



Spatial variability of the modern radiocarbon reservoir effect in the high-altitude lake Laguna del Peinado (Southern Puna Plateau, Argentina)

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Abstract. The high-altitude lakes of the Altiplano-Puna Plateau in the Central Andes often have large radiocarbon reservoir effects. This combined with the general scarcity of terrestrial organic matter makes obtaining a reliable and accurate
15 chronological model based on radiocarbon ages a challenge. As a result, age-depth models based on radiocarbon dating are often constructed by correcting for the modern reservoir effect, however, commonly without consideration of spatial variations of reservoir ages within the lake and across the basin. In order to get a better constrain on the spatial variability of the radiocarbon reservoir effects, we analyse ¹⁴C ages of modern terrestrial and aquatic plants from the El Peinado basin in the Southern Puna Plateau, which hosts the Laguna del Peinado lake fed by hydrothermal springs. The oldest ¹⁴C ages of modern
20 samples (>18,000 and >26,000 BP) were found in hot springs discharging into the lake likely resulting from the input of ¹⁴C-depleted carbon from old groundwater and ¹⁴C-free magmatic CO₂. In the littoral and central part of Laguna del Peinado, modern samples ¹⁴C ages were several thousand years lower (>13,000 and >12,000 BP) compared to the inflowing waters as a result of CO₂ exchange with the atmosphere. Altogether, our findings reveal a spatial variability of up to 14,000 ¹⁴C years of
25 the modern reservoir effect between the hot springs and the lake in the El Peinado basin. This study has implications for high-precision dating and accurate ¹⁴C-based chronologies in paleoclimate studies in the Altiplano-Puna Plateau and similar settings. Our results highlight the need to consider spatial and likely also temporal variations in the reservoir effects when constructing age-depth models.

1 Introduction

The Altiplano-Puna Plateau is the second highest and largest plateau in the world after Tibet (Allmendinger et al., 1997). It
30 extends along the Central Andes from southern Peru to northern Argentina and Chile at an altitude above 3,000 m a.s.l. and is characterised by endorheic basins that host numerous saline lakes, playa-lakes and salars. These systems are highly sensitive

to small fluctuations in the water balance making them promising sensors for studying recent and past environmental and hydrological changes (e.g. Grosjean et al., 1997; Valero-Garcés et al., 2000; McGlue et al., 2013; Santamans et al., 2021) associated with the dynamics of the South American Monsoon System and the more northerly influence of the Southern Hemisphere Pacific Westerlies (Vuille and Ammann, 1997; Garreaud, 2009; Vuille et al., 2012).

Our understanding of the regional and temporal hydroclimatic dynamics in the Altiplano-Puna Plateau is hampered by the difficulty in obtaining accurate chronologies from lacustrine sediments due to the scarcity of terrestrial organic matter and the large ^{14}C reservoir effect in the waters (Grosjean et al., 1995, 1997, 2001; Geyh et al., 1998; Valero-Garcés et al., 2000). In particular, in the southern sector of the Andean Plateau (i.e. the Puna region; Fig. 1), no other paleoclimatic archives (e.g. ice-glaciers) exist that can be studied and used to develop high-resolution paleoclimatic and paleoenvironmental reconstructions like those located further north in the Altiplano (e.g. Thompson et al., 1995, 1998, 2000; Zech et al., 2008). Therefore, obtaining reliable chronological models using lake sediments from this region is critical and requires an understanding of the ^{14}C reservoir effect variability in each particular lake system. Since the application of other dating methods is also strongly limited or not possible (like ^{210}Pb and ^{137}Cs due to the low concentration of these isotopes at these latitudes and altitudes; Argollo et al., 1994; Cisternas and Araneda, 2001), the construction of chronological models based on corrections for the modern reservoir effect is a common practice (e.g. Grosjean et al., 1995, 1997, 2001; Geyh et al., 1998, 1999; Moreno et al., 2007; Giralt et al., 2008; Jara et al., 2019). Sometimes, even assumptions on temporal variations of the reservoir effect are included in the construction of age-depth models. In contrast, spatial variations within a lake system are less considered although these can be equally crucial for reliable age-depth models.

Therefore, the aim of this study is to present and discuss new radiocarbon data from various types of modern samples from a range of different locations within the Laguna del Peinado lake system and catchment. This high-altitude lake in the Southern Puna Plateau is fed by hydrothermal springs and previous studies assumed a modern reservoir effect $>12,000$ years for a lake sediment record (Valero-Garcés et al., 1999, 2000). We analysed the ^{14}C ages of live/modern terrestrial and aquatic plants within the El Peinado basin to investigate whether significant variability exists and if it follows a spatial trend, and what are the likely sources of the reservoir effect. Furthermore, we report down-core ^{14}C ages from a lake core and compare them with the previously published dates to estimate possible temporal variability of the reservoir effect in the sedimentary record of this lake.

