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Research paper

Liquid–vapour homogenisation of fluid inclusions in stalagmites: Evaluation of a new thermometer for palaeoclimate research

Yves Krüger [a,c], Dominik Marti [a], Rita Hidalgo Staub [a], Dominik Fleitmann [b,c], Martin Frenz [a,*]

[a] Institute of Applied Physics, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland
[b] Institute of Geological Sciences, University of Bern, Baltzerstrasse 1&3, CH-3012 Bern, Switzerland
[c] Oeschger Centre for Climate Change Research, University of Bern, Zähringerstrasse 25, CH-3012 Bern, Switzerland

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ABSTRACT

We present a new approach to determine palaeotemperatures (mean annual surface temperatures) based on measurements of the liquid–vapour homogenisation temperature of fluid inclusions in stalagmites. The aim of this study is to explore the potential and the limitations of this new palaeothermometer and to develop a reliable methodology for routine applications in palaeoclimate research. Therefore, we have investigated recent fluid inclusions from the top part of actively growing stalagmites that have formed at temperatures close to the present-day cave air temperature.

A precondition for measuring homogenisation temperatures of originally monophase inclusions is the nucleation of a vapour bubble by means of single ultra-short laser pulses. Based on the observed homogenisation temperatures ($T_{h(obs)}$) and measurements of the vapour bubble diameter at a known temperature, we calculated stalagmite formation temperatures (T_f) by applying a thermodynamic model that takes into account the effect of surface tension on liquid–vapour homogenisation. Results from recent stalagmite samples demonstrate that calculated stalagmite formation temperatures match the present-day cave air temperature within ±0.2 °C. To avoid artificially induced changes of the fluid density we defined specific demands on the selection, handling and preparation of the stalagmite samples. Application of the method is restricted to stalagmites that formed at cave temperatures greater than ~9–11 °C.

1. Introduction

Information on climate prior to the instrumental records must be obtained from natural climate archives such as ice cores, lake sediments, tree rings, corals, and speleothems. During past decades speleothems (stalagmites, stalactites, and flowstones) have become a first class archive for continental climate variability and a major area of palaeoclimate research (*e.g.*McDermott, 2004; Fairchild et al., 2006; Henderson, 2006; Fleitmann and Spötl, 2008; Lachniet, 2009). Speleothems can grow continuously over several thousand years by precipitation of calcite from drip waters, and their age can be determined precisely with uranium-series dating (Thorium-230). They grow at cave air temperatures that are commonly very stable throughout the year and closely reflect the mean annual surface temperature outside the caves. Therefore, speleothems can deliver well-dated and highly resolved records of climate variations (*e.g.* Wang et al., 2001, 2005, 2008; Spötl et al., 2002, 2006; Bar-Matthews et al., 2003; Fleitmann et al., 2003, 2004, 2009; Genty et al., 2003; Cheng et al., 2009; Baker and Bradley, 2010; Jex et al., 2010).

To date, palaeoclimatic information from stalagmites has mainly been obtained from stable isotopes ($\delta^{18}O$ and $\delta^{13}C$), annual band thickness and trace element contents of the speleothem calcite. Although these climate proxies can be used to identify qualitative patterns of climate variability, they fail to deliver quantitative temperature reconstructions. Recently, different approaches have been proposed for a quantitative determination of palaeotemperature variations, based on:

(i) the combination of δD and $\delta^{18}O$ of fluid inclusion water and speleothem calcite, respectively (McGarry et al., 2004; Zhang et al., 2008).
(ii) the excess of ^{13}C–^{18}O containing molecules (so-called 'clumped isotopes') of the calcite (Ghosh et al., 2006; Affek et al., 2008).
(iii) the concentration of dissolved noble gases in the fluid inclusion water (Kluge et al., 2008; Scheidegger et al., 2010).

Up to now, none of these approaches could, however, take hold as a routine application in palaeoclimate research due to considerable uncertainties in the measurements.

Here we present a new approach to quantitatively determine palaeotemperatures based on liquid–vapour homogenisation

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[*] Corresponding author. Tel.: +41 31 631 8943; fax: +41 31 631 3765.
E-mail address: frenz@iap.unibe.ch (M. Frenz).

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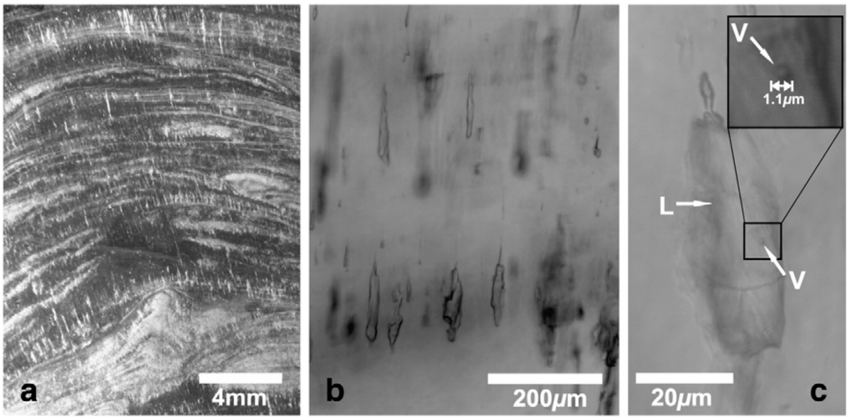

