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Climate of the Past 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 thoughtful comments and suggestions provided by referee # 2. In the following, we address the two major comments of the reviewer and then deal with some minor aspects in a point by point approach.

1) Use of noble gas temperatures (NGTs)

NGTs were used for drip-water reconstruction on time intervals for which reproducible noble gas results could be obtained. For example, the early Holocene NGT is based on 6 replicates (see Kluge et al., 2008), the Holocene NGTs that are used for

drip-water reconstruction are either based on replicates measured during different runs (BU1-D, BU1-G) or on several samples from the same growth period (BU1-B and C, BU1-D,E,F,G). For the Holocene only calcite samples of stalagmite BU1 were used for noble gas analysis. Stalagmite BU4 has not been analysed systematically. Unfortunately, BU1 did not grow continuously and therefore does not provide NGTs for the complete period in which drip-water δ^{18}O reconstruction is attempted. The older parts of stalagmite BU-UWE that grew during MIS3 and the Eemian yielded NGTs with generally high uncertainties unsuitable for precise drip-water δ^{18}O reconstruction (see Kluge, 2008) and were therefore not included here. Note however, that the relative temperature changes inferred from NGTs in these growth intervals of BU-UWE are also consistent with other reconstructions (e.g., Guiot et al., 1998).

We did not include a more detailed discussion of caveats of the noble gas technique as part of it was already addressed in the papers of Kluge et al. (2008) and Scheidegger et al. (2010, 2011) and we therefore referenced these (page 2863, lines 24-25). We agree that some additional sentences in the main text and a more detailed discussion in the supplement will improve the manuscript and will be included in the revised version.

NGTs from stalagmite BU1 (and BU-UWE) show consistently too low temperatures relative to the regional 1961-1990 mean. This deviation is likely due to analytical artefacts and unrelated to environmental influences. During studies that aimed at improving the technique it was realized that the combined analysis of all heavy noble gases in one measurement step leads to an overestimation of the Kr and Xe fraction (Marx et al., 2010; Wieser, 2011). Overestimated concentrations of heavy noble gases lead to lower temperatures and are one possible explanation for our results. A slight underestimation of water amounts during crushing steps (due to water adsorption on freshly crushed calcite) similarly causes too high apparent noble gas concentrations and too low NGTs. Tests showed that temperatures during the final heating step were high enough to completely release potentially adsorbed water. By combining water and gas amounts of all steps or all steps without the first one, that is dominated by

gases from air-filled inclusions, we exclude or at least minimize a possible influence of water adsorption on the determined NGT, obtaining more reliable NGT values. A constant offset correction, i.e. independent of the speleothem growth period, is justified because the deviations were consistently caused by analytical artefacts (as here potentially by the influence of Ar on the Kr and Xe signal) and not by environmental influences.
The temperature change determined by NGTs from the early Holocene (10-12 ka) compared to the rest of the Holocene seems relatively large. However, Pollen and chironomid studies generally support lower regional temperatures for the interval from 10-12 ka compared to the Holocene mean. The early Holocene was found to be cooler by:

- ~ 1°C (summer temperature), European Alps (Heiri et al., 2004)
- 1-4 °C, central western Europe (Davis et al., 2003)
- ~ 5°C, eastern France (Guiot et al., 1989).

Unfortunately, there are no other quantitative records from this time period and region available, but climate records from north-western Europe (2-3 °C: Davis et al., 2003; 2-4 °C lower July temperatures in Norway: Bakke et al., 2008; low North-Atlantic SSTs between 10 and 11 ka, Ebbesen and Hald, 2004) and some studies from Southern Europe (3-4 °C lower January and July temperatures in northern Italy: Finsinger et al., 2010) show a similar difference between these time intervals. It has to be noted that some studies focused on North Atlantic sea-surface temperatures found smaller or contrasting temperature differences (e.g., Calvo et al., 2002) which might be related to oceanic heat advection (Risebrobakken et al., 2011) that differs in its evolution and response from terrestrial climatic changes.
We will include the temperature reconstructions of the two above mentioned pollen studies of central Europe (Guiot et al., 1989; Davis et al., 2003) for calculating an early

Holocene reference temperature. Similarly, we complement the Holocene NGTs with temperature data from these studies and use in both cases the temperature range for calculation. Table R1 shows the re-evaluated data points that will be included in the revised manuscript.

2) Paleo-temperature reference and its uncertainty
Following the reviewer's suggestion we consider ranges of paleotemperature estimates for the investigated time intervals rather than mean temperature values (Table R1). This does not affect the general trend in the reconstructed drip-water δ^{18}O values, but it gives a better estimate of the uncertainty in drip-water δ^{18}O values that includes the analytical uncertainty and the temperature uncertainty.

Minor comments
1) Temporal drip-water δ^{18}O – temperature relationship
Section 5.2 can be seen as an additional test for the reconstructed δ^{18}O values beyond their direct comparison with other precipitation δ^{18}O reconstructions. As the calculated δ^{18}O-temperature relationships of the investigated time periods are consistent with independent studies, it in turn supports the co-variation method to provide reasonable drip-water values. Furthermore, this section is designed to give an outlook into a promising application regarding the temporal investigation of the δ^{18}O-temperature relationship. We will clarify these aspects in a revised version.
2) Figure 2
We will use more distinctive symbols in a revised version. The slopes related to the different calcites, in particular to the Holocene stalagmites and modern precipitates, were already addressed in detail in the reply to referee # 1.
3) Figure 5 Clumped isotope measurements can provide constraints for the kinetic isotope fractionation. The application of Δ_{47} measurements to investigate isotopic disequilibrium and its temporal evolution in speleothem calcite is discussed in detail in Kluge and Affek (2012) that has been recently published in QSR. In brief, a

higher offset in the Δ_{47} value relative to its expected value at a certain temperature corresponds to a stronger isotopic disequilibrium. This is exemplarily illustrated in the inset in Fig.5 and shortly addressed in section 5.4.
A comparison with δ^{13}C values was already done for stalagmite BU4 and is shown and discussed in Kluge and Affek (2012, section 5.5.4 and Fig. 5 therein). In brief, δ^{13}C values in BU4 were likely influenced by changes in drip rate, soil CO_2 concentrations and prior calcite precipitation. These directly affect super-saturation levels and determine the excursion from isotopic equilibrium during calcite precipitation.

Additional references:
(for the other references check manuscript CPD-8,2853-2892, 2012; doi:10.5194/cpd-8-2853-2012)

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Table R1:
Updated values regarding Table 2. Noble gas data are used in combination with results from the pollen studies of Davis et al. (2003) and Guiot et al. (1989). We give now ranges of temperature estimates (T_{used}) instead of a mean value. The resulting drip-water δ^{18}O values are slightly changed in few cases due to asymmetrical uncertainty estimates in the original publications that are used for temperature estimation. The table is included in the related supplement to this reply.

Please also note the supplement to this comment:
http://www.clim-past-discuss.net/8/C2563/2012/cpd-8-C2563-2012-supplement.pdf

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