Review of the paper entitled “A multimillennial Alpine ice core chronology synchronized with an accurately dated Arc0c Pb record” by Paolo Gabrielli and co-workers.

Overall comment: Whereas several points raised during previous reviews had permitted to improve and clarify the manuscript, there are still points that need to be considered as detailed below.

We thank very much Reviewer #3 for carefully reviewing our paper and sending constructive suggestions. This is greatly appreciated.

Introduction, Page 3, Line 8: Please specify that the ice-core record extracted from the Weißseespitze (3500 m, Austria) by Bohleber et al. (2020) covers some 5,900 years, and that in Western Alps the Dôme du Goûter record covers at least the last 12,000 years (Legrand et al., 2025). Reporting these previous findings here will permit to the readers to before understand the meaning of the first sentence in the introduction that “your record is of one of the oldest Alpine ice core records”. Reversely, it is not necessarily needed to refer again to Legrand et al. (2025) at line 13 (also page 3) for 14C.

We have now added the two references and deleted Legrand et al. (2025) at line 13 (page 3) as suggested. Since our study has a particular focus on the importance of absolute dating, we will cite those in the context of their oldest dated ^{14}C age which is 5.9±0.7 kyr cal BP for Weissseespitze and 9.4±0.4 kyr cal BP for Dôme du Goûter, with the latter estimated to reach at least an age of 12 kyr BP based on the $\delta^{18}O$ signal matched to corresponding records from a Greenland ice core and from German and Swiss lake sediments.

We have modified the manuscript text accordingly: “Our discovery of millennial-age ice in the Eastern Alps was confirmed by another ice core record extracted from the nearby drilling site of Weißseespitze (3500 m, Austria) where ^{14}C dating above the basal ice resulted in an age of 5.9±0.7 kyr cal BP (Bohleber et al., 2020). Together these two studies expand findings from the Western Alps, where even older bottom ice was discovered at Colle Gnifetti (^{14}C date of >15 kyr cal BP; Jenk et al. 2009) and at Dôme du Goûter (9.4±0.4 kyr cal BP, with ice below estimated to be at least 12 kyr; Legrand et al., 2025), to the Eastern sector of the Alps.”

The crustal Pb contribution: Page 15, line 20: Please specify that the site-specific Pb to Rb mass ratio of 0.51 that you derived is reasonably consistent with the mean sediment composition (Pb/Rb of 0.14 from Bowen, 1966).

H. Bowen, Trace Elements in Biochemistry (Academic Press, New York, 1966).

We fully agree that a reference is needed. We note that this ratio (Pb/Rb = 0.14) is also consistent with the one (0.15) provided for the Upper Crust by the more recent reference Wedepohl et al 1995 that we prefer to cite instead. The following was added to the manuscript: "… which is reasonably consistent with the ratio of 0.15 provided for the upper crust by Wedephohl (1995)".

The leaching queston:

In the atmosphere, Pb is present in dust particles and also comes from various natural and anthropogenic sources often involving processes at high temperatures during which Pb is first vola0lized and then condensed on pre-existing particles. This is true for main natural non-crustal sources of Pb (volcanoes and biomass burning) and numerous anthropogenic processes (liquid and solid fuel combustion, various metal smelters, pig iron and steel production, etc) (see Nriagu et al.,1979; Nriagu and Pacyna, 1988). As for many species crustal species, the crustal part of Pb is likely more refractory than components associated with combustion processes that are adsorbed onto smaller particles and so readily washed off during on-line acidification. It is therefore important when discussing the leaching question to know how abundant is the crustal fraction of Pb and its eventual change over the past. Since the difference between the two Pb Orles record is variable with time (see Figure 2 and my next comments on that below) it is important to show the contribution of crustal Pb to total Pb and its change along the records reported in Figure 2.

Nriagu, J. O. (1979). A global assessment of natural sources of atmospheric trace metals. Nature, 338, 47–49.

Nriagu, J. O., & Pacyna, J. M. (1988). Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature, 333(6169), 134–139.

