

Submission of reply to the comments made by Reviewer #3

Ms. Ref. No.: CP-2017-100

Title: Palaeoclimate significance of speleothems in crystalline rocks: a test case from the Lateglacial and Early Holocene (Vinschgau, northern Italy).

Reviewer #3

We thank the reviewer for providing thorough and constructive comments on our manuscript. Below we address each comment individually.

(reviewer text in italics)

General Comments:

The introduction is a bit short. The introducing part (Page 1, Line 22 to 35) could be more extended, with for example more details about the study of Frisia et al. (2017) about the analyses and results of similar studies. The part with the aim of your study (Page 1, Line 36 to Page 2 Line 17) is in relation to the introducing part quite long. Perhaps it is possible to move some of this to the methods part.

The introduction has been extended, but we have not shortened the description of the aims. We feel that the current description is appropriate in order to explain why these eight vein-lining deposits (out of a total of ca. 70 samples) were chosen for this study.

Overview pictures of the samples would be nice for the reader. In these pictures, it would be helpful for the reader, if all datings are marked and the ages are written next to them and the parts are marked used for this study. Therefore, it is clear that you used only specific time spans and that there is more material from other times spans.

A new figure (Suppl. Fig.1) showing the analysed hand specimens has been prepared. It is also indicated in the figure which section of each speleothem was examined in this study. We decided not to add the ²³⁰Th ages because this would overload the images.

Could you please mark the similarities of the isotope records in Figure 5. That would make it much easier for the reader to follow.

Fig. 5 has been modified for a better understanding. Dashed lines were added to show the similarities between the oxygen isotope records and the aragonite fabric is indicated by a pink background colour.

Could the occurrence of aragonite in the flowstone be interpreted as drier periods?

This is a very good point but we think that the reviewer might have missed this part in the text.

In our study aragonite should not be interpreted as a palaeoaridity indicator. A considerable effort was put into U-Th dating and petrographic analyses of these samples. The results do not show any systematic relationship between speleothem mineralogy and climate during the Lateglacial and the Early Holocene. Fig. 4 illustrates an example showing that while sample LAS 1 was deposited as an aragonite flowstone from ca. 13.0 to 12.3 ka, the coeval LAS 2 sample mostly formed as calcite.

Instead, petrographic analyses and hydrochemistry data of modern springs (Spötl et al., 2002) suggest that due to the high degree of total dissolved solids only a small change in water chemistry gives rise to either aragonite or calcite precipitation, partly reflecting the heterogeneity of this fractured aquifer. Accordingly, changes in speleothem mineralogy cannot be used to constrain the timing of past episodes of high vs. low precipitation.

In Section 2.3 we state (p.8 lines 12-15): “changes in speleothem mineralogy and growth rate are first and foremost driven by in-aquifer processes including PCP and/or PAP, as indicated by the TR samples and LAS 19 and LAS 72 (Figs. 4 and 6). Therefore, calcite-aragonite transitions and growth rate changes do not necessarily reflect an external (climate) signal, unless coeval samples show a coherent pattern.”

A sentence has been added to the Conclusions to emphasise this result.

Specific and technical Comments in chronological order:

Page 1, Line 13: Please replace “kinetic” with “disequilibrium”.

Corrected

Page 2, Line 29: Please replace “by mass movements” with “by the mass movements”.

An article has been added.

Page 2, Line 29: Please delete the “on” at the end of the line.

We think deleting “on” would slightly change the meaning of this sentence, therefore we prefer not to change this.

Page 4, Line 8: What calcite fabric occurs in LAS 72, 1, 2, 21 and 34? Please provide this information. Are these also columnar fascicular optic?

Yes, the characteristic calcite fabric in these samples is also columnar fascicular optic calcite. This information was added in the text.

Page 4, Line 29: Please replace “more enriched” with “higher”.

Corrected

Page 4, Line 30: Please replace “most depleted” with “lowest”.

Corrected

Page 4, Lines 33-34: I do not see two regression lines for LAS 2 in Figure 3. There should be one for the calcite part and one for the aragonite part, as I understood from the text.

