa and from the Pre-cordillera, Salar de Atacama and Chungará lake. **WMML**= world mean meteoric water line: δ²H=8δ¹⁸O+10‰.

are isotopically similar to precipitation in oceanic islands, with δ¹⁸O and δ²H values close to that of ocean water (Dansgaard, 1964). In fact, considering the isotopic data from the springs as values close to the value of the precipitation originating the recharge, the line joining these points has a slope close to 6, which is characteristic of heavy rainfall in oceanic islands (Plata, 1994; Clark and Fritz, 1997; Herrera and Custodio, 2008). Thus, it is possible to consider that, like in oceanic islands, the precipitation that recharged these aquifers were from coastal storms fed by quickly produced vapor in marine environment. This phenomenon has been described to explain the isotopic composition of precipitation and groundwater in coastal areas in Portugal and North Africa (Plata, 1994). Three of the springs show no significant evaporation during recharge, but Cuncun and La Chimba springs, with high salinity, show evaporation from an original value of about -2‰ for δ¹⁸O, similar to that of Perales spring. The evaporation effect can be related

to the presence of some soil while this evaporation effect does not show up when recharge is produced through cracks.

To assess the origin of the water vapor which caused the precipitation that recharged the coastal aquifers, the isotopic composition of coastal springs waters is compared with the isotopic composition of rainfall in other locations in the western edge of South America, as shown in figure 5, using data from the IAEA monitoring stations in the towns of La Cuca and Esmeraldas (Ecuador) and La Serena and Valparaíso (Chile). No isotopic data from the coast of Perú is included because the monitoring stations in this country are inland and in the highland. The δ¹⁸O and δ²H of precipitation in latitudes close to coastal Ecuador are more enriched than the isotopic composition of precipitation in higher latitudes, as in La Serena and Valparaíso, according to the isotopic patterns of δ¹⁸O and δ²H of global rainfall (Dansgaard, 1964; Custodio and Llamas, 1983; Clark and Fritz, 1997).
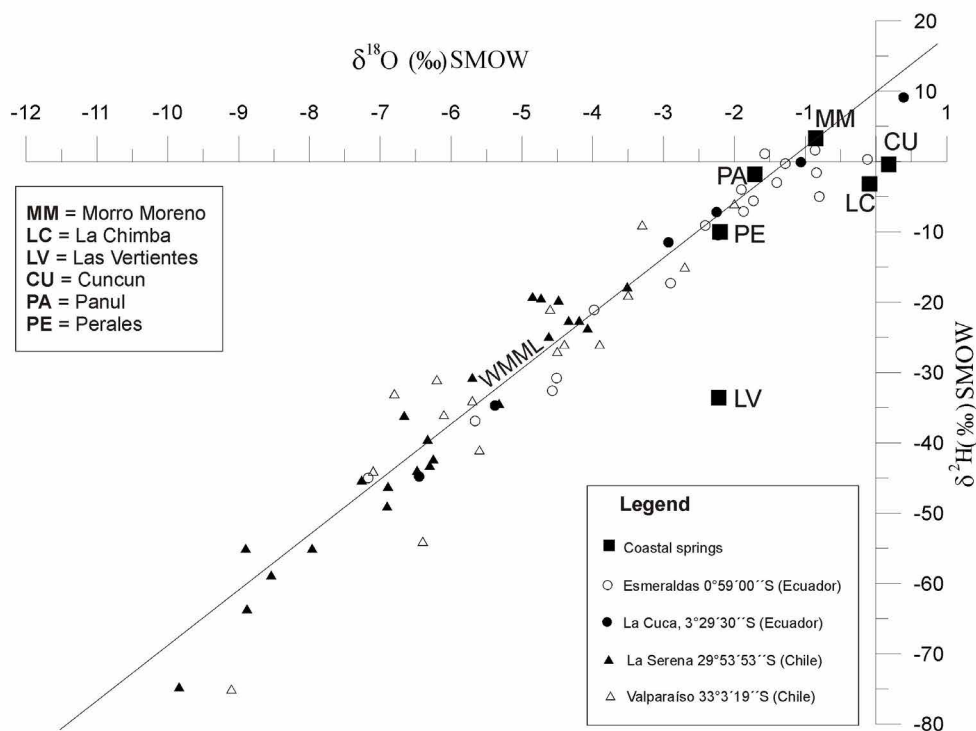
FIG. 5. $\delta^{18}O$-δ^2H plot of rainfall at coastal stations in La Cuca and Esmeraldas (Ecuador) and La Serena and Valparaíso (Chile), taken from the IAEA sampling network, and of Cordillera de la Costa springs. **WMML**= world mean meteoric water line: $\delta^2H=8\delta^{18}O+10‰$.

To assess the magnitude of the precipitation that probably recharged the coastal springs in northern Chile, a plot comparing the values of the average monthly precipitation of rain on the coast of Ecuador with the values of $\delta^{18}O$ in Esmeraldas station has been made. No rainfall records are available for Cuca station. The most enriched rainfall ($\delta^{18}O$ between 0 and -2‰) corresponds to monthly accumulated rainfall values less than 10 mm (Fig. 6). The highest rainfall recorded in Esmeraldas Station have the lightest $\delta^{18}O$ isotopic values and correspond to the rainfall occurring in the January, February and March, when the moist air masses from the Amazon attain the western part of South America at that latitude.

6.4. Tritium in spring water

Tritium is the radioactive isotope of hydrogen (^3H) that decays to ^3He by beta particle emission with a half-life of 12.43 years. The tritium produced in the atmosphere, either natural or artificial, becomes part of the water molecules and joins the hydrological cycle, where it behaves as a nearly ideal tracer. Thermonuclear explosions, mainly conducted in the early 1960s, injected into the atmosphere large amounts of tritium, to greatly exceeded natural concentrations. This generated conspicuous worldwide tritium increases in precipitation. In 1963-1964 tritium concentration peaked at 8,000 TU (tritium units=10^{-18} ^3H/^1H) in Ottawa (Canada). The effect was less marked in South America, with a maximum of 290 TU in Rio de Janeiro (Herrera *et al.*, 2006). Since then, a worldwide steady decline has been produced and today rainfall is close to natural background.

