

Response to anonymous Referee #1 comments:

We are very grateful to Referee #1 for taking the time to carefully review our manuscript and providing positive comments that help to improve this manuscript. We provide a response to each of them below. All comments have been considered and will be included in a revised version of this manuscript.

L16-17: You obviously go on to talk about TEMPORAL variation in reservoir effects too, but I felt that this should also be mentioned right at the start here, along with your noting of “spatial variations”.

Thanks for your comment, to mention temporal variations in reservoir effects we have now added “and possibly temporal” into that sentence.

L24-25: You’re absolutely right about the implications of this study affecting both precision and accuracy of ¹⁴C-derived chronologies, and they’re obviously interwoven, but I wonder if these should be inverted to reflect the greater importance of accuracy over precision? (I.e., accuracy is fundamental – there’s no point having inaccurate chronology is there?! – and, after that, increased precision then makes the data increasingly useful, no?)

We have modified the sentence and now reads “This study has implications for accurate ¹⁴C-based chronologies and high-precision dating in paleoclimate studies in the Altiplano-Puna Plateau and similar settings”.

L31: You list “endorheic basins that host numerous saline lakes, playa-lakes and salars”; is there scope for these basins to episodically dry out completely, with consequent impacts (hiatuses!) upon age modelling/palaeoenvironmental reconstruction?

Thank you for this question. Indeed, especially playa-lakes and salars can dry out episodically causing hiatuses in the sedimentary record. In order to minimize the likelihood of such hiatus, we collected the short core from Laguna del Peinado close to the deepest point of the lake at a water depth of 3.2 m. Further, we did not find any sedimentological indications in our record for a hiatus. This confirms a previous study of a sediment core that was taken even at shallower water depth (2 m) and in which no hiatus has been recognized (Valero-Garcés et al., 2000, 2003). Nevertheless, we are aware that it is difficult to detect a hiatus so that we cannot fully exclude that it has been overlooked. We address this point in the revised version of the manuscript where line 263 now reads “We do not observe lithological indications in the sediment core neither for a substantial sedimentation rate change nor for a hiatus in the record. However, since detection of a hiatus is not always straightforward, we cannot fully exclude the existence of one”.

L48-49: “Sometimes, even assumptions on temporal variations of the reservoir effect are included in the construction of age-depth models”; please could you include one or two references to support this statement.

We have added references “(e.g. Grosjean et al., 2001; Moreno et al., 2007)”.

L119-124: In order to interpret any radiocarbon data, it is essential to specify what chemical pre-treatment procedures have been applied. (I take on trust that this has been performed robustly, but this needs to be fully clarified, and is probably the most significant of my comments.)

Chemical pre-treatment on the samples was carried out in the Poznan Radiocarbon Laboratory where they were dated. Samples were washed with demineralised water in our lab before sending them out for dating. We have modified lines 119-121 to “Samples preparation, chemical pre-treatments, and accelerator mass spectrometry (AMS) ^{14}C measurements were carried out in the Poznan Radiocarbon Laboratory. A full description of the procedures can be accessed at <https://radiocarbon.pl/en/sample-preparation/>. After mechanical removal of macroscopic contamination under binoculars, the samples underwent a sequential acid-base-acid (ABA) treatment following the protocols established for each material (UW protocol for the wood sample PEI19-P-3 and UV protocol for all other plant remains samples). Samples were first treated with 1 M HCl at 80°C for 20 min or longer if needed until gas bubbles emanations finished (UV, UW), followed by 0.1 M NaOH treatment at room temperature for fragile plant remains (UV) and 80°C for wood (UW); and then 0.25 M HCl at 80°C for 1 hr. After each treatment, samples were rinsed with deionised water (Millipore) to pH=7. The NaOH treatment step is repeated a few times until no more colouring of the solution caused by humic acids is observed. For the wood sample PEI19-P-3 (UW) an additional treatment with 5% NaClO₂ at room temperature was applied for 30 min.”

L123-124 (and also for Table 1): Why only calibrate the post-bomb ^{14}C measurements, but not the pre-bomb?

We do not calibrate the pre-bomb ages because the reservoir effect of these dates is not known. In order to homogenise the table, we deleted the column with calibration.

L125-127: Again, what chemical pre-treatment procedures were applied to these samples prior to $\delta^{13}\text{C}$ analysis?

We did not apply chemical pre-treatment prior to analysis in the Kiel IV Carbonate Device coupled to the IRMS. We added some information about samples and sample preparation in the methods section. Lines 125-129 now read “Additionally, $\delta^{13}\text{C}_{\text{carb}}$ was analysed in four samples from the carbonatic matrix sediments at 0-2, 24-26, 46-48, and 71-72 cm depth from the core where the plant macrofossils have been taken and in one sample from the microbial mats in the southern hot spring. Samples were freeze-dried for 24

to 48 hours, freeze-dried for 72 hours, and ground to powder. Carbon isotopes analysis of carbonate powders ($\delta^{13}\text{C}_{\text{carb}}$) 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. In brief, acid digestion of carbonates with phosphoric acid takes place in the KIEL IV to produce CO_2 that is ultimately analysed for $\delta^{13}\text{C}_{\text{carb}}$ in the coupled MAT 253 IRMS. 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 precision better than ± 0.07 ‰ (σ).