Yes, there is only one regression line for LAS 2 in Fig. 3. We did not distinguish the two polymorphs graphically, because the two slopes are very similar to each other: $\delta^{13}\text{C} = 2.85 \cdot \delta^{18}\text{O} + 35.2$ (calcite) and $\delta^{13}\text{C} = 2.70 \cdot \delta^{18}\text{O} + 32.4$ (aragonite). $R^2 = 0.60$ and 0.79 for calcite and aragonite, respectively. Fig. 3 has been improved.

Page 5, Line 6: Please replace “more negative” with “lower”.

Corrected

Page 5, Line 8: Please replace “more positive” with “higher”.

Corrected

Page 5, Lines 12-13: Please add that the referred Table 1 is the Supplement Table 1.

Corrected

Page 5, Line 29: I think you mean “Suppl. Fig. 2a” instead of “Suppl. Fig. 5”.
Yes, the reference was corrected.

Page 6, Lines 9-10: Please give the exact temperature as a number.
This has been added to the text.

Page 6, Line 14: What do you exactly mean with “...primarily regarded as a proxy for $\delta^{18}\text{O}$ of local precipitation.”? There is no amount effect in the $\delta^{18}\text{O}$ of the precipitation in the Alps. Therefore, the $\delta^{18}\text{O}$ of the precipitation should have a relation to temperature. Due to the quite long transfer time of the water you mentioned, the water should contain long-term changes in the $\delta^{18}\text{O}$ of precipitation and therefore, of long-term changes in temperature. Please add some more information to this topic at this point.

We agree with the reviewer that there is no amount effect in the $\delta^{18}\text{O}$ data of precipitation in the Alps. We interpret the oxygen isotopes in our record primarily as a proxy of $\delta^{18}\text{O}$ in precipitation. A temperature rise of 1°C would lead to $0.59\pm 0.09\text{‰}$ higher isotope values in precipitation in the mid and high latitudes (Rozanski et al., 1992). This would be partially counterbalanced by the isotope fractionation when calcite/aragonite forms. The temperature dependence of the oxygen isotope fractionation during calcite precipitation is $-0.24 \text{‰}/^\circ\text{C}$ based on experimental studies (Kim and O`Neil, 1997), while a somewhat higher value ($-0.18 \text{‰}/^\circ\text{C}$) was determined by a cave-based study (Tremaine et al., 2011). Kim et al., 2007 reported a similar value ($-0.22 \text{‰}/^\circ\text{C}$) for the temperature coefficient for the oxygen isotope fractionation of aragonite. Consequently, for the study area a net isotope change of $0.35\text{--}0.41\text{‰}/^\circ\text{C}$ and $0.37\text{‰}/^\circ\text{C}$ is expected for calcite and aragonite, respectively.

Since the flowstone-forming water has a residence time of up to a decade (Spötl et al., 2002), we propose that these secondary carbonates record changes in the $\delta^{18}\text{O}$ of the precipitation and thus temperature on decadal to multi-decadal timescales.

LAS 6 is an annually laminated calcite sample. On an intra-annual time scale its $\delta^{18}\text{O}$ variability records surface temperature changes that were transmitted to the shallow subsurface by heat advection (Koltai et al., 2017). On a multi-annual time scale $\delta^{18}\text{O}$ variability of LAS 6 is replicated well by LAS 19, suggesting that the two flowstones were deposited close to isotopic equilibrium (Dorale and Liu, 2009). Thus, LAS 6 also provides insights into the changes of $\delta^{18}\text{O}$ of precipitation on (multi-)decadal timescales.

In response to the reviewer`s comment we clarify this in the revised text.

Page 6, Line 19: Please replace “kinetic” with “disequilibrium”.
Corrected

Page 6, Line 27: Please replace “more enriched” with “higher”.
This sentence had a mistake, which has been corrected.

