

## **Response to anonymous referee #2**

### **General comments**

This manuscript combines multi-proxy analyses ( $\delta^{13}\text{C}$ ,  $\delta^{44}\text{Ca}$ , paired U-Th and  $^{14}\text{C}$  ages) and geochemical modelling of vegetation-soil respiration within the soil-karst-cave system in the northern Iberian Peninsula over the last glacial-to-interglacial transition (ca. from 26 ka to 4 ka).

Authors have irrefutable knowledge on the subject and are familiar with the region, data and tools applied. They have performed comprehensive analytical work on three speleothems from two caves [Candela, El Pindal Cave (Moreno et al., 2010; Rudzka et al., 2011; Stoll et al., 2013; this study); Laura, El Pindal Cave (this study); Galia, La Vallina Cave (Stoll et al., 2013; this study)], including three pieces of the overlying bedrock.

The focus is on the  $\delta^{13}\text{C}$  speleo signal (Fohlmeister et al., 2020) to decipher whether it can be a possible paleo-soil respiration proxy (pCO<sub>2</sub>). CaveCalc (Owen et al., 2018) and ISTAL (Stoll et al., 2012) are used to account for effects of prior calcite precipitation (PCP), mean soil carbon age - dead carbon fraction (DCF), karst hydrology, bedrock dissolution, seepage zone and drip interval length changes. The referential temperature pattern is taken from Iberian Margin marine sediments (Darfeuille et al., 2016), the radiometric chrono-stratigraphy of which is sufficiently robust, and multiproxy studies have been performed on its strata.

Results point to increasing soil pCO<sub>2</sub> over the last deglaciation (from late glacial ca. 530-1030 ppmv to ca. early interglacial 1155-5780 ppmv) heavily dependent on temperature (Q<sub>10</sub> ~ 2.7-7; i.e., a factor by which soil respiration increases with a 10°C rise in temperature). This is in line with previously documented changes in vegetation cover and substrate from open glacial grassland, steppe taxa and low arboreal percentages to interglacial high arboreal pollen (data compilations in Fletcher et al., 2010 and Moreno et al., 2014; simulations in Scheff et al., 2017). Authors present and discuss other possible processes which are not found to exert a huge impact on the  $\delta^{13}\text{C}$  speleo signal. Their results, interpretations and conclusions are justified by data and are consistent with previous monitoring data that showed seasonal variations in cave pCO<sub>2</sub> driven by external temperature variations (Moreno et al., 2010; Stoll et al., 2012).

The science of the manuscript is excellent (significance and quality) and the overall presentation well structured. The organisation and length of the manuscript are good: 1 Table and 6 Figures in main text and 4 appropriate supplementary Figures (see below for specific comments). The title clearly reflects the contents of the paper and the abstract provides a concise and complete summary. The subject addresses relevant scientific questions within the scope of CP. My opinion is that it merits publication with minor changes once few clarifications are added. Please see below for constructive suggestions.

[Response: We thank the reviewer for these supportive comments and provide more detailed responses to their suggestions for improvement below.](#)

### **Specific comments and technical corrections**

#### **Tables**

Suppl. Table 1, Suppl. Table 2

I was unable to find the 2 supplementary Tables mentioned in the text.

Response: Apologies for this, we will provide the tables with the next version of the manuscript.

## Figures

### Current Figure 1 (Speleothem $\delta^{13}\text{C}$ records covering the last deglaciation in temperate Western Europe)

- Remove lines when 'hiatus' or 'no data' in panels A, C

Response: We believe the reviewer refers to the record from Villars cave (blue), which is very low resolution and therefore looks odd, although there is no hiatus. We will add a sentence clarifying this to the figure caption to avoid further confusion.

- Change "El Pindal (study site)" to "El Pindal & La Vallina (this study)" in legend of panel A

- Complete figure caption. Something like: "El Pindal Cave – stalagmite Candela (Moreno et al., 2010, this study), – stalagmite Laura (this study) and La Vallina Cave – stalagmite Galia (Stoll et al., 2013; this study)."

Response: The records shown here are only previously published studies, therefore we are now showing the new data from Laura and Galia. We will update the caption to clarify this.

-  $\delta^{13}\text{C}$  Villars (Genty et al., 2006; Wainer et al., 2011) does not appear to be consistent with El Pindal ca. 19 ka. Issue with resolution of the former? Any comment?

