

## CP-2020-28 – Reply to comments from referees 1 and 2

*Our replies are in blue italic fonts.*

### **Referee 1 - General comments**

The manuscript reviews recent development of isotopic dendroclimatology, addressing possible divergence problem in tree-ring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . In my opinion, this kind work is very important when isotopic dendroclimatology has been paid more attention and plays more important role in high-resolution paleoclimate reconstruction. However, the current manuscript should be reorganized and concentrated in  $\delta^{13}\text{C}$ . Physiological mechanisms between tree-ring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are quite different, therefore, comparing with tree-ring  $\delta^{13}\text{C}$ , tree-ring  $\delta^{18}\text{O}$  did not show recognizable effects from rising  $p\text{CO}_2$  (Lines 240-241) and pollution (Lines 424-425). Just as the authors said in Lines 514-515, tree-ring  $\delta^{18}\text{O}$  is a more appropriate proxy for climate reconstruction. And, the phenomenon of divergence between the  $\delta^{18}\text{O}$  and climate is really few worldwide.

*REPLY - Regarding presenting the review on  $\delta^{18}\text{O}$  series, indeed, rising  $p\text{CO}_2$  does not create divergence with climate for the  $\delta^{18}\text{O}$  series, as we pertinently explain, but other causes do: changes in climatic regimes and pollution (sections 4.1 and 4.3). That is why we judge pertinent to keep the  $\delta^{18}\text{O}$  series in this review (see Table 1).*

I also suggest the authors adding one section discussing uncertainty. Isotopic dendroclimatology is a subject based on chemical experiment. Unlike tree-ring width or density, the result of tree-ring  $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  measurements are different to verified again from their core or disk samples, due to time consuming and great expense. It is possible to introduce mistakes during many steps of experiments, for example, impure cellulose and unreliable measurements caused by bad condition of the isotope ratio mass spectrometer.

*REPLY - Uncertainties do exist for any kind of physical measurement, including tree ring width or density determination. We agree that in isotopic dendroclimatology, the chemical extraction of cellulose and the spectrometric measurements are critical steps. Impure cellulose and unreliable measurements yield bad data, which indeed more than likely diverge from climate.*

*We have added a sentence of caution at the beginning of section 2.2 and refer to several papers devoted to good analytical practices, including the five new references cited. However, we do not think this subject has to be extensively discussed in this paper. The text on new lines 97-101 now reads as follows: « A preliminary word of caution on tree-ring isotopic series is that the chemical extraction of cellulose and the spectrometric measurements are critical steps. Impure cellulose*

and unreliable measurements may yield erroneous data, which more than likely will diverge from climate. It is understood here that dendroisotopists should make sure to follow good analytical practices (see for instance Loader et al., 1997; Boettger et al., 2007; Wieloch et al., 2011; Kagawa et al., 2015; Andre-Hayles et al., 2019).»

Some other uncertainties also exist. First is sampling strategy. We should understand what kind of tree could be used for climate reconstruction. As recommended by classical “The principle of limiting factors” (Fritts 1976), site selection is very important when one would employ trees to infer climate change. It is also important to isotopic dendroclimatology. Because mixed (deep phreatic water, shallow ground water, precipitation...) ground water may disturb tree-ring d18O (A tree in flowing figure), tree-ring d18O of B tree only absorb precipitation. Although cellulose d13C and d18O could be measured for any tree from any site, but for purpose of climate correlation, it should be carefully selected.

*REPLY – Thank you for raising that up. Indeed site selection is a crucial step in paleoclimate research. If trees and/or sites are not well selected, one of the main risks is that their  $\delta^{18}\text{O}$  and/or  $\delta^{13}\text{C}$  isotopic series show no significant relation with climate. In that case, reconstruction is not possible. Therefore, we judge that using poor criteria for site selection does not have to be dealt with in this paper as we assume that the readership is well aware of the initial step of adequate site selection.*

Second uncertainty may be introduced by different samples for measurement (extractive-free samples,  $\alpha$ -cellulose, whole wood or holocellulose). And, for different chemical extraction methods (Green’s method, Brendel’s method...). Third uncertainty may be introduced by “pooling” or “not pooling”.