Page 6, Line 29: I am not sure if a co-variation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ indicate in-aquifer processes. Therefore, please delete “as indicated by the co-variation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopes.”.

We slightly disagree with the reviewer on this. Although prior calcite/aragonite (PCP/PAP) mostly influences the carbon isotopic composition of the speleothem, laboratory studies show

that calcite precipitation results in the progressive enrichment in both ^{13}C and ^{18}O (e.g. Polag et al., 2010; Dreybrodt and Scholz, 2011). Consequently, we suggest that PCP may lead to progressively higher $\delta^{18}\text{O}$ values along the flowpath, even if this change may be much smaller in amplitude than that of $\delta^{13}\text{C}$. Laboratory studies investigating the influence of PAP on the stable isotope composition of the precipitating aragonite are lacking, but a simultaneous enrichment in ^{13}C and ^{18}O is to be expected.

In response to the reviewer's comment, we provide further discussion on this in the text.

Page 6, Line 35: Please replace "kinetic" with "disequilibrium".
Corrected

Page 7, Line 5: Please replace "kinetic" with "disequilibrium".
Corrected

Page 7, Line 9: Please replace "kinetic" with "disequilibrium".
Corrected

Page 7, Line 23: Please replace "kinetic" with "disequilibrium".
Corrected

Page 7, Lines 34-35: Please delete "and thus provide short snapshots of local climate.". For me a multi-decadal to centennial resolution to not provide snapshots, which are some very short time-intervals for me.

We rewrote this sentence in order to emphasise that such fracture-lining flowstones may provide a fragmented record of the local climate history, but have only a limited potential to deliver a long (multi-millennial), continuous record.

Page 8, Line 9: Please replace "kinetic" with "disequilibrium".
Corrected

Page 8, Line 13: You refer to Fig. 8, however, there is no Figure 8 in the manuscript.
Corrected to Figs. 4 and 6.

Page 8, Lines 16-18: Please show this in a figure. That makes it easier for the reader.
A new supplementary figure (Suppl. Fig. 4) has been prepared.

Page 8, Line 20: Please refer also to the specific panel in Figure 6.
Done

Page 8, Line 20: Please mark the Younger Dryas and the Boling-Allerod in Figure 6.
Fig. 6 has been improved.

Page 8: Line 30: Please replace "more negative" with "lower".
Corrected

Page 8, Line 35: Please replace "kinetic" with "disequilibrium".
Corrected

Page 9, Line 2: Please specify the in-aquifer processes.

We do not think this is needed, because they are specified in the previous paragraph (p. 8 lines 36-37).

Page 9, Lines 3-4: You write here about changing hydrological condition. This could be discussed a bit more in detail in the discussion. For me it did not come up so clearly from the discussion. This is more a general comment.

The sentence has been modified for better understanding.

Table 1: Could you perhaps mark values from aragonite and calcite in different colours? That make it straight forward for the reader.

It would be difficult to mark the values for aragonite and calcite, because some of the samples are comprised of both polymorphs. Alternatively, we added a new column about mineralogy to make it easier for the reader.

Figure 1: Are there samples from the vein-filling flowstones from the two other sites at Spoding and Eysr? Do they perhaps provide time-spans missing in the other and could complete the record or give a better overlap?

Unfortunately, there are no other flowstones samples available from the other two fractures that cover the same time period. All the flowstones covering the 14.2-10.0 ka period were part of this study with the exception of one calcite-aragonite sample (LAS 71) from SQ site. This sample was not analysed in details due to its complex growth structure.

Figure 3: Please replace “kinetically” with “disequilibrium”.
Corrected

Figure 4: Please replace “230Th” with “²³⁰Th”.
Corrected

Figure 6: Please replace “shown in (e) and (d)” with “shown in (d) and (e)”.
Corrected

Figure 6: There is something missing in “represents the of LAS2,”.
Corrected

Figure 6: I think the blue rectangle marks the Younger Dryas, but this is not indicated in the figure or the figure caption.
Corrected

Yours sincerely,

Gabriella Koltai
(on behalf of all co-authors)