Response: We are not sure why the Villars record deviates from El Pindal and Chauvet before 19 ka. The issue is specifically with the record Vil-car1 (Wainer et al., 2011), which does indeed seem to show a different behaviour than other records from Villars cave. The authors of the Vil-car1 paper note that the record appears significantly affected by disequilibrium isotopic fractionation, which might explain the discrepancy.

-  $\delta^{13}\text{C}$  Buraca Gloriosa (Denniston et al., 2018) appears opposite to El Pindal (Moreno et al., 2010) ca. 13 ka and around 19 ka. Dating issues? Other reasons?

Response: Again, we are not sure about the reason for these high frequency discrepancies. The Buraca Gloriosa  $\delta^{13}\text{C}$  record is interpreted in the same way as El Pindal, but it is possible that chronological uncertainty leads to the observed discrepancy.

-  $\delta^{13}\text{C}$  Cova da Arcoia (Railsback et al., 2011, PPP 305) is not included. It seems to have quite different absolute values during the time span Galia grows (ca. 9 ka). Any comment? Could this be relevant to the comparison with temperatures derived from the marine record located further south? Atlantic versus Mediterranean climatic zones? (see for instance Fig. 1 in Denniston et al., 2018)

Response: Our study focuses on caves in settings where soil  $\text{pCO}_2$  is temperature limited, and therefore we argue that our findings have more broader significance than the specific region of northern Iberia. The reviewer makes a good point that stalagmites from caves located further south on the Iberian Peninsula have different trends in  $\delta^{13}\text{C}$ , as here soil  $\text{pCO}_2$  will likely be moisture limited, leading to very different phasing over glacial-interglacial cycles than temperature. We will make this clarification in the next version of the manuscript.

- In this regard, what about adding  $\delta^{13}\text{C}$  La Mine (Genty et al., 2006) as a contrasting environment?

This is important to highlight the "regional" extent of the exercise submitted in the present study.

Response: The reviewer is correct that our study focuses on a specific region, but we would like to emphasize that our findings do have broader impact, as they will apply to any system where soil  $p\text{CO}_2$  is temperature limited. Moreover, we combine the use of  $\delta^{13}\text{C}$ , DCF and  $\delta^{44}\text{Ca}$  measurements to better constrain initial soil conditions, which is a novel use of the speleothem archive. We will clarify this in the next version of the manuscript, but we think adding another record to figure 1 that is not from the Western European region would add confusion.

### **Additional Figure (new Figure 1? Current numbers would change accordingly up to 7 Figures)**

A non-specialist reader would very much appreciate being able to recognise all the variables measured and modelled under discussion. Thus, I earnestly request that authors include an illustrative scheme with the processes and reactions in question. As far as possible, the text must be self-explanatory: labelling the parameters as in the Figures, i.e.  $\delta^{13}\text{C}$ ,  $p\text{CO}_2$ , specifying sources and including the notion of dead carbon (modern-to-fossil reservoir effect) so the reader can follow the reasoning step by step: (i) atmospheric  $\text{CO}_2$  and rainwater (highlight seasonal effects in temperature and rainfall density/amount); (ii) biogenic  $\text{CO}_2$  from vegetation-plant litter-microbial activity-soil respiration (emphasize role of moisture availability, vegetation type and cover in soil gas  $p\text{CO}_2$ ); (iii) infiltration through soil water to karst and water flow paths, bedrock dissolution, drip water,  $\text{CO}_2$  degassing-calcite precipitation to form the speleothem (link to cave air  $p\text{CO}_2$ , cave ventilation dynamics, etc). Perhaps two panels are needed: one for a 'summer' scenario (assimilated to interglacial situation?) versus a 'winter' one (for the glacial conditions?). Ideally, this must lead the reader through the diverse situations deduced from the results, without digging too much in dispersed literature, which is somewhat scarce for  $\delta^{13}\text{C}$  specifically (indeed this is a strong point of the present manuscript value). Consider adding the seasonality of the caves in question with the series of instrumental measures available for the area (see below for additional comments on that).