60 2 Study area

Laguna del Peinado is a shallow lake located at 3,760 m a.s.l. in the Southern Puna Plateau in the Central Volcanic Zone of the Andes of Argentina ($26^{\circ} 30' 16.87''$ S, $68^{\circ} 5' 49.95''$ W; Fig. 1). The lake is located in a topographically closed basin along the Peinado lineament, a NNE-SSW dextral transcurrent fault system that runs along the Antofalla salar axis and presumably



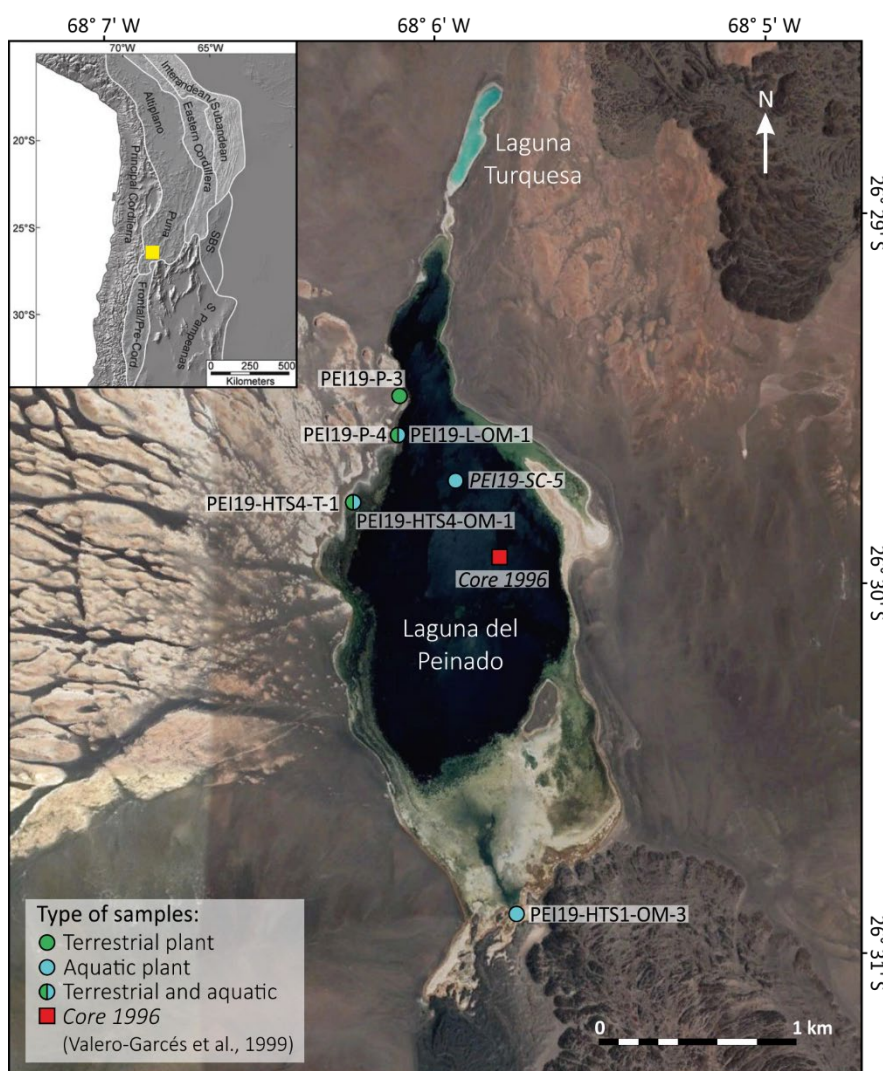
continues under the Peinado composite volcano (Seggiaro et al., 2006; Grosse et al., 2022; Fig. 1). Peinado is a young
65 potentially active volcano (last activity dated to 36.8 ± 3.8 ka; 5,890 m a.s.l.) located ~5 km south of Laguna del Peinado
(Grosse et al., 2022). It consists of a very steep cone surrounded by a ring of lavas originating from several lateral vents, loose
scoria and subordinate pyroclastic flows of dominantly mafic compositions (basaltic andesites and andesites; Grosse et al.,
2014, 2017, 2022). The Peinado volcanic field also hosts 17 mafic monogenetic centres, with seven of them located between
the Antofalla salar and the Peinado stratovolcano and of Pleistocene ages (0.6 ± 0.1 Ma to 0.15 ± 0.02 Ma; Grosse et al., 2020).
70 Lavas from one of these monogenetic centres (0.38 ± 0.02 Ma; Grosse et al., 2020) limit the southern part of the Laguna del
Peinado system (Fig. 1). To the west of the lake, the Pliocene rhyolitic Laguna Amarga ignimbrites (3.7-4 Ma, >70 km³)
originated from the Laguna Amarga caldera crop out (Kay et al., 2010 and references therein). Four lacustrine terraces have
been described, the uppermost consisting of volcanic sandstones and conglomerates cemented with calcite, and the lower ones
composed by intraclastic and biomicritic limestones (Valero-Garcés et al., 2001).