L129: Surely this is “precision” rather than “accuracy”?

Thanks, we have replaced “accuracy” with “precision”.

L143: Your samples were collected in 2019... and so the latter age (2018-2019 cal CE) makes sense. But how do you explain the former age (1994-1996 cal CE)? A freshwater reservoir effect wouldn't ENHANCE the 14C (112.39 pMC c.f. 101.61 pMC). Precisely what was the material sampled (for both of these samples)? Is the former sample more woody material (with an associated inbuilt “storage age”)? Please give more information around these samples, and suggest what has led to this.

The material collected for both samples is indeed different. The sample with an age 2018-2019 cal CE (101.61 pMC) was a Poaceae (Gramineae), possibly *Festuca ortophylla* (sample PEI19-P-4, Table 1, Fig. 2b). The sample with an age 1994-1996 cal CE (112.39 pMC) was a woody plant of the genus *Adesmia*, possibly the species *horrida* (sample PEI19-P-3, Table 1, Fig. 2a). Two possible causes could explain the older age (or higher pMC) of sample PEI19-P-3: 1) the plant was not alive at the time of sampling as it had no new sprouts (see Fig. 2a, the front plant was sampled); 2) the structure of this woody plant is formed over an extended time and the higher pMC than the atmosphere for 2019 results either from the integration of ^{14}C during the growing years or from the measurement in the sample heartwood (old wood). However, since both samples (PEI19-P-3 and PEI19-P-3) reveal modern ages and the difference between the two calibrated ages is only minor this is not relevant for the main statement that these samples are not influenced by reservoir effects. Therefore, we will not further discuss this in the revised version of the manuscript.

L166-167: I would say that this wording is misleading; Yes, terrestrial plants are “expected to provide modern radiocarbon ages without any reservoir effect involved” (generally speaking! Although there could be rare examples where the expectation may differ...) BUT aquatic plants obviously take on their carbon from the water, and so they wouldn't be “expected to” provide modern radiocarbon ages, surely? Isn't that a fundamental premise of the present paper? I just find the wording of this sentence unnecessarily misleading, taken in isolation.

We agree and have modified it to “Present-day terrestrial plants are commonly expected to provide modern radiocarbon ages, while aquatic plants potentially take up old carbon”.

L168-169: This is really interesting. I am not a biologist – is the aged C being taken in by the grass from the air (localised atmospheric depletion from C release from the hydrothermal spring), or is the aged C being taken in through the roots (in the water taken up by the plant)?

Although this is difficult to ultimately prove, we assume that this plant must have absorbed aged carbon through the air by the release of $\text{CO}_{2(g)}$ from the nearby hydrothermal spring because it was not in direct contact with the hydrothermal water. Uptake of aged carbon from soil DIC could have only had a minor effect because uptake by roots commonly is 1-3% or even less of the total CO_2 fixed by the plant (Loczy et al., 1983; Ford et al., 2007).

L169: Clarify again that here you are referring to aquatic species(?).

We have added “aquatic” for clarification.

L182-184: Give an approximate representation of the values given for the cited study.

We have added “with differences of up to 19,000 ^{14}C years between different locations within individual lakes”.

L191-194: “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”. Does this contradict what was written earlier on (“Abundant carbonate precipitation takes place in the El Peinado basin...”, L81), or do I misunderstand? (Even if the latter, perhaps clarification is still needed?)

Thank you very much for the comment that requires clarification. The main sources of water that feed Laguna del Peinado lake are the hydrothermal springs that provide the dissolved elements. As in other lakes in the Altiplano-Puna Plateau with scarce or absent carbonate outcrops in the catchment (e.g. Laguna Pastos Grandes) we interpret calcium as derived from the alteration of the volcanic bedrock by fluids at high temperatures (Muller et al., 2020). Plagioclase is dominant in the mafic rocks and ignimbrites of the El Peinado basin (Grosse et al., 2020, 2022; Kay et al., 2010). Calcium availability together with volcanic CO_2 supply and different processes trigger the precipitation of carbonates in these environments. In the hot springs, CaCO_3 precipitation is triggered by hydrothermal CO_2 degassing and microbially-driven elevation of local pH at crystallisation while in Laguna del Peinado, CaCO_3 precipitation is induced by evaporative supersaturation, CO_2 degassing and microbiological processes (Vignoni et al., 2022).

