

Zaragoza, 16th October 2020

Dear Dr. Farinotti,

I am submitting the revised version of our TC-2020-107 manuscript entitled "**The case of a southern European glacier that survived Roman and Medieval warm periods but is disappearing under recent warming**", co-authored by myself and colleagues, to be considered for publication in *The Cryosphere*.

In this new version we have followed closely the suggestions indicated by two previous reviewers. The main changes can be summarized as follows:

- Sampling methodology: our sampling procedure, including details about (1) the relation among the cores and the transect, (2) the translation of sample ID to thickness or (3) the order of the stratigraphical sequence (from old to young ice layers), were not clear in previous version (comments from RC1 and RC2) and are improved in this new one. In addition, new Figure 2 includes details of sampling and ice bedding.
- Chronology: we have included more clearly the criteria we followed to discard several 14C samples and more details on the methodology to select the samples for dating. How the age model was constructed is more detailed now, including the role of the dark debris-rich layers and their meaning as isochrones.
- Organization: we have followed RC1 advice about several changes in the manuscript structure such as including more information about MPG in the introduction, separating Results and Discussion and removing the supplementary material. Now all the information is in the main text, together with four tables and five figures.
- Trace elements: interpretation of Pb/Al ratio as the result of mining activities is reduced as suggested by RC2 and used the comparison to Marbore Lake record to highlight the lack of ice from the Industrial Era.

We hope this new version was suitable for *The Cryosphere*, and hope that it will fulfil your expectations. I will be happy to answer any question you might have regarding this study.

Yours sincerely,

annenero

Ana Moreno Caballud

Avda. Montañana, 1005 50.059Zaragoza (España) TEL.:976-369-393 Answers to tc-2020-107 RC1 "The case of a southern European glacier disappearing under recent warming that survived Roman and Medieval warm periods".

Note: Reviewer 1 comments start with RC1 while author responses start with AR (in blue).

RC1. General comments: The paper is interesting and reports worthwhile chronological and elemental data, interpreted in terms of recent intense ablation removing~600 years of ice from MPG (despite the glacier surviving warm times before then). Unfortunately, as presented, I am not convinced the data analysis supports the main conclusions and I cannot recommend the manuscript be published in its current form.

AR. We appreciate the interest on our manuscript and on the data presented. We provide our answers here to the three main points raised by Reviewer 1 hoping to solve his/her main concerns. Importantly, we approach the chronological issue in this new revised version following his/her advice regarding (1) the translation from lateral surface samples to depth, (2) explanations about the samples that we discarded from the chronology, (3) detailed interpretation of the "debris-rich" layers and (4) relation among the 100 studied samples and the three recovered ice cores. Ideas about the order and organization of the main text have been included in this new version of the manuscript and certainly have improved its readability.

RC1. First and most importantly, I believe the chronology needs to be addressed with greater structure and formal rigour. For example:

- Since this is so central to the paper's message, I find the translation from lateral surface samples to depth too difficult to follow in detail.

AR. We agree with this appreciation. Figure S2 showed a basic scheme of how we sampled the glacier ice and how we translate the surface samples to a depth profile. This figure was probably insufficient and not clear enough to understand our method. We provide an improved version of that figure (Figure 2 in the new manuscript). In that figure the bedding of the glacier ice is included with a downward slope of about 20 degrees. Although such a value has not been derived from local ice-thickness measurements, they are consistent with those derived from neighbouring GPR profiles further to the east (López-Moreno et al., 2019) . This figure will qualitatively help the readers to better understand the problem under study and how the sampling was done. A more complete information on this topic is included in the text of the revised version (section 3.1; lines 147-178). Please, see our responses to the following questions and the figures 1 and 2 of this letter to go further in depth into this topic.

RC1. It appears seven of 17 age samples were dismissed from the analysis; these need detailed comment on each.

AR. This information was already included in lines 309-327 of main text, but at a location within the paper that was not suitable. We greatly value the suggestions by the reviewer regarding restructuring of the manuscript contents, and have followed his/her suggestions. Of course providing the reasons to discard 7 out of 16 dates is one of the most important aspects of our discussion on chronology, so in the revised version we elaborate on the reasons to discard every sample (see text in lines 237-258). In addition, in Table 3 with all the 14C dates, we include a new column with comments regarding the quality of the dates.

Basically, we keep 8 samples from the first set of 9 bulk samples we dated. Those samples were the ones with more amount of organic material and we expected to get good 14C dates from them. The only one from that set we had to discard was MP46 that was out of order (younger than expected) and attributed to the presence of small pieces of plastic (too small to be removed) contaminating the sample. After obtaining the first 9 dates, we selected some other intervals where the dating information was insufficient but, unfortunately, the samples

were not so good in terms of quantity and quality of the organic material. Then, two samples dated by WIOC technique provided too large errors due to the low amount of carbon (still, we included one of them in the age model); three samples from pollen concentrates were too old (several millennia older than the others) likely due to associated problems to concentrate pollen (Kilian et al., 2002) and, finally, two samples from material contained in filters where the mixing among carbonate debris, dust and variable organic matter provided incongruent results. In summary, we constructed the age model from 8 samples from the first set of 9 bulk samples and 1 from WIOC. The other ones were not good enough to be considered in the chronology following the explained issues.

RC1. The interpretation of debris-rich englacial layers as periods of ablation (concentrating the debris) needs a far more rigorous argument based on physical analysis and exclusion of alternative possibilities. At present, the reader does not know whether these are isochronous, or whether they deform passively or cut-across primary layering/stratification. Could they be basally-derived? How are supply-rate variations excluded?

AR. Although alternative explanations cannot be completely excluded, we have firm reasons to believe that the sequence of debris-rich layers observed along the sampled profile correspond to the primary stratification of debris deposited at the surface of the glacier and are therefore isochronous layers (except for the cases in which the primary layers became merged due e.g. to intense melting episodes and/or low surface accumulation periods).

Note, first, that the distribution of layers is rather regular and extends laterally as shown in new Figure 2 in the manuscript, as would be expected for a stratification stemming from the original deposition at surface of snow and debris. Also note that the isochronal layers in a glacier emerge in the ablation area, but this is consistent with our case study, as our sampled profile corresponds entirely to the ablation zone. The reality is more complex, as our glacier has been shrinking and retreating since the end of the LIA, but the situation would be approximately as depicted in the attached figure (Figure 1).



[Figure 1 caption: In (1) we see the particle trajectories (blue) and the associated isochrones (red), emerging below the ELA; in (2) the trajectories have been removed to show only the

isochrones; (3) shows subsequent stages t1, t2, t3 of glacier shrinkage and retreat; (4) shows the current situation, similar to that illustrated in Figure 2 in the manuscript].

Additionally, we have prepared and run a dynamic flow model for a flowline as close as possible to our sampling profile using the available ground-penetrating radar data. Results are represented in Figure 2 where a collection of isochrones is shown in a similar way as they were represented schematically in Figure 2 of the manuscript. The limitation of this model is that it uses the current glacier geometry as if it was stationary during the whole modelled period. Still, it is interesting to see the approximate tilt of the ice bedding and the way in which the surface slope cuts the isochrone layers. If we carry out our sampling procedure along the slope represented here, we would sample the oldest material in the bottom part and the newest ice towards the top, as indicated by the area inside the black square. This illustrates perfectly the rationale of our sampling strategy.



[Figure 2 caption: Output of a dynamic flow model run in a closer area to the sampling transect where few georradar data were available. Colour lines are isochrones. The black square indicates a potential sampling transect along the slope cutting first the oldest ice beds and later the newest ones].

The reviewer questions whether the observed debris layers could be basally-derived. We believe that they are not. The main reason is that, in general, debris layers transverse to the glacier flow direction correspond to thrust faults developed near the glacier margin due to the compressional stress regime, most often associated to the transition, when we approach the glacier terminus, from warm-based to cold-based ice near the terminus. The warm-based ice slides over its bed, while the cold-based one does not, so strong compressional stresses develop, which cannot be accommodated by creep and thrusts develop. These thrust faults may reach the surface or terminate englacially (blind thrusts; see figure 3a below). Basal debris is incorporated into these thrusts, sometimes reaching the surface. When they do so, due to surface melting, they often produce large accumulations of debris (often in the form of pinacles or pinnacle ridges along the debris layer; see figs. 3a and 4 below); intense melting episodes can spread this debris over the glacier surface.



[Figure 3 caption: Fig. 7 of Graham and Midgley (2000).]



[Figure 4 caption: Fig 9.6 of Bennet and Glasser (1996) – modified from Fig. 2.36 of Hambrey (1994).]

We believe that the debris layers observed at the surface of MPG are not subglacially-derived, because the hypothetical thrust faults supplying subglacial till to the glacier surface would be limited to the terminal zone, while in MPG the debris layers are observed all-along the sampled profile covering the entire lower glacier. Neither the mentioned large accumulations of debris, nor pinacles, are observed in MPG. Furthermore, if such thrust faults close to the ice margin would form in an advancing glacier (such as MPG during the LIA), they would form progressively in front of each other as the ice margin advances. Upon retreat, they would appear as a moraine-mound complex as shown in figures 3b and 4. However, in the proglacial zone of MPG, the only hummocky moraines have been identified as push moraines created by glacier advance before 1850 CE (Serrano and Martín-Moreno, 2018).

Finally, we note that, as indicated in lines 283-287 of the original manuscript, "The debris layers were composed of detrital, silty-sandy size deposits, likely coming from wind-blown particles (e.g. black carbon-rich particles, dust) and from erosive processes of the limestone catchment, including the fall of gravel-sized particles from the surrounding cliffs" and they show no evidences of subglacially-derived glacier till.

Regarding the last concern of the reviewer, on how are supply-rate variations excluded, we note that our hypothesis does not necessarily exclude variations of debris supply-rate. In fact, higher supply rates are expected during warmer periods, in which more exposed rock surface should be available to supply falling debris from adjacent slopes and a larger extent of

ice/snow-free terrain would supply a higher amount of wind-blown dust. This is not inconsistent at all with our comment in lines 288-291 of the original manuscript that "the frequency of debris layers increases towards the top of the glacier, where these layers are most abundant. We consider the accumulation of debris layers to be indicative of reduced ice accumulation and dominance of ablation periods."

The text regarding debris-rich layers is now in lines 316-330 in the new version of the manuscript.

RC1. How were the three core samples (and two deep samples) combined with the 100 surface samples?

AR. The cores and the two samples from the front belong to a different area of the glacier, more dynamic, and for this reason they have not been combined with the 100 surface samples analysed in the present study. We recognise that, in the first submitted version of the manuscript, our writing could suggest that there was a relation among the cores and the 100 samples. Thus, in the new version we present here, we focus on explaining the sampling on the slope as the method selected to sample the glacier ice, and justify the lack of coring by noting that glacier conditions did not allow obtaining a complete ice sequence by coring (lines 149-154).

RC1. Since the annual 0 deg. C contour is at~3,000 m why wasn't snow/firn/ice sampled from the upper glacier. This glacier seems all to lie above this elevation and may therefore be accumulating, providing an undisturbed record of accumulation change?

AR. We could not reach the upper glacier in a safe way for sampling. Thus, up to now, there are no available samples, neither any age information from the upper glacier.

RC1. For me, too much key material seems to be given in the supplementary information rather than forming a central part of the argument of the main paper.

AR. We agree with this appreciation and have included all the supplementary information in the main paper.

RC1. For comparison, what elemental values have been measured in recent ice (not snow/firn)?

AR. Unfortunately, we cannot compare elemental values from current ice in Monte Perdido glacier since ice is not being formed at present as the glacier has virtually no accumulation zone (the accumulation-area ratio tends to zero). We obtained the same information derived from the lack of 210Pb on the surface ice samples. Neither we have analyses of MPG snow. However, we have several measurements of snow from other zones in the Pyrenees at similar altitude, and found that the variability in elementary values from one site to another, or even from a sampling campaign to another, is enormous (see recently published paper Pey et al. 2020). It would be incorrect to use such values to compare with fossil ice in MPG. On the contrary, sampling atmospheric aerosols in Ordesa National Park station appears better suited to compare with MPG, since we can average over two years to get a more comparable value. Doing this, several elements appear clearly enriched in present-day atmosphere compared with MPG samples.

RC1. Second, substantial relevant material relating to the chronology of MPG appears later in the manuscript when I believe it should be summarised in full in the Introduction, directing the specific aim and objectives of this study. In my view, it's fine to introduce related information in the Discussion (such as the chronology of lakes in the area or of broader Alpine glaciers), but material directly relating to MPG - and particularly the focus of this submission (i.e., its chronology) - should form relevant background material in the Introduction.

AR. The only materials related to the chronology of MPG are the few dates corresponding to the moraines. We include them now in the Introduction as suggested by Rev. 1 and use them to state more clearly our aims (lines 95-109).

RC1. Third, I found several of the sections and their contents to be confusing. For example, what I consider to be results are presented in the Field Site and Methods section, and I would separate Results from Discussion.

AR. Following this suggestion, we have separated Results and Discussion and included some dating information that was previously in Methods as Results. We hope that this new organization of the contents, together with the inclusion of all of the material from the Suppl. Materials in the main text, makes this paper more clear and readable.

RC1. Specific comments

Note, the manuscript includes many slight grammatical and typographical errors, as a few stylistic imperfections, which I have mostly not corrected. For me, the meaning was almost always clear, if not grammatically perfect.

AR. We have carefully reviewed the text looking for grammatical and typographical errors and corrected them.

RC1. Line/Location Comment/Suggestion

1 Title is awkward because 'that' is unspecified.

AR. We have changed the title to "The case of a southern European glacier that survived Roman and Medieval warm periods but is disappearing under recent warming". Thus, we better specify that is the glacier the one disappearing today but surviving during other warm periods.

RC1. 47 I'd avoid 'proves' unless the sentence states 'if we assume the chronological model is correct...'.

AR. We do not think that we need to assume that the chronological model is correct... it is based on 14C dates and the uncertainty is also considered. Yet, we can change the word "proves", which is probably too strong, to "evidences".

RC1. 54-55 This claim needs to be supported by a rigorous analysis.

AR. We claim that the current warming is unprecedented in the context of last 2 kyr because the loss of ice from MPG in the last decades has been the greatest since we have records. The last sentence was probably not properly placed in the abstract, as it is based on conclusions from previous studies ("We demonstrate that we are facing an unprecedented retreat of the Pyrenean glaciers whose survival is compromised beyond a few decades") and thus we have removed it.

RC1. 94-105 I'd invert this: state the aim of the paper and then state how it was achieved.

AR. We think the reviewer was confused by the wrong use of tense of verbs in this paragraph. Now, those explaining previous studies have been changed to past tense, and we state the aim of this paper, and how it was achieved, as suggested by Rev. 1 (lines 90-95).

RC1. 141 Data need to be presented and analysed to substantiate the claim that '(GPR and modelling)...suggested that the oldest ice could be located in these areas.' This claim is central to the chronology presented in the manuscript.

AR. That section has been removed, since it referred to the three cores which did not cover the whole sequence and thus were not studied.

RC1. 161 1 m of what? A Jacob's staff should be described, or just use 'staff'.

AR. We prefer to keep Jacob's staff since it is a common tool for geologists when sampling an outcrop and helps to understand the sampling here. This is the definition: "In geology, the Jacob's staff is mainly used to measure stratigraphic thicknesses in the field, especially when bedding is not visible or unclear (e.g., covered outcrop) and when due to the configuration of an outcrop, the apparent and real thicknesses of beds diverge therefore making the use of a tape measure difficult". Source: <u>https://en.wikipedia.org/wiki/Jacob%27s_staff</u>

RC1. 175 Which 'uppermost five samples'?

AR. We selected 5 samples towards the top of the sequence to have the most recent ones. In the text we now indicate which are those samples (line 183).

RC1.175-6 These are Results

AR. Ok, moved to results

RC1.176-8 This is Interpretation

AR. Ok, moved to discussion

RC1. 186-96 These are a mixture of Results and Interpretation. What values would be expected or have been measured on accumulating glaciers in similar settings?

AR. We moved some sentences to Results and some to Discussion.

RC1. 209 How and where did these samples come from? How were they treated?

AR. They are just two samples in the sequence of 100 samples. They correspond to samples 67 and 81 and were selected because in that portion of the record the dating obtained by the first 9 samples of bulk material was insufficient. We thought those samples may have more organic material and were easy to date.... The pre-treatment is already indicated in the text and the treatment in the 14C lab was similar to any other sample just removing the filter at the first stage.

RC1. 231-2 Why a second-order polynomial/quadratic? If there is a theoretical basis for such a relationship, then that should be presented. If there is not, then what justification is there for this form?

AR. Before explaining the reasoning behind this approach, we note that the model was not built using a second-degree polynomial, and thanks to the referee we have spotted this error. We initially took this model as a quality control for the 7 dates amongst the 16 from which we presumed low quality due to various reasons (discussed in main text –lines 237-258- and along this letter). Using a second-degree polynomial approximation, instead of spline or other interpolations, higher degree polynomials, or a Bayesian approach, has been evidenced to be the best approach when there is a low proportion of dates in comparison with the potential changes in sedimentation rate (Telford et al., 2004). In such a way we still account for potential non-linear accumulation, though it rarely happens in nature, while we reduce the number of assumptions when increasing the regression into higher orders. We insist that this approach was used just to double test the quality of the samples that we were discarding.

Our final model was then made with the 9 remaining dates, where we set a hiatus at sample D-AMS 025298 (uncalibrated 14C 1011± 25, 2700 cm, equivalent to 73 m depth following a bottom-up sampling strategy, as explained in Figure 2 in the manuscript). We then run a linear regression that, given our scarce prior knowledge on the record sedimentation and according to the particular nature of our archive, seemed the most reasonable one, reducing the overfitting to noise of splines or higher-order regressions, still not forcing the model though all dates as a piecewise linear interpolation would do.

RC1. 234-8 This argument relating to debris concentration by ablation/low accumulation needs substantial background and argument, including arguments for this interpretation and against alternative interpretations of englacial debris bands. For example, how are supply-rate variations or a source at the glacier bed excluded?