Fig. 1. a) Stalagmite section from Sofular Cave (Northern Turkey; 41°25′N, 31°56′E) displaying numerous growth bands decorated with fluid inclusions. The picture was taken under combined transmitted and reflected light illumination. b) Enlarged detail from Fig. 1a in transmitted light displaying the typical elongated, monophase fluid inclusions in two clearly separated growth bands. The long axis of the inclusions is oriented parallel to the main growth direction of the calcite. c) Previously monophase fluid inclusion after laser-induced bubble nucleation at 5.1 °C. The inclusion homogenises at 9.8 °C and the inclusion volume is approximately 6000 μm^3.

temperatures of primary fluid inclusions in stalagmites. In contrast to noble gas concentrations and δD measurements, this new palaeothermometer does not rely on the temperature-dependence of the composition but instead on the volumetric properties of the trapped water, *i.e.*, its density. Microthermometric measurements of fluid inclusion homogenisation temperatures have been used for a long time to assess mineral formation temperatures (*e.g.* Lemmlein, 1956; Roedder, 1971a; Mullis, 1975). However, the method has usually been restricted to homogenisation temperatures above ~80–130 °C due to the extensive metastability of liquid water that inhibits a spontaneous nucleation of the vapour bubble in high-density aqueous inclusions (*e.g.*Roedder, 1984 (Chapter 10); Weisbrod and Leroy, 1987; Roedder and Belkin, 1988; Zheng et al., 1991; Goldstein and Reynolds, 1994). Thus, the temperature range of surface and near sub-surface environments was not accessible to microthermometric measurements. Recently, a new technique has been developed to overcome metastable phase states in fluid inclusions by means of single pulses of a tightly focused Ti:sapphire femtosecond laser (Krüger et al., 2007). This technique allows us to selectively and efficiently induce vapour bubble nucleation in individual fluid inclusions, without causing any irreversible volume changes of the inclusions.

The aim of this study is to explore the potential and the limitations of this new palaeothermometer and to develop a reliable methodology for routine applications in palaeoclimate research. First, we describe the principles of the new palaeothermometer and the laser-induced bubble nucleation. Based on the measured homogenisation temperatures $T_{h(obs)}$ we discuss the mechanisms that may lead to density alterations of the trapped water and we describe the effect of surface tension on liquid–vapour homogenisation by means of a thermodynamic model. Finally, we present the procedure to determine stalagmite formation temperatures T_f from the measured fluid inclusion data.

2. Description of the method

2.1. Basic principles of the new palaeothermometer

Fluid inclusions in stalagmites are typically arranged along the calcite growth bands with their long dimension parallel to the main calcite growth direction (see Fig. 1a–c). They form by imperfect lateral coalescence of individual crystallites, which in case of uniform crystallographic orientation can build up large composite macrocrystals (Kendall and Broughton, 1978). Thus, the fluid inclusions are of primary origin and their age is equal to that of the surrounding calcite host, which can be determined precisely by uranium-series dating. The temporal resolution of palaeotemperature time series therefore depends on the frequency and distribution of growth bands containing measurable inclusions.

The fluids that have been preserved in the inclusions are remnants of the air saturated and calcite over-saturated drip waters from which the stalagmites have grown at cave air temperature under ambient atmospheric pressure conditions. The density of the trapped water and therefore the formation temperature T_f of the inclusions can be determined from measurements of the liquid–vapour homogenisation temperature $T_{h(obs)}$. Note that $T_{h(obs)}$ is not equal to T_f due to the effect of surface tension on liquid–vapour homogenisation (see Section 3.3).

2.2. Laser-induced vapour bubble nucleation

Because of the low formation temperatures of the stalagmites the fluid inclusions are typically monophase and contain only a liquid phase. Two-phase liquid–vapour inclusions may occur as well, either originally due to coincidental trapping of air bubbles or due to spontaneous nucleation of the vapour bubble in inclusions that are subject to leakage or volume changes. The fluid densities of these two-phase inclusions are not related to the stalagmite formation temperature T_f and thus only the monophase inclusions exhibit the potential to provide reliable palaeotemperatures from liquid–vapour homogenisation. In order to measure homogenisation temperatures in initially monophase inclusions, they have to be transferred into the two-phase liquid–vapour state by means of ultra-short laser pulses. The experimental setup used for laser-induced vapour bubble nucleation and subsequent microthermometric measurements is described in detail in Krüger et al. (2007). The principle of the method is illustrated in Fig. 2 on the basis of the pure water phase diagram derived from IAPWS-95[1] (Wagner and Pruß, 2002) that is used as an approximation to describe the p–V–T properties of natural cave drip waters. Note that in the diagram shown we initially neglect the effect of surface tension on liquid–vapour homogenisation by assuming an infinitely large inclusion volume. Under this assumption, the hypothetically observed homogenisation temperature $T_{h(obs)}$ would be equal to the nominal homogenisation temperature $T_{h\infty}$(*cf.*Section 3.3).

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[1] The IAPWS-95 formulation is an international standard for the thermodynamic properties of water, approved by the International Association for the Properties of Water and Steam.