We have modified L81 “Carbonate precipitation takes place within both lakes and the hydrothermal springs environments as a result of hydrothermal CO_2 degassing, evaporation, and biological processes

with deposits comprising a wide variety of facies...". We have also added "...and extreme aridity conditions prevail" at the end of L194 and a sentence in L196 "Furthermore, calcium available for carbonate formation in this lacustrine system is interpreted to derive from the alteration of the volcanic bedrock by fluids at high temperatures as it has been observed in other systems of the Altiplano-Puna Plateau with similar characteristics (e.g. Laguna Pastos Grandes; Muller et al., 2020)".

L213 and 216: Can you clarify what you mean by the terms "old" and "ancient" groundwater? (Is it the "100-10,000 years or longer" noted below, L219?)

This may indeed lead to confusion and we replaced "ancient" by "old" in the revised text. We have added in L214 "old waters that may be 100-10,000 yr old" and "modern water (<60 yr old)" to clarify this.

L279: Is it possible to measure ^{14}C on (the DIC/dissolved gasses of) the water itself? And would/could this, in combination with other isotope measures (including d^{13}C and d^3H , mentioned earlier) help to understand the "dominant process" question?

In principle, ^{14}C on water DIC and dissolved gasses could be measured. However, it would not help much in our case because of local dilution effects from the input of ^{14}C -free carbon (e.g. volcanic CO_2) into the groundwater. Moreover, as mentioned in the previous answer, ^3H analysis would only allow us to know the proportion of modern water (<60 yr old) in the system but not the age of groundwater older than a few decades (e.g., Moran et al., preprint).

In order to attempt to resolve this issue, further multi-tracer studies would be needed to characterise the groundwater system, the processes in the recharge zones, and the volcanism of the area, which is beyond the scope of this study.

L287: I would actually say that "corrections of ^{14}C chronologies based on a single reservoir age for an entire lake..." would result in INACCURATE results, rather than just "large uncertainties" (which, as I noted earlier would be a bigger problem). You would only end up with "large uncertainties" if these uncertainties were ACTUALLY accounted for and, the point that I think you're making (which I totally agree with!) is that often these "large uncertainties" are NOT properly accounted for (...producing small uncertainties, but inaccurate chronologies).

Thank you very much for this comment that clarifies our statement. We have changed "large uncertainties" to "inaccurate chronological models".

Finally, a more general question relating to your Discussion: If the C assimilated by the species in the hydrothermal pool were solely sourced from magmatic C (rather than "old groundwater"), this would yield "infinitely old" ^{14}C ages... And so, in that scenario, even the older ^{14}C sample would

still include some proportion of "modern" C input? (Is that reasonable to assume?) Why not perform a quick endmember "mixing model" to estimate the proportion of C (for each sample) that is from a modern (2019 CE atmospheric) source and what proportion from geologically old (14C dead) C? (N.B. this is a simple "back of an envelope" calculation, rather than requiring "proper" modelling!) I suggest that this will give a "better" impression of the differing contributions (of old vs modern C), which can be skewed by the exponential nature of the 14C decay curve, which can then carry through to all of your samples through the lake. (I.e., for each sample, what proportion of C is sourced from "modern" vs geologically "dead" sources?)

Thank you for this suggestion. We have now included a simple "mixing model" (Table 1) to assess the approximate contribution of old carbon to each sample following Pasquier-Cardin et al. (1999). We introduce this in the methods section and revised the discussion accordingly. It is true that even the sample with the oldest ¹⁴C age should include a proportion of modern carbon (~ 4% according to the model). We have now added a sentence in L233 regarding this: "Moreover, the aquatic plant with the oldest ¹⁴C age has a proportion of modern carbon (~4%; Table 1, Fig. 2d) supporting that the reservoir ages result from dilution with ¹⁴C-free volcanic CO₂".

(Non-comprehensive) typo/wording suggestions:

L14: Insert comma after "This".

Thanks, we inserted the comma after "This".

L17: Change "constrain" to "constraint".

"Constraint" has been corrected.

L24: Here, do you mean the "centre of the lake" specifically?

We have clarified the text and specified the core location as 'in the northern part of the lake basin' and refer to Fig. 1 where the core location is shown.

L114: Missing word: "littoral [zone]"?

We have added the missing word "zone".

L115: Spell out "macrofossil"... Perhaps even "plant macrofossil".

We have changed "macro remain samples" to "plant macrofossil samples".

L127: “Mile” should read “mille”.

Thanks, we have corrected “mile” to “mille”.

L143: “cal CE” is a suffix, and so should come after the date (e.g., “1994-1996 cal CE”).

Thank you for your comment. Although we no longer include calibrated dates to homogenise the data, we will consider your suggestion for future work.

L246: Even though I agree that your explanation is the overwhelmingly most likely one, is “proving” still too strong a word to use?

We agree and changed wording to “revealing”.

L278: I would say that “>26,000 14C years” is more than “up to several thousand years”?!

Thanks for the comment. We have removed “up to several thousand years”.

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