AR. We are referring to the primary ice stratigraphy, which is evidenced by the alternance of layers with more debris (darker layers) and debris-poor cleaner ice (lighter in colour). This alternance occurs at a metric scale and appears all along the ice sequence (Figure 2 in the manuscript). We interpret that these layers result from periods (summer?) with less ice formation and more "debris" supply. Interestingly, we observe this alternance more clearly between 67 and 72 "meters", where dark layers are thicker and are more closely spaced. From that interval we dated several samples (MP-67, MP-68, MP-69, MP-70, MP-73), obtaining dissimilar results, not in order, and covering a time interval from 600 to 1200 CE. Our hypothesis is that ice was formed at a very low rate during that period (600-1200 CE). Or, even if it was formed at a similar rate as in other periods, at some point it melted. Once most of the ice is melted, the accumulation of the debris particles becomes more evident. Here, the "debris" does not seem to correspond to material eroded at the glacier bed and entrained in the basal ice or transported to the glacier surface through thrust faults near the terminus, but just to material mostly transported by winds and deposited on the ice surface. Further comments on the debris layers have been included in the answer to the general comments.

RC1. 288-91 These arguments need formalising, expanding and presenting as a logical progression of argument; currently, it is difficult to evaluate the accuracy of the chronology because this logical progression in argument (supported by illustrated data) is missing or split up through the paper and supplementary information.

AR. We agree with this comment about the lack of a logical progression in our argumentation, since the discussion on chronology was indeed split up in various sections of the manuscript. This is now corrected and, after an explanation of the methods employed and the criteria to discard several dates, all the discussion concerning the age model is included as Results in the revised version. We have substantially changed the structure and organization of the manuscript, and are confident in that the revised version has improved its readability.

RC1. 281- I find this section difficult to follow since in some places Results have already been presented and they are only referred to here (e.g., 306-8) or Results are mixed with Interpretation, and in some case Methods are included here (318-27). In relating to the last point, I'd discuss sample removal from analysis in Methods and not Results.

AR. Yes, we agree and have worked in that direction in the new version (lines 237-258).

RC1. 333 I'd bullet or number these three main periods and interpret consistent/repeated data across all three.

AR. Ok, we have indicated the three periods by roman numbers.

RC1. 361- I'd move much of this into a dedicated Discussion section

AR. We have moved part of this into the Results section (explanation of trace elements values in present-day aerosols and in the glacier ice), and partly into a new section in the Discussion (comparison with another paleoclimate record nearby, the Marboré lake).

RC1. 412-26, 434-7 & 467-70 I'd move this published material relating specifically to the chronology of MPG to the Introduction. That way it would contribute to, and form the framework/rationale for, the aims and objectives of the present study.

AR. Done. That information in the introduction helps to state the objectives of the present study (lines 90-109).

RC1. Fig 1 Needs panel letters and I would find it easier to interpret if both had a similar orientation. Precise sample locations are needed. Are the locations of the three cores and the two deep samples noted here?

AR. Panel letters are included and map changed to have the same orientation as the picture. The three cores are not indicated, since we have not studied them, so just the transect with the 100 samples is shown.

RC1. Fig. 2 Y axis states 'h' but caption states 'depth'. 'h' is undefined, but appears to be height above bed. I know this depth scale is determined by translating the surface transect but it needs formal presentation and geometrical-dynamic argument and an error analysis. What flow model was used? If a flow model was not used, then at the very least the 3D surface geometry of the sample profile needs to be presented and the geometrical translation illustrated – in the main text. Is the glacier 100 m deep at present? Where in the glacier does this model relate to?

AR. All these questions posed by Rev1 indicate that the way we translated sample number to depth scale was not clear at all. As indicated in the main point of this letter, more text is added to explain this issue and Figure 2 is now included in the main text and improved with more information about glacier ice bedding (See Figure 2 in the manuscript).

RC1. Fig. 3 Show uncertainly in elemental ratios. Panels need labelling.

AR. Panels are labelled. Uncertainty is indicated in methods, we do not think that it is necessary to include it in the figures for every sample.

RC1. Recommendations

I would combine all that is currently published relating to the chronology of MPG into the Introduction and then recast the aims to address a clear knowledge gap. For example, it is already known that the glacier has lost~40 m of ice since 1980. If so, roughly how many years of accumulation does this cover and, if we are not sure, then can that –along with the existing chronology - form the basis of rationale for a chronological study based on flow-line surface sampling. Why here and not in the upper glacier? An age-depth model derived on the basis of the analysis of samples from the ablation area of an ablating glacier is not a trivial glaciological advance. I think this should form the main aim of the paper and be presented and argued in a logical and formal way, with relevant data presented in the main text and not supplementary information. Having done this, I would like to see a rigorous assessment and inclusion of all uncertainties involved in the age and depth scales, included in Figures such as current Fig. 2. I realise this cannot be achieved with great confidence, but I imagine it can be approximated.(i) Methods, (ii) Results, and (iii) Interpretation/Discussion/Conclusions need to be separated clearly. As a minimum, Results need to be separated from Interpretation and Discussion.

AR. We really appreciate this final summary from Rev1 and have followed his/her advice in this new revised version of the manuscript. The most problematic point regarding age-depth relationships is improved by including previous Fig S2 in the main text (in fact, all information in the Supp. Materials is now in the main text) and by more detailed explanations. However, we cannot present a rigorous assessment of uncertainties in depth scale since we do not know the inclination angle of the glacier ice layers to translate our sample numbers to real depth. We can approximately calculate the bedding tilt to finally have 30 m of ice sequence as happens in the easternmost section of the glacier. But still it would be unprecise and speculative. Therefore, we do not use the term "depth" anymore in the age model construction but "sample number" or "sample ID", which is more accurate. Regarding age uncertainties, they are included in the age-depth model. The organization separating methods / results / discussion really helps to understand the ideas and outcomes of this study. Similarly,

including in the introduction more information about what we know about this glacier helps to better state our aims.

AR. References cited:

Bennet, M.R., Glasser, N.F., 1996. Glacial Geology. Ice Seets and Landforms. John Wiley and Sons, Chichester.

Hambrey, M., 1994. Glacial Environments. UCL Press, London.

Graham, D.J., Midgley, N.G., 2000. Morain-formation by englacial thrusting: the Younger Dryas moraines of Cwm Idwal, Noth Wales. In: Maltman, A.J., Hubbard, B., Hambrey, M.J. (Eds.). Deformation of Glacial Materials. Geological Society Seccial Publication No. 176, p. 321-336. Geological Sciety, London.

Kilian, M.R., van der Plicht, J., van Geel, B., Goslar, T., 2002. Problematic 14C-AMS dates of pollen concentrates from Lake Gosciaz (Poland). Quaternary International 88, 21–26. https://doi.org/10.1016/S1040-6182(01)00070-2

López-Moreno, J.I., Alonso-González, E., Monserrat, O., Del Río, L.M., Otero, J., Lapazaran, J., Luzi, G., Dematteis, N., Serreta, A., Rico, I., Serrano-Cañadas, E., Bartolomé, M., Moreno, A., Buisan, S., Revuelto, J., 2019. Ground-based remote-sensing techniques for diagnosis of the current state and recent evolution of the Monte Perdido Glacier, Spanish Pyrenees. J. Glaciol. 65, 85–100. https://doi.org/10.1017/jog.2018.96

Pey, J., Revuelto, J., Moreno, N., Alonso-González, E., Bartolomé, M., Reyes, J., Gascoin, S., López-Moreno, J.I., 2020. Snow Impurities in the Central Pyrenees: From Their Geochemical and Mineralogical Composition towards Their Impacts on Snow Albedo. Atmosphere 11, 937. https://doi.org/10.3390/atmos11090937

Telford, R.J., Heegaard, E., Birks, H.J.B., 2004. All age-depth models are wrong: but how badly? Quaternary Science Reviews 23, 1–5. https://doi.org/DOI: 10.1016/j.quascirev.2003.11.003

Answers to tc-2020-107 RC2 "The case of a southern European glacier disappearing under recent warming that survived Roman and Medieval warm periods"

Note: Reviewer 2 comments start with RC2 while author responses start with AR (in blue).

RC2. General. The authors provide results from a focused local study on remains of a glacier at Monte Perdido (MPG) in the Pyrenees. Their comprehensive analyses concern a question of quite fundamental relevance: are glaciers and, hence, the climate system now changing beyond natural, pre-industrial variability ranges? The main results of the analyses are that the maximum age of MPG can be constrained to the Roman period, and that no ice dating to the Little Ice Age remains present today. The results are interesting and certainly merit publication. They especially have the potential to encourage similar studies in other regions of the world. Some parts need clarification and more precise presentation as explained below.

AR. We acknowledge the positive view of Drs. Haeberli and Bohleber regarding the importance of this study and the interest to publish it in the TC journal. We provide answers below to their main concerns about sampling and age structure and about radiometric and glacio-chemical analyses.

RC2. Sampling and age structure

RC2. Since the inferred age structure is central to the manuscript's main conclusions, it deserves a more clear and detailed presentation. The description of the ice sampling (e.g. on lines 151-163) is difficult to follow and should be clarified. The samples are obviously taken perpendicular to the stratigraphy along a profile at the surface of the stagnant, regularly layered ice patch. The assumption that this ice is cold and frozen to its bed may be reasonable, because this ice cannot warm up above OC in summertime but cool down far below OC in winter. This effect can explain the low flow velocities but not the ice stratigraphy, which must have been influenced by the active flow of the much larger glacier during the past millennia in question. This leads us to the following concrete questions that should be addressed in more detail:

(1) What exactly is the reasoning behind the inferred age structure of the remaining ice patch? Is it purely empirical from the dating or is it based on considerations of ice flow? The 14C dates are clustered in three different age groups, but the use of a linear interpolation needs better justification. In particular, why can the existence of further (presumably shorter) periods of hiatus or ice loss really be excluded from the presented evidence? Relatedly, if the only support for the hypothesis of a hiatus at 73 m is coming from a distinct dark layer (lines 233 ff., 302-303) – how does this interpretation of concentrated, impurity-rich dark layers fit with what is observed at the glacier surface today?

AR. We agree about the problems posed by the unknown ice stratigraphy, which certainly was the result of the glacier evolution during the last millennia. This problem is quite common to many high-mountain glaciers, even when coring is possible, since their detailed inner structure by physical analyses such as GPR is rarely available. When we applied ice flow models to MPG (using Elmer-ICE, in particular) the results indicated that the ice in MPG was at most 200 years old (the longest possible travel time of an ice particle deposited at the upper part of the current lower glacier), which was in contradiction with the obtained ages (210Pb, 137Cs, 14C). However, these models were just applied -given the lack of input data- assuming a steady-state surface (that of the current glacier), which is clearly incorrect. One explanation contributing to explain the old ages found is that the ice has been for long periods frozen to bedrock, and hence nearly stagnant. Moreover, we can just speculate about the inclination of the glacier bed necessary to account for the 30 m of maximum ice thickness previously measured by GPR in other sector of the glacier (López-Moreno et al., 2019). Our hypothesis that the oldest ice is found towards the base of the sequence and the newest towards the top

is based on general arguments on ice flow of mountain glaciers. 14C dates confirmed this hypothesis, but we agree with Reviewers in that we cannot totally exclude the presence of other shorter hiatus besides the one at 67-73 m, which was the most evident. We set the hiatus at 73 m to be able to construct an age-depth model and use different interpolations below and above (before and after) it, depending on the growth rate indicated by the dating results.

RC2. (2) How are distances along the surface profile transformed into values of (ice?) depths? Does "depth" relate to a former, thicker and less inclined ice body and, if yes, to which geometry/time exactly?

AR. The reviewer is right about the "depth" concept here. It is related to our consideration of horizontal ice layers, since we obtained one sample every meter, measuring these meters with the Jacob's staff without taking any inclination into consideration. Therefore, the 100 samples would represent 100 m of thickness in the ice sequence if the ice bedding was horizontal. The exact thickness is unknown, but in the order of 30 m in the easternmost sector of the glacier. So, the internal layers of the MPG must be very inclined. An improved version of Figure S2 is now included in the main text as Figure 2 and certainly helps to understand this problem and how we sampled the glacier ice.

RC2. (3) What are "stratigraphic thicknesses" and how are they determined?

AR. We are not using stratigraphic thickness anymore since we cannot measure it, as indicated in our response just above. We have now included "Sample ID" instead of "Depth" in the age-model figure (Figure 3 in the manuscript).

RC2. (4) If the ice is frozen to bedrock and stagnant, why did the authors find no evidence of neoglacial ice at the base and which process would have led to its removal?

AR. We have constructed the figures about the evolution of the glacier (Figure 5) based on what we have found sampling and dating the ice. Then, since we have not found the Neoglacial ice it likely was melted away at some point between 5000 years BP and the Roman Period. It is also possible that some ice from the Neoglacial periods remains in the base of the glacier but it was not cut by the vertical section of our surface sampling profile, so we did not sample it. We have included this possibility in the new version of Figure 5 and associated text (see lines 464-467).

RC2. (5) It also needs to be made more clear which part of the glacier was sampled (the lower portion?) and why the other (the upper portion?) was disregarded. Figure S2 should be included in the main text and supplemented with a zoom-in to the visual stratigraphy around the sampling sites for better visibility of the layering. Figure 4 suggests that neoglacial ice in the upper portion did not survive the Roman period, which is not supported by evidence in the manuscript. Are the authors assuming that this ice was removed by basal melting when the larger glacier was still warm-based, by thinning or ice flow? How does this align with the evidence for ice being frozen to bedrock now?

AR. The upper portion of the glacier was disregarded because it is really small today, with a slope very steep and the access for sampling was dangerous. Unfortunately, we do not have any date from that sector. Fig. S2 is now improved and included in the revised version of the manuscript (Fig. 2) with more details about layering and a closer picture of the glacier.

Regarding the Neoglacial ice survival, we can just hypothesize that it melted away at some point before or during the Roman period, since we don't find it in our dated samples. But, of course, it can remain in the upper glacier. It is also true that it may be found below the Roman ice that we sampled and is not exposed at the glacier surface today. We have considered all of these possibilities in the new revised version of the manuscript and accordingly updated Figure 5. We do not know when the glacier was frozen to bedrock. That situation might have happened once the glacier became sufficiently thin (after the Roman period? After the MCA?) and probably did not become warm-based anymore.

RC2. Radiometric and glacio-chemical analyses

RC2. The allocation of the samples to a position needs to be revised, at present much is left unclear to the reader. There seem to be two coordinates to consider: First, the position of the sampling site along the transect (MP1-100). Second, the depth below the surface / distance from bedrock. This information should be included in Table 1 to replace "sample depth (m from base)" – which is presumably referring to the distance from the glacier terminus? Again, a clear hypothesis should be stated why a systematic gradient in age of the samples in relation to their position on the glacier is expected? If the ice is stagnant, why is older ice expected closer to the terminus? The depth information should also be provided for the glacio-chemical datasets (especially Pb/Al and Hg of Figure 3).

AR. We totally agree with this comment about the difference among "position in the transect", "depth from the base" and "sample ID". The reviewer is right and we have replaced any reference to ice thickness or ice depth to sample position or sample ID. We expected the older ice closer to the terminus as a consequence of the bedding and due to the steep slope present today. Glacier ice layers are cut by the present-day surface and older layers should appear closer to the terminus if they are tilted (see Figure 2 in the manuscript). Since we don't know the tilt we can not calculate the thickness and just have information of the sample position in the transect. It is evident that more information on this was needed in the manuscript and has been included in the revised version (lines 147-178). We do not have the depth information for previous Figure 3 (now figure 4) and including sample ID (from 0 to 100) appears now unnecessary.

RC2. The selection of 14C data for dating needs clarification, especially because a substantial number of samples is disregarded. The WIOC technique is state-of-the-art but only one WIOC sample is used to construct the chronology. Known difficulties with the interpretation of dating derived from macroscopic 14C, such as reservoir effects need to be addressed in more detail. Dark and dust-rich layers can be biased either through incorporation of already "old" carbon (e.g. Saharan dust) or accumulate at the surface over a longer time period without ice formation. Regarding the pollen dating, which are presumably too old, the authors hypothesize that they originate from older ice which had melted and percolated through the ice. If this is true, how can such a process be excluded for the other radiocarbon dates?

AR. More detail on the criteria to discard 7 14C samples is included in this new version (lines 237-258). Our first option for dating would have been the WIOC technique, but we had not enough material in most cases. We did not preserve all the ice samples frozen, just a few of them for studying bacteria and virus. Thus, we were able to attempt WIOC dating in just two samples that were frozen and were of larger size. Unfortunately, they had still very low amount of carbon for dating and the errors were too large. One had to be discarded because of that reason, and the other is included in the age model. More and better organized information is now included about the reasons to reject some of the samples (lines 237-258 and new column in Table 3). We agree about the possible reservoir effect when dating dark and dust-rich layers where organic and inorganic material is mixed but this unfortunately is still difficult to avoid. For the future, Dissolved Organic Carbon (DOC) technique for dating may replace WIOC and provide more accurate results with less amount of sample (Fang et al., 2020).

We are not too sure about the reasons to obtain so old dates with pollen samples. In addition, the three pollen samples had very large errors likely related to the low amount of datable material. Dating with pollen concentrates can be an accurate tool for chronological

reconstruction, employed in many studies (González-Sampériz et al., 2006). However, obtaining old dates from pollen is a quite common problem not yet solved in the literature (Kilian et al., 2002). Another reason to exclude pollen samples for 14C consideration in MPG age model -not discussed in the manuscript- is that the obtained palynological spectra from the same samples that were dated is not coherent with well-known palynological records from the region. In the MPG area we have a detailed palinological study in Marboré lacustrine sequence (Leunda et al., 2017) which is totally different in taxa and abundance of that obtained from coetaneous MPG samples. Therefore, we suspect the pollen samples were contaminated somehow and we can not use them. Additionally, the information of pollen studies in active glaciers (specially related to the mechanisms of deposition and preservation) is scarce and thus not solves this problem. In any case, the three dated samples in MPG coming from pollen concentration are not consistent with the other ones and should be excluded.