For the current low tritium concentrations in natural water at least a 500 mL sample is needed for analysis. Due to the low amount of precipitation in the study area it was only possible to get one rain sample of 2006 to determine tritium content. A concentration of 1.03±0.32 TU was obtained in Antofagasta, consistent with what is currently expected at a maritime station.
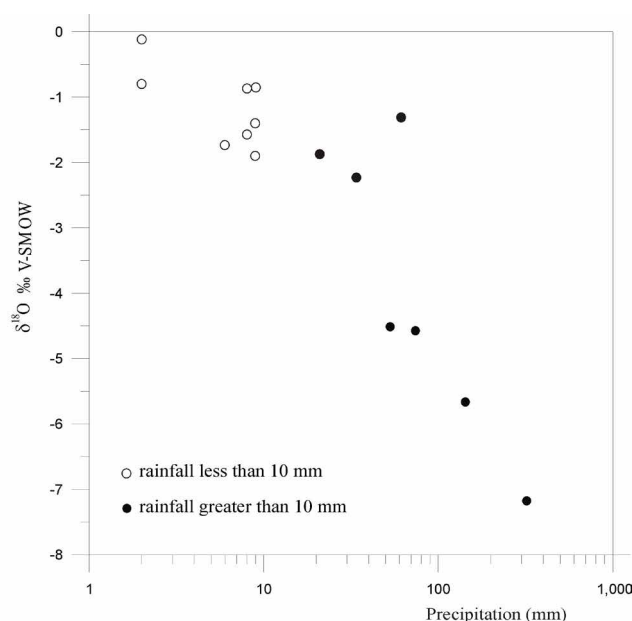
FIG. 6. $\delta^{18}O$ *versus* rainfall amount (mm) in Esmeralda coastal station (Ecuador). Data from IAEA network. Rainfall less than 10 mm correspond to the dry period between May and November, and rainfall greater than 10 mm are of the wet period between January and April.

Most spring samples have tritium concentrations below the laboratory measurement threshold, about 0.2 TU (Table 6). Thus, it can be assumed that most recharge was produced before year 1960, with the exception of Panul spring (0.88±0.2 TU, a significant fraction of meteoric tritium) and perhaps La Chimba spring (0.27±0.2 TU). It is likely that the sample obtained in Panul spring reflects the discharge of an area receiving small localized orographic precipitation events; in fact it is a fluctuating spring with increased discharge after local important rainfall periods and this may explain the significant fraction of recent recharge. In La Chimba spring a small contribution to recharge could be produced in the last 50 years. Since this spring is located in a canyon, it is probable that after large rainfall events runoff water could infiltrate in the vicinity of the spring and thus provide some tritium, albeit it is difficult to establish a consistent conceptual model of the spring due to the poor knowledge of the aquifer.

6.5. ^{13}C of dissolved inorganic carbon in spring water

The ^{13}C values of local coastal vegetation have been determined by Quade *et al.* (2007) from 24 spe-

cies of cactus in the vicinity of the town of Paposo. Most of them have an isotopic composition according to the Calvin photosynthetic path (C3) and also of Crassulacean acid metabolism (CAM), and they also recognized vegetation of type Hatch-Slack (C4) in lower proportion.

At the pH of spring water, the DIC (dissolved inorganic carbon) is dominated by HCO_3 and consequently the equilibrium fractionation with respect to CO_2 in soil gas is close to 9‰ at ambient soil temperature. Figure 7a shows $\delta^{13}C$ *versus* pH.

Las Vertientes and La Chimba springs have very light ^{13}C values that correspond to soil CO_2 derived from C3 to vegetation, non-fractionated with respect to soil gas CO_2 (system closed to CO_2). This requires close-to-saturated soil in the recharge area, which does not occur in the current conditions, but that could happen in the past in wetlands or in easily water-logged soils. The light value can also be explained by very light ^{13}C contribution from methane oxidation in ancient wetlands, but this is unlikely.

The other three springs show $\delta^{13}C$ values in isotopic equilibrium with soil gas derived from C3 vegetation, or recharge produced in a closed system receiving CO_2 from CAM or C4 plants, which is unlikely. The high pH values agree with water evaporation
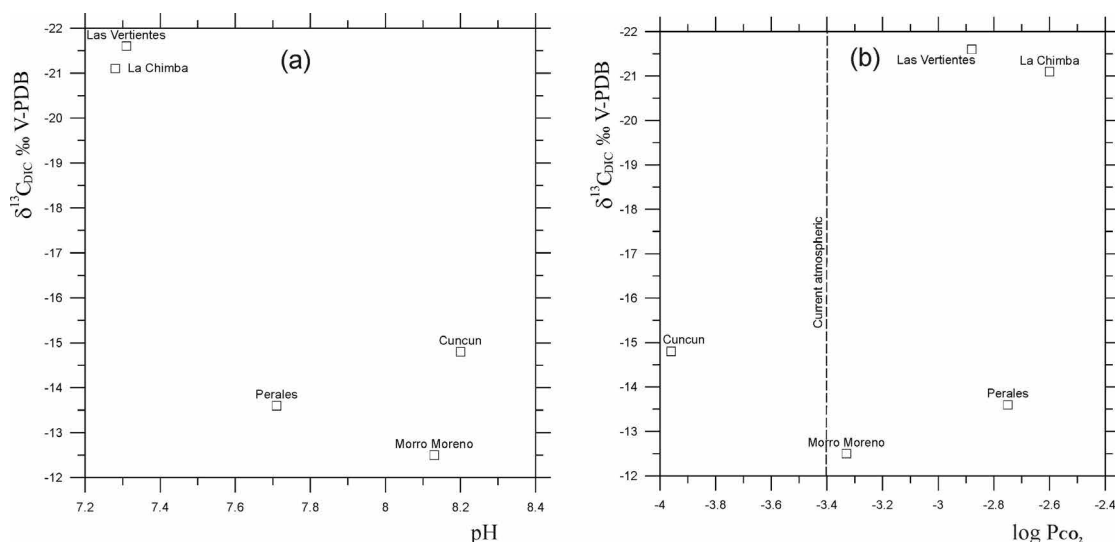
FIG. 7. Plot of **A.** $\delta^{13}C_{DIC}$ *versus* pH and **B.** $\delta^{13}C_{DIC}$ *versus* PCO_2 (atm).

and carbonate precipitation under arid conditions. The $\delta^{13}C$ content could reflect the incorporation of soil carbon of biogenic origin, despite the very low current vegetation, but not necessarily so in the past, and perhaps the dissolution of recent marine biogenic carbonate particles from the littoral area supplied by the wind, but this last is unlikely significant as shown by water chemistry. Plotting the value of PCO_2 *versus* $\delta^{13}C_{DIC}$ (Fig. 7b) a group of points close to the partial pressure of CO_2 in the atmosphere are found, which correspond to the heaviest values of $\delta^{13}C$. This could point to a moderate influence of atmospheric CO_2, whose $\delta^{13}C$ is near -8‰. This is acceptable since an important part of the Cordillera de la Costa has no permanent vegetation. A second group of samples has lighter values of $\delta^{13}C$ and the highest values of PCO_2 that indicate greater biological activity at the time when recharge was produced.

