Reply to comments of referee #1 Dominique Genty

Referee #1: *This is an excellent work that will mark a milestone. Lot of people were waiting for upgrading the former fluid inclusion devices to the new laser instruments, S. Affolter and co-authors did it in a very good way. First, the procedure appears relatively simple to setup and I guess that we will have several similar systems in the next few months in different labs that work on speleothems, at least. Second, the authors present clever innovations, like the vaporization of a standard water in the line to keep high enough the water background for an accurate and stable measurement. Moreover, desorption tests, laser calibration, stabilization of the system demonstrate the innovation and the carefulness of the approach in order to get the most reliable measurement. Beside the technical aspect of this study, authors present a very good and complete review of the former technical works made on FI. It is well written and figures are clear and all of interest.*
I would only criticize the beginning and the end of the article: the introduction part should be more careful about what we know on present day systems (i.e. rainfall/drip rate/FI d18O relationships), the last sample analysis on a recent calcite deposit, which, to my opinion is not enough described and, in any case, is not sufficient to draw such conclusion on a possible oxygen exchange between water and calcite. This is a great study that must be published as soon as possible.

We would like to thank for your appreciation of our work.

Referee #1: *p. 431, L11-26 : Despite the fact that the fluid inclusion isotopes has an enormous potential for paleoclimatic reconstructions, I think that the presentation in the Introduction part is sort of idealistic and I would be more careful here : 1) Most of speleothems are out of isotopic equilibrium, the paleotemperature calculation is thus not straightforward with fluid inclusion and calcite isotopes only (see Mickler et al. 2006). A promising way is certainly to combine D47 measurements with fluid inclusions ones (Daeron et al., 2011). 2) What do we know about the exact relationship between : a) rainfall d18O and drip d18O ?; b) drip d18O and FI d18O on modern calcite that precipitated at the same place and on stalagmite-shapped sample ? The Harmon 1979 was certainly a pioneer work, but, first the dD error at that time was quite large, and second, they did not study in details the relationship between present day drip and modern calcite FI d18O fed by the same water.*

We agree with Genty that all aspects of the complexity of calcite $\delta^{18}O$ are sparsely discussed in our first version, in particular the issue of non-equilibrium calcite deposition is hardly. Therefore we added the following sentences after line 16:
L16: However, one must keep in mind that speleothem calcite $\delta^{18}O$ values are often affected by kinetic fractionation (Mickler et al., 2006). It has therefore been suggested to use the empirical relationship between cave temperature and measured calcite $\delta^{18}O$ values in many different caves that already inherently documents the disequilibrium during the calcite precipitation (Tremaine et al., 2011). The calcite-water system fractionation can be calculated from the calcite and water isotope delta values. Another way would be to combine clumped isotopes ($\Delta47$) and isotopic compositions from fluid inclusions to correct for isotopic disequilibrium (Daeron et al., 2011;Wainer et al., 2011). Moreover the relationship between $\delta^{18}O$ in the atmosphere, drip water and fluid inclusions has been described in close detail by Lachniet et al. (Lachniet, 2009).

Referee #1: *p. 435, L25-26: Moreover, does the "pool spar" samples used in Dublyansky and Spotl (2009) to demonstrate the correspondence between FI and parent water d18O reflects*

the same conditions of a calcite precipitation on stalagmite tip ? Even if these questions do not concern the main topic of this work, they raise more complicated interpretations of FI isotopes. Certainly, the great advance of this study will contribute to clarify most of them.

We agree with the reviewer that this remains to be shown, therefore we changed the sentences as follows:
More recently, experiments have shown that fluid inclusions in "pool spar" preserve the both the oxygen and hydrogen isotopic composition of parent drip water (Dublyansky and Spotl, 2009). It remains to be shown that their findings are also valid for fluid inclusions of stalagmites.

Referee #1: *p. 435, L2 : do you estimate the variability of the vapour flow 65 mL/min + or - ?*

65 ± 0.1 ml/min corresponds to the mean flow reaching the detector (Picarro system) under measuring conditions.

Referee #1: *p. 435 : L21 : it seems that a quite large fraction of the calcite is not well crushed, likely reducing the efficiency, i.e. less FI water is extracted*

In two additional grain size determinations done on crushed stalagmite samples we observe the same grain size distribution as given in the CPD manuscript, i.e. approximately 17-24 % for the fraction under 200 μm for samples of 0.6 and 1.1 gram, slightly less that of Dublyansky and Spötl (2009). Therefore, the efficiency of our system is still improvable which potentially could lead to a significant reduction of sample amount required.

