Submission of reply to the comments made by Reviewer #1
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 #1

We are grateful for the positive and helpful comments and we address below the points raised by this referee (in italics).

First, the complete data for oxygen and carbon isotope analysis is not available in either manuscript, or supplementary documents. The data table only listed min and max isotope values for each of the nine samples. This greatly restricted exploration of the data by readers who intend to do so.

Due to the large amount of data we prefer not to include a long separate table in the supplementary materials, unless the editor tells us otherwise. We will make the results of stable isotope analyses available on the NOAA website once the manuscript is published.

Second, the presentation of oxygen isotope record is fragmented and difficult to read. Because aragonite and calcite fractionation factors are known, it may worth converting aragonite stable isotopes values to equivalent calcite values and construct a composite record. This may produce a more readable time series, which can be more easily compared with ice core record. On these time series, it is also apparently that some samples represent much larger time windows than others (e.g., fig 5, first SQ time series, between 10-10.5 ka). For these samples, line graph masked the uncertainty in the magnitude and frequency of the variations. Authors may consider not connecting the individual data points in these locations.

Yes, the stable isotope record is fragmented. We decided to present the samples belonging to each fracture separately, because the figure is difficult to read if the eight time series overlap each other. We are aware of the possibility of converting the aragonite oxygen isotope values to equivalent calcite values. Our main concern about a composite $\delta^{18}O$ record is the lack of sufficiently long overlapping segments. We run the ISCAM algorithm (Fohlmeister, 2012) for all coeval samples, but due to the shortness of common depositional periods no stacked records could be built. Thus, we prefer not to construct a stack record.

The chronology of LAS 72 suggests that there may be a hiatus between 10.57 ± 0.3 and 10.12 ± 0.2 ka. In the revised manuscript separate age models are provided for the two sections of the flowstone. The text and the figures have been corrected.

Third, I have reservations on the reliability of using covariance of oxygen and carbon isotopes as an indicator of the presence of kinetic effects. As pointed out in Feng et al. (2012) and Myers et al. (2014), oxygen and carbon isotopes of calcite are affected by difference factors: PCP/PAP is the major control on calcite isotope values, where it has virtually no impact on oxygen isotopes, which is controlled by evaporation, growth rate. A strong covariance between oxygen and carbon isotopes does not necessarily indicate a significant impact of oxygen isotope kinetic fractionation.

We are not entirely sure if the reviewer is referring to the paper by Meyer et al. (2014) published in GCA or a different paper. Also, it is unclear to us if the reviewer means carbon isotope values instead of calcite isotope values (line 4). In our response, we consider that she/he meant carbon isotope values.

First of all, we mostly agree with the reviewer. Evaporation has a major control on oxygen isotope values, resulting in higher $\delta^{18}O$ levels in the remaining water and consequently in higher oxygen isotope values of the calcite/aragonite. We also agree that PCP/PAP has a significant influence on carbon isotopes values but has very little impact on the oxygen isotopes. Yet, as recent laboratory experiments indicate, PCP may have an effect on both isotope systems of the precipitating calcite (Polag et al., 2010; Dreybrodt and Scholz, 2011). We suggest that PCP may lead to progressively higher $\delta^{18}O$ values along the flowpath, even if this change may be much smaller in amplitude than that of $\delta^{13}C$. 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.

Although the covariance of carbon and oxygen isotopes values may therefore not necessarily point to disequilibrium isotope effects, it has been widely used as an indicator of kinetic isotope fractionation (e.g. Hendy, 1971). Hendy (1971) attributed this covariation to Rayleigh distillation enrichment of ^{13}C and ^{18}O in the HCO_3^- reservoir due to CO_2 degassing and secondary carbonate precipitation. Even though the “Hendy test” has been criticised (e.g. Dorale and Liu, 2009), we propose that in samples LAS 2, LAS 34 and LAS 72 the observed correlation between the two isotopes most probably suggests strong disequilibrium isotope fractionation based on the arguments below.

(1) The slope of regression of $\Delta\delta^{13}C/\Delta\delta^{18}O$ varies 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). The theoretical model of Guo et al (2009) calculates a slope of 2.3 when $CaCO_3$ precipitation, dehydration and CO_2 degassing were dominant.
(2) Coeval flowstones dominated by calcite do not show such a strong correlation between $\delta^{13}C$ and $\delta^{18}O$.
(3) Monitoring of springs in the Vinschgau suggests that calcite precipitation occurs close to isotope equilibrium with respect to $\delta^{18}O$ (Spötl et al., 2002), but note that at none of these springs aragonite is forming today. On the other hand, $\delta^{13}C$ values of both modern speleothems and DIC show difference between pool and vadose settings, pointing towards more pronounced CO_2 degassing and related disequilibrium isotope fractionation in the vadose zone.

Thus, without coeval flowstones showing a consistent signal, the $\delta^{18}O$ variability of the aragonite samples should be treated with caution. In the revised manuscript we provide further discussion on this topic.

Fourth, lack of image of the samples studied. Most speleothem samples from cave have regular growth patterns and readers are familiar with them. A flowstone grew in the fracture of non-karst settings is more difficult to visually grasp. A photo of the sample (if it’s taken as a whole) or a diagram (if a core was taken) could help readers understand the work being done.

Good point. An additional figure (Suppl. Fig. 1) showing the hand specimens has been prepared.

Fifth, Large part of section 5.3 seems belong to the introduction section rather than discussion section. The introduction section, as written, is a bit light. Moving some part of the text from 5.3 to introduction may provide more background for readers before presenting the details of the study.

In response to the reviewer`s suggestion both the Introduction and section 5.3 of the Discussion have been modified.

Lastly, author should address the problems surrounding the flowstone. Most studies avoid flowstone due to concerns of kinetic effects, what steps have authors taken to avoid this pitfall?

In the Vinschgau, speleothems form exclusively as flowstones. We evaluated our data critically and assessed if calcite and aragonite deposition occurred in isotopic equilibrium (5.1. Stable isotope systematics). Secondly, the influence of PCP/PAP and evaporation on the different speleothem proxies (stable isotopes, growth rate, mineralogy) is also discussed in detail (under 5.2. Aquifer-internal processes). Thirdly, we compared changes in mineralogy and oxygen isotope composition between coeval flowstones (both from the same fracture and from different fractures) to provide replication tests as suggested by Dorale and Liu (2009). Given that the $\delta^{18}O$ variability of the coeval carbonates is comparable (e.g. LAS 6 and LAS 19) we argue that these samples reflect primarily an external (climate) signal.

Lastly, we would like to point out that similarly to stalagmites flowstones have been shown to be valuable palaeoclimate archives (e.g. Baker et al., 1995; Holzkämper et al., 2005; Drysdale et al., 2006; Boch and Spötl, 2011; Meyer et al., 2012; Regattieri et al., 2014; Koltai et al., 2017).

Yours sincerely,

Gabriella Koltai
(on behalf of all co-authors)