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The main water body in the El Peinado basin is Laguna del Peinado with a maximum length in the N-S direction of 3.4 km, a
width of 1.2 km, and a maximum water depth of ~4 m (Fig. 1). The lake is fed by hydrothermal springs located on the southern
and western shores. The southern part of the lake is characterised by an extensive shallow wetland area where hot spring seeps
and a pool discharge through a stream into the lake, while on the western shore several smaller hot spring seeps occur. To the
80 north of Laguna del Peinado, the smaller and shallower Laguna Turquesa is located which currently is disconnected due to the
low water level (Fig. 1). Abundant carbonate precipitation takes place in the El Peinado basin with deposits comprising a wide
variety of facies including microbialites (travertines, microbial mounds, microbial mats and others) and fine-grained mineral
precipitates (Valero-Garcés et al., 2001; Fariás et al., 2020; Della Vedova et al., 2022; Vignoni et al., 2022).

85 The location of the El Peinado basin in the southern portion of the Puna Plateau covers the climatic transition zone between
the South American Monsoon System (SAMS) and the more northerly influence of the Southern Hemisphere Pacific
Westerlies (SHPW). Due to the meridional extension and prominent orography, the Central Andes act as a topographic barrier
to the moisture-bearing easterly winds resulting in a steep E-W rainfall gradient with high precipitation on the eastern flanks
and increasing aridity westwards into the Puna Plateau (Strecker et al., 2007; Garreaud, 2009; Castino et al., 2017). In the
90 study region, mean annual precipitation values are <120 mm yr⁻¹, whereas evaporation has been estimated to be $>1,500$ mm
yr⁻¹ in Laguna del Negro Francisco located ~150 km southeast of Laguna del Peinado (Grosjean et al., 1997; Strecker et al.,
2007). The scarce precipitation events that reach these dry high elevation zones are associated to seasonal changes in the
position and intensity of the two dominant atmospheric circulation systems (SAMS vs. SHPW). Approximately 80% of the
annual precipitation occurs during summer when the strengthening of the SAMS and the heating effect over the Puna Plateau
95 are responsible for convective rainfall events (Garreaud, 2009; Vuille et al., 2012). During winter, precipitation is associated
with northward incursions of the SHPW and snowfall events result from Pacific cold fronts often combined with blocking

episodes in the South Pacific and polar air isolated cells that migrate north interacting with warmer tropical air masses (Vuille and Ammann, 1997).



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Figure 1: Location and type of samples collected in the El Peinado basin during 2019 (© Google Earth 2020, Maxar Technologies, CNES/Airbus). Sediment core samples are indicated in italics. Left top corner: The yellow square marks the location of the El Peinado basin in the Puna Plateau of NW Argentina on a shaded relief map with the principal morphotectonic provinces of the southern central Andes (SBS: Santa Barbara System; S. Pampeanas: Sierras Pampeanas; Frontal/Pre-Cord.: Frontal Cordillera and Precordillera; modified from Strecker et al., 2007).

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3 Materials and methods

3.1 Fieldwork and sampling

During fieldwork in January and November 2019, sediment and organic matter samples including living terrestrial and aquatic plants were collected for radiocarbon analysis from different parts of the lake basin (Fig. 1). Short sediment cores (<1 m) were
110 retrieved from Laguna del Peinado in two profiles at different water depths using an Uwitec coring device. The cores were split into two halves, photographed and described at the GFZ Potsdam (Germany). Four bulk samples were sieved for organic macro remains used for radiocarbon dating from a short core in the central part of the basin at 3.2 m water depth (PEI19-SC-5, Fig. 1). In total, we collected 10 samples: seven modern samples (three terrestrial plants, two microbial mats from the hot springs, aquatic macrophytes from the lake littoral, and aquatic macrophytes from the sediment core-top at 0-2 cm depth) and
115 three macro remain samples (from the sediment core at 22-23, 48-49, and 71-72 cm depth). All samples were washed with demineralised water and dried in the oven at 60 °C. Plant materials are reported in Table 1 and modern samples are shown in Fig. 2.

3.2 Radiocarbon and carbon isotopes analysis

Accelerator mass spectrometry (AMS) ^{14}C measurements of the ten samples were carried out in the Poznan Radiocarbon
120 Laboratory (Poland). The resulting ^{14}C ages are listed in Table 1 with one standard deviation (σ). Samples with percentage of modern carbon (pMC) were converted to fraction modern ^{14}C ($F^{14}\text{C}$) values (Stuiver and Polach, 1977; Reimer et al., 2004; Stenström et al., 2011). Dates were calibrated with CALIBomb (Reimer et al., 2004; Reimer and Reimer, 2023) using the Southern Hemisphere Zone 1-2 atmospheric radiocarbon data (Hua et al., 2013, 2021).

125 Carbon isotopes analysis of carbonates ($\delta^{13}\text{C}_{\text{carb}}$) associated with macro remain samples from the sediment core and southern hot spring were carried out on an automated carbonate extraction device (KIEL IV) coupled to a Finnigan MAT 253 IRMS (Thermo Fisher Scientific) at the GFZ Potsdam. Results are expressed in the conventional δ -notation in per mille (‰) relative to VPDB (Vienna Pee Dee Belemnite; Table 1). Repeated measurements of the reference material NBS 19 ensured an analytical accuracy better than ± 0.07 ‰ (σ).