Referee #1: *p. 436 : I guess that the saw wire is 0.3 mm and not 0.3 _m (?)*

Yes, the saw wire is 0.3 mm. We will correct this in the revised version of this manuscript.

Referee #1: *p. 437 : please indicate also the diameter in cm*

The inch unit is commonly for these parts, therefore we will leave those, unless the editor requires it. (3/8'' = 0.9525 cm; 1/4'' = 0.635 cm).

Referee #1: *p. 440 : you decided to fix the mixing ratio at 13000 ppmv, but why not slightly higher, i.e. 18000 ppmv, where the stability is more sure from figure 5 ?*

13000 ppmv is a compromise between the stability of the instrument in terms of water vapour mixing ratio (after 13000 ppmv, background water is less stable with a standard deviation of around 30 ppmv). As the delta values stabilities are good after 13000 for both δD and $\delta^{18}O$, the limiting factor seems to be the stability of the water background. This value is most probably dependent on the line properties and therefore requires a determination for each individual line.

Referee #1: *p. 442 : how to you proceed to go down to 2H for one sample analysis while it is 5H for a secure procedure ?*

The protocol presented was established to understand precisely how the line reacts/behaves in the various measurement steps. For example, we can trace whether the presence of a sample or powder in the tube has an influence on the behavior for δD and $\delta^{18}O$. With this procedure,

we had a technical control to check various influences on the delta values and water vapor mixing ratio.

Moreover, measurements are independent and mainly dependent on three factors: the stability of mean δD and $\delta^{18}O$ values as well as the water vapor mixing ratio, but as the Picarro system is stable on a weekly basis (experienced), we can safely assume that there is no trend during sample analysis period. Furthermore, the background values give a fair amount of information on the instrument stability due to the recordings throughout the measurements.

Having this in mind, we are convinced that we can process up to five measurements of single speleothem samples in a row per day. 70-90 minutes to desorb/recover measuring conditions and around 30-60 minutes for the sample measurement per sample, including a standard determination in the morning and in the evening. In addition series of standard measurement could be run once a week to control the stability and possible drift of the instrument with time.

Referee #1: *p. 443, L5 : we skip from figure 7 to figure 10 here, I did not found reference to figures 8 and 9 in the text*

Reference to Fig. 8 will be added. Reference to Fig. 9 is given on page 442, line 16.

Referee #1: *p. 445, L25-27 and p. 446, L2-5: you should give more information about the modern sample because you first results on it is of first importance. How old is this sample and what constrained its growth age and duration? Did it grew exactly under the stalactite that produced the analyzed drip water? Also, is the drip water d18O constant all over the year at this station?*

We will add the following section in the revised version of this manuscript:
The stalagmite was active and the measurement corresponds to a mixture of fluid inclusions coming from the top comprising the last 40 years. The sample grows exactly under the stalactite where drip water was collected and monitored. The collection was made on a three month interval during the last two years and the isotopic composition of the drip water show fairly small variations ranging between -8.71 ‰ and -9.20 ‰ in $\delta^{18}O$.

Referee #1: *Your last sentence that suggests a possible oxygen exchange between calcite and inclusion water seems to ruin most of the interest of doing FI isotopes because in such a case, the importance of the exchange will not be predictable. I think you don't have enough modern samples to make such a conclusion.*

We agree with Genty that we do not have sufficient information to draw such a conclusion. Indeed, there are several potential causes that could explain the observed difference in $\delta^{18}O$, such as a kinetic fractionation during the enclosure of the fluid inclusion water which would result in an easy observable shift for $\delta^{18}O$ (i.e. 1 ‰ shift as observed compared to 0.4 ‰) but not for δD (1 ‰ shift similar as for $\delta^{18}O$ compared to 1.5 ‰) due to their larger measurement uncertainty.

We propose to change the text in the manuscript as follows:
The observed isotopic offset between drip water and fluid inclusion for $\delta^{18}O$ of around 1 ‰, while δD values of drip and fluid inclusion water are identical might indicates an exchange between calcite and inclusion water after its formation or it could document a kinetic fractionation (similar in magnitude for both oxygen and hydrogen isotopes) during the

enclosure of the fluid inclusion water. The latter would be easy observable for $\delta^{18}O$ within its uncertainty of 0.4 ‰ but not for δD due to its larger uncertainty of 1.5 ‰.

References:

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