

Interactive comment on “Simulated oxygen isotopes in cave drip water and speleothem calcite in European caves” by A. Wackerbarth et al.

Anonymous Referee #1

Received and published: 13 August 2012

General Comments In the paper "Simulated oxygen isotopes in cave drip water and speleothem calcite in European caves", Wackerbarth et al. have presented model results of the $\delta^{18}\text{O}$ characteristics of precipitation, cave drip water, and cave calcite in European Caves, as well as climate output of temperature and precipitation amount. The modelling exercise was completed in order to compare modelled versus observed $\delta^{18}\text{O}$ and climate data. The authors extend their model/observation comparison to the mid-Holocene, a time period with different orbital boundary conditions than today, to test for spatial changes in climate and cave parameter that could be used to infer changes in the North Atlantic Oscillation.

Specific comments Overall this was a well-written paper, and a useful modelling exercise, and should be published with minor modifications.

C1132

Such modelling exercises are needed to evaluate the spatial variations in $\delta^{18}\text{O}$ at different time periods, to test hypotheses of climate variations at key time intervals, such as the mid-Holocene. The new emphasis on spatial variations in $\delta^{18}\text{O}$ has been emphasized in recent work by McDermott et al.'s 2011 GPC paper, which could be discussed in some more detail in the introduction to provide important context for the current study.

The model results compare reasonably well to observations. Perhaps the most critical comparison is the modelled vs. observed $\delta^{18}\text{O}$ value of speleothem calcite (panel e of Figure 1). The differences in the modelled and observed $\delta^{18}\text{O}$ values are strongly dependent on the model assumptions, most importantly through the equilibrium fractionation equations and climate input (e.g., temperature at the cave site). As with any modelling exercise, the full range of uncertainties in the model assumptions is important for the final output.

One key aspect that needs clarification is the use of the "equilibrium" $\delta^{18}\text{O}$ drip to calcite fractionation equation. There are now a multitude of such equations (both empirical and theoretical) which produce very different results. Simply stated, there remains a significant amount of uncertainty as to which equation provides the approximation of the true 'equilibrium' fractionation value. The citation to the specific fractionation equation used in the model should be presented and discussed, as the reader may not have read the previous papers on the ODSM that describe it in more detail. The equation apparently used in the model is the Friedman and O'Neil equation, but that one has largely been superseded by more recent work, in particular the Kim and O'Neil equation.

The reason this is important is that the new (kinetic?) fractionation equation of Feng et al. 2012 gives higher calcite $\delta^{18}\text{O}$ values than existing fractionation equations (such as Kim and O'Neil): Feng, Weimin; Banner, Jay L; Guilfoyle, Amber L; Musgrove, Mary-Lynn; James, Eric W, Chemical Geology, ISSN 0009-2541, 04/2012, Volume 304-305, pp. 53 - 67.

C1133

Finally, it is also worth noting the fractionation equation from Coplen using the Devils Hole calcite speleothem: T.B. Coplen, Calibration of the calcite–water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory, *Geochimica et Cosmochimica Acta*, 71 (2007), pp. 3948–3957. Tyler Coplen's equation also shows significantly higher d18O values than the Kim and O'Neil equation.

These new studies, and others that are cited in these two publications, suggest that our understanding of "equilibrium" d18O values in calcite is poorly known. It is clearly beyond the scope of the present paper to evaluate all of these details on d18O equilibrium. Nor would adoption of a different fractionation factor in the model explain away the discrepancies between the modelled and observed values. However, a short discussion should be included to point the reader to the respective literature.

Finally, the observations supporting a NAO+ state during the mid-Holocene seem warranted. Indeed, this is one of the major contributions of the current manuscript, and it could be emphasized more heavily in the abstract and conclusions.

Technical corrections The authors need to clearly reference the VPDB and VSMOW scales in the text. As written, one would think only one reference scale is being used. Also, there is a need to use correct stable isotopic terminology. A good reference is Zach Sharp's textbook "Stable Isotope Geochemistry". For example, being ratios, d18O values can not be enriched or depleted. Water can be enriched or depleted in 18O (or 16O), but ratios can neither be enriched nor depleted. "Higher" and "lower" are preferred adjectives to describe changing d18O values, and "heavier" and "lighter" are also ok.

Page 2783, Line 7: It is interesting to set the time scale of epikarst averaging at four years. What are the data citations to support this length of time averaging? One recent estimate was published for a ca. 9-year averaging in Lachniet et al., 2012, *Geology* 40 (3), pp. 259-262, but that result is empirical not observed.

Page 2784, Line 8: Add that another confounding effect may be changes in atmo-

C1134

spheric circulation associated with anthropogenic climate change since the 1980s.

Page 2786, Line 1 and 3 should read: "Thus, precipitation d18O values become lower along the transport path from the ocean to Bunker Cave, thus counteracting the temperature effect", and "The d18O values of an air mass decrease during its rise to the cave site".

Page 2787, Line 6: The magnitude of the RMSD values is pretty good considering the assumptions in the model. However, it is worth pointing out that many stalagmite records show only about 1-2 permil d18O variability over the length of their records, for comparison.

Page 2788, Line 20: An added complication regarding ET is that ET estimates are time averages, but precipitation is highly episodic. A heavy precipitation event over a short period would be essentially unaffected by long-term ET. Thus, the 'isotopically effective' infiltration may not correspond to the mean precipitation at any given cave site. This was discussed in some recent papers.

Page 2795, Line 1: There is some support in the literature for the influence of the Black Sea on the d18O value of precipitation in the region near Poleva Cave: see Badertscher et al *Nature Geoscience*: S Badertscher; D Fleitmann; H Cheng; R L Edwards; O M Göktürk; A Zumbühl ..., *Nature Geoscience*, ISSN 1752-0894, 04/2011, Volume 4, Issue 4, p. 236

Interactive comment on *Clim. Past Discuss.*, 8, 2777, 2012.

C1135