Response: We appreciate this comment from the reviewer, and we agree that it is difficult to keep track of all variables under discussion when modelling carbon isotopes. Rather than a new schematic figure here, we propose to refer to similar figures that have previously been published that we can refer to in the text, e.g. in Rudzka et al., (2011), or in Matthey et al., (2016). Instead, we suggest that the main points evaluated here would be clarified by the inclusion of a set of simple figures illustrating the isolated influence on speleothem  $\delta^{13}\text{C}$  of changes in a) the degree of openness of dissolution, b) the effect of soil  $p\text{CO}_2$  given a constant dead carbon fraction, and c) the effect of prior calcite precipitation (Figure 1). This figure will serve as a useful reference point to comment how independent proxy record of DCP from  $^{14}\text{C}$  allow constraining the open system effect, and how independent constraints on PCP from  $\delta^{44}\text{Ca}$  allow constraints on PCP effect, making it possible to narrow the range of possible soil  $p\text{CO}_2$  effects on speleothem  $\delta^{13}\text{C}$ .

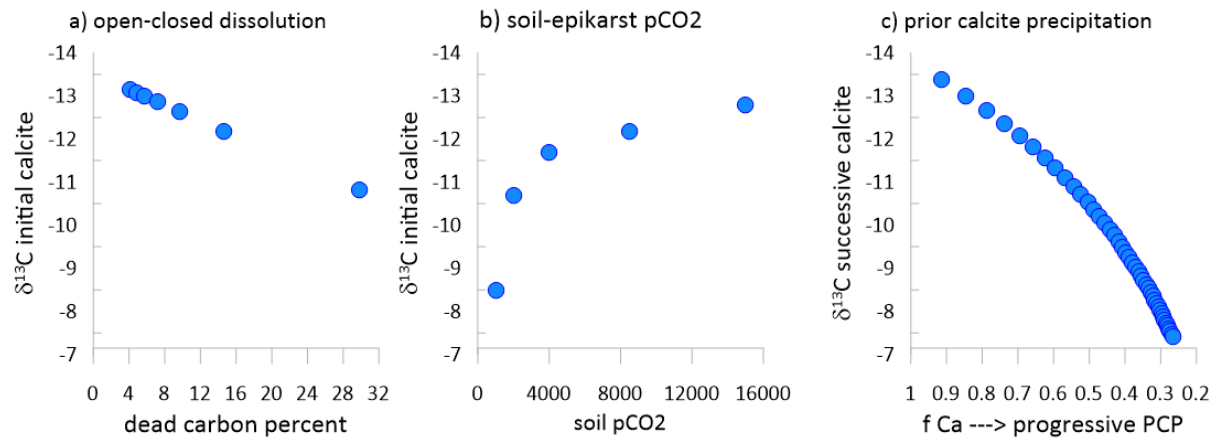


Figure 1: Processes dominantly affecting stalagmite  $\delta^{13}\text{C}$ . a) Carbonate bedrock dissolution under open-closed system conditions (shown by percent of dead carbon added to solution), b) soil  $\text{pCO}_2$  that the solution equilibrates with, c) prior calcite precipitation, i.e., how much carbonate is precipitated before reaching the stalagmite. The dissolution process can be constrained using DCF, while PCP is constrained using  $\delta^{44}\text{Ca}$ . Soil  $\text{pCO}_2$  affects all three proxies, but can be constrained further using the coupled relationship with  $\delta^{13}\text{C}$  from the mixing lines.

### Figure 3

- Complete figure caption to highlight the paired U-Th and  $^{14}\text{C}$  ages shown at the bottom of the figure. Refer to the Suppl. Table 2 (if it exists?)

Response: Thank you for this suggestion, we will add a note to the figure caption and refer to Suppl. Table 2.

### Figure 6

This figure seems too compacted. Try to uniform the criteria for all Figures, so the period of interest (from 26 ka to 4 ka?) and the relevant events of the study are clear.

Response: We will update this figure accordingly.

### Main text

References are made to the text by giving [line numbers: “text quotes”].

[Line 15 “underwent dramatic climatic and environmental change”]

Please remove “dramatic”. If qualifying the change is needed, any alternatives? “profound” is used for the Introduction, what about “significant” here?

Response: Done

[Lines 17-19 “global carbon cycle” ... “on local soil respiration”]

My recommendation is that neither the word “global” nor the point to “local” fit in here or at least may add confusion. The present work may have “regional” application (and unvaluable as such!) for similar temperate environments of Western Europe when results are properly reproduced in subsequent studies.

