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Discussions

Interactive comment on "Reconstruction of drip-water δ^{18}O based on calcite oxygen and clumped isotopes of speleothems from Bunker Cave (Germany)" *by* T. Kluge et al.

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We acknowledge the helpful comments and suggestions provided by referee # 1. In the following, we address the comments of the reviewer in a point by point approach.

New figures included in this comment are marked with an R to distinguish them from the figures in the original manuscript.

1) Variability of the co-variation slope

The basis of the presented method is the co-variation of δ^{18}O and Δ_{47} offsets relative to equilibrium values. The relationship between both parameters (the co-variation slope) was determined on modern material from Bunker Cave and different caves in close vicinity. The most convincing argument for a temporally constant Δ_{47}-δ^{18}O co-variation slope in speleothems comes from the underlying process. The offsets in Δ_{47} and δ^{18}O values are related to the degassing of CO_2 from a super-saturated solution, which was examined in the theoretical work of Guo (2008), suggesting only a weak temperature dependence of the slope. As long as the underlying process, that causes deviations in Δ_{47} and δ^{18}O values, stays the same there is no reason to assume temporal or sample-to-sample variability of the co-variation slope. In addition, the value of the co-variation slope has been investigated empirically in modern material reflecting different degrees of kinetic isotope fractionation. The co-variation slope determined here is consistent with values from other locations in Europe, the Mediterranean, and South America (Affek et al., 2008; Daëron et al., 2011; Wainer et al., 2011) and shows no significant temperature dependence in the temperature range from 4-20°C. The consistency in the co-variation slope determined on modern material from different caves and speleothems (this study; Affek et al., 2008; Daëron et al., 2011; Wainer et al., 2011) argues against significant variability from sample to sample.

The application of the Δ_{47}-δ^{18}O co-variation method for paleoclimate reconstruction is based on the assumption of a constant co-variation slope over time. The precise investigation of this assumption is difficult as it requires high-precision temperature and water δ^{18}O data from the sample location for the past. The offsets of the Holocene parts of stalagmites BU1 and BU4 shown in Fig.2 were calculated for illustration purposes assuming a constant drip-water δ^{18}O value of -7.9 ‰ and a constant temperature of 9.5°C (8.5°C for sample BU4-9). This assumption was made for simplicity and is only applied for offset calculation for BU1 and BU4 samples and not for the actual drip-water reconstruction. For drip-water reconstruction the water δ^{18}O value is the unknown, whereas the temperature is taken from independent paleotemperature studies.

The actual climatic parameters likely deviated slightly from the assumed values for offset illustration (as seen in the reconstructed water δ^{18}O values of this study). Also, regional temperature variations of up to 2°C are likely. Global or hemispheric recon-

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structions (as e.g., by Mann et al., 2008) show a smoothed picture that suppresses climatic excursions on the regional scale. Such deviations may shift the δ^{18}O offset by 0.5 ‰ for 2°C. This value is substantial compared to the extent of the kinetic isotope fractionation in speleothems ($\sim$ 1 ‰). Thus, the deviation of the Δ_{47}-δ^{18}O co-variation slope of BU1 and BU4 from the modern values and each other is likely due to the uncertainty of the past reference temperature (and to a smaller extent to the drip-water δ^{18}O uncertainty). Furthermore, displaying the Δ_{47} and δ^{18}O offsets for both stalagmites separately (Panel A and B in Fig.1R) shows that most samples indeed agree with the modern Δ_{47}-δ^{18}O co-variation slope within uncertainty (the dotted line in Fig.1R corresponds to the $\pm$ 0.3 ‰ uncertainty of the modern drip-water measurements). Samples that deviate from the modern slope likely reflect climatic conditions that deviate from the assumptions (e.g., during the Holocene Climatic Optimum).

2) Equilibrium δ^{18}O and Δ_{47} calibrations

The question of which δ^{18}O-temperature calibration truly represents equilibrium conditions is highly significant, but not yet resolved. Several recent publications (e.g., Coplen et al., 2007; Dietzel et al., 2009) suggest that the commonly used oxygen isotope calibration does not correspond to equilibrium conditions due to ^{18}O depletion in fast growing minerals. It is important to note, however, that speleothems are affected by thin-film CO_2 degassing, leading to ^{18}O enrichment, a process that is missing in the Dietzel experiments, so that those results may not be directly applicable to speleothems.

The co-variation method projects a kinetically influenced value back to an assumed ‘equilibrium’ reference line. In this respect, the reconstructed values will not be affected significantly by the exact equilibrium value as long as the same equilibrium reference values are used for calculation of the co-variation slope and for application of the method to ancient samples. A more detailed discussion of what is true equilibrium is beyond the scope of this article.

