

Fluid inclusion II: Liquid–vapour homogenisation

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Introduction

Fluid inclusions in stalagmites are typically arranged along the calcite growth bands with their long dimension parallel to the main calcite growth direction. They form by imperfect lateral coalescence of individual crystallites, which in case of uniform crystallographic orientation can build up large composite macro-crystals (Kendall and Broughton, 1978). Thus, the fluid inclusions are of primary origin and their age is equal to that of the surrounding calcite host. The inclusions contain remnants of the calcite supplying drip water from which the stalagmites have grown under atmospheric pressure conditions. Because the pressure can be treated as constant, the density of the encapsulated water depends directly on the cave temperature at the time the inclusions sealed off from the environment. In principle, this density information can be preserved in the inclusions over geological time scales and we can use it as an independent proxy for paleotemperature reconstructions. However, this applies only to fluid inclusions that were not subject to post-entrapment volume alterations or leakage.

Liquid–vapour homogenisation

In practice, we do not measure the fluid density but instead, we measure the *liquid–vapour homogenisation temperature* T_h of the fluid inclusions using a microscope heating/cooling stage. To measure T_h , we need two-phase inclusions containing liquid water and a vapour bubble. Due to the low formation temperature of the stalagmites, however, the fluid inclusions are typically monophasic and contain only the liquid phase. Spontaneous nucleation of the vapour bubble in these monophasic inclusions is inhibited by metastability and, therefore, we use ultra-short laser pulses to stimulate bubble nucleation in the metastable liquid, thus creating a stable two-phase inclusion appropriate for subsequent T_h measurements (Krüger et al., 2007). As a first approximation, fluid inclusions can be considered as isochoric systems ($V = \text{const.}$). Upon heating a two-phase inclusion, we can observe that the liquid phase expands at the expense of the vapour bubble until the bubble finally vanishes and the inclusion homogenises to the liquid phase again. The temperature at which we observe the liquid–vapour homogenisation is denoted as $T_{h(\text{obs})}$ and depends not only on the fluid density but also on the volume of the inclusion. For inclusions with identical fluid density, $T_{h(\text{obs})}$ decreases with decreasing inclusion volume because of the effect of surface tension on the liquid–vapour equilibrium.

Effect of surface tension

The surface tension σ at the liquid–gas interface of the vapour bubble works towards a minimisation of the liquid surface and creates a pressure difference Δp between the liquid and

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the vapour phase, which is proportional to the curvature radius r of the interface, according to the Young-Laplace equation:

$$\Delta p = \frac{2\sigma}{r}$$

In the case of a vapour bubble the radius r is negative and thus Δp also becomes negative, which means that the vapour pressure p_V in the bubble is higher than the liquid pressure p_L . In the isochoric system, the bubble radius r decreases upon heating and Δp increases until the bubble becomes mechanically unstable and collapses from a non-zero radius at $T_{h(obs)}$. The thermodynamic stability limit of the vapour bubble is called the bubble spinodal T_{sp} ($\approx T_{h(obs)}$). Figure 1 illustrates the change of the liquid pressure p_L as a function of the temperature, for instance, during microthermometric measurements. The example shown was calculated for a fluid inclusion of $10^3 \mu\text{m}^3$ that formed in a stalagmite at 15°C , using the thermodynamic model proposed by Marti et al. (2012). Based on $T_{h(obs)}$ and at least one additional measurement of the vapour bubble radius r at a known temperature, the model allows us to calculate the volume of an inclusion and a hypothetical homogenisation temperature $T_{h\infty}$ of an infinitely large inclusion, in which the bubble radius is infinite and Δp becomes zero. $T_{h\infty}$ is located on the liquid-vapour saturation curve (L+V) and, in the specific case of stalagmites, $T_{h\infty}$ equals the formation temperature T_f of the stalagmite, provided that the initial volume properties of the inclusion are preserved.

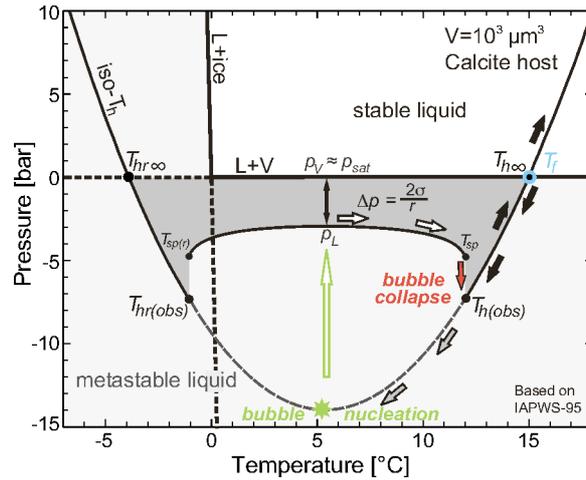


Fig. 1: P-T phase diagram of water displaying the liquid–vapour saturation curve (L+V), the liquid–ice coexistence curve (L+ice) and the stability fields of the stable (white) and the metastable (grey) liquid water. An Iso- T_h curve illustrates the pressure changes of monophasic liquid inclusion as a function of temperature. T_f of the inclusion is 15°C . The Iso- T_h curve is corrected for the temperature dependent volume change of the calcite host and does not represent an isochore. The curve intersects the liquid–vapour saturation curve twice due to the density maximum of water. T_h denotes the prograde homogenisation upon heating, T_{hr} the retrograde homogenisation upon cooling. In regard to stalagmites, however, the retrograde homogenisation is not of concern because they do not grow at temperatures below 0°C . The solid line of Iso- T_h curve indicates the stable liquid state, the dashed line the metastable liquid state of the inclusion.