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Table 1: ^{14}C ages from El Peinado basin. Post-bomb ages were calibrated using the Southern Hemisphere Zone 1-2 calibration dataset (Hua et al., 2013, 2021). The $\delta^{13}\text{C}$ values in *italic* correspond to samples at 24 to 26 cm and 46 to 48 cm, and differ at the sampling depths for ^{14}C .

Sample	Water influence and type	Material	Lab ID	Lab reported ^{14}C date $\pm \sigma$ (BP)	Calibrated date (cal CE)	$\delta^{13}\text{C}_{\text{carb}}$ (‰ VPDB)
PEI19-P-3	No water influence, ~2 m above lake level	Terrestrial plant (<i>Adesmia horrida?</i> , " <i>Añagua</i> ")	Poz-122590	112.39 \pm 0.31 pMC	1958-1959 and 1994-1996	-
PEI19-P-4	No water influence, ~1 m above lake level	Terrestrial plant (Poaceae, <i>Festuca ortophylla?</i>)	Poz-123623	101.61 \pm 0.34 pMC	1956-1957 and 2018-2019	-
PEI19-L-OM-1	Lake water (littoral, ~20 cm below water level)	Aquatic macrophyte (Potamogetonaceae, <i>Potamogeton sp.</i> or <i>Zannichellia sp.?</i>)	Poz-123624	13,840 \pm 70	-	-
PEI19-HTS4-T-1	Hot spring 4? (~15 cm away from the shore)	Terrestrial plant (Poaceae, <i>Festuca ortophylla?</i>)	Poz-123625	1,580 \pm 30	-	-
PEI19-HTS4-OM-1	Hot spring 4 (shallow, mix with lake water?)	Microbial mats in hot spring	Poz-122473	18,510 \pm 90	-	-
PEI19-HTS1-OM-3	Hot spring 1 southern shore (pool bottom)	Microbial mats in hot spring	Poz-123626	26,500 \pm 1,300	-	7.09
PEI19-SC-5_0 to 2 cm			Poz-132432	12,360 \pm 60	-	8
PEI19-SC-5_22 to 23 cm	Lake water (short core, 3.2 m water depth)	Aquatic macrophyte (Potamogetonaceae, <i>Potamogeton sp.</i> or <i>Zannichellia sp.?</i>)	Poz-132519	16,180 \pm 80	-	8.6
PEI19-SC-5_48 to 49 cm			Poz-132520	16,720 \pm 90	-	9.2
PEI19-SC-5_71 to 72 cm			Poz-132433	17,680 \pm 90	-	8.9
Core 1996 (Valero-Garcés et al., 1999)	Lake water (core)	Macrophyte (0 to 1 cm)	WHOI 17536	12,750 \pm 90	-	-

140 4 Results

Radiocarbon dating results of modern terrestrial and aquatic plants showed a wide variety of ages in the lake and catchment area (Table 1). Only two samples of terrestrial plants located approximately 15 and 5 m from the lake shore gave modern ages, PEI19-P-3 (*Adesmia sp.*) dated to cal CE 1994-1996 (112.39 \pm 0.31 pMC) and PEI19-P-4 (Poaceae) to cal CE 2018-2019 (101.61 \pm 0.34 pMC; Fig. 1, 2a, and 2b). Another terrestrial plant (Poaceae) collected near a hot spring (~15 cm) on the western shore (Fig. 1 and 2c) resulted in an older age of 1,580 \pm 30 BP. In contrast, a microbial mat sample of this hot spring dated to 18,510 \pm 90 BP (Fig. 1 and 2c). The oldest measured age was found in microbial mats from the southern shore hot spring pool (26,500 \pm 1300 BP; Fig. 1 and 2d). Living aquatic macrophytes (Potamogetonaceae) on the northwestern lake shore (~20 cm water depth) and from the surface sediment taken from the core located ~370 m away (3.2 m water depth) showed similar ages of 13,840 \pm 70 BP and 12,360 \pm 60 BP, respectively (Fig. 1, 2e and f). The three down-core samples from aquatic macrophytes (Potamogetonaceae) are in chronostratigraphic order and revealed ages of 16,180 \pm 80 BP (22 to 23 cm), 16,720 \pm 90 BP (48 to 49 cm) and 17,680 \pm 90 BP for the basal layer (71 to 72 cm; Fig. 3).