Response: Thank you for this suggestion. We have removed the term “local” from the sentence, but retained “global carbon cycle” as this refers to the significance of understanding soil respiration at a global scale.

[Lines 21, 73, 88, 92, 325, 336, 337, 349 ... “Northern Spain”, “NW Spain”, “northern Spain”...]

Check for consistency and consider changing to geological terms such as “NW Iberian Peninsula”.

Response: Thank you for the suggestion. We have changed the term to “NW Iberian Peninsula” throughout the text.

[Lines 34-35 “Between 22 and 10 ka BP (ka: thousands of years, BP: “before present”, with the present referring to 1950 CE),”

[Lines 103-104 “Minimum average temperatures are reconstructed for Heinrich event 1 (H1; 18-15 ka BP) and are ~8°C cooler than those of the Holocene Thermal Maximum (~8 ka BP; Darfeuille et al., 2016).”]

[Lines 246, 252, 256, 260, 298, 301, 333, 427 ... “LGM (26.8 ka BP)” “the LGM (24 ka BP)” “(LGM, H1, and YD)” “during the LGM and YD” “~530-1030 ppmv during the LGM, and ~1155-5780 ppmv during the EH”]

[Line 316 “for the Early Holocene (EH, post 10 ka BP) and the Late Glacial (LG, pre 10 ka BP and including deglacial)”]

These excerpts use terms and chronostratigraphic units that must be clarified.

For instance, “last glacial maximum” (LGM) is used, though I am afraid I do not find the complete acronym meaning anywhere in the manuscript. In any case, both characterisation and timing of the LGM are complex enough for including the term here (see different approaches and stratigraphy ranging from ca. 33 ka to 26.5 or 23 ka to 19 ka, depending on literature e.g., Peltier & Fairbanks, 2006, QUAT. SCI. REV. 25; Clark et al., 2009, SCIENCE 325; Batchelor et al., 2019, NATURE COMM. 10; Gowan et al., 2021, NATURE COMM. 12; and references therein). Decoupling between temperatures and ice volume is specifically pronounced during deglaciations. Temperature estimations at the Iberian Margin suggest that the LGM was not a real stadial but a kind of weak interstadial. Although undoubtedly cold, it was not the coldest interval. The coldest intervals are observed during Heinrich events. Following the reference used in the manuscript (Lambeck et al., 2014), the main phase of deglaciation occurred from ca. 16.5 ka to 8.2 ka. My advice would be to delete any reference to “the LGM” and stick to two phases Late Glacial (LG) and Early Holocene (EH). Similarly, avoid the reference to a “Holocene Thermal Maximum”, which is an even more diffuse designation. The “Holocene temperature conundrum” debate will likely remain highly contentious over many years to come (Liu et al., 2014, PNAS 111; Bader et al., 2020, NATURE COMM. 11; Martin et al., 2020, QUAT. SCI. REV. 228; and references therein).

Additionally, the base of the Holocene must be placed ca. 11.7 ka, not 10 ka (Walker et al., 2009, J. QUAT. SCI. 24) and the EH spans from 11.7 ka to 8.2 ka (Greenlandian; Walker et al., 2019, J. QUAT. SCI. 34), though technically speaking the present study shows results up to 4 ka in Fig. 3, i.e. the Mid-Holocene (Northgrippian; Walker et al., 2019, J. QUAT. SCI. 34). This does not alter the results of the manuscript but respects the formal definition and dating established, in line with the useful INTIMATE event stratigraphy of Greenland interstadials and stadials (GI and GS, respectively; Lowe et al., 2008, QUAT. SCI. REV. 27; Rasmussen et al., 2014, QUAT. SCI. REV. 106; Mojtabavi et al., 2020, CP 16, 2359). For the LG events, please consider this nomenclature (i.e., use GS-1, not YD; and GS-2.1a, not H1), which implies showing a Greenland  $\delta^{18}O$  profile in the Figures where these intervals are discussed. These are aspects of relevance to the subject because, the manuscript works on and paves the way to well dated speleothem material, with chronologies specifically reviewed within the SISAL database, version 2 (Comas-Bru et al., 2020a,b).