In the geological environment where water samples were obtained there are not recognized carbonate rocks that may have interacted with groundwater during its flow, but the presence of calcite possibly associated with ancient hydrothermal phenomena in the filling of the fissures of volcanic and intrusive rocks cannot be ruled out. In fact, in the southern part of the study area many copper veins containing quartz, actinolite, magnetite, tourmaline, and calcite are emplaced in diorite and granodiorite intrusive rocks of Jurassic age (Boric *et al*., 1990). Thus, water interaction with the calcite cannot be plainly discarded and therefore

some effect on $\delta^{13}C$ contents. However, the geological knowledge of the areas where the springs are located and the hydrogeochemical interpretation of spring water of the low aggressiveness due to the scarce vegetation in the area rule out a significant incorporation of carbon of lithological origin or isotopic exchange with it.

6.6. ^{14}C of dissolved inorganic carbon in spring water

Five determinations of activity of ^{14}C of dissolved inorganic carbon (DIC) in spring water have been done to try to determine the groundwater residence time. The apparent ages must be analyzed in the context corresponding to groundwater flow through fractures in volcanic and intrusive rocks of low permeability with possible large water storage in the matrix, with diffusive exchange of carbon species between them. Furthermore recharge feeding the springs occurs over a large area and thus springs are supplied by a wide range of path-lines implying very different transit times. Therefore, it can be expected that the water discharged by the springs corresponds to a mixture of waters of very different ages. So it is more appropriate to speak of water residence time in the system.

The ^{14}C concentrations vary between 55 and 75 pmC (Table 6). They are relatively high and considering the very different local circumstances they are little scattered. The apparent ages of spring water

vary between about 5,000 and 2,500 years (Table 7). The flow model explaining them is discussed below.

As explained before ^{13}C shows that most of the CID comes from the dissolution of biogenic and atmospheric CO_2. Thus, the classical correction models of apparent ages that consider mineral C input from carbonate formations do not apply in this case. Unfortunately carbon isotope values for Panul spring are not available. Their relatively large fraction of recent water would be a reference value for ^{14}C activity. For the Chimba spring, with some influence of recent recharge, the value of [14]A=65 pmC ([14]A=activity of ^{14}C) and a light $\delta^{13}C$ lighter value (-21.1‰) allows to assume that the average apparent age of ^{14}C is relatively high.

The $^{13}C_{DIC}$ *versus* $^{14}C_{DIC}$ plot (Fig. 8) show that the water samples are not binary mixtures of two end members of biogenic and dead mineral carbon, so the apparent radiogenic ages would likely be water ages in the case of a piston flow system. However, in the actual situation of recharge all over the surface, the groundwater flow system is dominantly of good mixing (exponential model) and what is called age is a function of mean residence time, as discussed below.

7. Discussion

7.1. Permeability characteristics of the Cordillera de la Costa formations

It is expected that volcanic and intrusive rocks of the Cordillera de la Costa behave in practice as almost impermeable formations, with macroscopic hydraulic conductivity (k) lower than 10^{-6} m/day, except near the surface, where saturated k could be about 0.01 m/ day but decreasing downwards. However, some major faults and fractures across the Cordillera de la Costa may locally increase permeability but only to some limited extent since they are not expected to be open

TABLE 7. δ¹³C, ¹⁴C AND APPARENT AGE OF SPRING FROM CORDILLERA DE LA COSTA.

Spring	δ¹³C (‰ *versus* V-PDB)	¹⁴C pmC	Apparent age (years)
La Chimba	-21.1	65	3,562
Morro Moreno	-12.5	55	4,943
Cuncun	-14.8	65	3,562
Las Vertientes	-21.6	74	2,490
Perales	-13.6	70	2,949

and often contain alteration minerals. Top volcanic rocks may be more permeable and thick, but with conditions similar to those described above. Saturated k may exceed 0.001 m/day, perhaps up to 0.1 m/day in the top. Under current conditions much of the more permeable rock is in the unsaturated zone, except under favorable circumstances for high water-table elevation, as near the coast. The hydraulic transmissivity (T) of the saturated zone rarely would exceed 0.1 m²/day regionally, and possibly may be at least one order of magnitude lower, according to the results obtained for the Miocene shield basalts in the Canary Islands (Custodio, 1985, 1989, 2007). This enables, even with very small average distributed recharge, the existence of a groundwater body that, when close to the surface, may sustain small discharges in springs, in addition to invisible diffuse discharges because of evaporation or due to outflowing along the coast.

7.2. Possible groundwater contribution from inland areas

The physiographic and climatic context of springs' location is essential for the interpretation of spring water origin. In this vast area under present and past hyper-arid climate, especially in the Central Depression, along more than 1,000 km of coastline, the recharge should be very small and limited to sporadic rare wet events, which according to what has been explained in section 3 were probably more frequent and important about 5,000 to 3,000 years ago.