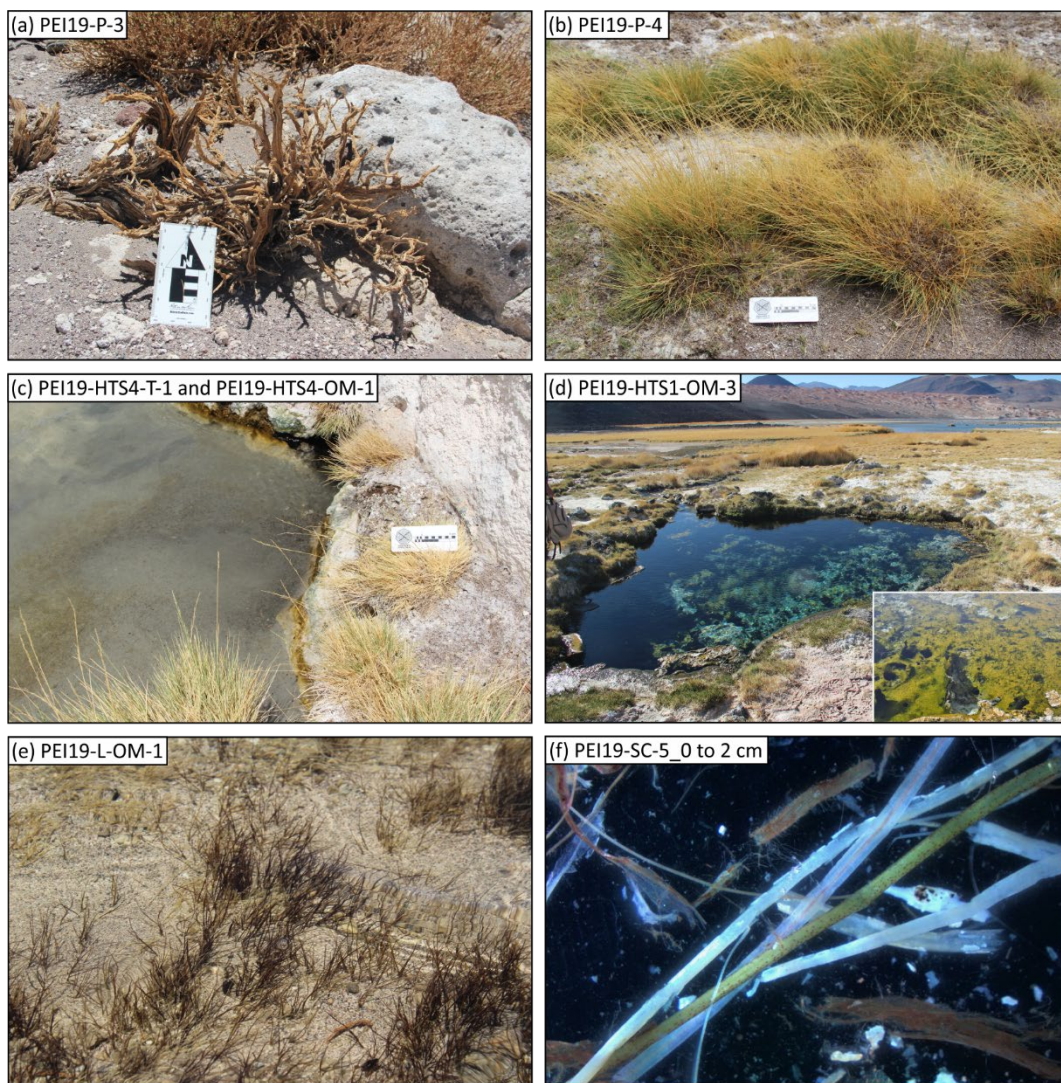
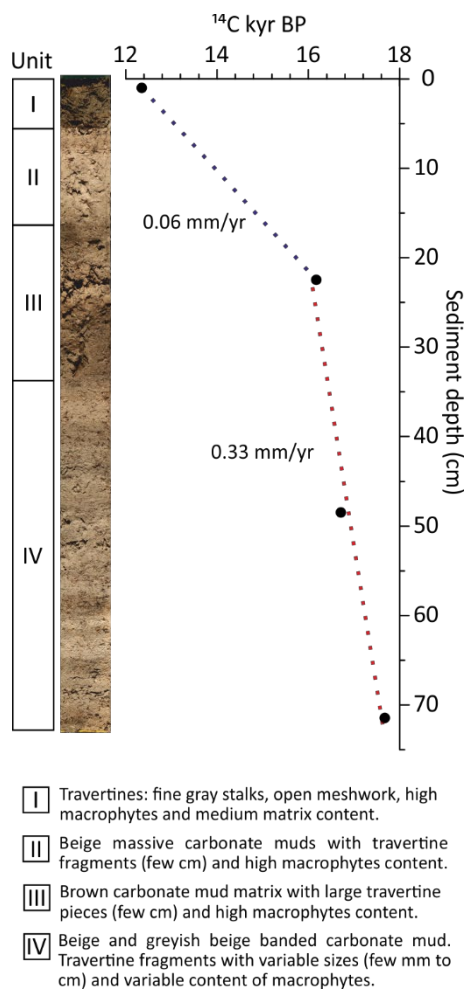


Figure 2: Modern samples: (a) and (b) terrestrial, (c) aquatic and terrestrial by the western shore hydrothermal spring, (d) aquatic from the southern shore hydrothermal spring, (e) lake littoral, (f) aquatic from the top of the lake short core.



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Figure 3: Short core PEI19-SC-5: down-core non-corrected ^{14}C ages obtained from aquatic macrophytes (Potamogetonaceae) remains (see Table 1) and calculated sedimentation rates. The top sample corresponds to live aquatic macrophytes (Potamogetonaceae).