We appreciate and agree with these general considerations. However, we feel it is more appropriate to further expand this topic within our publication (in preparation) detailing the environmental interpretation of the Pb records in the Alto dell'Ortles ice cores. Here we anticipate that a variety of previous studies have attempted to decouple the various effects of acidification times on the Pb concentration record (please see the relevant citations as already provided in the manuscript); still questions linked to the differential leached fraction of the various trace element source (in this case of Pb) remain and will remain unresolved also in this case due to, as Reviewer 3 noted, multiple Pb sources (not just crustal) to the total Pb concentration. We acknowledge that differential fractionation due to acid leaching is important from an environmental point of view, however we reiterate that the present study does not seem the most appropriate venue to address this topic in more detail to keep the manuscript at a reasonable length and to maintain a clear focus on the dating aspects.

We believe the current discussion - based on the afore mentioned studies on acidification time and leaching – is sufficiently detailed for a paper focused on the chronology as we already provide a likely/possible explanation (depending on the point of view), for the observed differences in absolute Pb concentrations between the two parallel ice cores from Mt. Ortles. At this time, we explain most of this difference to be related to the application of two different analytical methods

since they result in different acidification times. We reiterate that we base this explanation on the results from previous studies on differential leaching effects (see above and citations within the manuscript), showing that a difference in acidification time can lead to a difference in the derived absolute concentrations. Inter-lab differences from e.g., calibration, background and limits of detection – which are all particularly important in the very low concentration level - also might contribute to some extent. However, based on the high and significant correlation between the Pb concentration records from the two Ortles cores, we further argue that these effects do not significantly modify their temporal pattern.

Finally, just for general context and perspective, here we point to the facts that:

(i) the two Pb records in which this concentration difference is discussed originate from the two parallel Ortles cores drilled in very close proximity (10 meters apart)

(ii) they can thus be assumed to reflect the same emission and air pollution history resulting in the accordingly observed alike main features in the records

(iii) they are used to improve the depth alignment of a core section already aligned by other means above and below ($\delta^{18}O$; see below), resulting in a reasonably small shifts, typically less than 10 cm in depth.

(iv) we note that, whether Pb is from crustal or non-crustal sources is irrelevant in the context of this chronological paper (the use of the main total concentration features for depth alignment of the parallel cores).

In the Supplementary text 2 (Methodologies adopted to determine Pb), you specify that "In a more recent manuscript, these shorter timescales, from minutes to a few hours, were investigated (1.5-250 minutes) for alpine ice core samples (Münster et al., 2025). Those results show a 2-to-3-fold increases in the measured Pb concentration over that short time range and can explain the observed difference in absolute Pb concentration between Alto dell'Ortles cores #1 and #3 due to differences in the method dependent acid times applied."

First, please specify that the recoveries derived by Münster et al., 2025 were done on CG ice cores that contain relatively large dust content (see the Table 2 in Münster et al., 2025) and thus these results you cannot be generalized to the all Alpine ice cores. Therefore, as already mentioned, it would be important to see how abundant is the crustal Pb contribution in the Ortles ice.

We respectfully point out that there might be a misinterpretation regarding the concentration levels in Münster et al., 2025. The concentration levels, and certainly not the particle size, of the samples used for investigation of the leaching effect are not reflected in the mentioned Table 2. There, the average concentration is shown for all samples, including samples from sections with input from Saharan dust events. The sum of all these samples was analyzed for an entirely different purpose than investigating the leaching effect (focusing on instrument comparison). In contrast, the relevant figure for this discussion can be found in the Supplement of the Münster et al., 2025 study (Figure S1). As shown there, the acidification time/leaching effect on the short time scales of a few minutes was observed for samples exhibiting Pb concentrations of around 100 ng L^{-1} (i.e., around 1 ng g^{-1}).

This is within the same concentration range discussed in this study . In any event, we fully agree that results from one core cannot be generalized to all Alpine ice cores. This is now clearly stated in the relevant section of the Supplementary Text 2:

"In a more recent manuscript, these shorter timescales, from minutes to a few hours, were investigated (1.5-250 minutes) for Alpine ice core samples of similar concentration as analysed in this study (Münster et al., 2025). While these results cannot be automatically generalized and extended to other drilling sites, they do show a 2-to-3-fold increase in the measured Pb concentration over that short time range, which would explain the observed difference in absolute Pb concentration between Alto dell'Ortles cores #1 and #3, due to differences in the method-dependent acidification times applied."