Current recharge in the less extremely arid, mountainous regions of the Altiplano and Pre-cordillera is small but could produce lateral groundwater transfer to the Central Depression. This groundwater flow is stopped by the low permeability Cordillera de la Costa, thus forming a large groundwater reservoir which shows up at the surface as crypto-wetlands and salt deposits at elevations ranging between 500 and 1,000 m. This is the case of the Salar del Carmen, located in the Central Depression, directly to the east of the city of Antofagasta, where the water table is only a few meters beneath the surface and salts precipitate from evaporating water brought to the surface by capillary action. Similar cases are recognized further north, in the Pampa del Tamarugal aquifers, where runoff and groundwater from the Altiplano is also trapped against the Cordillera de la Costa, generating the large salt pans of Bellavista and Pintados.
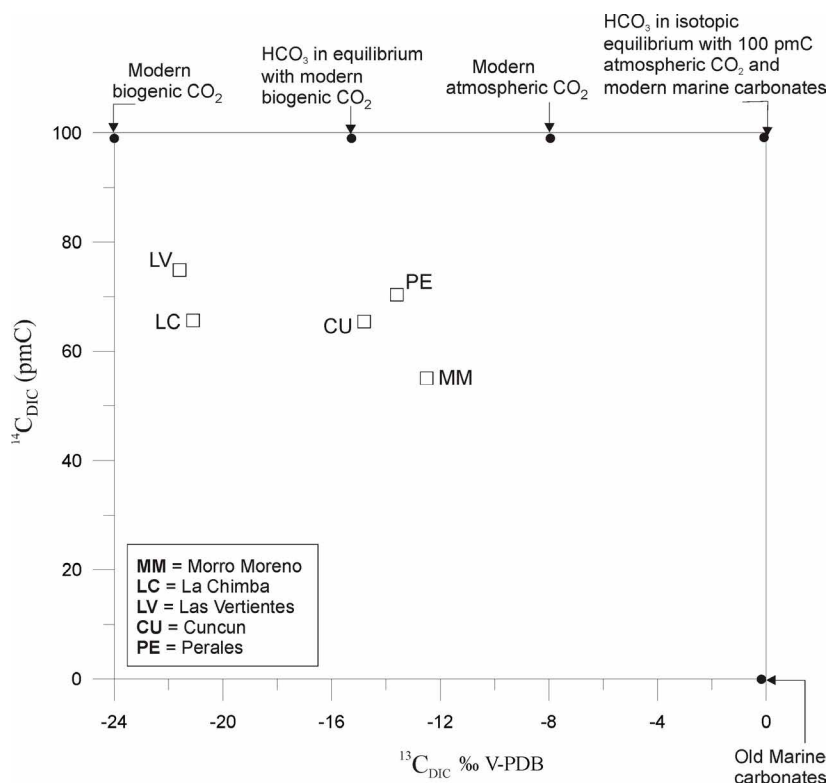
FIG. 8. [14]C activity (pmC) *versus* δ^{13}C data of the Cordillera de la Costa water samples. Some possibilities for water binary mixtures end-members are indicated.

Due to lack of detailed data and in order to constrain the hydrogeological conceptual model, a simplified groundwater hydraulic treatment in a homogeneous medium is presented. It is hypothesized that the small springs along the coastline, in addition to invisible diffuse discharges, may be due to local recharge by past or present rainfall events that originate in the Pacific Ocean, and perhaps some underground transfer from the mainland originated in the the Altiplano. For the Cordillera de la Costa at the latitude of the city of Antofagasta, a width of L=10 km and a water-table elevation in the Salar del Carmen of h=500 m can be assumed. A mathematical formulation that could explain the hydraulic conditions under which groundwater flows from the Central Depression to the coast can occur is presented in the Appendix.

7.3. Recharge in the Cordillera de la Costa

Recent climate research have shown that the high rainfall events in the Atacama Desert coast are far apart in time and only occur as a result of the presence of El Niño (Houston, 2006). Precipitation in the Cordillera de la Costa consists in rain and low fog (Camanchaca), the more intense events producing diffuse recharge on land with little or no soil and in areas covered with low water retention eolian deposits, although, as before said, the isotopic studies carried out on the coast of central Chile rule out fog condensation as a significant recharge mechanism (Squeo *et al.*, 2006) but in local situations. Occasional intense and far in time rain events are capable of some quick runoff, but due to the high slopes of the Cordillera de la Costa these runoff would not produce any locally significant infiltration at general level. Since current vegetation cover is very sparse or nil, most of rainfall stored near the land surface as soil and cracks moisture evaporates, with possible significant isotopic fractionation, strong evapoconcentration and the derived high salinity, especially where there is an important airborne saline contribution and low precipitation.

In general, the unsaturated zone can be expected to be tens of meters thick, without permanent perched

aquifers or only active after occasional rare rainfall events. In principle it is expected that recharged water moves vertically downward in diffuse form, preferably through the rock matrix, except after very heavy rainfall events, when flow through fractures could dominate up to certain depth. There is also the possibility that water penetrating through fractures temporarily accumulate above some very low permeability, tilted and sealed laterally level, which can favor concentrated recharge along fault planes, as in the ignimbrites of Yucca Mountain in Nevada (Zhu *et al.,* 2003). In such situations, if shallow, occasional storm water may move fast to the water table.

7.4. Flow in the unsaturated zone and residence time in the saturated zone

It is expected that the flow into the saturated zone moves preferably through a fracture network in relatively fast hydraulic equilibrium with blocks, but with exchange of solutes and isotopes by diffusion with the rock matrix, in which, in the case of volcanics, resides most of the groundwater storage. Thus, water feeding the springs is preferably water supplied by the fissure network but originated in the rock blocks (matrix).

The discharged water is assumed to be in equilibrium or near equilibrium with the composition of water stored in the matrix, except perhaps after intense rainfall events, in which the water recharged in an environment close to the recharge area could reach the spring with little or moderate diffusive effect. Thus, discharge water in the springs is a water mixture representing a wide range of residence times in a system that would resemble that of good mixing (Custodio, 1997), with delayed recharge due to the flow through the unsaturated zone, as was already analyzed in the Amurga phonolitic massif in south-eastern Gran Canaria island (Custodio-Ayala and Custodio, 2001).