5 Discussion

160 The reservoir effect of ^{14}C dates in lacustrine environments is a function of the CO_2 exchange rate between the lake water and the atmosphere, the internal system mixing dynamics, and the input of ^{14}C -dead, ^{14}C -depleted, or ^{14}C -free carbon (Macdonald et al., 1991; Ascough et al., 2010; Keaveney and Reimer, 2012; Jull et al., 2013; Lockot et al., 2015). In this section, we discuss the variability observed in the ^{14}C ages of modern plants in the El Peinado basin and the possible sources that lead to the reservoir effect that may also be of relevance for other basins in the Altiplano-Puna Plateau as well as basins in similar settings.



165 5.1 Spatial variability of the ^{14}C reservoir effect in the El Peinado basin

Present-day terrestrial and aquatic plants are expected to provide modern radiocarbon ages without any reservoir effect involved. However, in our investigation, only two terrestrial plant samples yielded recent ages and thus were free of any reservoir effects (Table 1). One sample of Poaceae growing in the vicinity of a hydrothermal spring revealed an age of $1,580 \pm 30$ BP indicating that even terrestrial plants incorporate ^{14}C -depleted carbon. The ages of all other modern samples varied substantially between $12,360 \pm 60$ BP and $26,500 \pm 1300$ BP, showing distinct reservoir effects depending on the location within the basin. The oldest age was found for the modern microbial mats from the southern shore hydrothermal pool, whereas microbial mats from a hot spring at the western shore displayed an approximately 8,000 ^{14}C years younger age (Table 1, Fig. 4). Ages from aquatic plants from a near-shore site and surface sediment from the central part of the lake reveal significantly younger ages than those from microbial mats in both hot springs (Table 1, Fig. 4). From those two, the shallow water sample is ca. 1,500 years older ($13,840 \pm 70$ BP) than the sample from the central part of the lake ($12,360 \pm 60$ BP). The general trend of decreasing ages from the inflowing hydrothermal waters and littoral positions towards the deeper lake likely reflects longer residence time of water in the lake and prolonged exchange of the dissolved inorganic carbon (DIC) with the atmospheric CO_2 compared to the hydrothermal inflows, resulting in higher ^{14}C concentrations and consequently lower reservoir effects (Fig. 4). In contrast, the higher reservoir effect recorded in the plants from the hot springs and the littoral zone of the lake reflects poorly equilibrated DIC. The difference of ca. 8,000 ^{14}C years between both hot springs (Table 1, Fig. 4) could result either from some influence (i.e. mixing) of lake water with higher ^{14}C concentrations in the western shore hot spring (Fig. 1), or from the existence of separate hydrothermal systems bounded by the Peinado lineament with distinct ^{14}C content in the DIC. A similar pattern of spatial variability has been observed in lakes in the Tibetan Plateau, with high reservoir effect in tributaries and spring waters and lower reservoir effect in the central regions of lakes (Mischke et al., 2013).

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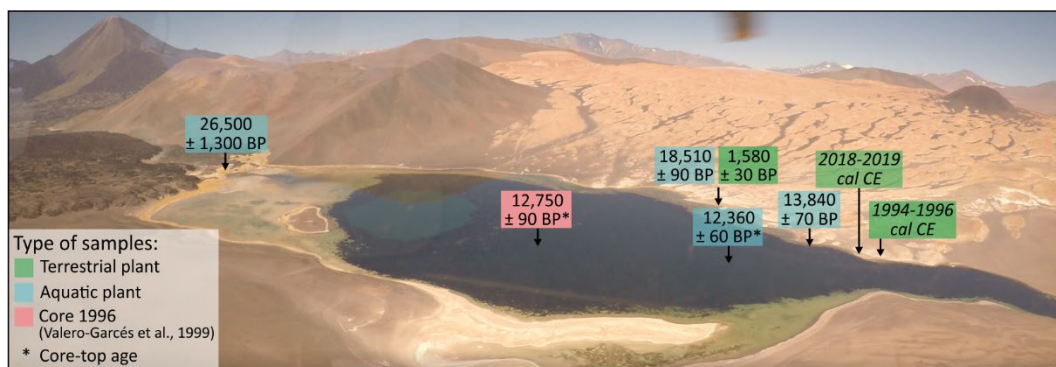


Figure 4: Aerial view of Laguna del Peinado from the northeast and all radiocarbon dates obtained from surface samples. Calibrated post-bomb ages are indicated in italics.

5.2 ^{14}C reservoir effect sources in the El Peinado basin

190 5.2.1 Catchment geology

The dissolution of carbonate-rich sediments or rocks in the catchment area is usually considered a main source of ^{14}C -dead carbon influx into a lake (Macdonald et al., 1991; Ascough et al., 2010). However, the dissolution of catchment carbonates can only be a minor source of ^{14}C -dead carbon into Laguna del Peinado because the lithology of the basin is dominated by volcanic rocks (Seggiaro et al., 2006; Grosse et al., 2020, 2022). Carbonatic outcrops are scarce and limited to few ancient
195 lake terraces consisting of conglomerates and sandstones with volcanic clasts cemented/coated with calcite, intraclastic and biomicritic limestones, and microbialites (Valero-Garcés et al., 2001; Villafañe et al., 2021).