*REPLY - Different extraction methods, as well as measurements produced in different laboratories with different spectrometers and procedures, should produce comparable results. There are very few inter-lab calibration experiments. To our knowledge the only study dealing with such a comparison was produced by the ISONET group (Boettger et al., 2007). Another one is in progress in the frame of the THEMES project conducted by one of the two authors (Daux, Andreu-Hayles et al., in progress). These inter-laboratory comparisons show that isotopic shifts may exist between laboratories (high correlations but different absolute value) due to differences in extraction methods, reference materials, instruments, etc. However, as long as the data included in an isotopic chronology have all been produced following the same protocols, by the same experimentalists, at the same laboratory, the data are consistent with one another and if they diverge from climate variations, the cause should be sought elsewhere.*

Special comments are as follow.

Lines 13-19, changes on physiology ( $f_0$  and *pecler effect*...) should be mentioned here.

*REPLY* -These items are covered in section 2.1. Here we cite the main CAUSES for divergences, not the mechanisms through which they operate. No change to these lines.

Line 32, need a reference

*REPLY* -We have added D'Arrigo et al., 2008. The text now reads as follows: « ... climatic data shows a 'divergence' (D'Arrigo et al., 2008). »

Lines 38-42, it is no need to describe growth divergence

*REPLY* -The referee probably means lines 38-42. Here we just present some background using growth divergence. No change to these lines.

Line 72, "concentration" is better than "pressure" , also in Line 236

*REPLY* – Atmospheric CO<sub>2</sub> pressure or pCO<sub>2</sub> are well accepted and widely used. No change to these lines.

Lines 94-95, need references

*REPLY* -The references covering this topic are through equations 1-3, for which the citations are in the previous text. No change to these lines.

Line 157, 5 year is not enough

*REPLY* – Understood. The parenthesis underlines the fact that some researchers may opt for longer overlaps. No change to this line.

Lines 175-177, one advantage for tree-ring isotope chronology is no need to detrending. If detrending for the isotope chronology, some climate signals may be lost.

*REPLY* – We agree. That is exactly what the text explains. No change to these lines.

Line 263, "1850s" is easy to understand than "last 170 years"

*REPLY* – We have modified the sentence (see new line 279), which now reads «... of rising pCO<sub>2</sub> since 1850.»

Line 302, relative humidity and RH, repeat

*REPLY* – we just present the abbreviation (RH) for relative humidity here. No change to this line.

Line 376, tropic/

*REPLY* – Tropical is a well accepted English adjective. No change to this line.

Lines 399-412 – multi-proxy approach and more climate noise?

**REPLY** - We do not understand what the reviewer means. We write the contrary in the text: 'Indeed, combining proxies with the same dominant control, but different secondary controls, tends to accentuate the common climate signal'. No change to this line.

Section 3.3. there is only one sentence to state the situation of cellulose d18O (Line 240). I recommend to delete d18O discussion in this manuscript. In addition, removing effect of increasing CO2 from the d13C series has been discussed in many literatures. Please shorten this section.

**REPLY** – It is true that the literature raised the issue abundantly, but there is still no consensus on how to approach and correct the problem. This manuscript designed to be a review article should cover the matter and section 3.3 intends to do just that. Concerning the effects on  $\delta^{18}O$  values, it is worth explaining which articles address the potential pCO<sub>2</sub> effects, even if nil or minimal. In addition, referee 2 pertinently suggests to integrate new references to this section. So we decide not to shorten the section.

Table 1, check which one use pooling method.

**REPLY** – good point. We identified the studies using pooled series (asterisks in Table R below), without identifying any specific common factors. Note that many of these studies validated that the use of pooled trees gave similar results to individual trees merged mathematically. We have kept Table 1 in its original form, but modified the end of section 3.1 (new lines 196-199): «Note that when the pooling approach is envisaged for producing series of a specific tree species in a given region, verifying its reliability by comparison with averaged individual series is required prior to embracing the approach. This validation appears to allow producing isotopic series devoid of methodological artefacts (Table 1).»