In your answers to the comments raised by the two reviewers on the leaching you said: "While we think the acid leaching topic will be of interest in a future manuscript focused on past Pb sources and emissions, the acid-leaching process is of minor relevance in the context of this manuscript where only the shape of the record can affect the conclusions (revised chronology)." I disagree since, as far as you show a Pb record in your manuscript, the reviewer is supposed to examine the validity of the reported data. Also, I am less optimistic than you here since your comparison (Figure 2) is reported as a log scale. In fact, the difference between the two Pb profiles sometimes (and for unknown reasons) are as large as the temporal variability.

Here we address the rest of the comment on the acidification/leaching issue point-by-point:

1) The log scale has the advantage to visualize changes also in the low concentration range. That is the reason why the data are shown on the log-scale in Figure 2 (they are however shown on the normal scale in later figures).
2) We do not argue that differences in concentration between the two Pb records exist. However, the concentration changes of the main features used as ties are certainly larger than "…the difference between the two Pb profiles…".
3) Finally, we would like to put the comment by the reviewer on the comparison of the two Pb concentration records in Figure 2 into context. These two records are used for depth alignment of the two parallel Ortles ice cores. (a) These two cores were drilled only 10 m apart. (b) Above and below the short sections (15 m) aligned using Pb, these two cores are aligned based on their $\delta^{18}O$ profile (Figure 1). However, because features of the $\delta^{18}O$ record between 59 m and 74 m depth are less obvious, the two Pb records have been used in addition to corroborate the $\delta^{18}O$ alignment. (c) The shift in depth between the two cores, according to the alignment based on both $\delta^{18}O$ and Pb, is typically in the order of 10 cm. This

is a small discrepancy in depth and certainly not an uncommon observation for parallel cores. Considering a) the very close proximity of the two cores, b) the robust constraints by $\delta^{18}O$ above and below the ice core section under discussion (therefore already putting this section into a likely correct temporal frame) and c) the reasonably minor shift in depth between the two cores, we believe that the leaching topic has sufficiently been addressed in regard of its relevance for this chronological paper while it will be certainly further expanded in the coming publication about the environmental interpretation.

You also said "In any case, it is possible that differences might be larger at low Pb concentrations where the Pb leaching from mineral dust particles of relatively large size can become relatively more important". Whereas I basically agree with that, the Figure 2 does not totally supports that: At 59-60 m depth in core 1 there are ~0.5 ng g-1 instead of ~0.12 ng g-1 in core 3, and at 69.5-70 m in core 1 there are ~ 0.09 ng g-1 instead of ~ 0.02 ng g-1 in core 3. So again, to clarify this point it would be more straightforward to report in Figure 2 (using a linear scale) a dust related species (Rb for instance that you used to calculate ncPb) instead of making speculation on what extent the variable difference between the two profiles is due to a variable amount of dust.

I saw in your answer that you envisage that "Rb concentrations and Pb leaching are not necessarily linked": This statement needs to be demonstrated (or documented with references). I don't really understand this argument since you used Rb concentrations to derive the ncPb fraction and we would expect that when dust is abundant the record indicates higher Rb concentrations. Please comment.

We observe that Reviewer 3 essentially agrees with us on our statement which he/she cited here. However, we do not fully understand what "Figure 2 does not totally supports" means in this context. For the numerical examples provided by the reviewer, the difference between the higher concentration is around a factor 4.2 and for the lower concentration it is consistently around a factor 4.5. This is in general agreement with our explanation for this difference (acidification time). We are concerned that this discussion is getting focused to a level of detail that is more appropriate in the context of the environmental interpretation of our Pb record but is unlikely to be relevant for this paper linked to dating using the most prominent Pb concentration features.

The recent trend:

To explain the large departure between Ortles and AN over the recent period you now specify that “It is also important to note, that the Mt. Ortles glacier archive at the study site is temperate in the upper firn part only (down to 30 m depth; see Gabrielli et al 2012) and post depositional effects, causing a partial loss of the most recent Pb signal by melt-water runoff are possible (see e.g., Huber et al., 2024; and Avak et al., 2018, estimating up to 50% loss for the Pb signal)”.

I am not totally convinced that the melting in the upper Ortles layers can explain the huge difference seen in your figure 8 after 1700 CE.

We agree the post depositional effect explanation reported within the manuscript likely concerns at least a fraction of the difference in Pb concentration between Ortles and other Alpine records, as already extensively discussed in the cited sentence within the manuscript. Regarding the comment about the “huge difference” please see our comment below.