5.2.2 Groundwater effects

Another common source of ^{14}C -depleted carbon in lakes can be the contribution of ancient groundwater (Macdonald et al., 1991; Riggs, 1984; Godfrey et al., 2021). In the Altiplano-Puna Plateau, the contribution of old groundwater to lacustrine
200 systems might be substantial given the present-day negative water balance regime (Grosjean et al., 1995). Furthermore, water tables can be very deep and develop groundwater flow paths with long transit times that often cross topographic boundaries prior to emerging at the basin bottoms (Moran et al., 2021). The old ^{14}C ages of modern aquatic organisms in the hot springs (Table 1, Fig. 4), can be partially explained by an old origin and high residence times of water in the hydrothermal groundwater system. This is supported by geochemical studies suggesting a meteoric origin of water in the hydrothermal reservoir (Vignoni
205 et al., 2022), which must have occurred in the past given the extreme low present-day precipitation. Groundwater in this region is thought to have formed during wet periods at the end of the last glaciation and early Holocene like the widespread Central Andean Pluvial Event (17.5–14.2 ka and 13.8–9.7 ka; Latorre et al., 2006; Placzek et al., 2009; Gayo et al., 2012), which overlap with the ages obtained for modern samples from the northwestern shore and the top of the lake core. Water from these wet periods, however, would be too young to explain the two older dates of $18,510 \pm 90$ BP and $26,500 \pm 1,300$ BP obtained
210 from organisms directly in the hot springs (Table 1, Fig. 4). Therefore, additional sources of ^{14}C -dead, ^{14}C -depleted or ^{14}C -free carbon must be involved (see Section 5.2.3).

The influence of old groundwater in the lake is consistent with ^3H analysis in wetland systems in the Southern Puna Plateau proving that these environments are mainly sustained by old waters, with only minor contribution of modern water not
215 exceeding 10 % (Moran et al., 2019, 2021; Frau et al., 2021). For example, the zero ^3H activity in the lake waters of the Carachi Pampa basin (~50 km east of the El Peinado basin) indicates that it is almost entirely sustained by ancient groundwater (Frau et al., 2021). Also, geochemical (^3H , $\delta^{18}\text{O}$, $\delta^2\text{H}$) and hydrophysical studies in springs and groundwater feeding the Salar de Atacama basin, located ~325 km north of the study area, revealed a large regional groundwater system integrated over timescales of 100-10,000 years or longer (Moran et al., 2019).



220 5.2.3 ¹⁴C-free volcanic CO₂

Another potential source for the large reservoir effects in El Peinado basin, in particular for those dates exceeding the ages of the Central Andean Pluvial Events, is a contribution of ¹⁴C-free magma derived CO₂ (Macdonald et al., 1991 and references therein; Pasquier-Cardin et al., 1999). In the young volcanic El Peinado basin (Grosse et al., 2020, 2022), magma degassing is a likely source of CO₂ into the hydrothermal system as assumed for the Cerro Blanco geothermal system located 40 km to the
225 ESE (Chiodi et al., 2019). Geophysical studies also suggested the existence of magma reservoirs in the crust beneath the El Peinado area (Bianchi et al., 2013; Ward et al., 2017). An influence of volcanic CO₂ is further supported by permanent bubbling in the southern shore hot spring pool as well as in the seepage areas on the west coast. Furthermore, strong ¹³C-enrichment in the lake carbonates up to +13 ‰ VPDB has been explained by degassing of volcanic CO₂ (Table 1; Valero-Garcés et al.,
230 magmatic CO₂ in the southern hydrothermal reservoir compared to those on the west would explain the oldest age of 26,500 ± 1,300 BP recorded in the basin. For example, ¹⁴C ages of the DIC exceeding 20,000 years due to dilution by geogenic DIC sources have been reported also from the Loa and Calama basins located north of the Salar de Atacama (~450 km NNW of the El Peinado basin; Godfrey et al., 2021).

235 Degassing of magmatic CO₂ might have also caused the age of 1,580 ± 30 BP for a modern terrestrial plant from the western shore (Table 1, Fig. 1 and 2c). It has been reported that diffuse emanations of magmatic CO₂ through soils lead to a substantial ¹⁴C depletion in terrestrial plants when ¹⁴C-free CO₂ is assimilated during photosynthesis (Pasquier-Cardin et al., 1999). This might explain the old age of the abovementioned terrestrial plant sample since it grew at a distance of only ~15 cm from the local hot spring. The other two dated terrestrial plants were not affected by volcanic CO₂ contamination probably because they
240 grew about 5 m and 15 m further away from the lake shore and from potential sources of volcanic CO₂ as no hot springs were identified in that area (Table 1).

5.3 ¹⁴C reservoir effect in surface sediments

The core-top age obtained from aquatic macrophytes (Potamogetonaceae) from core PEI19-SC-5 (12,360 ± 60 BP) is ~400 ¹⁴C years younger compared to that of a core taken in 1996 (Valero-Garcés et al., 1999, 2000; Table 1, Fig. 4). A likely
245 explanation for a stronger reservoir effect in the previous core is its location closer to the southern hydrothermal spring. This would be in agreement with our observations in the modern environment proving decreasing reservoir effects with increasing distance to the hydrothermal springs due to extended DIC equilibration with atmospheric CO₂.