RC2. Dark and dust-rich layers

RC2. Percolation of meltwater can also lead to redistribution of chemical impurities – would this be relevant at MPG and if not, why not? Along the same lines, it is important to give more attention to the glaciological settings of the site when interpreting the glacio-chemical records. Based on the presented hypothesis (Fig. 4), the MPG would have undergone substantial changes regarding its ice formation, possibly from a typical firnication process during cold periods to hiatus and melting during warm periods. An exposed glacier surface can lead to concentrated values of impurities, which would be more frequently the case in warm periods such as the roman or medieval period. In this sense, it is not clear that the heavy metals and their ratios should directly reflect any regional mining or smelting activities – this should either be removed or supplemented significantly by further discussion and justification. Notably, the connection between mining activities and heavy metal ice core records in the Alps was made at very high elevation locations (>4000 m asl) with a quasi-continuous snow sampling behavior.

AR. We appreciate these comments and partially agree about the problems of percolation and redistribution of chemical impurities, which are relevant for many mountain glaciers in the current climate context. Still, we think that we can assume that most of the material is in place since it correlates well with the Marboré geochemical record, now published (Corella et al., 2021), and supports the chronology indicating the absence of ice from the industrial period. We agree that an exposed glacier surface can lead to concentrate impurity values, but these impurities would still have the same origin if they come from atmospheric aerosols, and can still be interpreted as a result from mining activities. Nevertheless, taking into account the problems of redistribution of chemical impurities due to percolation, we have to be more moderate with our interpretation of Pb/Al peak in the Roman times as Roman mining only as a possibility, and including the issue of percolation (lines 399-405). We also reflect in this new version that the ice cores in the Alps where Pb/Al was considered as resulting from Romantime mining activities were more continuous and located at higher altitudes, thus not strictly comparable to our site.

RC2. Considering these points, the respective part of the manuscript dealing with the interpretation of the glacio-chemical analyses needs to be substantially revised and shortened.

AR. Yes, we agree, as indicated above and modified the text accordingly (see section 5.1).

RC2. The main support for the conclusions of the manuscript provided by the impurity analysis is the absence of ice dating to the industrial period. This point has value for the manuscript. The relation to mining activities and chronological support through the comparison with the Marboré Lake record seems, at present, speculative.

AR. The comparison with Marboré Lake was carried out using an age scale obtained independently (age model from MPG presented in this study and age model from Marboré

lake presented in Corella et al., 2021). Thus, the similarity of the Pb/Al records in both archives (lake and glacier) is at least interesting to show. We have given less weight to the interpretation of Pb/Al as mining in this new version, since we agree in that it can come from other sources (lines 390-405). But we would like to keep the graph showing Marboré and MPG records together. From that graph, we will highlight the absence of ice dating to the industrial period, as suggested by the Reviewers (lines 406-410).

RC2. Some minor technical comments can be found in the annotated file.

Wilfried Haeberli and Pascal Bohleber, 3 July 2020

AR. Many thanks for all these comments and suggestions to improve our manuscript.

AR. References cited

- Corella, J.P., Sierra, M.J., Garralón, A., Millán, R., Rodríguez-Alonso, J., Mata, M.P., de Vera, A.V., Moreno, A., González-Sampériz, P., Duval, B., Amouroux, D., Vivez, P., Cuevas, C.A., Adame, J.A., Wilhelm, B., Saiz-Lopez, A., Valero-Garcés, B.L., 2021. Recent and historical pollution legacy in high altitude Lake Marboré (Central Pyrenees): A record of mining and smelting since pre-Roman times in the Iberian Peninsula. Science of The Total Environment 751, 141557. https://doi.org/10.1016/j.scitotenv.2020.141557
- Fang, L., Jenk, T., Singer, T., Hou, S., Schwikowski, M., 2020. Radiocarbon dating of alpine ice cores with the dissolved organic carbon (DOC) fraction. The Cryosphere Discussions 1– 26. https://doi.org/10.5194/tc-2020-234
- González-Sampériz, P., Valero-Garcés, B.L., Moreno, A., Jalut, G., García-Ruiz, J.M., Martí-Bono, C., Delgado-Huertas, A., Navas, A., Otto, T., Dedoubat, J.J., 2006. Climate variability in the Spanish Pyrenees during the last 30,000 yr revealed by the El Portalet sequence. Quaternary Research 66, 38–52. https://doi.org/10.1016/j.yqres.2006.02.004
- Kilian, M.R., van der Plicht, J., van Geel, B., Goslar, T., 2002. Problematic 14C-AMS dates of pollen concentrates from Lake Gosciaz (Poland). Quaternary International 88, 21–26. https://doi.org/10.1016/S1040-6182(01)00070-2
- Leunda, M., González-Sampériz, P., Gil-Romera, G., Aranbarri, J., Moreno, A., Oliva-Urcia, B., Sevilla-Callejo, M., Valero-Garcés, B., 2017. The Late-Glacial and Holocene Marboré Lake sequence (2612 m a.s.l., Central Pyrenees, Spain): Testing high altitude sites sensitivity to millennial scale vegetation and climate variability. Global and Planetary Change 157, 214–231. https://doi.org/10.1016/j.gloplacha.2017.08.008
- López-Moreno, J.I., Alonso-González, E., Monserrat, O., Del Río, L.M., Otero, J., Lapazaran, J., Luzi, G., Dematteis, N., Serreta, A., Rico, I., Serrano-Cañadas, E., Bartolomé, M., Moreno, A., Buisan, S., Revuelto, J., 2019. Ground-based remote-sensing techniques for diagnosis of the current state and recent evolution of the Monte Perdido Glacier, Spanish Pyrenees. J. Glaciol. 65, 85–100. https://doi.org/10.1017/jog.2018.96

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40	Keywords	
41	Pyrenees, mountain glacier, current global warming, Medieval Climate Anomaly,	
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		pto, Interlineado: 1,5 líneas

44 Abstract

Mountain glaciers have generally experienced an accelerated retreat over the last 45 46 three decades as a rapid response to current global warming. However, the response to previous warm periods in the Holocene is not well-described for glaciers of the of 47 southern Europe mountain ranges, such as the Pyrenees. The situation during the 48 Medieval Climate Anomaly (900-1300 CE) is particularly relevant since it is not certain 49 whether the southern European glaciers just experienced significant ice loss or 50 whether they actually disappeared. We present here the first chronological study of a 51 glacier located in the Central Pyrenees (NEA Spain), the Monte Perdido Glacier (MPG), 52 carried out by different radiochronological techniques and atheir comparison with 53 geochemical proxies fromwith neighboring paleoclimate records. The result of the 54 55 chronological model evidencesproves that the glacier endured during the Roman Period and the Medieval Climate Anomaly. The lack of ice record dated from the last 56 600 years suggestsindicates that the ice formed during the Little Ice Age has melted 57 away. The analyses of the content of several metals <u>with</u>of anthropogenic <u>source that</u> 58 59 characterize the Industrial Periodorigin, such as Zn, Se, Cd, Hg and, Pb, revealappear in concentrationsamounts in MPG ice, which provides further evidence 60 low aboutsupports our age model in which the absence ofrecord from the most recent 61 62 iceindustrial period is lost. This study confirms the exceptional warming of the last 63 decades in the context of <mark>the</mark> last two millennia. We demonstrate that we are facing an unprecedented retreat of the Pyrenean glaciers which survival is compromised beyond 64 a few decades. 65

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68 1. Introduction

Mountain glaciers are sensitive to climate variations on temporal scales from decades 69 to centuries. It is well known that summer temperature and winter precipitation are 70 71 the most important climate parameters influencing glacier mass balance (Oerlemans, 72 2001). Therefore, continuous records of past glacier size fluctuations provide valuable 73 information about the timing and magnitude of Holocene climate shifts, which 74 contributed to explain the characteristics and evolution of plant cover, human movements and land use (Solomina et al., 2015, 2016). Several glacier advances during 75 the Neoglacial (which started around 6000-5000 years ago) have been identified and 76 77 associated to sustained cooling periods across the North Atlantic (Wanner et al., 2011). The most recent period of global glacier expansion took place during the Little Ice Age 78 (LIA), beginning in the 13th century and reaching a maximum between the 17th and 19th 79 centuries (Solomina et al., 2016). Afterwards, most glaciers worldwide have retreated 80 rapidly, as indicated by measurements of ice volume and ice-covered area, and this 81 trend seems to have accelerated over the last three decades (Marzeion et al., 2014; 82 83 Zemp et al., 2015, 2019). Mountain glaciers are often sensitive to climate variations on temporal scales from decades to centuries. It is well known that summer temperature 84 and winter precipitation are the most important climate parameters influencing glacier 85 86 mass balance (Oerlemans, 2001). Therefore, continuous records of past glacier size 87 fluctuations provide valuable information about the timing and magnitude of Holocene climate shifts (Solomina et al., 2015, 2016), which contributed to explain the 88 89 characteristics and evolution of plant cover, human movements and land use. Several 90 glacier advances during the Neoglacial (which started around 6000-5000 yr ago) have 91 been identified and associated to sustained cooling periods across the North Atlantic (Wanner et al., 2011). The most recent period of global glacier expansion took place 92 during the Little Ice Age (LIA), beginning in the 13th century and reaching a maximum 93 between the 17th and 19th centuries (Solomina et al., 2016). Afterwards, most glaciers 94 worldwide have retreated rapidly, as indicated by measurements of ice volume and 95 96 ice-covered area, and this trend seems to have accelerated over the last three decades 97 (Marzeion et al., 2014; Zemp et al., 2015, 2019).

98 Despite broad agreement on millennial-scale trends in global glacier fluctuations and 99 Holocene climate variability (Davis et al., 2009; Solomina et al., 2015), regional 100 variations are not so well constrained. The Pyrenees is a mountain range that currently hosts the majority of the southernmost glaciers in Europe. In this mountain chain there 101 102 is a significant lack of knowledge about Holocene glacier fluctuations, with few 103 evidences of Neoglacial advances (García-Ruiz et al., 2020). Based on Pyrenean treering chronologies, summer temperatures during the Medieval Climate Anomaly (MCA, 104 <u>circa 900–1300 CE) were estimated to have been as warm as those of the 2</u>0th century 105 106 (Büntgen et al., 2017), but no information is available on the glacier response to MCA warming. Conversely, glacier advance during the LIA is well constrained in the 107 Pyrenees (García-Ruiz et al., 2014; González Trueba et al., 2008; Hughes, 2018; Oliva et 108 109 al., 2018) and a significant deglaciation is also evident in recent times (López-Moreno 110 et al., 2016; Rico et al., 2017). In particular, the period from the 1980s to present has been the most intense in terms of the number of glaciers that disappeared (from 39 111 inventoried Pyrenean glaciers in 1984 to 19 at present; Rico et al. 2017). Given the 112 small size of the Pyrenean glaciers and their current critical situation in the context of 113 global warming, we hypothesize that they could have disappeared completely during 114 warm periods such as the MCA. Despite broad agreement on millennial-scale trends in 115 116 global glacier fluctuations and Holocene climate variability (Davis et al., 2009; Solomina 117 et al., 2015), regional variations are not so well constrained. For instance, for the 118 Pyrenees, a mountain range that currently hosts the majority of the southernmost glaciers in Europe, there is a significant lack of knowledge about Holocene glacier 119 120 fluctuations, as indicated scarce evidences of glacier advances during the Neoglacial 121 period (García-Ruiz et al., 2014; Gellatly et al., 1992). Based on Pyrenean tree-ring 122 chronologies, summer temperatures during the Medieval Climate Anomaly (MCA, circa 900–1300 CE) were estimated to be as warm as those of the 20th century (Büntgen et 123 124 al., 2017), but no information has been obtained on the glacier response to MCA 125 warming. Conversely, glacier advance during the LIA is well constrained in the 126 Mediterranean mountains (García-Ruiz et al., 2014; González Trueba et al., 2008; 127 Hughes, 2018; Oliva et al., 2018) and a significant deglaciation is also evident in recent times (López-Moreno et al., 2016; Rico et al., 2017). Thus, Pyrenean glaciers have 128 129 exhibited during the 20th and 21st centuries multi-decadal variations similar to those of other mountain ranges in the world. In particular, the period from the 1980s to
present has been the most intense in terms of number of glaciers that disappeared
(from 39 inventoried Pyrenean glaciers in 1984 to 19 at present) (Rico et al., 2017).
Given the small size of the Pyrenean glaciers and their current critical situation in the
context of global warming, we hypothesize that they could have disappeared

135 completely during the aforementioned warm periods

This study is focused on Monte Perdido Glacier (MPG), located in the Marboré Cirque 136 in the Spanish Central Pyrenees. MPG is currently one of the best monitored small 137 glaciers (<0.5 km²) worldwide (López-Moreno et al., 2016, 2019). Previous research 138 139 based on different ground-based remote sensing techniques has demonstrated a rapid retreat of this glacier, with an average loss of ice thickness of about one meter per year 140 141 since 1981 (López-Moreno et al., 2016, 2019). This glacier is located in one of the few 142 valleys in the Pyrenees where information about Holocene glacier fluctuations exists. The outermost moraine in Marboré Cirque was recently dated at 6900 ± 800 ³⁶Cl yr BP 143 (García-Ruiz et al., 2020), which is the oldest Holocene date available for glacial 144 deposits in Spain, and indicates a glacier advance during the Neoglacial period. Other 145 minor advances would have occurred in MPG prior to the LIA, as inferred from three 146 147 polished surfaces dated at 3500 \pm 400, 2500 \pm 300 and 1100 \pm 100 36 Cl yr BP (García-148 Ruiz et al., 2020). Unfortunately, no information has been obtained on the glacier 149 response to Roman or MCA warming periods, remaining an open question whether 150 MPG just experienced significant ice loss or melted away totally. Most likely, the 151 voluminous moraine at the foot of the Monte Perdido Massif was deposited during the 152 LIA, indicating an important glacier advance. These results, together with the evidences of long-term retreat from its LIA position indicated by pictures and 153 154 moraines, suggested that this glacier could disappear over the next few decades 155 (López-Moreno et al., 2016).

The present study aims to reconstruct the chronology of MPG ice sequence by using a
 variety of dating techniques and the analysis of several proxies associated to
 environmental and anthropogenic changes measured on a set of samples taken from a
 transect. Such analyses will fill the existing knowledge gaps and answer the key
 guestion of whether Pyrenean glaciers may have survived previous Holocene warm

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161 periods. This study is focused on Monte Perdido Glacier, located in the Spanish Central 162 Pyrenees, which is currently one of the best monitored small glaciers (<0.5 km²) 163 worldwide. Recent research based on different ground-based remote sensing 164 techniques has demonstrated a rapid retreat of this glacier, with an average loss of ice 165 thickness of about one meter per year since 1981 (López-Moreno et al., 2019). These 166 results, together with the evidences of long-term retreat since the LIA glacier position indicated by pictures and moraines, suggest that this glacier could disappear over the 167 168 next few decades (López-Moreno et al., 2016). The present study relies on a variety of dating techniques and on the analysis of several proxies associated to environmental 169 170 and anthropogenic changes to construct, for the first time, the chronology of an ice sequence from a Pyrenean glacier. Such analyses will respond the key question of 171 172 whether Pyrenean glaciers may have survived previous Holocene warm periods.

173 2. Study area

174 The MPG (42°40'50"N; 0°02'15"E) is located in the Central Spanish Pyrenees, in the Ordesa and Monte Perdido National Park (OMPNP) (Fig. 1). It currently consists of two 175 176 separate ice bodies, which were connected in the past. Both are north facing, lie on 177 structural flats beneath the main summit of the Monte Perdido Peak (3355 m a.s.l.) 178 and are surrounded by vertical cliffs of 500-800 m in height. At the base of the cliffs, 179 the Cinca River flows directly from the glacier and the surrounding slopes, and has 180 created a longitudinal west–east basin called the Marboré Cirque (5.8 km²). This is the 181 area within the Pyrenees with the highest variety of recent morainic deposits (García-182 Ruiz et al., 2014, 2020). Additionally, a 6 m thick sediment core obtained in 2011 from a lake inside the cirque (Marboré Lake) provided valuable information from the last 183 14,600 years of the depositional evolution of the lake (Oliva-Urcia et al., 2018) and of 184 185 the regional variations in vegetation cover (Leunda et al., 2017). The Marboré Lake 186 (2595 m a.s.l.) is located in the Marboré or Tucarroya Cirque, in the northern face of 187 the Monte Perdido massif. The distance between the lake and the MPG is 188 approximately 1300 m and, therefore, both have been affected by similar 189 palaeoenvironmental conditions. The Monte Perdido Glacier (MPG, 42°40'50"N; 0°02'15"E.) is located in the Central Spanish Pyrenees, in the Ordesa and Monte 190 Perdido National Park (OMPNP) (Fig.1). It currently consists of two separate ice bodies, 191

192 which were connected in the past. Both are north facing and lie on structural flats 193 beneath the main summit of the Monte Perdido Peak (3355 m a.s.l.) and surrounded by vertical cliffs of 500-800 m in height. At the base of the cliffs, the Cinca 194 195 River flows directly from the glacier and the surrounding slopes, and has created a 196 longitudinal west-east basin called the Marboré Cirque (5.8 km²). This is the area 197 within the Pyrenees with the highest variety of recent morainic deposits (García-Ruiz et al., 2014). Additionally, a a 6-m thick sediment core obtained in 2011 from a lake 198 199 inside the cirque (Marboré Lake) contains valuale information from the last 14,600 200 years of the depositional evolution of the lake (Oliva-Urcia et al., 2018) and of the 201 regional variations in the vegetation cover (Leunda et al., 2017). The Marboré Lake 202 (2595 m a.s.l.) is located in the Marboré or Tucarrova Cirgue, in the northern face of 203 Perdido massif. The distance between the lake and the MPG is Monte 204 approximately 1300 m and, therefore, both have been affected by similar 205 palaeoenvironmental conditions.