The clumped isotope thermometer was calibrated by laboratory experiments in which calcite was precipitated under controlled conditions and constant temperature (Ghosh et al., 2006). These experiments have been replicated recently, yielding a similar relationship (Zaarur et al., in prep.). It is relevant to note, that the δ^{18}O values associated with these precipitation experiments are close to those obtained by Kim and O'Neil (1997). Most importantly, a large number of biogenic samples confirm the calibration in the range of typical Earth surface temperatures (Eiler et al., 2007, 2011; Tripati et al., 2010). The current Δ_{47}-temperature calibration can be taken as reliable based on these data sets, although there remains a small uncertainty at the lower and upper end of the calibration curve due to the limited number of samples derived from inorganic laboratory experiments and the variability in the biogenic data. The calibration of Ghosh et al. (2006) is so far the best available reference for Δ_{47}-T, and is consistent with the majority of carbonate samples analysed so far.

3) Kinetic isotope fractionation in carbonates other than speleothems

The process leading to kinetic isotope fractionation during speleothems formation is known and can be modelled to a certain extent for oxygen, carbon, and clumped isotopes (Guo, 2008; Dreybrodt 2008; Mühlinghaus et al., 2009; Scholz et al., 2009; Dreybrodt and Scholz, 2011). Its effect on clumped isotopes in speleothems was investigated by Daëron et al. (2011), Wainer et al. (2011), and Kluge and Affek (2012). The increase in δ^{18}O and decrease in Δ_{47} is related to the degassing of CO_2 from a thin film of a solution that is not buffered by isotope exchange with water due to $CaCO_3$ formation being faster than the isotope exchange. Carbonate material from marine sediments originates from a completely different environment with very distinct carbonate precipitation mechanisms. A simple and direct transfer of the Δ_{47} co-variation technique from speleothems (e.g., using the same Δ_{47}-δ^{18}O co-variation slope) is therefore not possible. However, the approach of the combined assessment of offsets in clumped and oxygen or carbon isotopes can also be very helpful in cases of disequilibrium in stratigraphic studies in the marine environment. Similar to the application to stalagmites, a Δ_{47}-δ^{18}O co-variation slope may be determined for the according processes and be used for back-correction to the nominal equilibrium values. Precondition is, however, the knowledge and detailed understanding of the processes causing disequi-

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librium.

4) Figures
The referee correctly observed that there is a certain point-to-point variability in the Holocene part of Fig.4 that could reflect either true climatic variability or the uncertainty of the technique. The uncertainty in the reconstructed drip-water δ^{18}O value is about 0.3 ‰ . The average deviation of single sample values from the Holocene drip-water trend (three point smoothing in Fig.4 and Fig.5) is <0.3 ‰ indicating that the individual samples cannot be distinguished from the trend line. However, a higher-frequency climatic pattern cannot be excluded due to the limited analytical precision and especially the low time resolution. A climatic signal is suspected for the late Holocene (page 17, line 10-14), but requires validation by additional stalagmites sampled at higher resolution. This is not available at this time.

The plots in Fig.4C are cut off in order to show the Holocene values of Lake Ammersee and NGRIP in reasonable detail. The δ^{18}O changes in the mid-latitudinal groundwater and drip-water values are small compared to the large changes observed in Greenland ice over a glacial cycle and are barely visible if shown on the same scale. Nevertheless, we will add another figure (Fig.2R) for comparison in the supplementary material of the revised version to show both records completely and on the same scale as the drip-water reconstruction.

Additional references: (for the other references check manuscript CPD-8,1-40, 2012; doi:10.5194/cpd-8-1-2012)

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Figure captions:

Figure 1R: Δ_{47} and δ^{18}O offsets of stalagmites BU1 (A) and BU4 (B). The offsets are calculated on the assumption of a constant drip-water δ^{18}O value of -7.9 ‰ and a constant temperature of 9.5°C (8.5°C for BU4-9). Samples that deviate from the modern Δ_{47}-δ^{18}O co-variation slope are marked with ages.

Figure 2R: Reconstructed drip-water δ^{18}O values (A), rainfall δ^{18}O values inferred from Lake Ammersee ostracods (B, light grey; von Grafenstein et al., 1999) and water isotopes evolution in Greenland (B, black; NGRIP members 2004). All data sets are shown on the same scale. The Holocene trend of the drip-water reconstruction is shown for comparison in panel B as a blue line.

Interactive comment on Clim. Past Discuss., 8, 2853, 2012.