**Table R. Reported critical divergences of correlations between isotopic results and instrumental climatic series (other than sampling, stand dynamics and juvenile effects).**

Isotopes	Climate Parameters	Tree species	Causes	Region	Author(s)
$\delta^{13}C$	Summer T	<i>Quercus robur</i>	CC: longer growth season	Eastern England	Aykroyd et al., 2001
$\delta^{13}C, \delta^{18}O^*$	Summer T, Pc	<i>Quercus petraea;</i> <i>Pinus sylvestris</i>	CC: physiological adaptation to higher T, change in moisture origin	Switzerland	Reynolds et al., 2007
$\delta^{13}C^*$	Summer T	<i>Pinus sylvestris</i>	CC: earlier Summer	Eastern Finland	Hilasvuori et al., 2009
$\delta^{13}C^*$	Summer T & Pc	<i>Quercus robur,</i> <i>Pinus sylvestris</i>	Poll: SO <sub>2</sub> from close emitter	Southeastern England	Rinne et al., 2010
$\delta^{13}C$	Summer cloud cover, T	<i>Pinus sylvestris</i>	CC: AO, decoupling of T and radiations	Northwestern Norway	Young et al., 2010
$\delta^{13}C, \delta^{18}O^p$	Tmax, RH	<i>Larix decidua</i>	CC: drier climate; deeper soil water	French Alps	Daux et al., 2011
$\delta^{13}C, \delta^{18}O^*$	Summer T & Pc	<i>Pinus sylvestris</i>	CC: change in T, irradiance & cloud circul.	N. boreal zone	Seftigen et al., 2011
$\delta^{13}C^*$	Summer T & Pc	<i>Larix decidua</i>	Poll: traffic/vehicles	Italian Alps	Leonelli et al., 2012
$\delta^{18}O$	Summer Pc	<i>Pinus halepensis</i>	CC: increase of drought; deeper soil water	Greece	Sarris et al., 2013
$\delta^{13}C$	No link	<i>Juniperus virginiana</i>	Poll: distant SO <sub>2</sub> emitters	Appalachians, USA	Thomas et al., 2013
$\delta^2H, \delta^{13}C, \delta^{18}O$	RH	<i>Abies alba</i>	Poll: distant SO <sub>2</sub> emitters	Southwestern Germany	Boettger et al., 2014
$\delta^{13}C^*$	RH, T	<i>Abies georgei</i>	CC: water stress	Western China	Liu et al., 2014
$\delta^{13}C^*$	Tmax	<i>Picea mariana &amp; glauca</i>	Poll: oil sands mining operations	Alberta, Canada	Savard et al., 2014

$\delta^{13}\text{C}$ , $\delta^{18}\text{O}$	Summer T Spring Pc	<i>Picea mariana</i>	CC; NAO longer growth season	Northeastern Canada	Naulier et al., 2015b
$\delta^{13}\text{C}^*$	Spring-Sum. T	<i>Sabina przewalskii</i>	CC: change in cloud circulation	Tibet	Wang et al., 2016; 2019
$\delta^{13}\text{C}$ , $\delta^{18}\text{O}$	VPD	<i>Pinus ponderosa</i>	CC: increase of drought	Southw. USA	Szejner et al., 2018
$\delta^{18}\text{O}$	Spring AO, spring NAO	<i>Cryptomeria japonica</i>	CC: spring AO-EASM changes	Northeastern Japan	Sakashita et al., 2018
$\delta^{13}\text{C}$	No link	<i>Picea rubens</i>	Poll: distant $\text{SO}_2$ emitters	Appalachians, USA	Mathias & Thomas, 2018
$\delta^{18}\text{O}^*$	May-July T, RH, PDSI	<i>Abies forrestii</i>	CC: change in moisture origin	Southwestern China	An et al., 2019
$\delta^{13}\text{C}$ (WUE) <sup>p</sup>	Summer Tmax	<i>Picea mariana &amp; glauca</i>	Poll: bitumen mining, metal smelter emissions, global $\text{CO}_2$ rise	Alberta & Québec, Canada	Savard et al., 2020

T : temperature. Tmax : maximum temperature. RH : relative humidity. Pc: precipitation. VPD: vapour pressure deficit. AO : Arctic oscillations. NAO : North Atlantic Oscillations. PDSI: Palmer drought severity index. CC : climate change. Poll : pollution stress. EASM: East Asian summer monsoon. \* indicates series exclusively involving pooled tree rings; <sup>p</sup>, series partially composed of pooled rings.

## Anonymous Referee #2

### Comment on the review from referee 1

Received and published: 1 May 2020

First, I would like to thank the authors for conducting this synthesis. The authors did a great job on synthesizing and explaining all the different sources of divergence caused by multiple factors recorded in Carbon and Oxygen isotopes in the wood.