The total surface area of MPG in 2016 was 0.385 km², with an average decrease in 206 207 glacier ice thickness of 6.1 m during the period 2011 - 2017 (López-Moreno et al., 2019). According to recent measurements of air temperature (July 2014 to October 208 209 2017), the 0 °C isotherm lies at 2945 m a.s.l., suggesting that the potential glacier 210 accumulation area is very small, even inexistent during warm years. The average 211 summer (June to September) temperature at the foot of the glacier from 2014 to 2017 has been of 7.3 °C (López-Moreno et al., 2019). No direct observations of precipitation 212 213 are available at the glacier location, but the maximum accumulated snow by late April 214 in the three available years (2014, 2015 and 2017, when no scanning limitations 215 occurred and the whole glacier was scanned) was 3.23 m, and field-measured average snow density was 454 kg m⁻³, indicating that total water equivalent during the main 216 accumulation period (October to April) could be equivalent to 1500 mm (López-217 218 Moreno et al., 2019).

Recent measurements indicate that the total surface area of MP glacier in 2016 was
 0.385 km² (López-Moreno et al., 2016). During the period 2011–2019, the glacier ice
 thickness decreased by 7.4 m on average, though such losses exhibit a marked spatial
 and temporal variability (Fig. S1, Supplementary Material). According to recent

223 measurements of air temperature (July 2014 to October 2017), the 0 °C isotherm lies 224 at 2945 m a.s.l., suggesting that the potential glacier accumulation area is very small, 225 even inexistent during warm years. In an average summer (June to September; 226 temperature measurements were conducted from 2014 to 2017), the temperature at 227 the foot of the glacier is 7.3 °C. No direct observations of precipitation are available at the glacier location, but the maximum accumulation of snow in late April during the 228 three available years was 3.23 m, and average snow density was 454 kg m⁻³ measured 229 in the field, indicating that total water equivalent during the main accumulation period 230 (October to April) could be close to 1500 mm (López-Moreno et al., 2019). 231

232 3. Material and methods

233 *3.1. Ice sampling and storage*

Ice sampling on MPG was carried out in September 2017 along a chrono-stratigraphical 234 sequence covering from the oldest to the newest ice preserved in the glacier, following 235 236 the isochronal layers that emerge in the ablation zone (Fig. 2A). Unfortunately, the 237 extraction of vertical cores was not possible because the glacier does not currently 238 meet any of the usual glacio-meteorological and topographical criteria required to obtain a preserved ice-core stratigraphy. The unfulfilled criteria include low 239 240 temperatures to prevent water percolation or a large extension and flat surface 241 topography to minimize the influence of glacier flow (Garzonio et al., 2018). Samples 242 were collected in an area with no evidence of current ice movement (or very low), as 243 confirmed by results from interferometric radar and GNSS measurements (López-Moreno et al., 2019). Due to the small size of this glacier, we expected the ice to be 244 245 frozen to bedrock, and hence nearly stagnant, to become of substantial age, as 246 indicated by previous studies in similar glaciers (Gabrielli et al., 2016; Haeberli et al., 2004). The sampling sector lies in the ablation zone of MPG and has been eroded to 247 form a current steady slope of 20° where it is possible to observe the primary 248 stratigraphy, marked by clear debris-rich layers. The distribution of these debris-rich 249 layers is rather regular and extends laterally (Fig. 2B), as would be expected for the 250 primary stratification resulting from the original deposition at surface of snow and 251 debris. Therefore, these layers are considered isochrones, and confirm and facilitate 252

the sampling along the slope, from the oldest to the newest ice preserved in the
glacier.

255 We measured one-meter thickness using a Jacob's staff at each sampling point along 256 the slope (Fig. 2B). The tilt of the ice layers was unclear but, since previous studies 257 calculated about 30 m of ice thickness (López-Moreno et al., 2019), the ice layers are 258 probably quite tilted downward as detailed in Fig. 2A. Once cleaned the most 259 superficial ice (ca. 50 cm) to avoid possible ice formed recently, we recovered at every 260 sampling position 3-4 small horizontal cores (6 cm in diameter and 25 cm in length) using a custom stainless-steel crown adaptor on a cordless power drill (Fig. 2C). 261 262 Following this sampling procedure we recovered a total of 100 samples. The ice samples were stored in a freezer room at the IPE-CSIC in Zaragoza until they were 263 melted and analysed to obtain their chronology combining ²¹⁰Pb, ¹³⁷Cs and ¹⁴C 264 techniques, and their geochemical composition in trace metals, such as Pb or Hg (see 265 below). Ice drilling in MPG was carried out in September 2017 using a Kovacs ice coring 266 267 device at three sites. These sites were selected based on previously obtained groundpenetrating radar (GPR) results, which, combined with glacier dynamics modelling, 268 269 suggested that the oldest ice could be located at these locations since the thickness 270 was over 30 m and there was no movement of the ice (López-Moreno et al., 2019) (Fig. 271 1). Unfortunately, none of the glacio-meteorological and topographical criteria 272 required to obtain a preserved ice-core stratigraphy, such as low temperatures to 273 prevent water percolation, or a large extension and flat surface topography to minimize the influence of glacier flow (Garzonio et al., 2018), are currently met in the 274 275 glacier. With this technique, only three short ice cores of 4, 3 and 2 m in length could 276 be recovered, which could not provide a complete chrono-stratigraphical ice sequence. The cores were preserved intact and later stored at -60 °C at the BC3-IzotzaLab ice 277 278 core facility (Leioa, Spain) but not used in this study.

Based on the poor core recovery, we changed our drilling strategy and, to collect ice
 samples in an ordered chrono-stratigraphical sequence covering from the oldest to the
 newest ice preserved in the glacier, we took samples in an area with no evidence of
 current ice movement, as confirmed by results from interferometric radar and GNSS
 measurements (López-Moreno et al., 2019) (Fig.S2). This sector has been eroded to

284 form a current steady slope of 20° where it is possible to establish a relation between 285 the sample distances and the ice depth in a formerly much less steep glacier surface. Due to the small size of this glacier, the ice needs to be frozen to bedrock, and hence 286 287 nearly stagnant, to become of substantial age, i.e., a few hundred years or more, as 288 indicated by previous studies in similar glaciers Gabrielli et al., 2016; Haeberli et al., 289 2004). Therefore, we measured one-meter thickness using the Jacob's staff at every sampling point to measure stratigraphic thicknesses since bedding was unclear (Fig. 290 291 52). Once cleaned the most superficial ice to avoid new ice formed recently, we 292 recovered at every sampling position 3–4 small cores (6 cm in diameter and 25 cm in length) using a custom stainless steel crown adaptor on a cordless power drill (see Fig. 293 S2 in Supplementary Material). Following that sampling procedure we recovered a 294 total of 100 samples, every one constituted by 3-4 cylinders, which represent the 295 whole ice sequence in MP glacier. Those ice samples were stored in a freezer room in 296 Zaragoza and further analysed to obtain their chronology (combining ²¹⁰Pb, ¹³⁷Cs and 297 ¹⁴C techniques) and their geochemical composition (trace element and Hg 298 concentrations) (see below). 299

300 3.2. Dating by ²¹⁰Pb and ¹³⁷Cs.

The isotope ¹³⁷Cs usually associated to the fallout from nuclear tests during the 1950s 301 302 and the 1960s, as well as the Chernobyl (1986) and Fukushima (2011) accidents was investigated by γ -spectrometry in the uppermost five samples in MPG, but no trace 303 304 could be detected (Table S1 in Supplementary Material). This implies that all samples are older than 60-65 years and therefore they were not exposed to the atmosphere 305 after 1950 CE. The isotope ¹³⁷Cs, usually associated to the fallout from nuclear tests 306 during the 1950s and the 1960s, as well as the Chernobyl (1986) and Fukushima (2011) 307 accidents, was investigated by γ -spectrometry in five samples recovered towards the 308 top of the MPG chronological sequence (MP-61, MP-82, MP-97, MP-98, MP-100, Table 309 1). In addition, ten samples were selected to perform a ²¹⁰Pb analysis as an 310 311 independent dating method to obtain the age model of approximately the last hundred years of glacier ice (Eichler et al., 2000; Herren et al., 2013). These samples 312 were selected also from the top of the ice sequence to collect the younger ice (Table 313 2). Determination of ²¹⁰Pb activities was accomplished through the measurement of its 314

daughter nuclide, ²¹⁰Po, by α -spectrometry following the methodology described in 315 316 (Sanchez-Cabeza et al., 1998) (Table 2). Another possibility that was discarded once we had ¹⁴C dates, is that all samples were younger than 1950 CE. Additionally, up to ten 317 samples were selected from the 100 samples that constitute the whole ice sequence to 318 carry out ²¹⁰Pb analysis as an independent dating method to obtain chronologies for 319 about the last hundred years of glacier ice (Eichler et al., 2000; Herren et al., 2013). 320 Those samples were selected from the top of the sequence (Table S2). Determination 321 of ²¹⁰Pb activities was accomplished through the measurement of its daughter nuclide, 322 210 Po. by α -spectrometry following the methodology described in (Sanchez-Cabeza et 323 al., 1998) (Table S2 in Supplementary Material). Similarly, ²¹⁰Pb activity was also 324 undetectable in most cases, except in three samples (MP100, MP73 and MP76) with 325 concentrations above minimum detection activity (MDA; Table S2). Probably, the 326 MP100 sample contained the ²¹⁰Pb recently deposited because it was the most 327 328 superficial sample, therefore in contact with the atmosphere. However, this sample, as well as samples MP73 and MP76 contained a large amount of lithogenic particulate 329 material from atmospheric dust or ash deposits. The absence of ²¹⁰Pb activity in the 330 samples does not allow constructing an age-depth model for the last 100 331 analysed years indicating that MPG ice samples were very likely older and the ²¹⁰Pb had 332 completely decayed. We then built up the proposed MPG chronology using AMS ¹⁴C 333 dating. 334

335 3.3. Dating by ¹⁴C method.

336 Sixteen accelerator mass spectrometry (AMS) ¹⁴C dates from MPG ice were obtained 337 by combining bulk organic matter (9 samples), pollen concentrates (3 samples), bulk 338 sediment accumulated in filters (2 filters), and water-insoluble organic carbon (WIOC) 339 particles (2 samples) (Table <u>3</u>). The procedure to select these samples was as follows:

(i) Using1). First, using a binocular microscope [x10], we picked upselected organic
 particles for dating from the nine-selected icebulk samples, once the ice sample was
 melted. However, the small size of the handpicked organic remains prevented us from
 classifying them. As a result, we obtained 9 samples (MP-1, MP-42, MP-48, MP-67, MP 68, MP-69, MP-70, MP-73, MP-100, Table 3) thatthe organic remains. All the

amorphous particles were sent to the <u>Direct_AMSdating</u> laboratory (<u>Direct_AMS</u>,
 Seattle, USA) for dating. The selection of those nine samples was based on the amount
 of debris found in the sample, once the ice was melted

(ii)), Pollen concentrates were prepared from three selected samples (MP-30, MP-70 348 349 and <u>MP-</u>100-m depth) to complete the previous set with the aim of replicating some of 350 the results (MP-70 and MP-100) and obtaining new dates (MP-30). Preparation followed of samples following the standard palynological method, including a chemical 351 treatment and mineral separation in heavy liquid (Thoulet: density 2.0; Moore et al., 352 353 1991). The effects of meltwater percolation on pollen in snow, firn and glacial ice are 354 not fully understood and currently challenge the use of pollen in ice-core studies (Ewing et al., 2014). Just in few cases pollen has appeared as a potential dating 355 356 material, when seasonal layers are preserved (Festi et al., 2017). Yet, pollen concentrates have been used in other type of archives with high success (Fletcher et 357 al., 2017), opening the door to apply the same methodology here. 358

359 (iii) Two ice samples (MP-67 and MP-Moore et al., 1991). Additionally, two ice samples 360 previously melted (67 and 81), which appeared darker than others once melted, m 361 depth) were filtered throughout a filtration line connected to a vacuum pump using 47 362 mm quartz fiber filters (PALL tissuquarzt 2500QAT-UP), parameterized at controlled conditions (temperature: 22 - - 24 °C; relative humidity 25 - - 35_%) and weighted 363 364 twice in different days. Abundant material was obtained, but no control was made on the composition and amount of organic material versus other typestype of input. The 365 366 three concentrated inputs. Concentrated pollen samples and the two filters were dated at the same ¹⁴C dating laboratory (Direct AMS, Seattle, USA<u>) (Table 3).</u> 367

(iv) Finally, two more samples were dated at the Laboratory of Environmental
 Chemistry, Paul Scherrer Institute (Switzerland) removing the outer part of the ice core
 segment for decontamination purposes (Jenk et al., 2009).)- Since organic fragments
 (plants, wood, insects) are rarely found in mountain glaciers, a new, complementary
 dating tool was recently developed based on extracting the microgram-amounts of the
 water-insoluble organic carbon (WIOC) fraction of carbonaceous aerosols embedded in
 the ice matrix for subsequent ¹⁴C dating (Uglietti et al., 2016). These two samples,

Iabelled as MP10m and MP59m at the WIOC facility (Table 3), were selected as the
 only ones with sufficient ice volume available. (Uglietti et al., 2016). Two samples were
 dated by the WIOC technique at the Laboratory of Environmental Chemistry, Paul
 Scherrer Institute, Switzerland, following the usual procedures including removing the
 outer part of the ice core segment for decontamination purposes (Jenk et al., 2009).

380 Once the 16 radiocarbon ages were obtained, we converted them into calendar ages by using the CALIB 5.0.2 software, which uses the most updated dataset, INTCAL13 381 (Reimer et al., 2013) (Table 3). The median of the one- σ probability interval was 382 selected for these dates, resulting in highly variable errors in the calendar ages 383 obtained (from 30 years on the bulk organic samples to more than 200 years on pollen 384 and WIOC samples). While the first method to select organic remains at the 385 386 microscope resulted the best option, the pollen concentration and filtering methods used to isolate organic matter to be dated by ¹⁴C were, unfortunately, not successful. 387 Finally, from the initial 16 dates, we had to discard seven according to the following 388 criteria (see the "comments" column in Table 3): 389

390 <u>- Sample MP-46 (D-AMS 025295) was the only one discarded from the nine initial</u>
 391 <u>bulk organic matter samples. We suspect that the very recent age obtained</u>
 392 (1897 ± 20 CE, Table 3) is due to the sample contamination, since small plastic
 393 <u>debris coming off from the painting used in the coring device were identified</u>
 394 <u>under the microscope.</u>

395 From the two WIOC-dated samples, one was discarded (MP10m) due to the low carbon content (5.3 µg), thus providing too inaccurate results (854 ± 721 396 397 CE, with an unacceptable large uncertainty). The other sample (Finally, from 398 the initial 16 dates, we had to discard seven (see the criteria in section 4.1 399 below) and the age model was developed including nine samples (eight from 400 bulk organic matter and one from the WIOC technique; Table 1). Those nine 401 dates were converted into calendar ages by the CALIB 5.0.2 software, which uses the most updated dataset, INTCAL13 (Reimer et al., 2013) (Table 1). The 402 403 median of the one- σ probability interval was selected for these dates, resulting 404 in large errors (230 years on average) in the obtained calendar ages. The depth-age model was created using the R package CLAM 2.2 (Blaauw, 2010; 405

406	Blaauw et al., 2019) (Fig. 2). Given the scattered depths at which dates
407	concentrate, we chose to perform a non-smooth, second order polynomial
408	regression for preventing any model over-fitting and a spurious age-depth
409	relationship. In addition, we run the depth-age model setting a hiatus at 73 m
410	depth where we think an interruption in the ice accumulation was produced.
411	This idea is supported by the observation of several debris layers that increased
412	their frequency towards the top of the glacier. Those layers are interpreted as
413	the result of several phases of melting, dramatically changing the accumulation
414	rates and concentrating samples of similar ages (see section 4.1 below). Full
415	details on how the model was performed and a reproducible workflow with the
416	current chronological dataset are available in the Supplementary Material <u>MP59m)</u> ,
417	with higher organic carbon content (28.7 μ g), was incorporated into the age
418	model in spite of its error above 200 yr (1046 ± 242 CE).
419	- The three pollen concentrates provided unreliably old dates with very high
420	errors, likely due to the small amount of pollen that we were able to
421	concentrate (errors above 200 yr, Table 3). Obtaining old dates from pollen is a
422	guite common problem not yet solved in the literature (Kilian et al., 2002).
423	- Similarly, we discarded the two filter samples MP-67 and MP-81 (D-AMS
424	029894 and D-AMS 033972, respectively). The material accumulated in the
425	filters was a mixture of particles containing detrital carbonate eroded from
426	Eocene limestones or supplied by Saharan dust, which was not removed and
427	probably influenced the results incorporating allochthonous carbon to the
428	samples.
120	Finally, nine dates were employed to infer the chronology of the MPG sequence. The
423	depth are model was created using a linear regression in the B package CLAMA 2.2
430	uepth-age model was created using a linear regression in the K package CLAMI 2.2
431	(Blaauw, 2010; Blaauw et al., 2019).

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432 *3.4. Trace elements in soluble and insoluble material.*

35 selected ice samples from the altitudinal transect were melted and filtered through
a filtration ramp connected to a vacuum pump using 47 mm quartz <u>fibrefiber</u> filters
(PALL tissuquarzt 2500QAT-UP). Filters were pre-heated at 250 °C and thereafter

436 prepared in controlled conditions (temperature: 22 - - 24 °C; relative humidity: 25 - -437 35 %) before and after filtration. Subsequently, they were weighted in two different 438 days. Mass difference between blank and sampled filters was used to calculate the 439 amount of insoluble material entrapped in ice samples. For every sample, an aliquot 440 and a filter were obtained. From aliquots, anions and cations, as well as major and trace elements were determined. From filters, we determined major and trace 441 elements, as well as organic and elemental carbon, following the method devised by 442 Pey et al. (2013)(Pey et al., 2013) (Table 42). Basically, an acidic digestion 443 (HNO₃:HF:HClO₄) of half of each filter was conducted, driven to complete dryness, 444 being the remaining material re-dissolved in HNO₃. Inductively coupled plasma mass 445 spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy 446 (ICP-AES) were used to determine major and trace elements, respectively.- From the 447 other half of each filter, a 1.5 cm^2 section was used to determine Organic Carbon (OC) 448 and Elemental Carbon (EC) concentrations by using a SUNSET thermo-optical analyzer, 449 following the EUSAAR 2 temperature protocol. Table 1 also contains the Enrichment 450 Factors (EFs), calculated as follows: 451

$$EF_{iCODD} = \frac{X_{iCODD}/Al_{CODD}}{X_{iUC}/Al_{UC}} \qquad EF_{iMPGID} = \frac{X_{iMPGID}/Al_{MPGID}}{X_{iUC}/Al_{UC}} \qquad EF_{i} = \frac{X_{iCODD}/Al_{CODD}}{X_{iMPGID}/Al_{MPGID}}$$

452

where EF_{iCODD} is the Al-normalised Enrichment Factor with respect to the Upper Crust (*UC*, <u>Taylor and McLennan (1995)</u>(Taylor and McLennan, 1995)) of an *'i'* element in the current Ordesa's deposited dust (*CODD*); EF_{iMPGID} is the Al-normalised Enrichment Factor with respect to the *UC* of an *'i'* element in the current MPG ice dust (*MPGID*); and EF_i is the Al-normalised Enrichment Factor with respect to *CODD* of an *'i'* element in the *MPGID*.