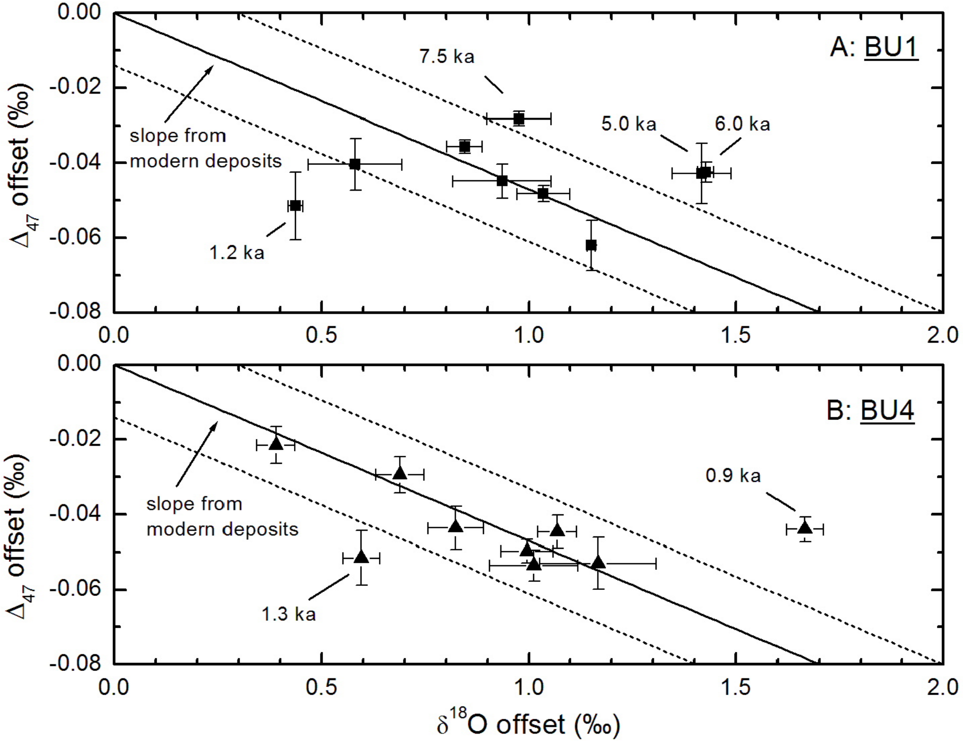

Fig. 1. R: caption on page C6

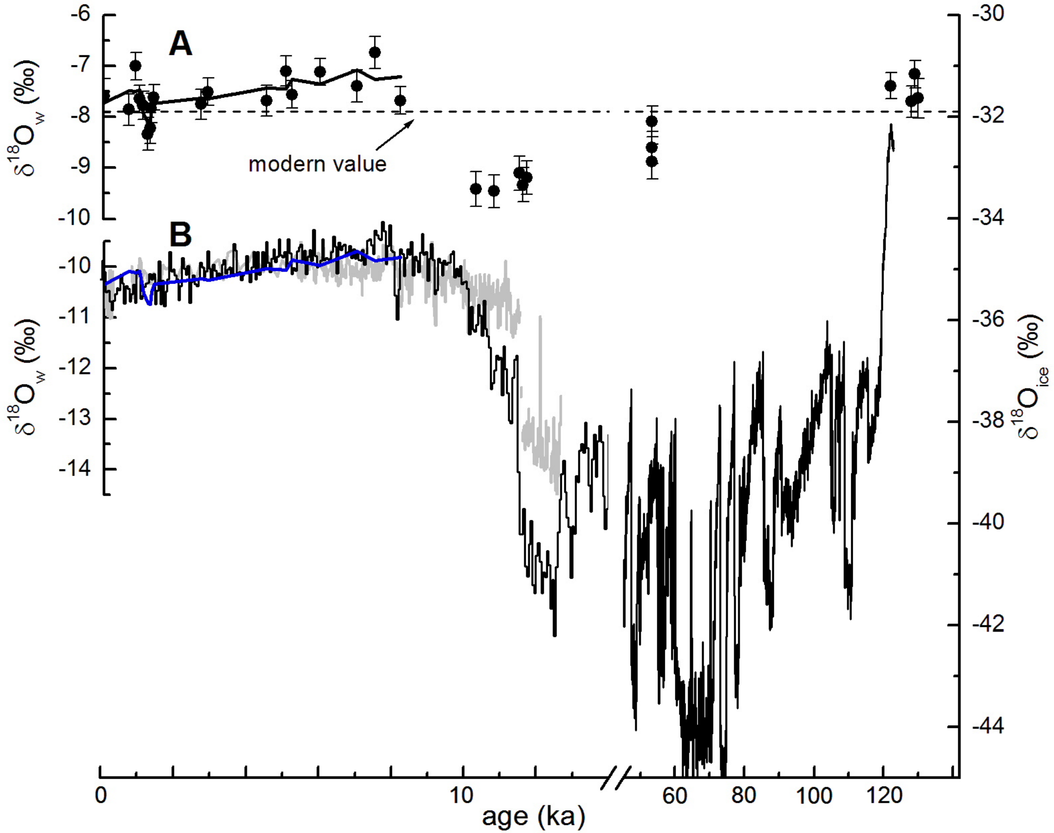

Fig. 2. R: caption on page C6