The diagram illustrates the effect of surface tension on the liquid–vapour homogenisation for an inclusion of $10^3 \mu\text{m}^3$. The arrows indicate the pressure–temperature path of the inclusion during the microthermometric measurement: Black denotes the stable liquid, gray the metastable liquid and white the liquid–vapour coexistence. To induce bubble nucleation the inclusion is cooled to approximately 5.1°C , where liquid water is metastable. Upon bubble nucleation induced by a single ultra–short laser pulse, the liquid pressure p_L increases and a pressure difference Δp between p_L and the vapour pressure p_V forms. The vapour pressure p_V is almost equal to the saturation pressure p_{sat} . Upon heating the bubble radius becomes smaller and Δp increases. At T_{sp} finally, the vapour bubble becomes unstable and collapses, the liquid pressure drops on the Iso- T_h curve and the inclusion homogenises to a stable liquid state. The diagram also shows that $T_{h(obs)}$ is almost 3°C lower than $T_{h\infty}$ and T_f . On further heating the pressure exceeds the saturation curve and a fluid overpressure builds up in the inclusion with increasing temperature.

Sample selection, handling and preparation

The location of the fluid inclusions at the crystallite grain boundaries makes them highly susceptible to mechanical stress causing density alterations either by volume changes of the inclusion cavity or leakage of water from the inclusions. Mechanical stress on the calcite host can be induced by internal fluid overpressure arising at temperatures greater than T_f and may result in a volume increase of the inclusions due to plastic or brittle deformation of the inclusion walls. Therefore the stalagmites should be maintained close to the present-day cave temperature during transport, storage, and sample preparation, to avoid large differential stress. The most critical step in matters of mechanical stress, however, is the preparation of the 300 μm thick sections used for the microthermometric measurements. The shear stress acting on the calcite host can induce micro-fractures close to the sample surface and along the crystallite boundaries, thus opening potential pathways for leakage. To minimise the mechanical stress on the calcite host, we use a low-speed circular rock saw for the cutting and we omit the polishing of the sections. Instead of polishing, we use immersion oil to reduce light scattering at the section surfaces and make them transparent for microscopic observations in transmitted light. However, despite these measures, we cannot avoid density changes in some of the inclusions. The resistivity of the inclusions towards mechanical stress strongly depends on the calcite fabric of the stalagmites: Columnar calcite fabrics turned out to be most suitable for our measurements. Additionally, we have some evidence that the age of the stalagmite can be an important factor related to the mechanical strength of the inclusions. Once the inclusions sealed off, a continuous calcite dissolution and re-precipitation process works towards a minimisation of surface energy of the inclusion walls. We suppose that this re-crystallisation process increases the mechanical resistivity of the inclusions. In recent stalagmite samples we found a proportion of presumably unaltered inclusions of less than 20%, whereas in a 400 ky old stalagmite the proportion increased to almost 90% based on our interpretation of the data.

Data interpretation

The main challenge of the data interpretation is the discrimination between inclusions with altered fluid densities and those that still provide the original density information. Density alterations, both by a volume increase of the inclusion or by leakage result in a decrease of the fluid density and thus, in an increase of $T_{h\infty}$. This means that the inclusions yielding the lowest $T_{h\infty}$ values within an individual calcite growth band provide the closest approximation to the stalagmite formation temperature T_f . We could demonstrate that this criterion works very well for recent stalagmite samples by direct comparison of the $T_{h\infty}$ data with the present-day cave temperature (Krüger et al, 2011). In old stalagmite samples, in contrast, we also have to consider the eventuality of natural density alteration caused by volume changes of the inclusions or the calcite host. At the present stage of our research, however, we can only speculate about potential processes but we have not yet a positive proof for significant natural density alterations in stalagmite fluid inclusions.

Limitations of the method

The thermodynamic model of Marti et al., 2012 has revealed that liquid–vapour homogenisation temperatures can only be measured in stalagmites formed at temperatures greater than 9 – 11 °C, depending on the size of the inclusions. In inclusions that formed below this temperature limit a stable vapour bubble cannot exist due to the surface tension at the liquid–gas interface. Thus, the application of the method is restricted to stalagmites that formed in warm temperate to tropical climate zones.

References

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