Regarding the Pb/Al ratio, we carried out a normalization with Al in both, ice and lake
records, to disentangle the anthropogenic lead variability from possible detrital inputs.
Aluminium has been selected for normalization since this lithogenic element is
immobile and abundant in carbonated watersheds (Corella et al., 2018). Regarding the
Pb/Al ratio, we carried out a normalization with Al in both, ice and lake records, to
disentangle the anthropogenic lead variability from possible detrital inputs. Aluminum

465 has been selected for normalization since this lithogenic element is immobile and
466 abundant in carbonated watersheds.

467 3.5. Hg determination.

Total Hg concentration measurements were carried out in 21 selected samples by 468 Atomic Absorption Spectrophotometry using an Advance Mercury Analyzer (AMA 254, 469 LECO Company). This equipment is specifically designed for direct mercury 470 determination in solid and liquid samples without sample chemical pre-treatment. 471 Certified reference materials were used to determine the accuracy and precision of the 472 Hg measurements. These reference materials were ZC73027 (rice, 4.8 \pm 0.8 μ g kg⁻¹) 473 and CRM051–050 (clayClay soil, 4.08 \pm 0.09 mg kg⁻¹). The standard deviation 474 (repeatability) was $\frac{Sr}{Sr} \le 15$ % and the relative uncertainty associated with the method 475 (with ak = 2; confidence level of about 95_%) was ±20 %. All analyses were run at least 476 three times. Total metal concentrations were expressed in $\mu g g^{-1}$ of dry weight 477 478 sediment due to the low amount detected.

479 **4. Results**

480 <u>4.1. Chronological model</u>

To date the ice sequence from MPG we compiled the results from ¹³⁷Cs, ²¹⁰Pb and ¹⁴C 481 methods. First, it is remarkable the absence of ¹³⁷Cs in the five samples analyzed (Table 482 1discussion). This implies that all samples are older than 60–65 years and therefore 483 they were not exposed to the atmosphere after 1950 CE. Another possibility that was 484 discarded upon obtaining ¹⁴C dates, is that all samples were younger than 1950 CE. 485 Similarly, ²¹⁰Pb activity was also undetectable in most cases, except in three samples 486 (MP-100, MP-73 and MP-76) with concentrations above minimum detection activity 487 488 (MDA; Table 2). These three samples contained a large amount of lithogenic particulate material from atmospheric dust or ash deposits, likely causing the observed 489 values. Thus, the absence of ²¹⁰Pb activity in the analysed samples suggests that MPG 490 ice samples were very likely older than 100 years and the ²¹⁰Pb had completely 491 decayed. We then built up the proposed MPG chronology using only AMS ¹⁴C dating. 492

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Regarding ¹⁴C dating, we took most of the ice samples for dating in sections where 493 494 dark debris layers alternated every ca. 5 m with cleaner and clearer ice (Fig. 2). The 495 debris-rich layers were composed of detrital, silty-sandy size deposits, likely coming from wind-blown particles (e.g. black carbon-rich particles, dust) and from erosive 496 497 processes of the limestone catchment, including the fall of gravel-sized particles from the surrounding cliffs. These debris-rich layers do not have a subglacially derived origin 498 since they are observed all along the sample profile and large accumulation of debris 499 or pinnacles, both characteristics of subglacially derived glacier till, were not found in 500 MPG. These debris layers contain more organic remains than those formed by clear 501 ice, making them ideal spots to find datable remains. 502

503 Interestingly, the frequency of debris layers increases towards the top of the glacier 504 sequence. We consider the accumulation of debris layers to be indicative of reduced 505 ice accumulation and dominance of ablation periods. In such situations, the detrital and organic material concentrates as the ice melts, giving its characteristic dark colour 506 507 to the ice layers. The major concentration of such layers occurred among samples MP-67 and MP-73 (Table 3), thus suggesting the dominance of ablation processes. 508 Therefore, we run the depth-age model setting a hiatus at 73 m depth, where we 509 think an interruption in the ice accumulation was produced. Finally, as explained in the 510 511 methods section, the age-model was constructed with 9 of the initially dated 16 512 samples (Table 3). Given the scattered depths at which dates concentrate, we chose to 513 perform a non-smooth, linear regression for preventing any model over-fitting and a spurious age-depth relationship (Fig. 3). Full details on how the model was performed 514 515 and a reproducible workflow with the current chronological dataset are stored at 516 https://zenodo.org/record/3886911.

517 <u>4.2. Trace elements</u>

518 We have used the averaged concentration values of major and trace elements 519 currently obtained at a monitoring station located at OMPNP (8 km away from the 520 MPG, at 1190 m a.s.l.), where deposited atmospheric particulate matter is sampled 521 monthly (Table 4) (Pey et al., 2020). Interestingly, the elements that are abundant 522 nowadays in the Ordesa station are not so frequent in the ice from MPG. Indicators

523	such as organic carbon, Zn, Se and Cd concentrations, all of which are potential proxies
524	of current anthropogenic emissions, are much higher in the samples from Ordesa,
525	which are representative of today's atmosphere, than in the ice samples from the
526	MPG. The low concentration of these elements in MPG samples could indicate their
527	disappearance from glacier surface layers due to its continuous melting. This supports
528	our suggested age model (Fig. 3), in which ages from the Industrial Period are not
529	recorded. Conversely, the Al-normalised enrichment factor (EF) of Ti, Mn, Cr, Co, Ni, Cu
530	and Pb, elements linked to the natural fraction (dust deposition, lithogenic elements)
531	and mining activities (Corella et al., 2018), are more abundant in the MPG ice samples
532	than in the present-day Ordesa aerosols (Table 4). From them, Cu and Pb were
533	markedly enriched (by a factor >6) in the MPG ice samples compared with the current
534	deposited aerosols in Ordesa station.
535	5. Discussion
536	54,1. Dating of ice from the Monte Perdido Glacier <u>ice sequence</u>
537	Dating the ice from non-polar glaciers is challenging and often problematic as annual
537 538	Dating the ice from non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to common
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537 538 539 540	Dating the ice from non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to common ice deformation caused by glacier flow (Bohleber, 2019; Festi et al., 2017). We have constrained the age model of MPG ice using nine ¹⁴ C absolute dating from different
537 538 539 540 541	Dating the ice from non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to common ice deformation caused by glacier flow (Bohleber, 2019; Festi et al., 2017). We have constrained the age model of MPG ice using nine ¹⁴ C absolute dating from different materials (Table 3), the absence of ¹³⁷ C and ²¹⁰ Pb in surface ice samples and integrating
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537 538 540 541 542 543 544 545 546 547 548	Dating the ice from non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to common ice deformation caused by glacier flow (Bohleber, 2019; Festi et al., 2017). We have constrained the age model of MPG ice using nine ¹⁴ C absolute dating from different materials (Table 3), the absence of ¹³⁷ C and ²¹⁰ Pb in surface ice samples and integrating in the chronology the characteristics of the ice stratigraphy, such as the presence of dark debris-rich layers. Dating of ice cores from temperate, non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to ice deformation caused by glacier flow (Festi et al., 2016; Thompson et al., 2006). Hence, we have constrained the age of glacier ice within the last 100 years by using ²¹⁰ Pb and ¹³⁷ Cs relative dating methods, and for the oldest sections we used ¹⁴ C absolute dating from different materials (<i>Sect. Material and</i>
537 538 540 541 542 543 544 545 546 547 548 549	Dating the ice from non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to common ice deformation caused by glacier flow (Bohleber, 2019; Festi et al., 2017). We have constrained the age model of MPG ice using nine ¹⁴ C absolute dating from different materials (Table 3), the absence of ¹³⁷ C and ²¹⁰ Pb in surface ice samples and integrating in the chronology the characteristics of the ice stratigraphy, such as the presence of dark debris-rich layers. Dating of ice cores from temperate, non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to ice deformation caused by glacier flow (Festi et al., 2016; Thompson et al., 2006). Hence, we have constrained the age of glacier ice within the last 100 years by using ³¹⁰ Pb and ¹³⁷ Cs relative dating methods, and for the oldest sections we used ¹⁴ C absolute dating from different materials (<i>Sect. Material and methods</i> and Tables S1, S2 in Supplementary Material). Additionally, characteristics of
537 538 540 541 542 543 544 545 546 547 548 549 550	Dating the ice from non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to common ice deformation caused by glacier flow (Bohleber, 2019; Festi et al., 2017). We have constrained the age model of MPG ice using nine ¹⁴ C absolute dating from different materials (Table 3), the absence of ¹³⁷ C and ²¹⁰ Pb in surface ice samples and integrating in the chronology the characteristics of the ice stratigraphy, such as the presence of dark debris-rich layers. Dating of ice cores from temperate, non-polar glaciers is challenging and often problematic as annual layer counting is precluded due to periods without net accumulation, and to ice deformation caused by glacier flow (Festi et al., 2016; Thompson et al., 2006). Hence, we have constrained the age of glacier ice within the last 100 years by using ²¹⁰ Pb and ¹³⁷ Cs relative dating methods, and for the oldest sections we used ¹⁴ C absolute dating from different materials (<i>Sect. Material and methods</i> and Tables S1, S2 in Supplementary Material). Additionally, characteristics of the ice stratigraphy, such as the presence of dark debris-rich layers, were integrated
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Con formato: Inglés (Reino Unido)

Con formato: Inglés (Estados Unidos) Con formato: Inglés (Estados Unidos) the Marboré Lake located nearby (Corella et al., 2018; Oliva-Urcia et al., 2018) (Fig.1)
helped to support the obtained MPG age-depth model .

554 We took most of the ice samples for dating in sections where dark debris layers 555 alternated every ca. 5 m with cleaner and clearer ice (Fig. S2 in Supplementary 556 Material). The debris layers were composed of detrital, silty-sandy size deposits, likely 557 coming from wind-blown particles (e.g. black carbon-rich particles, dust) and from 558 erosive processes of the limestone catchment, including the fall of gravel sized particles from the surrounding cliffs. These debris layers contain more organic remains 559 than those formed by clear ice, making them ideal spots to find datable remains. 560 Interestingly, the frequency of debris layers increases towards the top of the glacier, 561 where these layers are most abundant. We consider the accumulation of debris layers 562 563 to be indicative of reduced ice accumulation and dominance of ablation periods. In such situations, the detrital and organic material concentrates as the ice melts, giving 564 its characteristic dark colour to the ice layers. The age-depth model obtained indicates 565 566 the presence of ice since 2000 years ago and allows distinguishing three main periods for MPG (Fig. 3). Period I was an accumulation period from 0 to 700 CE. Period II 567 represents an ablation-dominated phase from 700 to 1200 CE, which corresponds to 568 569 the dark-rich layer interval where more dates are concentrated. Period III corresponds 570 to a new accumulation period from 1200 to 1400 CE. This period agrees well with an 571 increase in cold season (Oct–May) heavy rainfall events in the Southern Central Pyrenees between 1164 – 1414 CE (Corella et al., 2016) that most likely resulted on 572 higher snow accumulation at high elevation areas, leading to a net accumulation in 573 574 MPG. Finally, no ice formed during, at least, the last 600 years has been found today in 575 MPG. This indicates that the LIA ice has been melted away, pointing to an intense 576 ablation period since 1850 CE. The MPG age model is supported by, first, a quantitative 577 comparison with present-day atmospheric particulate matter (Table 4) and, second, by 578 the comparison with the paleoenvironmental sequence of the Marboré Lake for the 579 last 2000 years (Corella et al., 2021; Oliva-Urcia et al., 2018) (Fig. 4).

The chronology for the last 100 years was not eventually constrained using.²¹⁰Pb and
 ¹³⁷Cs as samples proved to be older than the decay period of both radionuclides
 (Tables S1 and S2, Supplementary Material). Thus, the lack of.²¹⁰Pb activity indicated

583 the lack of ice formed during the last 100 years. Regarding the 14C dated samples, 584 some sample limitations precluded the construction of a chronology (Table 1). The sample from 48 m depth (D-AMS 025295) was the only one from the nine bulk organic 585 586 matter samples to be discarded due to probable contamination, since small plastic 587 debris coming from the painting used in the coring device were identified under the 588 microscope. From the two WIOC-dated samples, one was discarded (MP10m), as it had too small amount of organic carbon (5.3 μg), thus providing too inaccurate results. The 589 other sample (MP59m), with higher organic carbon (28.7 ug), was incorporated into 590 591 the age model. The other two methods (pollen and filters) used to concentrate organic dated by ¹⁴C were, unfortunately, not successful. The three pollen 592 matter -to 593 concentrates provided unreliably old datings. We hypothesize that these old datings 594 are likely associated to melting processes of older ice layers accumulated in the upper 595 ice body of MPG (Neoglacial or Roman times), which later percolated through the ice, 596 as observed in other glaciers (Ewing et al., 2014). Similarly, we discarded the two filter 597 samples from 67 m and 81 m depth (D-AMS 029894 and D-AMS 033972, respectively). 598 The material accumulated in the filters was a mixture of particles containing detrital carbonate Eocene limestones or supplied by Saharan dust, which was not 599 removed and probably influenced the results incorporating dead carbon to the 600 601 samples.

602 Finally, from the original set of sixteen absolute dates obtained, we selected the nine 603 samples which did not present any problem related to the amount of carbon, possible 604 contamination, material from different sources or percolation within the ice sequence. 605 These nine samples were all chrono-stratigraphically coherent (eight from bulk organic 606 WIOC-technique). The age-depth model obtained indicates the matter and one from 607 presence of ice since 2000 years ago and allows distinguishing three main periods for 608 MPG (Fig. 2). First, an accumulation period from 0 to 700 CE. Second, an ablation-609 dominated phase from 700 to 1200 CE, which corresponds to the dark-rich layers 610 interval. Third, a new accumulation period from 1200 to 1400 CE. Finally, no ice formed during, at least, the last 600 years has been found today in MPG according to 611 612 this the melted indicator that thus ablation period since 613 demonstrating 1850 CE The MPG chronology is intense

supported by, first, a quantitative comparison with present-day atmospheric
particulate matter (Table 2) and, second, by the comparison with the
paleoenvironmental sequence of the Marboré Lake for the last 2000 years (Fig. 3) (see
text below).

618 We have used the averaged concentration values of major and trace elements 619 currently obtained at a monitoring station located in Ordesa and Monte Perdido National Park (8 km away from the MPG, at 1190 m a.s.l.), where deposited 620 621 atmospheric particulate matter is sampled monthly (Table 2). Interestingly, the 622 elements that abound nowadays in the Ordesa station are not so abundant in the ice 623 from MPG, Indicators such as organic carbon, Zn, Se and Cd concentrations, all of which are potential proxies of current anthropogenic emissions, are much higher in the 624 625 samples from Ordesa, which are representative of today's atmosphere, than in the ice samples from the MPG. The low concentration of these elements in MPG samples 626 627 could indicate their disappearance from glacier surface layers due to its continuous melting. This supports our suggested age model (Fig. 2), in which the industrial period 628 been recorded. Contrariwise, the Al-normalised enrichment factor (EF) of Ti. 629 630 Co, Ni, Cu and Pb, elements linked to the natural fraction (dust deposition, 631 lithogenic elements) and mining activities (Corella et al., 2018), are more abundant in 632 the MPG ice samples than in the present-day Ordesa aerosols (Table 2). From them, Cu 633 and Pb were markedly enriched (by a factor >6) in the MPG ice samples compared with

635 Present-day aerosols in the studied region are well-recorded in Ordesa site (Pey et al., 2020). Following previous studies on present-day atmospheric particulate matter 636 composition from natural, urban or industrial areas (Querol et al., 2007), the values of 637 638 some elemental ratios (e.g., Cu/Mn, As/Se, Pb/Zn) help to determine the origin of the 639 particulate matter accumulated today. The Ordesa site can accordingly be mostly 640 defined as remote in terms of atmospheric deposition ("rural background") while the 641 average composition of MPG ice samples could be defined as a site under the influence of Cu mining and smelting activities, due to the high values of the Cu/Mn, As/Se and 642 Pb/Zn ratios. It is noteworthy that Cu, Ag, and Pb mining and smelting have been 643 644 historically documented in Bielsa valley during pre-industrial times (Callén, 1996).

the current deposited aerosols in Ordesa station.