Assuming a constant concentration in space and time of DIC (dissolved inorganic carbon) and ^{14}C in the DIC, the simplified isotopic balance for steady flow in a volume, V, of saturated zone is:

$$Q \cdot C_O = Q \cdot C + \lambda \cdot V \cdot C$$

where C is the ^{14}C concentration (activity) in water, C_o is the input ^{14}C concentration in recharge water (the atmospheric ^{14}C concentration diminished by the

disintegration during the transit time through the unsaturated zone, assumed also constant), and Q is flow. As turnover time is

$$\tau = V / Q; \quad C = \frac{C_0}{1+\lambda\tau}; \text{ so that } \tau = \frac{1}{\lambda}\left(\frac{C_0}{C} - 1\right)$$

For ^{14}C, the half-life is 5,720 years, so $\lambda = \ln2/5720 = 1.21 \cdot 10^{-4}$ year $^{-1}$

A simple application to a system with turnover times of 1,000, 2,000, 5,000 and 10,000 years and an assumed initial ^{14}C recharge value of 100 pmC, the ^{14}C concentration in discharge water is respectively 89, 80, 62, and 42 pmC. This means that the radiocarbon concentrations found can be explained by assuming constant recharge and therefore the apparent age is a function of the residence time in the flow system. A series of simplified calculations in progress (Custodio and Custodio-Ayala, 2014) consider the effect of an increase in recharge in a hyper-arid area occurring some time ago. For the period between 5,000 and 3,000 years ago, considering several hypothesis of dynamic and dead water reserves in the aquifer system, a greater recharge would produce an increased discharge lasting up to today, with higher ^{14}C content than that corresponding to constant recharge system and resembling those obtained here. Therefore, the hypothesis of increased recharge between 5,000 and 3,000 years ago is consistent with the results obtained but several other interpretations are also possible. Additional studies are needed to try to better define aquifer functioning. Hereinafter the designation of apparent age is maintained.

For a recharge R and an unsaturated zone thickness H with soil moisture θ, assuming homogeneous concentration, the transit time through the unsaturated zone is $t = \theta \cdot H/R$, so that $C_o = C_o* \cdot e^{-\lambda t}$ is the initial ^{14}C value of soil gas at the water table, C_o* being the value near the surface.

If H vary between 10 and 100 m and θ between 0.5% (compact fissured rock) and 1% (volcanics), $\theta \cdot H = 0.5$ to 1 m. In case that all the reduction of activity is due to the passage through the unsaturated zone, C_o / C_o^* is the observed ^{14}C value in the samples, between 0.55 and 0.7. This limits the potential recharge to between 0.01 and 0.35 mm/yr, which is within the ranges shown in the Appendix. This means that ^{14}C aging may be explained simply

by the passage through the unsaturated zone. This does not agree with measurable tritium in Panul and possibly in La Chimba springs.

Recharge can also occur in a compact rock through the fractures, with little water storage change in the low porosity matrix. This is the case of recharge through sparsely distributed fissures when the occasional rain is concentrated on them by surface and subsurface runoff. In such a situation recharge can reach the aquifer in a short time compared to the half-life of the radioisotope; thus the turnover time τ of groundwater in the aquifer would simply be the value obtained by considering the ^{14}C concentration near the surface. In this case τ varies between 3,500 and 6,700 years. This range is similar to the period in which the climate was less arid, so the recharge hypothesis in that period, with much lower recharge before and after it, is also plausible.

The rate of groundwater reserve exhaustion can be assumed exponential and estimated through the parameter $\alpha \approx 4T/(L^2S)$, where L is the dimension of the system, T the hydraulic transmissivity and S the massif rock specific yield. The time to exhaust half the reserve is $\beta = \ln(2)/\alpha$. For L=10 km, T=0.01 m²/d to 0.1 m²/d and S=0.005 to 0.01, it results β= 2,000 to 45,000 years. The evolution of spring flow points to a few thousand years, and therefore a T whose value is close to that of the upper part of the aquifer and an S characteristic of fissured rock with low matrix water storativity.

7.5. Relationship between spring water 'apparent age' and paleoclimatic events

The isotopic composition of coastal spring water generally shows values very close to that of seawater, with small deuterium excess values. It points to high humidity conditions at the time of vapor generation in the oceanic atmosphere and condensation in close-by areas. This is common in oceanic islands. The isotopic data of coastal spring water agree with this hypothesis. To explain how atmospheric vapor was generated near the coast and produced precipitation with an isotopic composition typical of the first condensation, a change of ocean currents around 5,000 years ago can be argued, with a southward shift of the equatorial warm ocean currents. This implies that in the mid-Holocene a predominance of ENSO on the coasts of southern Perú and northern Chile may have occurred. Considering that precipitation

should be important enough to recharge the coastal aquifers, it can be concluded that the ENSO phenomenon in northern Chile was much more intense and frequent than today, with important changes in the oceanographic current system during the mid-Holocene. This explanation agrees to some extent with the results obtained by Ortlieb *et al*. (2011) from radiocarbon content in marine shells and associated charcoal fragments in archaeological deposits. These observations also agree with the study of alkenones in core samples off the coast of central and northern Chile, for which Kim *et al.* (2002) deduced a mid-Holocene warming of ocean surface waters resulting from changes in ocean currents.

There is an important relation between the recurrence of debris and mud flows produced by highest rainfall in the Cordillera de la Costa and ENSO events (Vargas *et al*., 2000). The highest rainfall that occurred 5,000 years ago coincides with effects on the terrain morphology, when alluvial fans and sediment-laden stream flows were active. They began 5,400 years ago and affected the entire coastline of northern Chile and southern Perú (Vargas *et al*., 2006). This also coincides with the hypotheses proposed by archaeologists for the coastline of northern Chile, according to which the discharge of coastal springs have decreased from pre-Hispanic times to the present day, causing the gradual abandonment of different sites inhabited by ancient peoples (Núñez and Varela, 1968). The time of activation of alluvial flows and the oldest apparent age of spring water do not fully coincide because water age is not a calendar value but a value that depend on groundwater turnover time, as explained before.

The time period of higher rainfall in the coastal area of northern Chile, between 5,000 and 3,000 yr B.P., also correlates with the wet weather recognized in the coastal strip of central Chile and coincide with those obtained from pollen in coastal wetlands south of the study area (Norte Chico), which indicate extensive development of swamp forest between 4,200 and 3,200 yr B.P. (Maldonado and Villagrán, 2002); from the year 3,200 B.P. they report a slow reduction in the extent of swamp forest associated with a decrease in rainfall, with xerophytic scrub vegetation typical of arid climate around 1,800 year B.P.. Other limnological records obtained further south, in central Chile, indicate that these events began before the greater precipitations of northern Chile, but ended in similar dates. This is the case of pollen

records from Aculeo lagoon, at 34° south latitude, which show that between 5,700 and 3,200 years ago there was an increase of tree species related to increased rainfall in this period (Villa-Martínez *et al*., 2003).

