Reply to Short Comment of A. Demény

A. Demény: *I would have some suggestions for the revision of the paper. 1) Citations. There have been soem papers published on the use of laser spectroscopy for water extracted from minerals. I would suggest to cite them - G. Koehler, L. I. Wassenaar. Determination of the Hydrogen Isotopic Compositions of Organic Materials and Hydrous Minerals Using Thermal Combustion Laser Spectroscopy. Analytical Chemistry 2012, 84, 3640. - D. A. Hodell, A. V. Turchyn, C. J. Wiseman, J. Escobar, J. H. Curtis, M. Brenner, A. Gilli, A. D. Mueller, F. Anselmetti, D. Ariztegui, E. T. Brown. Late Glacial temperature and precipitation changes in the lowland Neotropics by tandem measurement of d18O in biogenic carbonate and gypsum hydration water. Geochimica et Cosmochimica Acta 2012, 77, 352. – Demény A & Czuppon G (2013): Developments in hydrogen and oxygen isotope analyses of inclusion-hosted waters using laser spectroscopy: domination of crustal fluids in the formating of the Yungul-Willmott fluorite deposit, NW Australia. 12th Stable Isotope Network Austria (SINA) Meeting. Graz, Ausztria, 2013 - Demény A & Czuppon G (2013): A Novel Method of Stable H and O Isotope Analyses of Inclusion-Hosted Waters Based on Laser Spectroscopy. Mineralogical Magazine, 77(5) 970*

We thank Dr. Demény for the additional references. We will include Koehler (Koehler and Wassenaar, 2012) as well as Hodell (Hodell et al., 2012) but we hesitate to reference to the other publications since they are all referring to conference contributions only. Otherwise there would be many to be cited.

A. Demény: *2) Heating to 140 oC. It is possible that you were lucky with the Borneo stalagmite, but the preheating to 140 oC sounds too high for me. I have observed partial decrepitation even at 80 oC (actually it could be inclusion stretching and diffusion), shifting the isotopic compositions in positive directions.*

Similar temperature has been shown to give successful analyses using the pyrolysis coupled to mass spectrometry method (Vonhof et al., 2006;Dublyansky and Spotl, 2009). Heating to 140°C clearly leads to an overpressure of the fluid inclusions that may cause cracks in the surrounding calcite and decrepitation surely occurs during the process. However, the amount is so small that we haven't seen any clear signal/perturbation on the spectrograms. This is probably due to the fact that released water from fluid inclusions decrepitation slightly diffuses through cracks and the released tiny amount of water is smoothed by the line volume and by the mixture with standard and ambient vapor when escaping from the sample. During fluid inclusions decrepitation, the water will follow micro cracks to slowly diffuse out of the sample, nevertheless the question is, once fluid inclusions crack, whether the water has enough time (during the restoration of original conditions before the crushing) to escape or whether it diffuses so slowly through cracks that it stays in the sample. If decrepitation occurs at the periphery of the sample, tiny amounts of water will be released to the environment and lost. In our experience we found no indication of loss.

A. Demény: *3) Productivity. 2-5 hours per sample means that the method has much less productivity than for example the procedure described by Vonhof et al. (2006) or Arienzo et al. (2013).*

The presented procedure which lasts five hours intended to investigate and to understand precisely how the system is reacting to various measurement parameters and crushing. As the principle is new, we took care to test and avoid any source of errors. Of course, we think that this procedure can be optimized, an estimation of two hours is necessary for one sample (for

more information see reply to referee #1 from D. Genty). (Arienzo et al., 2013) wrote in their publication: *"…the entire process takes between 1 and 2 hours. After the measurement cycles… The line is purged with dry N_2 for approximately 30 to 60 min to remove adhered water vapor before the next measurement cycle."*, which sounds like a total measuring time including desorption between 1h30 and 3h. This is very similar to our improved measurement time per sample.

A. Demény: *4) Data verification. You have measured only two stalagmites. For the one from Borneo no dripwater data are available, and we don't know whether the Borneo dripwaters really follow the Global Meteoric Water Line, or this is just accidental agreement. The Swiss sample gave 1 permill lower d18O than the dripwater composition. Analysing more samples with "known" isotopic compositions would be desirable. Since Arienzo et al. have already described a PICARRO-based method, I think this paper should be extended with more samples analysed.*

The Borneo sample comes from the Gunung Mulu National Park and is between 460-330 ka old. Drip water data are not yet available for this cave (Moerman et al., 2013a). Nevertheless, few data of drip water from Borneo are available for the "Wind cave" located in the same region. These data show an isotopic composition of $\delta^{18}O$ drip water of -6.6 ± 1.0‰ and -7.0 ± 1.1‰, respectively for slow and fast drip waters which fits with the $\delta^{18}O$ in rainfall collected at three stations around the cave system, the mean $\delta^{18}O$ values of the rainfall is -6.7 ± 2.8 ‰ for the time period 2003-2006 (Cobb et al., 2007). Later, (Moerman et al., 2013b) showed that the local meteoric water line for Gunung Mulu National Park for a five years daily monitoring is $\delta D = 7.9*\delta^{18}O + 10.3$, which is close to the global meteoric water line. Moreover, Moerman (2013) showed averaged delta values throughout the five years for δD and $\delta^{18}O$ of respectively -51.7 ± 28.9‰ and -7.8 ± 3.6‰. These observations agree with our Borneo test measurements. Details and references will be added to the manuscript.

References:

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