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645 Indeed, MPG is only 7 km east from some of the largest lead and silver ore deposits in 646 the Central Pyrenees (historical mines of Parzán). The impact of ancient environmental 647 pollution in high alpine environments is archived in the lacustrine sequence of the 648 neighbouring Marboré Lake, providing first evidences of long-range transport of trace 649 metals from historical metal mining and smelting activities during the Roman Period 650 (RP) (Corella et al., 2018, 2021). Similar ice core records from the Alps have also demonstrated the suitability of glacier ice to record local and regional mining and 651 smelting activities during RP and pre-Roman times (More et al., 2017; Preunkert et al., 652 653 2019). Even if the enrichment of trace elements in MPG ice record may correspond to mining activities during ancient times, the different altitude of MPG glacier with 654 655 respect to records from Alpine glaciers where such activities were recorded (> 4000m 656 a.s.l.), together with the likely processes of redistribution of chemical impurities due to 657 percolation (Pohjola et al., 2002), prevents a firm interpretation of the origin of these 658 elements.Following previous studies on present-day atmospheric particulate matter 659 composition from natural, urban or industrial areas (Querol et al., 2007), the values of 660 some elemental ratios (e.g. Cu/Mn, As/Se, Pb/Zn) help to determine the origin of the 661 particulate matter accumulated today. The Ordesa site can accordingly be mostly 662 defined as remote in terms of atmospheric deposition ("rural background") while the 663 average composition of MPG ice samples could be defined as a site under the influence 664 of Cu mining and smelting activities, due to the high values of the Cu/Mn, As/Se and 665 noteworthy that Cu Ag. and Pb mining and smelting have been 666 historically documented in Bielsa valley during pre-industrial times (Callén, 1996). 667 Indeed, MPG is only 7 km east from some of the largest lead and silver ore deposits in 668 the Pyrenees (historical mines of Parzan). The impact of ancient environmental 669 pollution in high alpine environments is archived in the lacustrine sequence of the 670 neighbouring Marboré Lake, providing first evidences of historical metal mining and 671 processing activities during the Roman Period (RP) (Corella et al., 2018, 2020). 672 Therefore, the enrichment of trace elements in MPG ice record most likely to mining activities during ancient times. Recently, 673 core record 674 western Alps have also demonstrated the suitability of glacier ice to record 675 regional mining and smelting activities during RP and pre-Roman times 676 (Preunkert et al., 2019).

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677 On the other hand, the comparison of Pb/Al ratios from the independently dated 678 records of Marboré Lake and MPG provides further support to the obtained glacier 679 chronology (Fig. 4). In particular, the lack of a Pb/Al peak characterizing the Industrial Period in the upper sequence of the MPG confirms the absence of the last two 680 centuries in MPG ice record, in agreement with the ²¹⁰Pb and ¹³⁷Cs analyses. Similarly, 681 682 the Hg concentration in the glacier is very stable throughout the ice sequence (Fig.4). Hg concentrations in other ice core records show an increase during the onset of 683 Industrialization at 1800 CE with maximum values typically 3-10 times higher than 684 preindustrial values (Cooke et al., 2020). In Marboré Lake, the Hg increase occurred 685 over the last 500 years associated to the maximum activity in the Spanish Almadén 686 687 mines during the Colonial Period (Corella et al., 2021). Again, these results, lacking an 688 expected increase in Hg levels, support the age model from the MPG record where the 689 last six centuries of ice deposition are missing. The comparison of Pb/Al ratios from the 690 independently dated records of Marboré Lake and MPG (Fig. 3) shows a reasonable 691 agreement, supporting the obtained age model for MPG ice. Particularly, the high 692 Pb/Al values in both records between the 1st-5th centuries can be explained by 693 increased Pb emissions related to the aforementioned regional mining and smelting 694 activities during the RP. Maximum Pb/Al values have been found in several natural 695 archives in the Central Pyrenees since the onset of Industrialization at 1800 CE as well 696 as in other glacier ice core archives from the Alps (Corella et al., 2017. 2018). Thus. the 697 of a Pb/Al peak in the upper sequence of the MPG again confirms the absence of 698 the last two centuries in MP ice record. Similarly, the Hg concentration in the glacier is 699 very stable throughout the ice sequence (Fig.3). Hg concentrations in other ice core 700 records preserve an increase during the onset of Industrialization at 1800 CE with 701 maximum values typically 3–10 times higher than preindustrial values (Cooke et al., 702 2020). In Marboré Lake, the mercury increase occurred over the last 500 years 703 associated to the maximum activity in the Spanish Almaden mines during the Colonial 704 Period (Corella et al., 2020). Again, these results, lacking an expected increase in Hg levels, support the age model from the MPG record where the last six centuries of ice 705 706 deposition are missing.

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¹⁷ <u>5</u>4.2. Evolution of the Monte Perdido glacier over the last 2000 years

708 The analyzed ice from MPG provides valuable information about the evolution of the 709 glacier during the last two millennia, which deserves consideration in the regional 710 context. Based on published results, the oldest paleoclimatic information in the Marboré Cirque comes from the Marboré Lake, since no glacier deposits 711 712 corresponding to the Late Pleistocene have been found in the cirque (García-Ruiz et al., 713 2014). There is sedimentological evidence that the Marboré Lake was already ice-free at least since the onset of the Bølling period (Greenland Interstadial-1, 14,600 yr BP), 714 when clastic sediments were deposited in the lake basin (Leunda et al., 2017; Oliva-715 Urcia et al., 2018). This is coherent with the nearby La Larri juxta-glacial sequence 716 which showed that the main Pineta glacier had already retreated further up in the 717 718 <u>headwater by 11 kyr BP (Salazar et al., 2013). In fact, glaciological studies performed in</u> 719 the Central Pyrenees confirm the sudden retreat of glaciers during the Bølling period, 720 when they were reduced to small ice tongues or cirque glaciers (Palacios et al., 2017). The next piece of information comes from the outermost moraine that was dated at 721 6900 ± 80<u>0 ³⁶Cl yr BP (García-Ruiz et al., 2020), corresponding to the Neoglacial</u> 722 advance, a cold period identified in the sediments of Marbore Lake (Leunda et al., 723 724 2017). Other minor advances would have occurred in MPG prior to the LIA, as inferred from three polished surfaces dated at 3500 \pm 400, 2500 \pm 300 and 1100 \pm 100 36 Cl yr 725 726 BP (García-Ruiz et al., 2020). 727

With the new chronology of the MPG record, we can ascertain that MPG has persisted 728 at least since the RP (ca. 2000 years ago). At that time, which is a well-known warm 729 period in the Iberian Peninsula as recorded in both continental (Martín-Puertas et al., 730 2010; Morellón et al., 2009) and marine sequences (Cisneros et al., 2016; Margaritelli et al., 2020), the glacier was still present, but probably smaller than during previous 731 732 Neoglacial times (Fig. 5B). This situation probably continued during the following cold 733 period, the Dark Ages (DA, Fig 5C) when the glacier advanced as indicated by the polished surface dated at 1100 ± 100 ³⁶Cl yr BP (García-Ruiz et al., 2020). In the Alps, 734 735 reconstructions based on dating trees found within and at the edge of glacier forefields 736 have revealed a minimum glacier extent during the Iron Age and the RP (Holzhauser et 737 al., 2005), when glaciers were estimated to be smaller than during the 1920s (Ivy-Ochs et al., 2009). Afterwards, in the late RP and the early Middle Ages numerous glaciers in 738

739 the Alps advanced during the DA, also known as the Göschener II oscillation 740 (Holzhauser et al., 2005). The analyzed ice from MPG provides remarkable information about the evolution of the glacier in the last two millennia, which deserves be 741 considered in the regional context. Based on published results, the oldest paleoclimatic 742 743 information in the Marboré Cirque comes from the Marboré Lake, since no glacier 744 deposits corresponding to the Late Pleistocene have been found in the cirque (García-Ruiz et al., 2014). There is sedimentological evidence that the Marboré Lake was 745 already ice-free at least since the onset of the Bølling period (Greenland Interstadial-1, 746 747 14,600 yr BP), when clastic sediments were deposited in the lake basin (Leunda et al., 2017; Oliva-Urcia et al., 2018). This is coherent with the nearby La Larri juxta-glacial 748 sequence which showed that the main Pineta glacier had already retreated further up 749 750 in the headwater by 13,245 ± 120 vr BP (Salazar et al., 2013). In fact, glaciological 751 studies performed in the Central Pyrenees confirm the sudden retreat of glaciers 752 during the Bølling period, when they were reduced to small ice tongues, cirque glaciers 753 or rock glaciers (Palacios et al., 2017).

754 Like other glaciers all over the world (Davis et al., 2009; Solomina et al., 2015), MPG likely experienced numerous spatial fluctuations during the Holocene, although 755 756 absolute dates directly obtained from moraines are uncertain. A single boulder was 757 dated from the outermost moraine corresponding to the maximum glacier expansion 758 since the Younger Dryas (recalculated at 6900 ± 800-3 Cl yr BP) (García-Ruiz et al., 759 2020) in the Marboré Cirque. This is the oldest Holocene date available for glacial 760 deposits in Spain (García-Ruiz et al., 2014), and indicates a glacier advance during the 761 Neoglacial period (Fig. 4A). Other minor advances would have occurred in MPG prior to 762 the LIA, as inferred from three polished surfaces dated at 3500 ± 400, 2500 ± 300 and 1100 ± 100 ³⁶Cl vr BP, indicating the occurrence of different deglaciation phases, and 763 764 therefore glacial re-advances prior to these dates (García-Ruiz et al., 2020). Most likely, 765 the voluminous moraine at the foot of the Monte Perdido Massif, which undoubtedly 766 was deposited during the LIA, incorporates minor moraines and till from prior 767 Neoglacial advances, as has been reported in other Pyrenean cirgues (Crest et al., 768 2017; Palacios et al., 2017).

⁷⁶⁹ With the new chronology of the MPG record, we can ascertain that MPG has persisted

770 at least since the RP (circa 2000 yr ago). At that time, which is a well known warm 771 period in the Iberian Peninsula as recorded in both continental (Martín-Puertas et al., 772 2010; Morellón et al., 2009) and marine sequences (Cisneros et al., 2016; Frigola et al., 773 2007; Nieto-Moreno et al., 2011), the glacier was still active, but probably smaller than 774 during Neoglacial times (Fig. 4B). This situation probably continued during the following cold period, the Dark Ages (DA, Fig 4C) when the glacier advanced as 775 776 indicated by the polished surface dated at 1100 ± 100 ³⁶Cl yr BP (García-Ruiz et al., 2020). In glaciers in the Alps, reconstructions based on dating trees found within and 777 778 at the edge of glacier forefields have revealed a minimum glacier extent during the 779 Iron Age and the RP (Holzhauser et al., 2005), when glaciers were estimated to be smaller than during the 1920s (Ivv-Ochs et al., 2009). Afterwards, in the late RP and the 780 early Middle Ages numerous glaciers in the Alps advanced during the DA, also known 781 782 as the Göschener II oscillation (Holzhauser et al., 2005).

783 The MCA (900–1300 CE) is the most recent preindustrial warm era in Europe (Mann et 784 al., 2009). For instance, in the Alps, a general glacier retreat has been observed during 785 this period, mainly associated with a decline in precipitation (Holzhauser et al., 2005). 786 According to the age-depth model, the MPG experienced a spectacular retreat (Fig. 787 5D), including the complete melting of some minor glaciers in the Marboré Cirque 788 (García-Ruiz et al., 2020). Nevertheless, during the MCA part of MPG was preserved, as 789 we find ice from 0 to 700 CE. No doubt the ice loss was significant, as evidenced by the 790 accumulation of dark strata over a long time interval (600 – 1200 CE) (Fig.3). On this 791 basis, we propose that the MPG was dominated by ablation processes during the MCA, 792 leading to considerable ice loss as deduced from just six meters of ice remaining from 793 this period (blue horizontal line, Fig. 3). It is evident that at the end of the MCA the MPG still preserved ice from the RP and the first half of the DA (Fig. 5D). It is difficult to 794 795 assure if Neoglacial basal ice is still present in MPG since no ice sample was dated with 796 Neoglacial age or even older. Still, Neoglacial ice can remain in the glacier base without 797 being exposed by the slope where sampling procedures were carried out. The MCA 798 (900–1300 CE) is the most recent preindustrial warm era in Europe (Mann et al., 2009). 799 For instance, in the Alps, a general glacier retreat has been observed during this 800 period, mainly associated with a decline in precipitation (Holzhauser et al., 2005).

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811 Over such a diminished MCA glacier, ice started to accumulate again at a rapid rate during the LIA (1300 – 1850 CE). In most cases, the LIA was the period when mountain 812 813 glaciers recorded their maximum Holocene extent (Solomina et al., 2016), with remarkable advances in the alpine glaciers (Ivy-Ochs et al., 2009). From a large variety 814 815 of proxies, several warm and cold periods have been identified in the Iberian Peninsula during the LIA (Oliva et al., 2018). In the Marboré Cirque two generations of LIA 816 moraines have been mapped (García-Ruiz et al., 2014), whose emplacement coincided 817 818 with the coldest LIA phases, i.e. 1620 - 1715 CE, when the Pyrenean glaciers recorded 819 their maximum extent of the last two millennia, and at some time between 1820 -820 1840 CE, when a rapid advance of the ice mass moved over the large moraine leaving 821 parallel ridges and furrows, so-called flutes, as signs of erosion (García-Ruiz et al., 822 2020; Serrano and Martín-Moreno, 2018). These two cold phases are very well 823 identified in the Marboré Cirque and were confirmed by the study of the altitudinal 824 <u>fluctuations of the timberline in the neighboring Escuaín Valley (Camarero et al., 2015).</u> 825 In fact, according to the map of Schrader from 1874 CE and other historical sources, the MPG made direct contact with the large moraine in the second half of the 19th 826 827 century (García-Ruiz et al., 2014). Despite the fact that the MPG would have covered 828 an area of 5.56 km² at the end of the LIA (in 1894 (González Trueba et al., 2008), Fig. 829 5E), there is no record today of ice accumulated during the LIA, except for a few 830 meters at the top of the sequence corresponding to about 1400 CE. This means that more than 600 years of ice accumulation have been lost associated to the warming 831

832 after ca. 1850 CE. This situation is not so common in the Alps, where ice from the LIA, 833 and even from the last two centuries, is still preserved in many studied cold glaciers 834 (Eichler et al., 2000; Gabrielli et al., 2016; Gäggeler et al., 1983; Preunkert et al., 2019). Over such a diminished MCA glacier, ice started to accumulate again at a rapid rate 835 836 during the LIA (1300–1850 CE). In most cases, the LIA was the period when mountain 837 glaciers recorded their maximum Holocene extent (Solomina et al., 2016), with remarkable advances in the alpine glaciers (Ivy-Ochs et al., 2009). From a large variety 838 839 of proxies, several warm and cold periods have been identified in the Iberian Peninsula during the LIA (Oliva et al., 2018). In the Marboré Cirque two generations of LIA 840 841 moraines have been mapped (García-Ruiz et al., 2014), whose emplacement coincided with the coldest LIA phases, i.e. 1620-1715 CE, when the Pyrenean glaciers recorded 842 843 their maximum and moment between 1820-1840 CE, when a rapid 844 mass moved over the large moraine leaving parallel furrows, or 845 signs of erosion (García-Ruiz et al., 2020; Serrano and Martín-Moreno, 2018). These two cold phases are very well identified in the Marboré Cirgue and were 846 confirmed by the study of the altitudinal fluctuations of the timberline in the 847 848 neighboring Escuaín Valley (Camarero et al., 2015). In fact, according to the map of Schrader from 1874 CE and other historical sources, the MPG made direct contact with 849 the large moraine in the second half of the 19th century (García-Ruiz et al., 2014). 850 851 would have Despite covered an area of 5 56 of the LIA (in 1894 852 <u>IGonzáloz</u> Trucha 20081 today of ice 853 accumulated during the LIA excent for the sequence 854 about 1400 CE. This means corresponding to more than 600 vears 855 accumulation have been lost associated to the warming after ca. 1850 CE. This 856 situation is not so common in the Alps, where ice from the LIA, and even from the last two centuries, is still preserved in many studied glaciers (Eichler et al., 2000; Gabrielli 857 858 et al., 2016; Gäggeler et al., 1983; Preunkert et al., 2019).

Today the MPG is divided in two small ice bodies that together cover just 0.38 km² (<u>López-Moreno et al., 2016</u><u>López-Moreno et al., 2016</u>, Fig. <u>5F4F</u>). Comparing the MPG extent at the end of the LIA (ca. 1850 CE), <u>as given bythanks to</u> the moraine location, and <u>today's extent</u>today, more than 5 km² of MPG would have disappeared, thus

indicating that the last 150 years have likely been the period with the largest glacier
melting <u>overin</u> the last 2000 years.

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865 5. Conclusions

866 This study presents for the first time a continuous chronological model of a remaining smallthe chronology of a glacier in the Pyrenees, reconstructed from a set of ¹⁴C dates 867 on different organic remains, and supported by measurements of or current 868 atmospheric deposition and comparison with a nearby lake sequence (Marboré Lake). 869 The ice sequence from MPG covers the last 2000 years, allowing the identification 870 ofdefining cold time periods of growing glaciers and warm time periods of ice 871 loss.advance and warm periods of retreat. We demonstrate that the glacier was active 872 873 during the RP, a well--known warm period in the IberianIberia Peninsula. During the 874 MCA, the MPG experienced a spectacular retreat marked by the presence of dark 875 debris layers indicative of successive years when ablation processes predominated. The LIA was a period of glacier growthadvance but is not recorded today in the ice 876 from MPG, since more than 600 years of ice accumulation have been lost associated to 877 the warming after the end of the LIA, ca. 1850 CE. This evidence from the age-depth 878 879 model is supported by the lack of anthropogenic indicators usually associated to the 880 Industrial Era abundant today in current atmospheric deposition in a nearby site. 881 Additionally, both Hg concentration and Pb/Al ratio appear much higher in the Marboré Lake sediments, whereas the MPG record does not they don't reflect their the 882 883 anthropogenic increase in the MPG record.

884 Comparing the present-day glacier situation with that of previous warm intervals, such as the RP or the MCA, we conclude that the MPG is nowadays greatly reduced in area 885 and volume. Additionally, the recent rate of ice--mass loss rate-is definitely more rapid 886 than that ofduring the four centuries spanned by the MCA, thus suggesting that 887 888 present day warming in the Pyrenees is faster and more intense than in any previous 889 warm phase of occurred during the last 2000 years. Under the current such climatic 890 conditions, it is reasonable to expect the disappearance of this glacier, as well as other 891 glaciers in the Pyrenees and in Southern Europe, over the next few decades.

892 6. Data availability

The input data file for CLAM₇ as well as the output results are stored in <u>the open</u> repository Zenodo (https://zenodo.org/record/3886911).this journal for reviewing process and will be permanently deposited in the journal upon the acceptance of this manuscript. The <u>rest ofother</u> data are <u>givenincluded</u> in the <u>paper Tablestables and in</u> the Supplementary.