Response: We thank the reviewer for this in-depth comment. We apologise for the inconsistencies in terminology and chronostratigraphic units used in the text, and we agree that it is best to stick with the LG/EH time slices. Given our updated modelling framework with different mixing lines accounting for changes in atmospheric CO<sub>2</sub> over the glacial-interglacial transition, we now use three time slices: LG for the period older than 24 ka, DEG for the deglacial transition (15-11.7 ka), and EH for the period younger



than 11.7 ka. We have also changed the nomenclature for the LG events as suggested, and show the Greenland  $\delta^{18}\text{O}$  record together with the Iberian Margin SST record in figures 1 and 3.

[Lines 96-99 “(AEMET meteorological stations at Santander and Oviedo, period 1973-2010; AEMET, 2020)” “(AEMET meteorological station at Santander, period 1987-2000; AEMET, 2020)”]

[Lines 469-470 “AEMET, 2020. State Meteorological Agency (AEMET) [WWW Document]. URL <http://www.aemet.es/en/portada> (accessed 470 10.8.20)”]

Not sure I understand the data source used here. Are the time intervals 1973-2010, 1987-2000 chosen for a particular reason? Is there a gap between 2010 and 2020? Can the series be shown for instance in the new Figure? Something that illustrates the seasonality in the region and explains more clearly the assumptions for the parameters involved in the present study (cave-monitored  $\text{CO}_2$ ,  $\delta^{13}\text{C}$ , etc).

Response: This refers to the governmental meteorological agency data. We will add more clarifications with respect to the effects of seasonality on soil and cave parameters to the text and add the new figure (Figure 1).

[Lines 98, 101-102, 106-107, 197-198, 407-409 “winter months (December-February)”, “summer months (June-September)” “estimate of the deglacial temperature change in caves on the coastal plain, as the region’s modern seasonal cycle displays similar amplitude to sea surface temperatures (Stoll et al., 2015).” “caves are well ventilated in the cold season with close to atmospheric  $\text{pCO}_2$  values, but feature elevated  $\text{CO}_2$  concentrations during the warm summer season (Stoll et al., 2012).” · “Cave monitoring data from winter months (December-March) were excluded from the regression analysis”; “Two model scenarios mimic full glacial and Holocene conditions, including changes in temperature, cave  $\text{pCO}_2$ , and soil  $\text{pCO}_2$  for “winter” (i.e., atmospheric) and “summer” (i.e., elevated) cave  $\text{pCO}_2$  (Suppl. Fig. 4).”]

Response: Thank you for spotting this. We will refer to the months more clearly in the next version of the manuscript.

Please correct “mimick” to ‘mimic’; or better still, change the word to “simulate”?

Response: Done.

Seasonal changes, both in  $\text{CO}_2$  and temperature, appear crucial for interpretation of the results. Please clarify as much as possible throughout the manuscript. This would improve if illustrated with the new Figure. The reader would appreciate a clearly understandable and comprehensive discussion on that. For calibration purposes, I wonder if databases considering non global atmospheric  $\text{CO}_2$  values but continuous seasonal  $\text{CO}_2$  measurements from the ground-based network ICOS may be of some assistance here (Integrated Carbon Observation System, ICOS; Ramonet et al., 2020, Phil. Trans. R. Soc. B 375). Any comments?

Response: Thank you for this comment and the suggestion to use regional  $\text{CO}_2$  measurements. As suggested by reviewer 1 we do now include the measured modern (rather than Suess-corrected)  $\delta^{13}\text{C}$  data and a modern atmospheric end member. However, the seasonal variations in atmospheric  $\text{CO}_2$  are small relative to the range along the mixing line, and we find that using seasonally resolved modern atmospheric composition does not have any appreciable effect on the estimation of the modern respired end member. This use of a global  $\text{pCO}_2$  is also consistent with the approach we must take for the speleothem modeling, as we use ice core estimates of global  $\text{pCO}_2$  from glacial to early Holocene time periods.