The more humid climatic conditions in the coast about 5,000 years ago probably concentrated in the coastal strip and the Cordillera de la Costa since this significant orographic barrier prevents the easy passage of vapor masses inland. However, records from paleo-wetlands located in the eastern part of the Loa River basin and Salar de Atacama, show increased rainfall between 7,000 and 3,000 yr B.P. (Rech *et al.*, 2002). While the start date of the rainfall in these places does not match that for the Cordillera de la Costa, the end date coincide. This allows considering that the wettest events that occurred in the Cordillera de la Costa between 5,000 and 3,000 yr B.P. may also have reached the Central Depression and western slope of the Andes.

The physiographic barrier played by the Cordillera de la Costa for the incursion of rainy fronts from the Pacific Ocean is reflected in the isotopic composition of the groundwater in the Altiplano of northern Chile, where light values of $\delta^{18}O$ and δ^2H prevail; they are characteristic of Atlantic air masses moving through the Amazon Basin (Salati *et al.*, 1979; Aravena *et al.*, 1999; Gonfiantini *et al.*, 2001; Herrera *et al.*, 2006). However, the isotopic data of waters from the Pre-cordillera and Pre-Andean basins show a mixture of vapor from the Pacific Ocean and vapor from the Amazon Basin, and could explain the coincidence in the time of the increased spring flow in the Loa River basin and Salar de Atacama. Therefore, although increased rainfall occurred in the northern coastal area of Chile between 5,000 and 3,000 yr B.P., their timing does not fully agree with the wetter events in the Altiplano but could be related with higher rainfall in the Pre-cordillera and Pre-Andean basins.

7.6. Paleo-hydrogeology of Cordillera de la Costa

The small springs located at the coast that do not receive inland groundwater flow contribution have apparent ages ranging between 3,000 and 5,000 yr B.P. Since these springs are located far apart from each other and with very different geological and hydrogeological conditions, the apparent water ages fall in a small range. This can be related to climate as the

common factor for all these springs. The extreme aridity of the coastline makes the relatively small aquifers that support the springs very sensitive to any change in rainfall regime. As indicated above, an intense drought period occurred between 14,000 and 5,000 yr B.P. in the coast, with low groundwater levels and exhaustion of water stored in the aquifer at the end of this long period. Thus, it is likely that a significant portion of the water recharged and stored in coastal formations of northern Chile before 14,000 years ago was discharged during this extended period of drought lasting more than 9,000 years, with low groundwater levels in the coastal formations (Fig. 9a).

The water isotopic values indicate that coastal aquifer recharge occurred under wetter climatic conditions than today and radiocarbon content is compatible with recharge occurred at least 3,000 years ago. However the radiocarbon content can also be the result of the mixing of waters recharged along a very long time period.

The increased precipitation during the mid-Holocene produced recharge with water-table elevation possibly not reaching a stationary condition (Fig. 9b). In this scenario, a part of recharge could flow quickly through hydraulically well-connected fracture systems in the volcanic and intrusive formations, while another part moved sluggishly, increasing water storage in the rock matrix. As some springs, as La Chimba, have relatively high altitudes (450 m), it can be assumed that the water-table dome also attained high elevations.

When climate conditions changed to a lower rainfall regime about 3,000 years ago to conditions similar to those prevailing today, with very scarce recharge to aquifers but locally, a progressive decline in the water table begun and still goes on (Fig. 9c). The presence of tritium in one spring, and possibly in other spring, points to some current small recharge at local scale by some sporadic rainfall events.

8. Conclusions

The main conclusions are:
1. Coastal springs chemical and isotopic water composition and dissolved sulfate show that water was recharged in the coastal area of northern Chile and not inland, except for Las Vertientes spring, which has a composition characteristic of groundwater in the Central Depression.
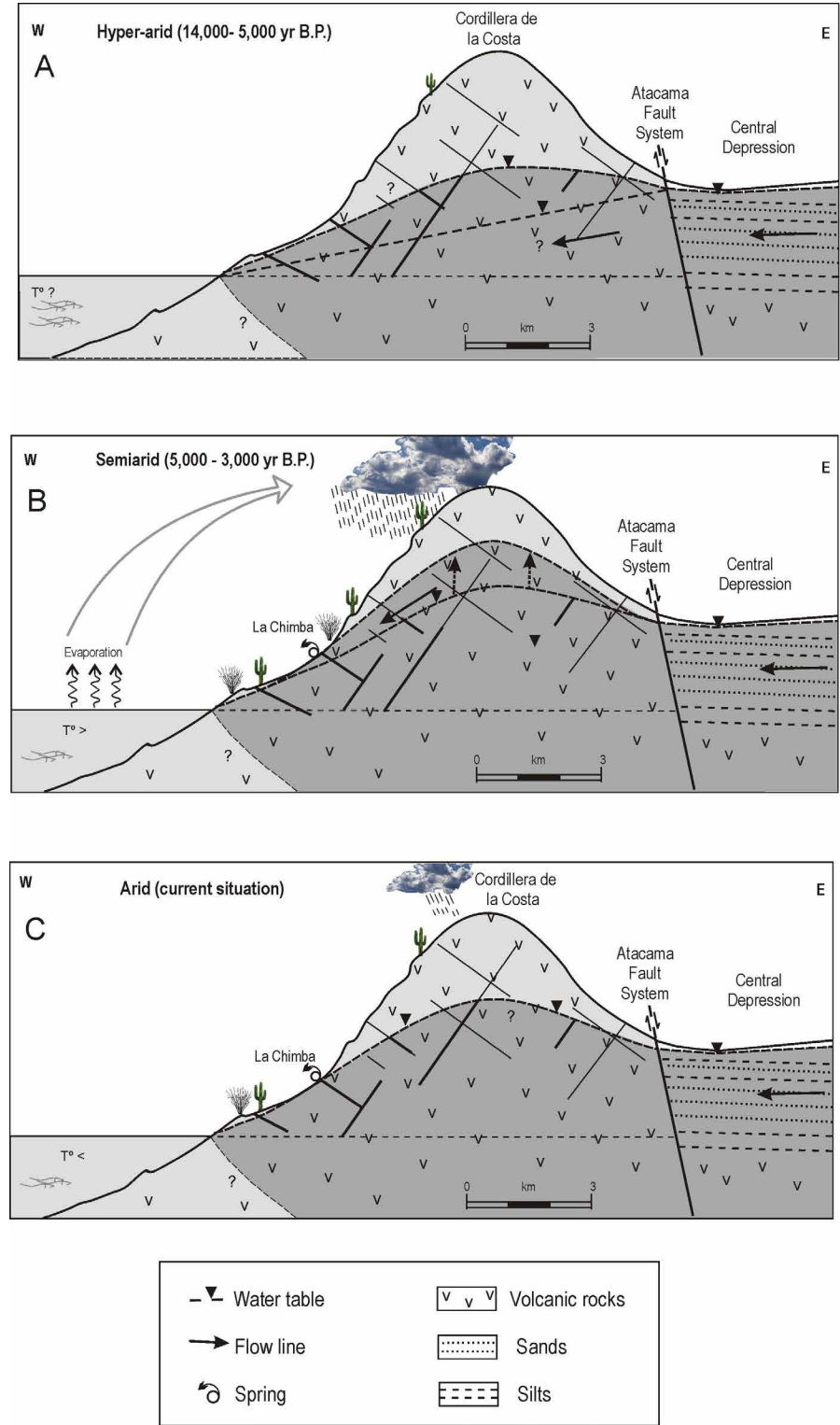
FIG. 9. Conceptual model showing the change of the water-table dome in the Cordillera de la Costa in the last 14,000 years and how this affects La Chimba spring.