898 7. Author contributions

899 The paper was conceived by A.M., M.B., C.S. and J.I.L--M. together with and-F.N., J.O-900 -G., J.L., P.G_-S., C.C., J.-L_-M., B.O_U_-S.H.F and J.G_-R. who contributed to design and develop this research project (PaleoICE). F.N., C.P., M.L., E.A. participated during field 901 work to recover the samples; A.M., M.B. and M.L. prepared the samples for ¹⁴C dating;-902 J.G.O. carried out the ²¹⁰Pb and ¹³⁷Cs analyses; J.P., X.Q. and A.A. provided the 903 geochemical data from Ordesa site and MPG; J.P.C., M.J.S. and R.M. provided the Hg 904 905 data from Marboré Lake and MPG; , C.P., M.L., E.A. helped during field work and G.G.--R. builtrun the R package CLAM 2.2 to build the age depth-model. All authors 906 contributed to discuss and interpret the data and to the writing of the original and 907 revised version of this paper. 908

909 8. Competing interest

910 The authors declare that they have no conflict of interest.

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929 10. References

- 930 Blaauw, M.: Methods and code for 'classical' age-modelling of radiocarbon sequences,
- 931 Quaternary Geochronology, 5(5), 512–518, doi:10.1016/j.quageo.2010.01.002, 2010.
- 932 Blaauw, M., Christen, J. A., Vázquez, J. E. and Goring, S.: clam: Classical Age-Depth Modelling of
- 933 Cores from Deposits. CRAN 2019, [online] Available from: https://CRAN.R-
- 934 project.org/package=clam, 2019.
- 935 Büntgen, U., Krusic, P. J., Verstege, A., Sangüesa-Barreda, G., Wagner, S., Camarero, J. J.,
- 936 Ljungqvist, F. C., Zorita, E., Oppenheimer, C., Konter, O., Tegel, W., Gärtner, H., Cherubini, P.,
- 937 Reinig, F. and Esper, J.: New Tree-Ring Evidence from the Pyrenees Reveals Western
- 938 Mediterranean Climate Variability since Medieval Times, J. Climate, 30(14), 5295–5318,
- 939 doi:10.1175/JCLI-D-16-0526.1, 2017.
- Callén, J. J. N.: El proceso sidero-metarlúrgico altoaragonés: los valles de Bielsa y Gistain en la
 Edad Moderna (1565-1800), Llull: Revista de la Sociedad Española de Historia de las Ciencias y
- 942 de las Técnicas, 19(37), 471–508, 1996.
- 943 Camarero, J. J., García-Ruiz, J. M., Sangüesa-Barreda, G., Galván, J. D., Alla, A. Q., Sanjuán, Y.,
- 944 Beguería, S. and Gutiérrez, E.: Recent and Intense Dynamics in a Formerly Static Pyrenean
- 945 Treeline, Arctic, Antarctic, and Alpine Research, 47(4), 773–783, doi:10.1657/AAAR0015-001,
 946 2015.
- 947 Cisneros, M., Cacho, I., Frigola, J., Canals, M., Masqué, P., Martrat, B., Casado, M., Grimalt, J.
- 948 O., Pena, L. D., Margaritelli, G. and Lirer, F.: Sea surface temperature variability in the central-
- 949 western Mediterranean Sea during the last 2700 years: a multi-proxy and multi-record
- 950 approach, Clim. Past, 12(4), 849–869, doi:10.5194/cp-12-849-2016, 2016.
- Cooke, C. A., Martínez-Cortizas, A., Bindler, R. and Sexauer Gustin, M.: Environmental archives
 of atmospheric Hg deposition A review, Science of The Total Environment, 709, 134800,
 doi:10.1016/j.scitotenv.2019.134800, 2020.
- Corella, J. P., Valero-Garcés, B. L., Wang, F., Martínez-Cortizas, A., Cuevas, C. A. and Saiz-Lopez,
 A.: 700 years reconstruction of mercury and lead atmospheric deposition in the Pyrenees (NE
- 956 Spain), Atmospheric Environment, 155, 97–107, doi:10.1016/j.atmosenv.2017.02.018, 2017.
- 957 Corella, J. P., Saiz-Lopez, A., Sierra, M. J., Mata, M. P., Millán, R., Morellón, M., Cuevas, C. A.,
- 958 Moreno, A. and Valero-Garcés, B. L.: Trace metal enrichment during the Industrial Period
- 959 recorded across an altitudinal transect in the Southern Central Pyrenees, Science of The Total
- 960 Environment, 645, 761–772, doi:10.1016/j.scitotenv.2018.07.160, 2018.

- 961 Corella, J. P., Sierra, M. J., Garralón, A., Millán, R., Rodríguez-Alonso, J., Mata, M. P., Wilhem,
- 962 B., Vivez, P., Duval, B., Amouroux, D., Vicente de Vera, A., Moreno, A., Cuevas, C. A., Adame, J.
- 963 A., Saiz-Lopez, A. and Valero Garcés, B.: Legacy pollution from roman and medieval mining in
- the Iberian Peninsula recorded in high mountain ecosystems, Science of The Total
- 965 Environment, under review, 2020.
- 966 Crest, Y., Delmas, M., Braucher, R., Gunnell, Y. and Calvet, M.: Cirques have growth spurts
- 967 during deglacial and interglacial periods: Evidence from 10Be and 26Al nuclide inventories in
- 968 the central and eastern Pyrenees, Geomorphology, 278, 60–77,
- 969 doi:10.1016/j.geomorph.2016.10.035, 2017.
- 970 Davis, P. T., Menounos, B. and Osborn, G.: Holocene and latest Pleistocene alpine glacier
- 971 fluctuations: a global perspective, Quaternary Science Reviews, 28(21–22), 2021–2033,
 972 doi:10.1016/j.quascirev.2009.05.020, 2009.
- 973 Eichler, A., Schwikowski, M., Gäggeler, H. W., Furrer, V., Synal, H.-A., Beer, J., Saurer, M. and
- Funk, M.: Glaciochemical dating of an ice core from upper Grenzgletscher (4200 m a.s.l.),
 Journal of Glaciology, 46(154), 507–515, doi:10.3189/172756500781833098, 2000.
- 976 Ewing, M. E., Reese, C. A. and Nolan, M. A.: The potential effects of percolating snowmelt on
- palynological records from firn and glacier ice, Journal of Glaciology, 60(222), 661–669,
- 978 doi:10.3189/2014JoG13J158, 2014.
- 979 Festi, D., Carturan, L., Kofler, W., dalla Fontana, G., de Blasi, F., Cazorzi, F., Bucher, E., Mair, V.,
- 980 Gabrielli, P. and Oeggl, K.: Linking pollen deposition, snow accumulation and isotopic
- 981 composition on the Alto dell'Ortles glacier (South Tyrol, Italy) for sub-seasonal dating of a firn
- temperate core, The Cryosphere Discussions, 1–16, doi:10.5194/tc-2016-221, 2016.
- 983 Frigola, J., Moreno, A., Cacho, I., Canals, M., Sierro, F. J., Flores, J. A., Grimalt, J. O., Hodell, D. A.
- 984 and Curtis, J. H.: Holocene climate variability in the western Mediterranean region from a
- 985 deepwater sediment record, Paleoceanography, 22(doi:10.1029/2006PA001307), 2007.
- 986 Gabrielli, P., Barbante, C., Bertagna, G., Bertó, M., Binder, D., Carton, A., Carturan, L., Cazorzi,
- 987 F., Cozzi, G., Dalla Fontana, G., Davis, M., De Blasi, F., Dinale, R., Dragà, G., Dreossi, G., Festi, D.,
- 988 Frezzotti, M., Gabrieli, J., Galos, S. P., Ginot, P., Heidenwolf, P., Jenk, T. M., Kehrwald, N.,
- 989 Kenny, D., Magand, O., Mair, V., Mikhalenko, V., Lin, P. N., Oeggl, K., Piffer, G., Rinaldi, M.,
- 990 Schotterer, U., Schwikowski, M., Seppi, R., Spolaor, A., Stenni, B., Tonidandel, D., Uglietti, C.,
- 22 Zagorodnov, V., Zanoner, T. and Zennaro, P.: Age of the Mt. Ortles ice cores, the Tyrolean
 23 Iceman and glaciation of the highest summit of South Tyrol since the Northern Hemisphere
- 993 Climatic Optimum, The Cryosphere, 10(6), 2779–2797, doi:10.5194/tc-10-2779-2016, 2016.
- Gäggeler, H., Gunten, H. R. von, Rössler, E., Oeschger, H. and Schotterer, U.: 210Pb-Dating of
 Cold Alpine Firn/Ice Cores From Colle Gnifetti, Switzerland, Journal of Glaciology, 29(101),
- 996 165–177, doi:10.1017/S0022143000005220, 1983.
- 997 García-Ruiz, J. M., Palacios, D., Andrés, N. de, Valero-Garcés, B. L., López-Moreno, J. I. and
- Sanjuán, Y.: Holocene and 'Little Ice Age' glacial activity in the Marboré Cirque, Monte Perdido
 Massif, Central Spanish Pyrenees, The Holocene, 24(11), 1439–1452,
- 1000 doi:10.1177/0959683614544053, 2014.
- 1001 García-Ruiz, J.M., Palacios, D., Andrés, N., López-Moreno, J.I.: Neoglaciation in the Spanish
- 1002 Pyrenees: A multiproxy challenge. Mediterranean Geoscience Reviews.
- 1003 https://doi.org/10.1007/s42990-020-00022-9, 2020.

- 1004 Garzonio, R., Di Mauro, B., Strigaro, D., Rossini, M., Colombo, R., De Amicis, M. and Maggi, V.:
- 1005 Mapping the suitability for ice-core drilling of glaciers in the European Alps and the Asian High 1006 Mountains, J. Glaciol., 64(243), 12–26, doi:10.1017/jog.2017.75, 2018.
- 1007 Gellatly, A. F., Grove, J. M. and Switsur, V. R.: Mid-Holocene glacial activity in the Pyrenees, The 1008 Holocene, 2(3), 266–270, doi:10.1177/095968369200200309, 1992.
- 1009 González Trueba, J. J., Moreno, R. M., Martínez de Pisón, E. and Serrano, E.: `Little Ice Age'
- 1010 glaciation and current glaciers in the Iberian Peninsula, The Holocene, 18(4), 551–568,
- 1011 doi:10.1177/0959683608089209, 2008.
- 1012 Haeberli, W., Frauenfelder, R., Kääb, A. and Wagner, S.: Characteristics and potential climatic
- 1013 significance of "miniature ice caps" (crest- and cornice-type low-altitude ice archives), Journal
- 1014 of Glaciology, 50(168), 129–136, doi:10.3189/172756504781830330, 2004.
- 1015 Herren, P.-A., Eichler, A., Machguth, H., Papina, T., Tobler, L., Zapf, A. and Schwikowski, M.: The
- 1016 onset of Neoglaciation 6000 years ago in western Mongolia revealed by an ice core from the
- 1017 Tsambagarav mountain range, Quaternary Science Reviews, 69, 59–68,
- 1018 doi:10.1016/j.quascirev.2013.02.025, 2013.
- Holzhauser, H., Magny, M. and Zumbühl, H. J.: Glacier and lake-level variations in west-central
 Europe over the last 3500 years, The Holocene, 15(6), 789–801, 2005.
- Hughes, P. D.: Little Ice Age glaciers and climate in the Mediterranean mountains: a newanalysis, CIG, 44(1), 15, doi:10.18172/cig.3362, 2018.
- 1023 Ivy-Ochs, S., Kerschner, H., Maisch, M., Christl, M., Kubik, P. W. and Schlüchter, C.: Latest
- Pleistocene and Holocene glacier variations in the European Alps, Quaternary Science Reviews,
 28(21–22), 2137–2149, 2009.
- 1026 Jenk, T. M., Szidat, S., Bolius, D., Sigl, M., Gäggeler, H. W., Wacker, L., Ruff, M., Barbante, C.,
- 1027 Boutron, C. F. and Schwikowski, M.: A novel radiocarbon dating technique applied to an ice
- 1028 core from the Alps indicating late Pleistocene ages, Journal of Geophysical Research:
- 1029 Atmospheres, 114(D14), doi:10.1029/2009JD011860, 2009.
- 1030 Leunda, M., González-Sampériz, P., Gil-Romera, G., Aranbarri, J., Moreno, A., Oliva-Urcia, B.,
- 1031 Sevilla-Callejo, M. and Valero-Garcés, B.: The Late-Glacial and Holocene Marboré Lake
- 1032 sequence (2612m a.s.l., Central Pyrenees, Spain): Testing high altitude sites sensitivity to
- millennial scale vegetation and climate variability, Global and Planetary Change, 157, 214–231,
 doi:10.1016/j.gloplacha.2017.08.008, 2017.
- 1035 López-Moreno, J. I., Revuelto, J., Rico, I., Chueca-Cía, J., Julián, A., Serreta, A., Serrano, E.,
- 1036 Vicente-Serrano, S. M., Azorin-Molina, C., Alonso-González, E. and García-Ruiz, J. M.: Thinning
- of the Monte Perdido Glacier in the Spanish Pyrenees since 1981, The Cryosphere, 10(2), 681–
 694, doi:10.5194/tc-10-681-2016, 2016.
- 1039 López-Moreno, J. I., Alonso-González, E., Monserrat, O., Del Río, L. M., Otero, J., Lapazaran, J.,
- 1040 Luzi, G., Dematteis, N., Serreta, A., Rico, I., Serrano-Cañadas, E., Bartolomé, M., Moreno, A.,
- 1041 Buisan, S. and Revuelto, J.: Ground-based remote-sensing techniques for diagnosis of the
- 1042 current state and recent evolution of the Monte Perdido Glacier, Spanish Pyrenees, J. Glaciol.,
- 1043 65(249), 85–100, doi:10.1017/jog.2018.96, 2019.

- 1044 Mann, M. E., Zhang, Z., Rutherford, S., Bradley, R. S., Hughes, M. K., Shindell, D., Ammann, C.,
- 1045 Faluvegi, G. and Ni, F.: Global Signatures and Dynamical Origins of the Little Ice Age and 1046
- Medieval Climate Anomaly, Science, 326(5957), 1256–1260, 2009.
- 1047 Martín-Puertas, C., Jiménez-Espejo, F., Martínez-Ruiz, F., Nieto-Moreno, V., Rodrigo, M., Mata,
- 1048 M. P. and Valero-Garcés, B. L.: Late Holocene climate variability in the southwestern
- 1049 Mediterranean region: an integrated marine and terrestrial geochemical approach, Clim. Past,
- 1050 6(6), 807-816, doi:10.5194/cp-6-807-2010, 2010.
- 1051 Marzeion, B., Cogley, J. G., Richter, K. and Parkes, D.: Attribution of global glacier mass loss to
- 1052 anthropogenic and natural causes, Science, 345(6199), 919-921,
- 1053 doi:10.1126/science.1254702, 2014.
- 1054 Moore, P. D., Webb, J. A. and Collinson, M. E.: Pollen Analysis, Second., Blackwell Scientific 1055 Publications., 1991.
- 1056 Morellón, M., Valero-Garcés, B., Vegas-Vilarrúbia, T., González-Sampériz, P., Romero, Ó.,
- 1057 Delgado-Huertas, A., Mata, P., Moreno, A., Rico, M. and Corella, J. P.: Lateglacial and Holocene
- 1058 palaeohydrology in the western Mediterranean region: The Lake Estanya record (NE Spain), 1059 Quaternary Science Reviews, 28(25-26), 2582-2599, 2009.
- 1060 Nieto-Moreno, V., Martínez-Ruiz, F., Giralt, S., Jiménez-Espejo, F., Gallego-Torres, D., Rodrigo-
- 1061 Gámiz, M., García-Orellana, J., Ortega-Huertas, M. and de Lange, G. J.: Tracking climate
- 1062 variability in the western Mediterranean during the Late Holocene: a multiproxy approach,
- 1063 Clim. Past Discuss., 7(1), 635–675, doi:10.5194/cpd-7-635-2011, 2011.
- 1064 Oerlemans, J.: Glaciers and Climate Change, CRC Press., 2001.
- 1065 Oliva, M., Ruiz-Fernández, J., Barriendos, M., Benito, G., Cuadrat, J. M., Domínguez-Castro, F.,
- 1066 García-Ruiz, J. M., Giralt, S., Gómez-Ortiz, A., Hernández, A., López-Costas, O., López-Moreno,
- 1067 J. I., López-Sáez, J. A., Martínez-Cortizas, A., Moreno, A., Prohom, M., Saz, M. A., Serrano, E.,
- Tejedor, E., Trigo, R., Valero-Garcés, B. and Vicente-Serrano, S. M.: The Little Ice Age in Iberian 1068 mountains, Earth-Science Reviews, 177, 175–208, doi:10.1016/j.earscirev.2017.11.010, 2018. 1069
- 1070
- Oliva-Urcia, B., Moreno, A., Leunda, M., Valero-Garcés, B., González-Sampériz, P., Gil-Romera, 1071 G., Mata, M. P. and Group, H.: Last deglaciation and Holocene environmental change at high
- 1072 altitude in the Pyrenees: the geochemical and paleomagnetic record from Marboré Lake (N
- Spain), J Paleolimnol, 59(3), 349–371, doi:10.1007/s10933-017-0013-9, 2018. 1073
- 1074 Palacios, D., García-Ruiz, J. M., Andrés, N., Schimmelpfennig, I., Campos, N., Léanni, L.,
- 1075 Aumaître, G., Bourlès, D. L. and Keddadouche, K.: Deglaciation in the central Pyrenees during
- 1076 the Pleistocene–Holocene transition: Timing and geomorphological significance, Quaternary
- 1077 Science Reviews, 162, 111–127, doi:10.1016/j.quascirev.2017.03.007, 2017.
- 1078 Pey, J., Pérez, N., Cortés, J., Alastuey, A. and Querol, X.: Chemical fingerprint and impact of
- 1079 shipping emissions over a western Mediterranean metropolis: Primary and aged contributions,
- Science of The Total Environment, 463–464, 497–507, doi:10.1016/j.scitotenv.2013.06.061, 1080
- 1081 2013.
- 1082 Preunkert, S., McConnell, J. R., Hoffmann, H., Legrand, M., Wilson, A. I., Eckhardt, S., Stohl, A.,
- 1083 Chellman, N. J., Arienzo, M. M. and Friedrich, R.: Lead and Antimony in Basal Ice From Col du
- 1084 Dome (French Alps) Dated With Radiocarbon: A Record of Pollution During Antiquity,
- 1085 Geophysical Research Letters, 46(9), 4953–4961, doi:10.1029/2019GL082641, 2019.