However, we cannot fully exclude a decrease in the reservoir effects in the last 23 years since the core from Valero-Garcés et al. (1999) was recovered probably related to a lake level lowering of at least 0.6 m (Villafañe et al., 2021) as it has been
250 assumed for other lakes in the Altiplano-Puna Plateau (e.g. Laguna Lejía, Laguna Miscanti, Lago Chungará; Geyh et al., 1998,

1999; Grosjean et al., 2001; Moreno et al., 2007; Giralte et al., 2008). In contrast, studies from other lake environments in NW China report an opposite mechanism, i.e. increasing reservoir effect related to lake level lowering (Zhou et al., 2020). Due to the lack of systematic studies, the influence of short-term lake level fluctuations on modern reservoir effects remains elusive. Other potential causes for temporal reservoir effect changes might be fluctuations in geothermal activity (Ascough et al., 2010) or changes in the lake primary productivity (Zhou et al., 2020), though we have no evidence to investigate these in more depth.

5.4 Down-core ^{14}C ages

The four down-core ^{14}C ages from aquatic macrophytes (Potamogetonaceae) in our core PEI19-SC-5 are in chronological order (Table 1, Fig. 3). The three radiocarbon ages between ca. 22 and 72 cm core depth suggest that these 50 cm of sediment comprise ca. 1,500 years with a rather constant sedimentation rate of 0.33 mm/yr (Fig. 3). The age of $12,360 \pm 60$ BP from the core surface suggests that the uppermost 22 cm of the sediment record cover a period of ca. 4,000 years. Assuming a largely constant reservoir effect, either the sedimentation rate must have decreased by a factor of about 5 or the sediment record includes a major hiatus. The only alternative interpretation would be a major decrease of the reservoir effect during the deposition of the uppermost 22 cm of the sediment record. Unfortunately, we do not have robust data to support any of these possibilities so that the age-depth relation of the core remains a matter of debate. Consequently, the age of the base of the core of $17,680 \pm 90$ BP (Table 1) might also be questioned. Interestingly, our data largely resembles the radiocarbon dates from the previous core taken in 1996 (Valero-Garces et al., 1999) except the few hundred years lower reservoir effect of the sediment surface likely due to spatial variations within the lake basin as discussed above. However, the age model of the previous core has been re-interpreted based on three preliminary U/Th dates suggesting a much younger age of ca. 450 a BP for the base of the 1996 core (Valero-Garces et al., 2000, 2003). Accepting this age, the radiocarbon reservoir age must have decreased in the last three centuries by about 4,000-5,000 ^{14}C years. Due to the lack of a critical assessment of potential bias of U/Th dating in this lake setting (Valero-Garces et al., 2000, 2003), the true age of the Peinado sediments remains unsolved. However, even if the good agreement of the radiocarbon dates in both cores does not necessarily prove the absence of major reservoir effect changes, the postulation of a several thousand year decrease of the reservoir effect in the last few centuries should be questioned and re-investigated. Further research is needed, not only in this lake but also along the Altiplano-Puna plateau to understand how these reservoir effect changes vary across the region.

6 CONCLUSIONS

Radiocarbon dating of modern plants revealed large reservoir effects of up to several thousand years ($>26,000$ ^{14}C years) within the El Peinado basin. These reservoir effects result from two dominant processes: the inflow of old groundwater that likely formed during pluvial phases at the end of the last glaciation and an additional contribution of ^{14}C -free magmatic CO_2 . We could further prove that the reservoir effect shows distinct differences within the lake basin depending on the distance to the source of old groundwater inflow and volcanic CO_2 . This can even influence the dating of sediment cores obtained from



different locations in the lake. Through comparison of surface sediments from a core taken for our study with a previously published sediment record, we found indications of a ca. 400 year difference in the reservoir ages between both cores. Such spatial variations in the ^{14}C reservoir effect may also occur in other lake records in the Central Andes and elsewhere and should also be considered for the construction of age models. In this sense, corrections of ^{14}C chronologies based on a single reservoir age for an entire lake are not reliable and would result in large uncertainties, as it can vary from hundreds to thousands of years within a lake leading to temporally misleading paleoclimatic interpretations. In contrast to proving spatial variability of reservoir ages, it remains challenging to determine temporal changes, in particular when alternative robust dating methods are not available. Therefore, radiocarbon dating of lake sediment cores from the Central Andes to obtain robust and reliable chronological models remains a major challenge, but the characterisation of spatial variations has the potential to better assess the underlying processes influencing the reservoir effect in a lake.

Author contribution

PV performed the samples processing, data analyses, and wrote the article with contributions from all co-authors. AB, FC, and RT designed the project and together with PV and CS organized fieldwork. LP helped to identify the families of the plants sampled. AB, FC and RT supervised analyses and article writing.

Competing interests

The authors declare that they have no conflict of interest.

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310 Data availability

All data used in this study is available in Table 1 of the manuscript.

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