First, Avak et al. indicated a rather weak effect on Pb (a loss from 5 to 50%) compare to others species such as Zn (70-80%) or Cd (85- 95%) in the warm ice from the Grenzgletscher site. They concluded “Based on their immobility with meltwater percolation, we propose that Ag, Al, Bi, Cu, Cs, Fe, Li, Mo, Pb, Rb, Sb, Th, Tl, U, V, W, Zr and the REEs (Ce, Eu, La, Nd, Pr, Sc, Sm, Yb) may still be applicable as robust environmental proxies in ice cores from Alpine glaciers partially affected by melting. In contrast, concentration records of Ba, Ca, Cd Co, Mg, Mn, Na, Ni, Sr and Zn are prone to significant depletion”. Based on your Figure 8, I calculated that we may expect an initial (prior to post depositional effect due to melting) ncPb concentration at Ortles at the surface of ~30 ppb to respect the rest of the record and its scaling to the AN record. Given the measured surface Ortles concentration of 1 ng g-1; that means a depletion reaching a factor of 30. That a lot and far larger than what was claimed by Aval et al. (a factor of 2 as an upper limit).

We thank very much the Reviewer for taking the time to explore in detail the Pb concentration record from Mt. Ortles. However, while it is not explained how Reviewer 3 made his/her calculation, the presented, high numbers of the expected Pb concentration (30 ppb) and, as a consequence, the depletion factor (30), are unlikely to be correct. The expected concentration can be read out directly from the CG03 record presented in Supplement Figure S6 and is around 2.65 ppb for the anthropogenic peak value (10-year average). This is the same data and thus consistent with the values reported in Eichler et al., 2023 (CG03 being one of the records presented there). Thus, the difference between the respective 20th century peak values for Ortles (around 1.3 ppb for the 10-year average; also readable from Figure S6) and CG03 is just around a factor of 2, and between

Ortles and Cole du Dome (CDD), which is also shown in Eichler et al. 2023, it is only around 1.5. Hence, these factors are within the upper limit of potential, melt related Pb loss reported by Avak et al. (2018).

Second, the difference is still a factor 20 in 1800 CE.

We respectfully observe that this statement does not reflect the findings. Please see the explanation above.

How conciliate that with what was claimed in the previous Ortles paper (Gabrielli et al., 2016): “We concluded that this glacier probably represents a unique remnant of the colder climate prior to ~ 1980, which has since been shifting from a cold to a temperate state.” Please comment.

We note that that statement from our 2016 paper is extracted and put out of context in this discussion, as that sentence was linked to borehole temperature measurements and certainly it was not excluded that some limited postdepositional events linked to summer melting could have happened at the Mt. Ortles drilling site also before 1980.

Finally, since it is well-known that in temperate ice species like NH4 and Ca are quasi- totally lost (Eichler et al., 2001) and because they were certainly measured in the Ortles ice core, it would be nice to document the absence of recent increase of Pb with a record of Ca or NH4 over the two or three last centuries to assess the strong effect of melting after 1700 CE in the Ortles record.

Eichler A, Schwikowski M and Gäggeler HW (2001) Meltwater- induced relocation of chemical species in Alpine firn. Tellus B Chem. Phys. Meteorol., 53(2), 192–203.

We appreciate the suggestion that will be certainly taken into consideration for a future paper where the ionic species will be presented. Here we want to remark that the dating of the most recent period, linked to the mentioned “absence of recent increase of Pb”, is entirely independent of the Pb record from Mt. Ortles as it has been determined based on annual layer counting (please see the text within the manuscript).

Conclusion:

“In conclusion, this revised more accurate time scale (CP2025/2) will allow to

provide additional new detailed climatic environmental histories of Central Europe during the

Holocene": That is overstated since the Holocene started at 10,500 yr BP not at 7,000 yr BP. So please modify the sentence since the Orles record did not extend to the Early Holocene.

We agree and we have modified the sentence accordingly. In conclusion, this revised and more accurate time scale (CP2025/2) will allow to provide additional detailed climatic and environmental histories of Central Europe during the second half of the Holocene".

I don't understand the last sentence: "In addition, CP2025/2 has the potential to become a reference chronology for multiple paleoclimate archives in Europe." Please be more specific (what do you mean with "reference chronology" ?).