2. Coastal spring waters are isotopically heavy, pointing to recharge from air masses generated near the coast, in the Pacific Ocean. There is no water isotopic composition showing the influence of rainfall though the Amazon basin, except for Las Vertientes spring, which have a lighter isotopic composition and would correspond to the discharge of the groundwater flow from the inner region (La Negra basin), derived from Atlantic air masses from the Amazon basin, and that could be associated to a fracture zone through the Cordillera de la Costa.

3. The isotopic values of spring waters are similar to rainfall along the western coastal area of Ecuador and different from rainfall in the central coastal Chile.

4. The radiocarbon content of the coastal spring waters is compatible with increased recharge between 5,000 and 3,000 years ago, but a mixture of groundwater recharged at a small rate along millennia is also a possible explanation.

5. The wetter conditions between 5,000 and 3,000 years ago, when recharge to coastal aquifer could happen, can be explained by the incursion of warmer currents from the coast of Ecuador to northern Chile associated with a southward displacement of El Niño-Southern Oscillation (ENSO).

6. The existence of small permanent springs, some at relatively high altitude, can be explained by a groundwater body in the very low permeability rocks in the Cordillera de la Costa, even with very limited recharge, and is compatible with remnant effects of a less arid past. The springs are not related with local or perched aquifers.

Acknowledgments

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APPENDIX

Elemental formulation of groundwater flow through the Cordillera de la Costa

A simplified groundwater flow calculation through the Cordillera de la Costa from the Central Depression to the coast is formulated. Due to the lack of detailed data, a homogeneous medium of low permeability is assumed, as shown in figure A1, with average recharge R and an imposed water-table elevation at x= L, in the area where the Central Depression is closed by the Cordillera de la Costa and representing the water-logged conditions in Salar del Carmen. The following symbols are used:

T = average transmissivity.
L = width of the Cordillera de la Costa.
R = annual average recharge.
q = groundwater flow through across the Cordillera de la Costa, per unit width along the coast.
x = distance from coast, perpendicular to it.
$\mathbf{h_o}$ = imposed inland water table elevation.

The water balance is: dq = Rdx, and after Dacy's law $q = -T\dfrac{dh}{dx}$;

Then $dq = -\dfrac{d^2h}{dx^2} = R \;\rightarrow\; -T = -\dfrac{dh}{dx} = Rx + A \;\rightarrow\; -Th = R\dfrac{x^2}{2} + Ax + B$
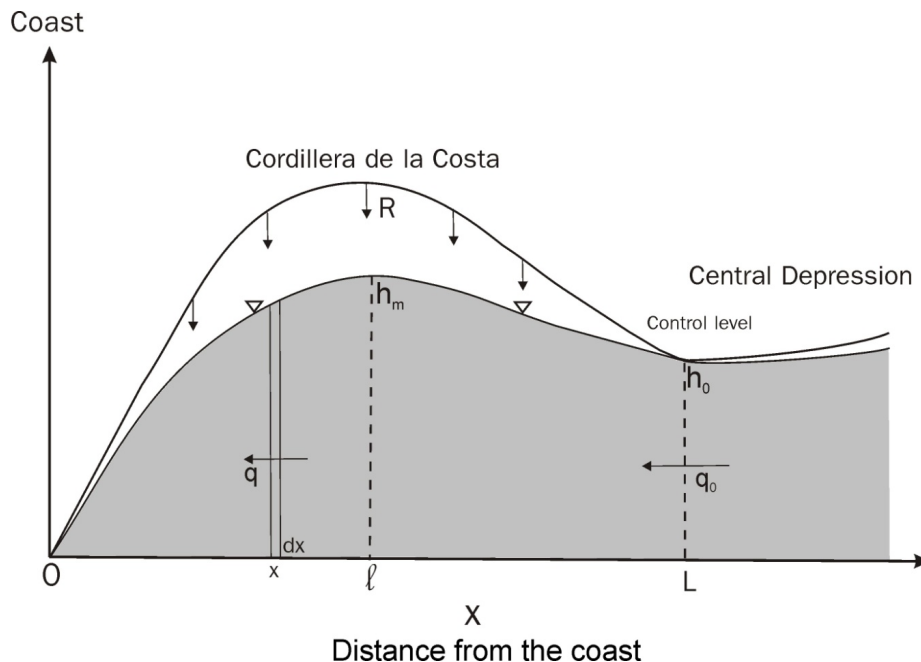

FIG. A1. West-east oriented hydrogeological cross-section sketch of the Cordillera de la Costa. from Antofagasta city coast (x=0) to the Central Depression (x=L). R is diffuse recharge, ∇ represents the water table elevation, q groundwater horizontal flow and q_o groundwater flow transferred from the Central Depression.

