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Correcting stalagmite fluid inclusion homogenisation temperatures for the effect of surface tension

Hidalgo Staub, Rita[*,**], Krüger, Yves[*,**], Frenz, Martin[*] and Fleitmann, Dominik[**,***]

[*]Institute of Applied Physics, University of Berne, Sidlerstrasse 5, CH-3012 Bern
[**]Institute of Geological Sciences, University of Berne, Baltzerstrasse 1&3, CH-3012 Bern
[***]Oeschger Centre for Climate Studies, University of Berne, Zähringerstrasse 25, CH-3012 Bern

We evaluate a new method to determine paleotemperatures (mean annual surface temperatures) from liquid-vapour homogenisation temperatures (T_h) of fluid inclusions in stalagmites. Our approach is to determine the density of fluid inclusions by measuring the liquid-vapour homogenisation temperature after inducing vapour bubble nucleation in the initially monophase inclusion. This is achieved by ultra short laser pulses to overcome the metastable state of water (Krüger et al. 2007). Fluid inclusions in stalagmites are primary inclusions containing remnants of the drip water from which the calcite precipitated under atmospheric pressure. Therefore their T_h is expected to equal the stalagmite formation temperature i.e. the cave air temperature. An important precondition being that the density of the fluid inclusions remains unaltered, it is important to avoid large fluid overpressure and to minimise mechanical stress during sample preparation.

MEASUREMENTS

To test our paleothermometer T_h measurements were carried out using 300–400 μm thick sections of an actively growing stalagmite from Milandre Cave (Switzerland). The observed homogenisation temperatures ($T_{h\,obs}$) display a large variability with a maximum around the actual cave temperature of 9.5 °C (see Fig. 1). The position of this maximum is, however, coincidental, because $T_{h\,obs}$ values are influenced by various parameters.

$T_{h\,obs}$ values above 9.5°C result from density changes in the fluid inclusions induced by mechanical stress during sample preparation. Therefore these inclusions do not represent the original fluid density and are not considered for the determination of the stalagmite formation temperature (T_f).

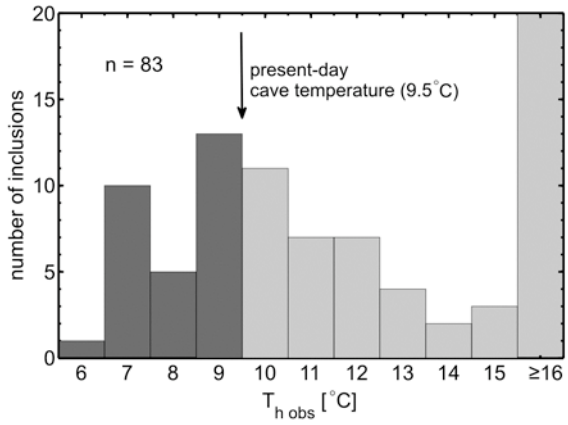

Fig. 1. Distribution of $T_{h\ obs}$ values measured in a recent stalagmite from Milandre Cave. Temperatures in light grey are higher than the actual cave temperature and result from density alterations in the inclusions. Temperatures in dark grey are from fluid inclusions that have potentially preserved their density. $T_{h\ obs}$ above 16°C were not determined in order to avoid overheating (and large overpressure in other inclusions).

$T_{h\,obs}$ values lower than 9.5°C can be explained by the effect of surface tension on liquid-vapour homogenisation. Surface tension leads to a collapse of the vapour bubble below the nominal homogenisation temperature. The extent of this effect depends on the inclusion volume as well as on the fluid density. Being negligible in large inclusions of low density it can amount to a temperature difference of several degrees in small inclusions with high bulk density. Thus, to determine T_f we have to correct the measured $T_{h\,obs}$ values for the effect of surface tension.

CORRECTION OF SURFACE TENSION EFFECT

To compensate for the effect of surface tension we applied a correction algorithm to derive the nominal homogenisation temperature (T_h and

the inclusion volume from $T_{h\,obs}$ and the vapour bubble radius measured at a known temperature. Fig.2 shows the result of this correction. Marti et al. have described the thermodynamic relations between bulk density, inclusion volume and the vapour bubble radius at a defined temperature (see abstract in this conference volume). Their model predicts that fluid inclusions with T_f of 9.5°C with a volume of less than 35000 μm^3 are too small for a stable vapour bubble to exist. Therefore we can eliminate these values in the diagram as the density in these inclusions must have been altered.

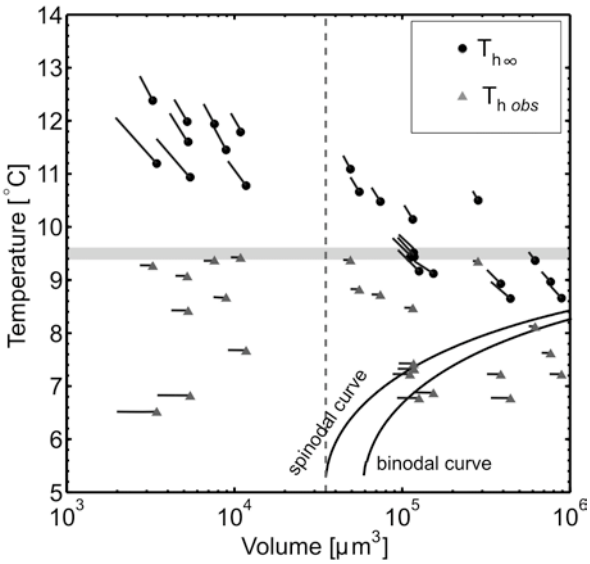

Fig. 2. Temperature-volume diagram showing the results of the surface tension correction. Grey triangles denote $T_{h\,obs}$, black dots the corrected temperatures T_h. The horizontal bar indicates the stalagmite formation temperature of 9.5°C. The correction is made on the assumption that $T_{h\,obs}$ corresponds to the spinodal temperature with error bars indicating the uncertainty arising from the bubble metastability. The solid curves denote the spinodal and binodal temperatures for a formation temperature of 9.5°C. The spinodal curve ends at 5.1°C at the minimum inclusion volume of 3500 μm^3 (dashed line) predicted by the model. Median of corrected T_h 9.42°C.

The model also shows that due to surface tension the bubble passes through a metastable state (beginning at the binodal temperature) before it becomes unstable and collapses (at the spinodal temperature). However, the bubble may also collapse before approaching the spinodal temperature and therefore the actual $T_{h\,obs}$ is not clearly defined. This leads to an uncertainty in the calculated volume and T_h shown in Fig.2.

A second error rises from the uncertainty in vapour bubble radius determination due to microscopic resolution and scattering effects around the vapour bubble.

CONCLUSION

Only the lowest $T_{h\,obs}$ values originate from inclusions that have preserved the original fluid density. These values have then to be corrected for the effect of surface tension in order to determine the stalagmite formation temperature. In the presented example this procedure yields a stalagmite formation temperature (median value) of 9.42°C, which is close to the present day cave temperature. Based on these results we expect an accuracy in paleotemperature determination of ±0.5°C.

REFERENCES

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