We agree that the sentence is unclear, and we have modified it: "In addition, CP2025/2 has the potential to become an important high-altitude reference for multiple paleoclimate archives extracted at lower elevation in Central Europe."

Your answer to previous reviewers: There some points where you did not yet answer adequately to the reviewers (points for which I also agree):
Supplementary Text S2: Previous remark from one of the previous reviewers said that the first sentence is very misleading: "The Colle Gnifetti ice core (Mt. Rosa, Western Alps) is currently the oldest record from the Alps, dating back >15000 years (Jenk et al., 2009)". This sentence gives the impression that the CG ice recorded environments (and/or climate) back to more than 15,000 years. This is however not correct: As argued by Jenk et al. (2009), while radiocarbon analyses of particulate organic carbon have indicated that Pleistocene ice is sometimes present in the bottom layers at CG, it is shown that prior to 3,000 years the climate d18O record was strongly disturbed by post- deposition liquid migration of 18O at the grain boundary of ice located in zones of strong strain-rate gradients above the inclined bedrock." Your answer is that you replace the word "record" with "archive". That is far too vague and still incorrect: Whereas the ice deposited at the bottom of the CG glacier is as old as 15,000 years, Jenk et al. (2009) demonstrated that the ice did not correctly archived past

climate and environment prior to 3,000 years BP, so again please modify your wording.

This is a detail in the supplement, and the reviewer uses the statement made in Jenk et al., 2009 out of context. Stated in Jenk et al. is:

"…a pressure induced $\delta^{18}O$ depleted liquid front along shear zones" might "…explain the observed depression in the lowermost part of the core."

And they conclude that "…the interpretation and understanding of the Colle Gnifetti $\delta^{18}O$ record is still incomplete and needs further investigation."

We see the possibility of other possible explanations for the $\delta^{18}O$ depletion which do not require disturbance of the archive, but could rather reflect certain climate conditions (i.e., changes in seasonality of accumulation due to changes in wind erosion of winter snow). Therefore, , we respectfully disagree that our sentence is "very misleading".

Nevertheless, the sentence has been changed to: "The glacier on Colle Gnifetti (Mt. Rosa, Western Alps) currently contains the oldest ice found in the Alps with a ^{14}C confirmed age (15000 years; Jenk et al., 2009)."

Units: Whereas you give now the formula to convert m into mwe, I also ask you to report on Figure 2 the depth scales using both m and mwe (since for most of the Figures and Tables the unit is mwe), so that the reader can more easily find the ages in your figure 5.

When uploading the data of Figure 2 in Zenodo.com we will also upload the linked depth scale in mwe, so that the reader can build any graph that reputes is most suitable for any additional observation.

Figure S6: (comparison CG03-Ortles): At around 1550 CE the difference between the two profiles reached a factor of 10. In your answer you commented as "While this discussion is out of the scope of this paper, we think that a factor 10 difference in absolute Pb concentrations is reasonable, considering different snow accumulation rates, distance, and transport path from the emission sources to the respective sites. Also, please see above the response related to CG." I am not convinced: A difference by a factor of 10 between CG03 and Ortles for a species that is mainly present in the atmosphere as micronic or submicronic aerosol is a lot (at the scale of the Alps). Also, how you explain that the difference is

sometimes as high as a factor 10 and sometimes far lower. Please comment.

We believe that it is possible that two separate matters are being mixed in this assessment by Reviewer 3. The answer cited refers to the general difference between the Ortles and the Arctic (AN) Pb concentration levels. For those, a factor of around 10 is what we referred to as “reasonable”. As for the difference between the Ortles and CG03 Pb records at around 1500 CE, we cannot provide a clear answer at this point. This is certainly of interest and will deserve thorough investigation and discussion, looking into regional and local sources, their location with respect to circulation patterns, their source strength, general emission factors and particle size for different mining processes, transport etc. In this context we believe this is out of scope of this manuscript.

I am not sure about the publication rules of the Climate of the Past journal but it

seems to me that, as far you show Pb profiles, the Pb data (not only the tie points) has to be

deposited in a data base (and not waiting your planned future publications). I let the editor

to decide on this point.

We agree this is a very important point that has now been clarified with the Editor and the data will be made available consistently to the Journal rules.

End of the review