A and B are constants to be determined applying the following boundary conditions:

in $x = 0$ is $h = 0$ $\rightarrow$ $B = 0$

in $x = L$ is $h = h_o$ $\rightarrow$ $A = -\dfrac{2Th_0 + RL^2}{2L}$

This results in the following steady-state water-table elevation:

$$h = -\frac{R}{2T}x^2 + \left(\frac{h_0}{L} + \frac{RL}{2T}\right)x$$

The highest water-table elevation is produced when $dh/dx = 0$ at a distance $l = \dfrac{h_0 T}{RL} + \dfrac{L}{2}$

l is real if $\dfrac{2h_0 T}{RL} \leq L$, or $R \geq \dfrac{2h_0 T}{L^2}$;

otherwise the water-table maximum elevation is not inside the problem domain; this means that groundwater flow is in the same direction from x=L to x=0.

The highest water-table elevation, when it is inside the problem domain, is:

$$h_m = \frac{RL^2}{8T} + \frac{h_0}{2} + \frac{h^2_0 T}{2RL^2};$$

By introducing the variable $\tau = RL^2/T$, it results $\tau^2 + 4\,(h_o - 2h_m) + 4\,h_o^2 = 0$

Part of the recharge produced in the Cordillera de la Costa flows inlandward, and what remains feeds the springs and produce diffuse discharge: $q_T = R \cdot l = RL/2 + Th_o/L$

When an groundwater divide in not formed inside the problem domain, the water flow transferred from the Central Depression is:

$$q_0 = -\left|\frac{dh}{dx}\right|_{x=L} = -\frac{Th_0}{L} - \frac{RL}{2}$$

and then the flow available to feed the springs and diffuse discharge is:

$$q_T = RL - q_0 = \frac{RL}{2} + \frac{Th_0}{L},$$

which is the same expression obtained above.

The above formulae are applied to Cordillera de la Costa conditions: L = = 10.000 m; h_o = = 500 m, under the following conditions:

a) R from nil (only water transfer from the Central Depression and the springs at an elevation below h_o) up to 1 mm/yr in the most favorable parts; really R is not homogeneous in the cross-section.

b) except in the case when the water table is placed close to land surface in a large fraction of the cross-section T is that corresponding to a medium of very small hydraulic conductivity, k, and quite thick (e), with the following tentative values:
   - non-tectonized massif, k=10^{-4} to 10^{-6} m/d; e=100 to 1,000 m; then T=10^{-4} to 0.1 m²/d (~0.036 to 36 m²/yr).
   - tectonized massif (the strip associated to a main transversal fracture); k=10^{-2} to 10^{-3} m/d; e=100 m; then T=0,1 a 1 m²/d (~36 to 365 m²/yr).

c) the highest springs are at 450 m elevation, but they are the discharge points of higher elevation basins. It can be expected that h is up to 800 m and not below 350 m in the non-tectonized parts, although it can be lower in tectonized areas.

d) spring discharge is reckoned to be 60,000 m³/yr in 200 km, or q_T= 0.3 m²/yr. Discharge could be actually greater in tectonized parts where groundwater flow concentrates or due to unaccounted diffuse recharge. Thus, a discharge between 0.3 and 2 m²/yr is estimated.

To have a water-table dome:

$$R \geq \frac{2h_0T}{L^2} = 10^{-5} \quad \text{T in consistent units, or } R(mm/yr) \geq T(m^2/d)/3.65$$

R varies between ≥0.3 mm/yr in the tectonized areas and ≥10^{-4} mm/yr in the more compact parts. According with this, a water-table dome may be expected in the Cordillera de la Costa, except in highly tectonized parts, the only ones through which groundwater may be transferred from the Central Depression to the coast.

To limit the water-table dome elevation to 800 m

$$\tau^2 + 4.4 * 10^{-3}\tau - 10^6 = 0 \quad \rightarrow \quad \tau = -2.2 + \sqrt{5.84} * 10^3 = 217 \text{ m}$$

$R \leq \frac{\tau T}{L^2} = 2.17 * 10^{-4}T$ in consistent units, or $R(mm/yr) \leq$500T (m²/d); this means T > 2•10^{-3} m²/d

To limit q_T to a value between 0.3 and 2 m²/yr, it results 20 q_T= 10^5 R + T in consistent units. Since the value of T has little influence, R≈ 2•10^{-4} q_T, resulting in R between 0.2 and 0.03 mm/yr.

This highly simplified analysis shows that the recharge rate that could explain actual current observations is in the range 0.03 to 0.2 mm/yr, which allows a water-table dome to be formed in the Cordillera de la Costa, except in the most tectonized areas, whereas the hydraulic transmissivity can be expected to exceed a 2•10^{-3} m²/d and groundwater may be transferred from the Central Depression; recharge produced in the Cordillera de la Costa is added to that flow, but some drainage transversal to the cross-section is produced since the flow pattern is three-dimensional. The upper limit of these recharge values cannot be explained with current rainfall. Two possible explanations can be considered: **a.** current higher recharge than assumed, due to occasional, poorly known, exceptional recharge in moments of rare intense rainfall events; and **b.** present situation is the remnant of a more rainy past period during which groundwater storage conspicuously increased and the effect has not fully decayed, this agrees with the decreasing spring outflow shown by historical and pre-historical data.

The water-table sensitivity to recharge deviations from the average value R, is:

$$\frac{\Delta h}{\Delta R} * \frac{1}{2T}(-x^2 + Lx)$$

In Cordillera de la Costa central position (x= L/2):

$$\frac{\Delta h}{\Delta R} = \frac{L^2}{8T} \quad \rightarrow \quad \Delta h = \frac{L^2}{8T}\Delta R \, ,$$

which in the considered case is $\Delta h(m) \approx 36 \, \Delta R(mm/yr)/T(m^2/d)$

For R= 0.1 mm/yr, when it doubles in the most compact part of the massif, with T= 2•10^{-3} m²/d, it results Δh= 175 m, which means saturation up to the surface. This situation is poorly real. This again means that R <<0.1 mm/yr, but at the higher T tectonized areas.