At the beginning of this review, the authors explain the differences between the “divergence” topic in the tree ring community versus the divergence that can be found in isotopic measurements in Tree rings. I see why the Authors are attributing the term divergence to the examples they show. However, it is not clear if the term divergence is the correct term. It is fine to use this term as long the authors make sure that they are referring to the divergence to the climate signal and eventually highlight that this "issue" falls into the problems we as scientists have when we want to interpret the isotopic records in Tree rings. I do appreciate the sections where they make recommendations and a strong call to the good practices so future researchers can take this advice to minimize the chances of losing the climatic signal.

**REPLY** – *We sincerely thank referee 1 for the constructive comments and suggestions compiled above and below. Regarding the usage of ‘divergence’, we agree with the referee that this term should be restricted to describing tree-ring isotopic departures from climatic parameters. That is what we rigorously do in the manuscript. The introduction explains lines 30-32: «When correlations between climatic parameters and tree-ring proxies show periods of instability such that correlations weaken, become non-significant or change in signs, the relationship between proxies and climatic data shows a ‘divergence’. » Further down (lines 44-45): «The present article deals with the ‘isotopic divergence’, which we define here as the middle- to long-term (>10 years) loss or change in signs of correlations between a climatic parameter and tree-ring isotopic ratios ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , or rarely  $\delta^2\text{H}$ ). » So no changes needed.*

## Anonymous Referee #2

### Some other suggestions

Received and published: 1 May 2020

One comment I should mention is that the review is highly focused on climate reconstructions, while the ecophysiological responses to environmental cues are somewhat left a little bit on the side, as something that is dampening or disrupting the climate signal.

*REPLY – It is right to reckon that the article focuses on the tree-ring isotopes-climate relationships with the main purpose of climatic reconstruction as explained in the introduction (lines 61-63): «Given the need for careful assessments of isotopes as climate proxies for various regional contexts and tree species, this synthesis of the up-to-date information on isotopic divergences aims at: (1) describing the main isotopic divergence types and discussing their potential causes, and (2) reviewing research avenues to identify them and account for them (Table 2). »*

*On one hand, wide ecological changes are not included in the manuscript on purpose as we want to restrict the review to TR isotopic divergences due to direct tree responses. On the other hand, we refer to the ecophysiological approaches for assessing tree responses to environmental changes as part of eventual solutions for circumventing some isotopic divergence issues (see for instance Section 5; paragraph before last). Therefore, we did not take actions in response to this comment.*

So, the more specific comments are more targeted to references in the literature (given this manuscript is a review) plus some other clarifications if the author agrees.

Line 125. The Model "MAIDEN" is not well explained, so I recommend explaining it a little bit, so the reader can understand what the model it's all about.

*REPLY – Lines 124-129 define the general approach to mechanistic modeling, which applies to MAIDEN as well as to the other models of the kind. We do not want to place too much emphasis on MAIDEN, but following the suggestion of referee 2, we now explain briefly the main structure of MAIDENiso as follows (new lines 129-135): « Most models make forward predictions and allow verifying that the measured tree-ring isotopic trends compare well with the isotopic outputs modelled with the meteorological and non-meteorological inputs, and identifying processes behind isotopic responses. For instance, MAIDENiso is an expanded growth model which includes C and O modules. The model allows reproducing fractionation of carbon isotopes due to atmospheric CO<sub>2</sub> diffusion to the site of carboxylation, enzymatic photosynthesis and respiration, and estimates oxygen isotopes in precipitation, soil water and xylem water, and the fractionation in leaves due to evapotranspiration and biochemical formation of cellulose (details in Danis et al., 2012; Boucher et al., 2014; Lavergne et al., 2017). »*

Line 131 The citation for the Vaganov model it should be correctly cited, or add the papers where Vaganov published originally, then, of course, you can use other citations as usage examples.