- 1086 Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J.,
- 1087 Sánchez de la Campa, A., Artíñano, B., Salvador, P., García Dos Santos, S., Fernández-Patier, R.,
- 1088 Moreno-Grau, S., Negral, L., Minguillón, M. C., Monfort, E., Gil, J. I., Inza, A., Ortega, L. A.,
- 1089 Santamaría, J. M. and Zabalza, J.: Source origin of trace elements in PM from regional
- 1090 background, urban and industrial sites of Spain, Atmospheric Environment, 41(34), 7219–7231,
- 1091 doi:10.1016/j.atmosenv.2007.05.022, 2007.
- 1092 Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E., Cheng,
- 1093 H., Edwards, R. L., Friedrich, M. and others: IntCal13 and Marine13 radiocarbon age calibration
- 1094 curves 0–50,000 years cal BP, Radiocarbon, 55(4), 1869–1887, 2013.
- 1095 Rico, I., Izagirre, E., Serrano, E. and López-Moreno, J. I.: Superficie glaciar actual en los Pirineos:
 1096 Una actualización para 2016, Pirineos, 172(0), 029, doi:10.3989/Pirineos.2017.172004, 2017.
- Salazar, A., Mata, M. P., Rico, M., Valero-Garcés, Oliva-Urcia, B. and Rubio, F. M.: El paleolago
 de La Larri (Valle de Pineta, Pirineos), Cuadernos de Investigación Geográfica, 39(1), 97–116,
 2013.
- 1100 Sanchez-Cabeza, J. A., Masqué, P. and Ani-Ragolta, I.: 210Pb and 210Po analysis in sediments
- and soils by microwave acid digestion, J Radioanal Nucl Chem, 227(1), 19–22,
- 1102 doi:10.1007/BF02386425, 1998.
- Serrano, E. and Martín-Moreno, R.: Surge glaciers during the Little Ice Age in the Pyrenees,
 Cuadernos de Investigación Geográfica, 44(1), 213–244, doi:10.18172/cig.3399, 2018.
- 1105 Solomina, O. N., Bradley, R. S., Hodgson, D. A., Ivy-Ochs, S., Jomelli, V., Mackintosh, A. N.,
- 1106 Nesje, A., Owen, L. A., Wanner, H., Wiles, G. C. and Young, N. E.: Holocene glacier fluctuations,
- 1107 Quaternary Science Reviews, 111, 9–34, doi:10.1016/j.quascirev.2014.11.018, 2015.
- 1108 Solomina, O. N., Bradley, R. S., Jomelli, V., Geirsdottir, A., Kaufman, D. S., Koch, J., McKay, N. P.,
- 1109 Masiokas, M., Miller, G., Nesje, A., Nicolussi, K., Owen, L. A., Putnam, A. E., Wanner, H., Wiles,
- 1110 G. and Yang, B.: Glacier fluctuations during the past 2000 years, Quaternary Science Reviews,
- 1111 149, 61–90, doi:10.1016/j.quascirev.2016.04.008, 2016.
- 1112 Taylor, S. R. and McLennan, S. M.: The geochemical evolution of the continental crust, Reviews1113 of Geophysics, 33, 241–265, 1995.
- 1114 Thompson, L. G., Mosley-Thompson, E., Brecher, H., Davis, M., Leon, B., Les, D., Lin, P.-N.,
- Mashiotta, T. and Mountain, K.: Abrupt tropical climate change: Past and present, Proceedings
 of the National Academy of Sciences, 103(28), 10536–10543, doi:10.1073/pnas.0603900103,
 2006.
- 1118 Uglietti, C., Zapf, A., Jenk, T. M., Sigl, M., Szidat, S., Salazar, G. and Schwikowski, M.:
- 1119 Radiocarbon dating of glacier ice: overview, optimisation, validation and potential, The
- 1120 Cryosphere, 10(6), 3091–3105, doi:10.5194/tc-10-3091-2016, 2016.
- 1121 Wanner, H., Solomina, O., Grosjean, M., Ritz, S. P. and Jetel, M.: Structure and origin of
- 1122 Holocene cold events, Quaternary Science Reviews, 30(21–22), 3109–3123,
- 1123 doi:10.1016/j.quascirev.2011.07.010, 2011.
- 1124 Zemp, M., Frey, H., Gärtner-Roer, I., Nussbaumer, S. U., Hoelzle, M., Paul, F., Haeberli, W.,
- 1125 Denzinger, F., Ahlstrøm, A. P., Anderson, B., Bajracharya, S., Baroni, C., Braun, L. N., Cáceres, B.
- 1126 E., Casassa, G., Cobos, G., Dávila, L. R., Granados, H. D., Demuth, M. N., Espizua, L., Fischer, A.,

1127 Fujita, K., Gadek, B., Ghazanfar, A., Hagen, J. O., Holmlund, P., Karimi, N., Li, Z., Pelto, M., Pitte,

1128 P., Popovnin, V. V., Portocarrero, C. A., Prinz, R., Sangewar, C. V., Severskiy, I., Sigurðsson, O.,

Soruco, A., Usubaliev, R. and Vincent, C.: Historically unprecedented global glacier decline in

1130 the early 21st century, Journal of Glaciology, 61(228), 745–762, doi:10.3189/2015JoG15J017,

- 1131 2015.
- 1132 Zemp, M., Huss, M., Thibert, E., Eckert, N., McNabb, R., Huber, J., Barandun, M., Machguth, H.,
- 1133 Nussbaumer, S. U., Gärtner-Roer, I., Thomson, L., Paul, F., Maussion, F., Kutuzov, S. and Cogley,
- 1134 J. G.: Global glacier mass changes and their contributions to sea-level rise from 1961 to 2016,
- 1135 Nature, 568(7752), 382–386, doi:10.1038/s41586-019-1071-0, 2019.
- 1136

Con formato: Fuente: 12 pto



Figure 1. (left) Location of Monte Perdido Glacier (MPG) within a digital elevation map
of Marboré Cirque₂- (right) Picture (©Google Earth) of MPG where the location of the
sampled profilesamples is indicated (see Fig. 2). - Note the different orientation of both
figures.



Con formato: Inglés (Estados Unidos)



1152 at the bottom of the lower glacier. Note the inset with a detailed view of the sampling

1153 procedure measuring a height difference of 1 m to obtain every sample. (B) Image of

1154 <u>the Monte Perdido glacier surface where the sampling was carried out (red line I- II</u>

1155 represents the sampled profile shown in Figure 1). Note the presence of dark debris1156 rich layers alternating with cleaner ice. (C). Detailed view indicating that every sample

1157 consisted in 3-4 small horizontally-drilled cylinders (see text for more details).





1159

Figure 2. Figure 3. Age model for the Monte Perdido ice sequence based on linear 1161 interpolation of ¹⁴C data (Table 3), obtained using the Clam software (Blaauw, 2010; 1162 1163 Blaauw et al., 2019). Y axis indicates the number of samples from MP-0 to MP-100 (see 1164 Fig. 2). The dates appear as the calendar-age probability distributions in blue, while the black line is the resulting depth-age model and the gray envelope shows the 95 % 1165 1166 confidence interval. Note the hiatus located at 73 m indicated by a dashed line. The error of sample MP59m is so high that appears as a horizontal line. Composite depth-1167 Monte Perdido ice sequence based on linear interpolation of ¹⁴C 1168 age 1169 data (Table 1), obtained using the Clam software (Blaauw, 2010; Blaauw et al., 2019). 1170 dates appear as the calendar-age probability distributions in blue, while the black The 1171 envelope shows the 95% confidence resulting depth model and the gray 1172 interval. Note the hiatus located at 73m indicated by a dashed line.

1173

Con formato: Inglés (Estados Unidos)











Figure 54. Geomorphic transects (south to north) taken from the Marboré Cirque, 1185 showing the tentativeschematic reconstruction of MPG during the six main stages 1186 discussed in the text. A) Neoglacial Period (ca. 5000 - 6000 cal yr BP) where the 1187 Neoglacial moraine is indicated (García-Ruiz et al., 2014)(García-Ruiz et al., 2014); (B) 1188 Roman Period (0-500 CE) when the glacier is shown considerably retreated; (C) Dark 1189 Ages (500-900 CE); (D) Medieval Climate Anomaly (900-1300 CE), a period when the 1190 1191 glacier retreated and ablation caused a concentration of made condensing debris and 1192 organic remains form dark layers in the glacier ice (discontinuous line aims to highlight 1193 the importance of melting processes); (E) Little Ice Age (1300-1850 CE), with the MPG 1194 reaching the LIA moraines position and (F) present-day situation characterized by the MPG divided into two ice bodies, no ice remaining from the LIA, and very steep slopes. 1195

Table 1. Concentrations of ¹³⁷Cs in the soluble water fraction of ice from Monte

1198 <u>Perdido samples.</u>

Sample	Mass of ice analyzed	MDA
Sample	<u>(g)</u>	<u>(Bq·L⁻¹)</u>
<u>MP-61</u>	<u>240</u>	<u>0.15</u>
<u>MP-82</u>	<u>178</u>	<u>0.16</u>
<u>MP-97</u>	<u>232</u>	<u>0.14</u>
<u>MP-98</u>	<u>376</u>	<u>0.09</u>
<u>MP-100</u>	<u>238</u>	<u>0.17</u>

Table 2. Determination of ²¹⁰Pb activity in the soluble water fraction of 100 g of ice

1201	from Monte	Perdido samples.	
	Comula	²¹⁰ Pb activity	MDA
	Sample	<u>(Bq·L⁻¹)</u>	<u>(Bq·L⁻¹)</u>
	<u>MP-73</u>	<u>17.4 ± 2.6</u>	<u>1.14</u>
	<u>MP-76</u>	<u>6.2 ± 1.3</u>	<u>0.70</u>
	<u>MP-82</u>	<u><mda< u=""></mda<></u>	<u>0.61</u>
	<u>MP-85</u>	<u><mda< u=""></mda<></u>	<u>0.84</u>
	<u>MP-88</u>	<u><mda< u=""></mda<></u>	<u>1.23</u>
	<u>MP-91</u>	<u><mda< u=""></mda<></u>	<u>1.05</u>
	<u>MP-94</u>	<u><mda< u=""></mda<></u>	<u>0.71</u>
	<u>MP-97</u>	<u><mda< u=""></mda<></u>	<u>0.77</u>
	<u>MP98</u>	<u><mda< u=""></mda<></u>	<u>0.58</u>
	<u>MP-100</u>	<u>8.5 ± 1.5</u>	<u>0.71</u>
1202			

1204 Table 3. Table 1. Radiocarbon dating of MPG samples indicating their origin, the 1205 radiocarbon age (¹⁴C age BP) and the calibrated date using INTCAL13 curve and 1206 presented in calendar years Common Era (CE). Samples in red and *italics* were not 1207 included in the age model (see <u>column "comments" and</u> text for explanation).

							_
sboratory ID pth (r base		Sample Image: state stat		Cal age (CE)	<u>Comm</u> <u>ents</u>		
÷	Bulk organic matter	<u>MP-1</u>	<u>D-AMS</u> 025291	2000±64	8±66	Used in the age <u>model</u>	
<u>MP-</u> <u>42</u> 10	<u>D-AMS</u> 025294 WIOC		812±755<u>15</u> 54±27	<u>854±72146</u> <u>2±32</u>	Used in the a	ige model	
<u>MP-48</u>	D-4 025295	AMS <u>031464</u>	30<u>73±33</u>	<u>1897±20</u> pol len concentrati on	3906±42 <u>Disc</u> arded due to <u>plastic</u> <u>contaminati</u> on,	= 2384±13 32	
<u>MP-67</u>	, D-4 025296	AMS 2 <mark>025294</mark>	<mark>42<u>876±29</u></mark>	bulk organic matter <u>1185</u> <u>±31</u>	1554±27<u>Use</u> d in the age model	462±32	
<u>MP-68</u>	D-/ 026592	AMS 2 <mark>025295</mark>	4 <u>81128±22</u>	bulk organic matter <u>942±</u> 24	73±33Used <u>in the age</u> <u>model</u>	1897±20	
MP5 <u>MP-</u>		<u>AMS</u> 3 WIQC	926±268<u>12</u> 30±23	1046±242<u>7</u> 30±14	Used in the a	ige model	
<u>MP-70</u>	D-4	AMS 2 <mark>025296</mark>	67 <u>1308±28</u>	bulk organic matter <u>680±</u> <u>16</u>	876±29<u>Used</u> in the age <u>model</u>	1185±31	
<u>MP-73</u>	D-/ 025298	AMS <u>8</u> 029894	67<u>1011±25</u>	bulk material (filter) <u>1012</u> <u>±16</u>	4 85±40 Used in the age <u>model</u>	1429±15	
<u>MP-</u> <u>100</u>	D-4 <u>025299</u>	AMS 2 <mark>026592</mark>	<mark>68</mark> 923±39	bulk organic matter <u>1074</u> <u>±31</u>	<u>1128±22Use</u> <u>d in the age</u> <u>model</u>	942±24	
	atory ++ <u>MP-48</u> <u>MP-67</u> MP-68 MP-70 MP-70 MP-73 MP-73	Sample originde originde pth (m from base) t MP- 4210 02529 MP-48 02529 MP-67 02529 MP-68 02529 MP-68 02529 MP-69 02529 MP-68 02529 MP-70 02529 MP-70 02529 MP-73 MP-73 MP-70 02529	Sample originde pth (m hose)Sample pase)Image: selection of the s	Sample originde pth (m from base)Sample Description ption Description ption Description 	Sample originde pth (mSample D Laboratory D $1^{14}Cage$ BP r_{+} $\frac{1}{20}$ $\frac{1}{10}$ $\frac{1}{$	Sample originde pth (m from base)Sample IDdescri ption ptionLaboratory ID 1^{4} Cage BPCalage Calage BP-++ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ Calage BP(CE)-++ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ -++ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ -++ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ MP- $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ MP-48 $\frac{D-AMS}{025295031464}$ $\frac{3073+33}{2025295031464}$ $\frac{1897+20004}{16}$ $\frac{1897+20004}{16}$ $\frac{19064432015c}{07464 due to to plasticcontaminati0\pi\frac{3073+33}{0\pi}\frac{1897+20004}{16}\frac{3064432015c}{07464 due to to plasticcontaminati0\pi\frac{3073+33}{0\pi}\frac{1897+20004}{16}\frac{35544274}{0\pi}\frac{19064432015c}{07464 due to to plasticcontaminati0\pi\frac{3073+33}{0\pi}\frac{1897+20004}{16}\frac{15544274}{12}\frac{19064432015c}{07464 due to to plasticcontaminati0\pi\frac{1120422427}{0\pi}\frac{19064432015c}{0\pi}\frac{1120422427}{12}\frac{1104642427}{12}\frac{1104642427}{12}\frac{1104642427}{14}\frac{1120422427}{14}\frac{1120422427}{16}\frac{116}{116}\frac{11204224215c}{116}\frac{11204224215c}{116}\frac{11204224215c}{116}\frac{11204224215c}{116}\frac{1120422215c}{116}\frac{1120422215c}{116}\frac{1120422215c}{116}11$	Sample originate pth (m base) Sample iDdescri ption base) Laboratory iD 14 C age BP Cal age Cal age BP Comm ents

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rial (filter)	<u>MP-</u> <u>67filte</u> <u>r</u>	D- <u>02989</u>	-AMS 9 <u>4026593</u>	69<u>485±40</u>	bulk organic matter <u>1429</u> <u>±15</u>	1230±23 Disc arded due to mixing with	730±14	• •
<u>Bulk mate</u>	<u>MP-</u> <u>81filte</u> <u>r</u>	D- <u>03397</u>	-AMS 2 <u>2025297</u>	70<u>1758±25</u>	bulk organic matter <u>287±</u> <u>68</u>	<u>detrital</u> <u>fraction</u>	680±16	4
<u>WIO</u>	<u>MP10</u>	<u>MP10</u>) <u>m</u> pollen	1787±37<u>81</u>	237±255<u>85</u>	<u>Discarded du</u>	<u>ie to too</u>	•
<u>C</u> Ð-	<u>m</u> 70	conce	entration	<u>2±755</u>	<u>4±721</u>	<u>high er</u>	error	
AMS 0314	<u>MP59</u> <u>m73</u>	<u>MP59m</u> bulk organic matter		1011±25<u>92</u> <u>6±268</u>	1012±16<u>10</u> 46±242	Used in the a	<u>ge model</u>	•
ation	<u>MP-</u> <u>30poll</u> <u>en</u>	D- <u>03146</u>	-AMS 5 <u>4033972</u>	81 <u>3906±42</u>	bulk material (filter) <u>-</u> 2384±1332	1758±25Disc arded due to technical	287±68	• •
len concentra	<u>MP-</u> 70poll <u>en</u>	D- <u>03146</u>	-AMS <u>55025299</u>	100 <u>1787±3</u> <u>7</u>	bulk organic matter <u>237±</u> <u>255</u>	too high <u>errors</u>	1074±31	•
lod	<u>MP-</u> <u>100pol</u> <u>len</u>	D-AMS 03146 6	100	pollen co i	ncentration	1854±30	158±80 7	• •

1209 Table 42. Elemental concentration (ppm) of major and trace metals in both Ordesa's 1210 current deposited dust and MPG ice deposits (averaged values for the 35 analyzed samples), as well as); Upper Crust (UC) elemental contents for comparison (Taylor and 1211 McLennan, 1995). On the right side, (Taylor and McLennan, 1995); and Al-normalised 1212 1213 Enrichment Factors (EF) for dust components and elements for: EF,Ef, the MPG ice 1214 dust versus the current Ordesa's deposited dust (CODD); EF_{iCODD}, the CODD versus the Upper Crust (UC:); and EF impgid, the MPG ice dust versus the UC. Numbers in bold type 1215 in the EF represent anomalous values (elements enriched in Ordesa samples or in MPG 1216 1217 ones).

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