

Submission of reply to the comments made by Reviewer #2

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 text in italics)

Reviewer #2

We appreciate the positive and constructive comments which helped to improve this manuscript. We went through the detailed comments (e.g. typos, wording) and changed the manuscript accordingly.

Relationship with water chemistry

Spötl et al. (2002) presented some water analyses from the study area. The water are said to be highly mineralised. Can more discussion be drawn from those data about the likely conditions of growth of the fracture-fills, e.g Ionic strength, Mg/Ca, oxidation state, supersaturation etc?

In the Vinschgau, modern springs relevant for this study are characterised by slow discharge (< 1 l/sec), high electric conductivity (720-2300 $\mu\text{S}/\text{cm}$) and elevated Mg/Ca molar ratios varying from 0.25 to 3.28. All springs are supersaturated with respect to calcite and also to aragonite except for one. SI values reach as high as +1.2 and +1.0 for calcite and aragonite, respectively.

Section 2.1 has been extended to provide more information on water chemistry, and for further data we refer to the original research paper by Spötl et al., 2002.

Macroscopic nature of the precipitates

I think it would be helpful for readers looking for analogous occurrences elsewhere to provide a figure with macroscopic images of the vein-lining deposits and to describe and comment on features at this spatial scale.

A new figure (Suppl. Fig. 1) showing the hand specimens of the eight vein-lining deposits has been prepared.

Secondary calcite

P4, lines 9-10 and Figure 2. I could not see why this calcite couldn't be primary from the information provided. If it has straight extinction rather than undulose extinction that might be a criterion (as would a low Mg content)

We re-investigated the discussed thin section (LAS 2) and found indication of competitive growth of aragonite and calcite. Both the text and Fig. 2. have been corrected accordingly.

Stable isotope compositions

1. P6, lines 13-14. Carbonate isotopes are primarily interpreted as a proxy for isotopic composition of atmospheric precipitation, but temperature changes in the 13-10 ka intervals surely may have been sufficient to have influenced the composition of calcite too?

Thank you for pointing it out that this paragraph may have been misleading. Yes, changes in ambient temperature and therefore in fracture temperature most probably have had an influence on the speleothem isotopes. Speleothem $\delta^{18}\text{O}$ values are a function of cave air temperature and the $\delta^{18}\text{O}$ value of the carbonate-precipitating drip water (e.g. Lachniet, 2009).

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.

In response to the reviewer's comment we rewrote this part of the discussion to avoid confusion.

2. The relationship between carbon and oxygen isotopes in some samples is for a strong covariation, but the slope is not mentioned in the text. Carbon isotopes change much more than oxygen. Needs a bit more discussion, including ideas of Hansen et al (GCA, 2017) of which Spötl is a co-author. Could there be some equilibration effects here?

In response to the reviewer's suggestion we improved the paragraph by discussing the slope of the regression lines. Although studies for aragonite are lacking, laboratory experiments on calcite precipitates resulted in a regression slope of $\Delta\delta^{13}\text{C}/\Delta\delta^{18}\text{O}$ of 1.4 ± 0.6 (Wiedner et al., 2008) in case of fast degassing, while a modelling suggested that during slow degassing the slope of $\Delta\delta^{13}\text{C}/\Delta\delta^{18}\text{O}$ should approach an infinite value (Mickler et al., 2006). The authors do not see a reason to include the study by Hansen et al. (2017) in the discussion which only refers to calcite. The evidence of non-equilibrium isotope fractionation is compelling.

The aragonite phases of the LAS samples exhibit slopes of regression between 2.7 and 3.4. This indicates that disequilibrium isotope fractionation occurred during aragonite precipitation, whereby CO_2 hydration and hydroxylation reactions promoting oxygen isotope exchange between HCO_3^- reservoir and H_2O were not fast enough to maintain isotopic equilibrium (cf. Mickler et al. 2006).

3. The discussion properly considers potential differences amongst the conditions in which aragonite and calcite form.

a) However, the two phases are not distinguished in the crossplots of Figure 3 and I think it would be helpful to do this.

b) I also think that the data for the other samples should also be cross-plot to illustrate more clearly the variation in the extent of covariation.

LAS 34 and LAS 72 are aragonite samples. Aragonite and calcite are only present in LAS 2. Initially 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. Following the reviewer's suggestion Fig. 3 was modified and isotopic cross plots for other samples were included.

c) LAS34 is shown in Fig. 3, but ages are not plotted in a figure – the reason for this is apparently not referred to in the text.

We do not fully understand what the reviewer is referring to. The ages of LAS 34 are plotted both in Fig. 5 and Suppl. Fig. 2 and the growth period of LAS 34 is also mentioned in the text (p. 5. lines 24-25).

Suggested minor corrections

P1, Line 23. The words: "by yielding high-resolution, multi-proxy data" are redundant. By no means all of the iconic records are multiproxy or high-resolution.

Corrected

P2, line 20 "E-W" is conventional, not "W-E"

Corrected

P2, line 24 To avoid repetition of the word valley in "the deglaciation of the valley", how about "local deglaciation".

Corrected

P2, line 29. Reference to "highly mineralised". More details would be useful. Section 2.1 was expanded.

P3, line 27. "chemical" rather than "chemistry"

Corrected

P4, line 5 "detritus-rich" not "detrital-rich"

Corrected

P4, line 6 "however" requires a semi-colon before it and does not need the comma afterwards. Alternatively substitute "but".

Corrected

P4, line 7. "thick" not "wide". [the habit of some authors of referring to the "width" of layers comes from the dendroclimatological literature, but the geometry of tree rings is different]

Corrected

P4, lines 29-30. "enriched" and "depleted" Higher and lower delta values are meant. [see Sharp (2007)!]

Corrected

P4, lines 33-34. The actual slope of the regression lines is not mentioned. Carbon isotopes changes much more than oxygen.

This paragraph has been improved (please see discussion above).

P6, line 8 "springs"

Corrected

Figure 1. *Neither this figure nor the text mention the altitude of the site or specify its precise location. The precise locations of the fractures have been added to the text.*

Figure 2. *This figure (part c) does not make it clear why the secondary calcite cannot be primary since simultaneous growth of aragonite and calcite is also shown elsewhere.*

As mentioned above, we re-examined the thin section showed in Fig. 2c and excluded the presence of secondary calcite. Both the figure and the text have been corrected accordingly.

Figure 4, caption. *Superscript needed: ^{230Th}.*

Corrected

Figure 5 *has references to colour, but these need to be made more explicit for the colour-blind. Add a background shade for the aragonitic sample, as in Figures 4 and 6.*

Thank you for the suggestion. Pink background colour has been added.

Figure 6 *reference to colour in the caption should be supplemented by writing the name of the sample next to the plots on the figure itself.*

Sample names have been added to the figure and the figure caption has been modified.

Supplementary information

Supplementary table 1. Excessive significant figures for ^{238U} and ^{230Th}/^{232Th} ratios?

It would be useful to present the STALAGE age models graphically in the supplementary information

StalAge models were graphically already presented in the original version of the manuscript as Suppl. Figs. 1-2.

Yours sincerely,

Gabriella Koltai
(on behalf of all co-authors)