[Lines 103-104, 343 “Heinrich event 1 (H1; 18-15 ka BP) and are ~8°C cooler than those of the Holocene Thermal Maximum (~8 ka BP; Darfeuil et al., 2016).” “Assuming a temperature change of roughly 8°C between the LGM and EH (Darfeuil et al., 2016)”] Please clarify. It seems the 8°C value accounts for the increase of temperatures between GS-2.1a (H1; ca. 18-15 ka) and the EH (before 8.2 ka). Other alternatives, i.e., from LGM to values after 8.2 ka seem closer to 6°C, though perhaps I am missing something here. I understand the selection criteria of the site used as a reference for temperature (Iberian Margin site MD95-2042; Darfeuil et al., 2016) is based on its chrono-stratigraphy? I’d suggest authors also highlight the fact that multiproxy studies have been performed on its strata. In Darfeuil et al., 2016, two complementary paleothermometers are discussed, the TEX86 and Uk’37 (annual mean sea surface temperatures, a potential shift towards summer production that may occur for glacial times?). Authors refer to the former only and the profile is shown in Fig 3. Any comment here considering seasonality? Please include considerations of the analytical and calibration errors of the estimates. What about alternative documentation provided by pollen transfer functions? Perhaps it would be preferable to have a sediment core further north, closer to the caves, though to my knowledge this is not available.

**Response:** Thank you for this comment. We will address this comment in the next version of the manuscript and clarify the underlying issues with these reconstructions (analytical and calibration errors, seasonality). It would indeed be very nice to have a sediment core closer to the caves, but as the reviewer points out, this is not available.

[Line 129 “Stoll et al., in review”].

If the paper is not publicly available at the time the present manuscript is published, I would suggest that the authors remove the reference in review and point to a different reference already peer-reviewed or add the information in this study.

**Response:** Thank you. This manuscript should be published soon and we will update the reference accordingly.

[Lines 142-145 “Reimer, 2013”; “Reimer et al., 2013”]

It may be advisable to work on the updated calibration curves, i.e. IntCal20 and Marine20; Reimer et al., 2020, Radiocarbon, 62; Heaton et al., 2020a,b, Radiocarbon, 62. For Marine20, marine reservoir ages are modelled as time-varying, though for IntCal20, speleothem dead carbon fractions are approximately constant over time but with an unknown level. Any comment here?

**Response:** We agree that in general the use of up to date calibration curves is advisable. However, since changes in the calibration curve over the studied interval are minor (and uncertainties related to chronology in the speleothems will be the dominant source of uncertainty in DCF) we refrain from updating the records.

The calculation of speleothem dead carbon fraction in our study is based on paired U-Th and <sup>14</sup>C measurements, which makes them especially robust as chronological uncertainty from age interpolation procedures is avoided. We are not sure what the reviewer refers to with respect to the dead carbon fractions in IntCal20: it is true that the DCF for the calibration curve intervals beyond atmospheric values is based largely on extrapolation of the well-constrained DCF at Hulu Cave, however, this does not directly affect our reconstruction (except for increased uncertainty in the calibration curve, which then translates to the DCF values).

[Line 360 “vegetation cove”]

Change to “vegetation cover”.

**Response:** Thank you for spotting this mistake, now corrected.

[Line 433 “ $\delta^{13}\text{C}_{\text{spel}}$  over the last deglaciation in Western Europe is best explained by c”]

Please complete the sentence.

Response: Apologies for this mistake, it is now corrected and the sentence reads: “... the temperature sensitivity of  $\delta^{13}\text{C}_{\text{spel}}$  over the last deglaciation in Western Europe is best explained by increasing soil respiration.”

**References cited:**

- Mattey, D.P., Atkinson, T.C., Barker, J.A., Fisher, R., Latin, J.-P., Durell, R., Ainsworth, M., 2016. Carbon dioxide, ground air and carbon cycling in Gibraltar karst. *Geochim. Cosmochim. Acta* 184, 88–113. doi:10.1016/j.gca.2016.01.041
- Rudzka, D., McDermott, F., Baldini, L.M., Fleitmann, D., Moreno, A., Stoll, H., 2011. The coupled  $\delta^{13}\text{C}$ -radiocarbon systematics of three Late Glacial/early Holocene speleothems; insights into soil and cave processes at climatic transitions. *Geochim. Cosmochim. Acta* 75, 4321–4339. doi:10.1016/j.gca.2011.05.022
- Wainer, K., Genty, D., Blamart, D., Daëron, M., Bar-Matthews, M., Vonhof, H., Dublyansky, Y., Pons-Branchu, E., Thomas, L., van Calsteren, P., Quinif, Y., Caillon, N., 2011. Speleothem record of the last 180 ka in Villars cave (SW France): Investigation of a large  $\delta^{18}\text{O}$  shift between MIS6 and MIS5. *Quat. Sci. Rev.* 30, 130–146. doi:10.1016/j.quascirev.2010.07.004