Noble gas measurements on fluid inclusions in stalagmites

Tobias M. Kluge¹, Werner Aeschbach Hertig¹

¹Institute of Environmental Physics, University of Heidelberg, 69120 Heidelberg, Germany

Background

Dissolved atmospheric noble gases in groundwater constitute a reliable paleothermometer, based on their precisely known temperature-dependent solubilities. The groundwater archive is limited due to the dispersive mixing and dating problems. In contrast to this, speleothems can be well dated using uranium-thorium dating. However, there is no paleothermometer comparable to the noble gas thermometer so far. The idea of this project is to combine the advantages of both archives.

If noble gases are extracted from fluid inclusions in stalagmites, similar excess-air patterns than in groundwater can be detected. In case of groundwater the effect of excess-air can be corrected [1,2]. However, compared to groundwater, stalagmite samples have much less water (4 orders of magnitude), but a 100 times higher excess-air to water rate. Therefore methods have been developed to account for this complication by trying to reduce the air/water ratio.

Methods and results

Noble gases have been extracted from stalagmites by crushing, respectively heating the sample in evacuated copper tubes. In the following step the amount of released water was determined using the water vapour pressure.

The extracted water amount is strongly dependent on the stalagmite (varying from 0.004 wt% (OBI 5, Austria) to 0.25 wt% (H12, Oman)) and on the extraction techniques (crushing, heating, microwave treatment). A typical value is 0.1% wt [3].

For the calculation of absolute noble gas amounts a diluted air standard is used. The statistical error for the standard is in the range of 1 - 2%. Sample uncertainties have been much higher, because of a high and variable background and additionally in some cases low noble gas signals. Nevertheless the background corrected Xe-Ne and Ar-Kr plot are indicating that the values are not far away from the expected mixing between noble gases from water filled inclusions and some unfractionated ”excess-air”.

Outlook

Calculation of noble gas temperatures in case of the best samples (from a cave with a recent cave temperature of 26 °C) leads to 26, respectively 30 °C (although with very large uncertainties) using the same inverse modelling approach as for groundwater [1]. This may be a hint that noble gases from fluid inclusions can be used to determine noble gas temperatures if the problems (high uncertainties, high air/water volume ratios) can be managed.

The last experiments have shown that the selection of adequate samples is important. Without using special extraction techniques the air/water ratio is very different in case of various stalagmites. Therefore the samples should be checked in advance concerning the water content and the microscopic structure, which is related to the air/water ratio. For instance a stalagmite from Cuba has a surprising low air/water ratio. In those cases no special methods to reduce the excess air have to be applied with regard to the calculation of noble gas temperatures.

The calculation of noble gas temperatures
seems to be possible, if adequate samples with low air/water ratios are used and a sufficient measurement precision can be achieved.

Figures

Noble gas concentrations calculated for stalagmite samples. The points in the blue circle are values of air-equilibrated water at temperatures between 0°C and 30 °C. The black lines indicate addition of “excess-air” (upper line: water at 0°C, lower line: water at 30 °C). Most of the samples show ratios in the expected area, that means they are situated on the mixing line of equilibrated water with unfractionated air. However the uncertainties are quite large and typically in the range of 10%. Only the best sample has an uncertainty of 2-3 %.

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References