*REPLY – Good point. We have corrected the name of the model and now refer to Vaganov et al., 2011. The text now reads as follows (new lines 140-141): « ... refer to the so-called proxy-system models (e.g., the Vaganov-Shashkin or VS model; Vaganov et al., 2011; Sánchez-Salguero et al., 2017).»*

Line 89 and Line 359 The percentage of oxygen isotope exchange during cellulose synthesis, as you mention, can indeed be variable. Recently there is a published paper addressing this same possibility and highlights some of the possible hypotheses that can be involved in such phenomena. Probably this is a reference you might be interested in exploring. New Phytologist (2020) doi: 10.1111/nph.16484



*REPLY – Good point; this newly published reference is pertinent. We have added a citation to this article at new line 377 and add the full reference to the final list. The text now reads: « However, this proportion may vary over growing seasons and longer periods due to relative humidity conditions (Gessler et al., 2009; Szejner et al., 2020). »*

Line 253 The PIN correction of the pCO<sub>2</sub> influence on the D13C discrimination should be double-checked. I think Gagen et al. 2007 made the first mention of the Pin correction that I know of. The Holocene, 17(4), 435–446. <https://doi.org/10.1177/0959683607077012>

*REPLY – Correct. We have added a citation to Gagen et al. (2007) before the citation to McCarroll et al. (2009), which describes six steps in the application of the method. The modified text on new lines 268-270 is: « A widespread corrective approach uses a conditional, pre-industrial (pin) correction (Gagen et al., 2007). This six-steps non linear detrending of the low-frequency changes (McCarroll et al., 2009) ...».*

Line 206 Another recent publication Citation that you might be interested in exploring about age effects in Tree ring isotopes is from Xu et al. 2020. I think this is relevant to your review as it addresses the age-related effect concerning Climate reconstructions. 2020 Journal of Geophysical Research: Biogeosciences, 0–2. <https://doi.org/10.1029/2019JG005513>

*REPLY – Good point; this freshly appeared reference is pertinent. We have added the text below with a citation to this article at the end of the paragraph before last in section 3.2 (new lines 238-242), and added the full reference to the final list.*

« Finally, in some cases, though there is no trend in the tree-ring isotopic series, the response to climate in the isotopic chronologies may be age-dependent. For instance, in *Picea Schrenkiana* from northwestern China,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values in trees under 125 years have a stronger response to relative humidity than trees older than 270 years (Xu et al., 2020). A diminishing strength of the correlations with tree age advocates for the incorporation of young trees only to develop a non-divergent composite chronology. »

Xu, G., Wu, G., Liu, X., Chen, T., Wang, B., Hudson, A., 2020. Age-related climate response of tree-ring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from spruce in northwestern China, with implications for relative humidity reconstructions 0–2. <https://doi.org/10.1029/2019JG005513>

Lien 262. I agree that there is no overarching consensus over how to correct the pCO<sub>2</sub> effects on the discrimination of 13C. But I find a bit troubling this sentence "A wise approach is to test the various corrective methods and assess the performance of the resulting series with climatic reconstruction model." This statement is for me, suggesting that we should select the best fit to climate. I think this is a bit biased and undermined the fact that we still do not fully understand how the pCO<sub>2</sub> is affecting gs and A. so I think this part needs to be careful on not incentivize researchers to select the best fit, but instead, incentive to investigate what is the mechanisms and how the pCO<sub>2</sub> is or not affecting the Carbon chronologies. Then I suggest reviewing Global Change Biology, 22(2), 889–902. <https://doi.org/10.1111/gcb.13102>

*REPLY – We agree. The text is modified as follows on new lines 276-279: « A wise approach is to investigate the potential influence of pCO<sub>2</sub> on isotopic ring series and the gas-exchange response mechanisms in trees prior to selecting a corrective method (Voelker et al., 2016; Savard et al., 2020). »*

Line 287 I think this part needs this reference. Dorado-Liñán, I et al. 2016. *Climate Dynamics*, 47(3–4), 937–950. <https://doi.org/10.1007/s00382-015-2881-x>

*REPLY – We agree. We have added the reference and the text modified on new lines 306-309 now reads:* « ... (Young et al., 2010), the Northern boreal zone (Seftigen et al., 2011) and Northern Spain (Dorado-Liñan et al., 2016) depicted divergences between temperature records and  $\delta^{13}\text{C}$  series of pines (*Pinus sylvestris* or *Pinus uncinata*) during episodes of decoupling between irradiance and temperature linked to either changes in large scale atmospheric circulation (in the first two references), or large volcanic eruptions (in the third one). »

Line 345 This reference also can be useful here Carbone, M. S. et al. 2013, *The New Phytologist*, 200(4), 1145–55. <https://doi.org/10.1111/nph.12448>

*REPLY – We agree. We have added the reference and the text modified on new line 361 now reads:* «... mainly as starch (Carbone et al., 2013; Kimak and Leuenberger... »