PALEOTEMPERATURES FROM FLUID INCLUSION LIQUID-VAPOUR HOMOGENIZATION IN STALAGMITES

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Introduction

Speleothems, such as stalagmites, provide a long-term record of continental climate variations, since they grow continuously over thousands to hundreds of thousands of years and can be dated precisely using absolute ^{230}Th-ages. Therefore, stalagmites are proving increasingly attractive to paleoclimate research. To date, paleoclimatic information from stalagmites has mainly been obtained from stable isotope compositions (δ^{18}O and δ^{13}C) and trace element contents of the calcite host mineral (e.g., Fleitmann et al., 2003) and from δD of the fluid inclusions (e.g., Zhang et al., 2008). However, stable isotopes and trace elements are influenced by several climatic and environmental factors, making it difficult to employ these climate proxies for quantitative temperature reconstructions. Therefore we propose a novel approach to determining paleotemperatures based on direct micro-thermometric measurements of liquid-vapour homogenization temperatures (T_h) of fluid inclusions in stalagmites.

Analytical Approach

Stalagmite samples suitable for paleotemperature determination consist of columnar, macro-crystalline calcites that contain a sufficient number of intra-crystalline fluid inclusions. Many stalagmites, however, are build up from fibrous columnar, partly micro-crystalline calcite and the fluid inclusions are located in intra-crystalline positions for which reason these inclusions generally tend to leak and thus do not provide reliable temperatures.

The liquid-vapour homogenization temperature (T_h) as a measure for the fluid density depends on the pressure-temperature conditions under which the fluid has been trapped. In the particular case of stalagmites, which grow from gas (CO_2, air) and calcite (over)-saturated drip waters at ambient atmospheric pressure, T_h should be equal to the formation temperature of the fluid inclusions, i.e. the cave temperature, which often corresponds closely to the mean annual surface temperature outside the cave.

Because of the low formation temperatures of stalagmites, the fluid inclusions that have preserved original fluid densities are all monophase liquid at room temperature and spontaneous nucleation of the vapour phase fails to occur on cooling below the homogenization (formation) temperature. In order to induce vapour bubble nucleation we use single amplified pulses of a tightly focused femtosecond laser at temperatures below T_h, i.e. in the metastable state of the liquid (Krüger et al., 2007). Fig. 1 shows a detail of the phase diagram of pure water based on the IAPWS 95 formulation (Wagner and Pruß, 2002) serving as an approximation of the stalagmite forming fluid to illustrate the laser-induced bubble nucleation method. P-T paths shown for fluids of various T_h are corrected for the volume change of the calcite host and thus do not represent isochores. The diagram also indicates the existence of two liquid-vapour homogenizations, a prograde (T_h) occurring upon heating and a retrograde (T_{hr}) that can be observed upon cooling. In the pure water system the temperature where T_h is equal to

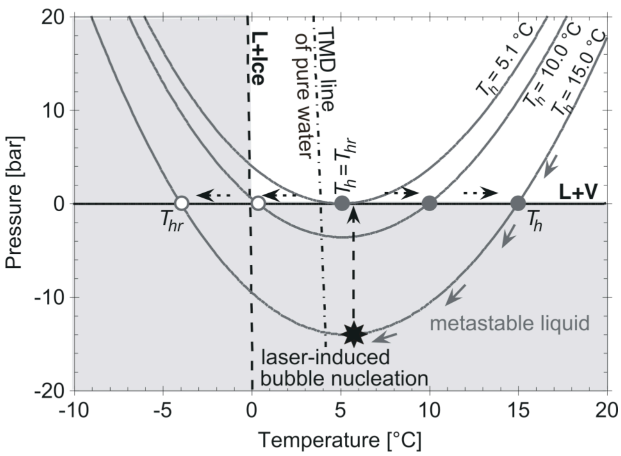

Figure 1. Detail of the phase diagram of water accounting for the volume change of the calcite host.

T_{hr} coincides with the **T**emperatures of **M**aximum **D**ensity (TMD) on the liquid-vapour curve at 4.0 °C. For fluid inclusions in calcite, however, T_h and T_{hr} become equal at ca. 5.1 °C, thus suggesting an seeming increase of the TMD (Marti et al. 2009). For this reason stalagmite formation temperatures below 5.1 °C are represented by T_{hr}. Thus, for formation temperatures immediately around 5.1 °C it will be difficult to decide which of the two liquid-vapour homogenizations is actually the correct one.

Results

In a study that was conducted to test the feasibility of this novel approach of paleotemperature determination we measured liquid-vapour homogenization temperatures of 130 previously monophase fluid inclusions hosted within the most recently formed calcite bands of an actively growing stalagmite from Sofular Cave, Northern Turkey (Krüger et al, 2008). Although we found that the T_h values show a wide and apparently unsystematic scatter ranging from 6 to > 30 °C, they display a clear maximum at around 10 °C which closely matches the present day cave temperature of 10.5 to 11.7 °C, as shown in Fig. 2. The observed variability in T_h has been proven not to result from the high intensity laser pulses used for vapour bubble nucleation since the reproducibility of T_h of individual inclusions is, with few exceptions, within ± 0.1 °C. Therefore it is likely that the scatter of the T_h values can partly be attributed to irreversible volume changes (stretching) or partial leakage of the inclusions caused by sample preparation and/or by internal fluid overpressure that builds up when the inclusions are exposed to temperatures well above their formation temperature during transport, storage or preparation. An increase of the T_h values above the actual formation temperature can also result from stretching of the fluid by capillary forces during formation of the inclusions. Finally, we assume that a surface tension mediated collapse of the vapour bubble provides a potential explanation for T_h values which are too low, but presumably also for values that are too high (stabilized bubble). A better understanding of the fundamental physical parameters that control bubble collapse in the fluid inclusion micro-systems can potentially help us to estimate the magnitude of this effect on T_h.

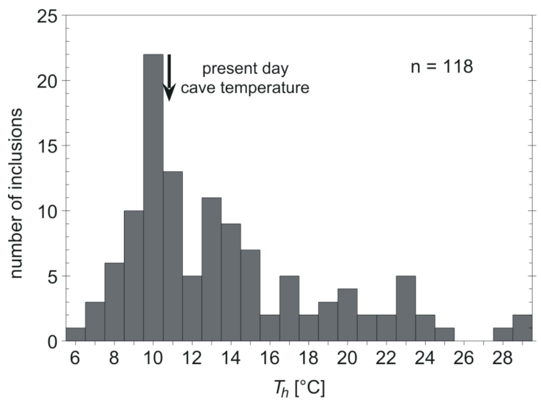

Figure 2. Distribution of the T_h values from a recent stalagmite sample from Sofular Cave (Northern Turkey).

Conclusion

The results of this study confirm that liquid-vapor homogenization temperatures of fluid inclusions can be used to determine stalagmite formation temperatures and thus represent a promising analytical approach to reconstruct paleotemperature variations. However, considerable effort is still necessary to develop a reliable methodology for sample handling and preparation that provides a reduced scatter of the T_h values and useful criteria for acquisition, processing and refinement of the data. The goal is to achieve an accuracy in temperature determination within ± 1.0 °C or better, at a high temporal resolution. In our study we measured T_h values from fluid inclusions that are hosted within several growth bands that cover approximately the last 20-50 years. Future work will focus on inclusions that formed during distinct climatic events (e.g., the Younger Dryas) to reconstruct paleotemperature evolution.

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