Tensile Stress in Metastable Monophase Fluid Inclusions: Implications for Determining Gypsum Growth Temperatures

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Gypsum is a challenging host mineral for fluid inclusion studies because of its easy deformability and the perfect cleavage along {010}, which makes the inclusions susceptible to post-entrapment volume alterations. In addition, the fluid inclusions are often in a metastable liquid state, which makes measurements of the liquid-vapour homogenisation temperature Th impossible. To transfer these metastable monophase inclusions to a stable two-phase state appropriate for subsequent Th measurements, we use femtosecond laser pulses to stimulate bubble nucleation (Krüger et al., 2007). In the present study, we test the suitability of Th measurements for an accurate determination of gypsum growth temperatures using synthetic and natural gypsum crystals (Krüger et al., 2013) .

Synthetic gypsum crystals were grown in the laboratory at 40.0, 50.3, 60.9 and 78.9°C under atmospheric pressure conditions. Fluid inclusions of 10^2 to 10^4 µm^3 in size formed during crystal growth. Most of them are monophase liquid at room temperature. Two-phase inclusions that do not result from leakage are found only in crystals grown at 78.9°C. In the two-phase inclusions the vapour bubble forms spontaneously upon cooling the crystals to room temperature. The temperature of bubble nucleation was measured to be 30–45°C below the gypsum growth temperature Tg.

Natural gypsum crystals were taken from two sites in the underground mine of Naica (Mexico). Most of the fluid inclusions are monophase liquid at room temperature and only a small percentage of two-phase inclusions is present. The size of the inclusions ranges between 10^3 and 10^6 µm^3.

Results

The results from the synthetic gypsum crystals show that the measured homogenisation temperatures of monophase (Th(1ph)) and two-phase inclusions (Th(2ph)) are systematically lower than the crystal growth temperatures Tg. The deviation of Th(2ph) from Tg is relatively small and primarily attributed to the effect of surface tension on liquid–vapour homogenisation (Fall et al., 2009; Marti et al., 2012). In monophase inclusions, however, an additional, strong decrease of Th(1ph) is attributed to post-entrapment volume changes caused by plastic deformation of the inclusion walls. The deformation results from large internal tensile stress occurring in the metastable liquid state of the inclusions. At room temperature, the tensile stress acting on the inclusion walls reaches –120 bar in inclusions formed at 40.0 °C and –540 bar in inclusions formed at 78.9°C. The deviation as well as the variation of Th(1ph) increases with increasing Tg, i.e., with increasing tensile stress. The variation of Th(1ph) indicates that differential stress is not the only parameter that determines the deformation and volume change of the inclusions. Further parameters are the size and shape of the inclusions, the thickness of the inclusion walls, and the orientation of the inclusions within an anisotropic crystal (Burnley and Davis, 2004). Finally, the volume change induced by plastic deformation depends also on the duration of the tensile stress, which explains the comparatively small variation of the Th(2ph) values.

We have applied these findings to natural gypsum crystals from Naica to determine the crystal growth temperatures. Figure 1 shows the characteristic distribution of the Th values in a temperature–volume diagram. The nominal homogenisation temperatures Th∞ were calculated to compensate for the effect of surface tension using the thermodynamic model proposed by Marti et al. (2012). In the present example, the temperature difference between Th∞ and the measured Th values never exceeds 1.0 °C. Based on the results from the two-phase inclusions, we determined a crystal growth temperature Tg of 47.5 ± 1.5 °C. Regarding the monophase inclusions, the diagram indicates that the original volume properties have only been preserved in the smallest inclusions, and that the volume alteration due to deformation increases with increasing inclusion volume. Note that a volume reduction of 1‰ decreases Th by 2.8 °C.

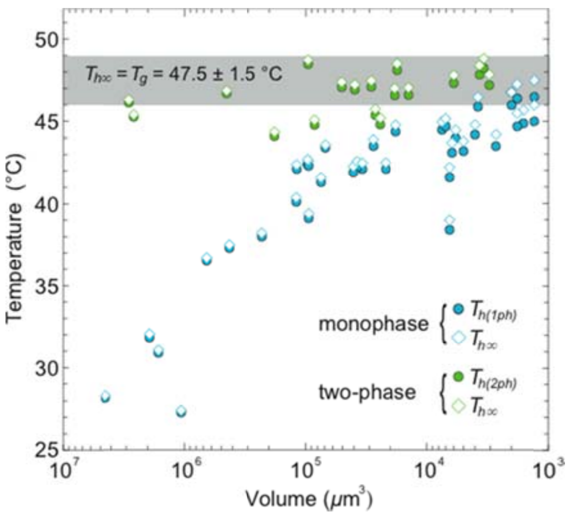

Fig. 1: Determination of the growth temperature of a natural gypsum crystal from Naica (Cave of Swords, 120 m below surface). Measured Th data from monophase (blue dots) and two-phase inclusions (green dots) are plotted against the inclusion volume. Diamonds denote the calculated nominal homogenization temperatures Th∞ that compensate for the volume–dependent decrease of Th due to surface tension. The gray band indicates the estimated gypsum growth temperature Tg. The pronounced decrease of Th(1ph) with increasing inclusion volume is attributed to post-entrapment volume alterations due to internal tensile stress causing plastic deformation of the inclusion walls.

Conclusions

The occurrence of tensile stress in the inclusions can be caused by natural temperature variations during uplift and cooling, but can also be artificially induced by inadequate sample handling. The distribution of Th shown in Fig. 1, for example, essentially reflects the temperature decrease after the crystals were taken out of the mine. Similar variations of Th were previously reported by Lowenstein et al. (1998) from initially monophase fluid inclusions in synthetic and natural halite crystals. Prior to the Th measurements, the authors stored the halite crystals at –20 °C for several days to stimulate spontaneous bubble nucleation by inducing large tensile stress in the metastable liquid. As a consequence, the inclusion volumes decreased due to plastic deformation, resulting in a decrease and large variation of the Th values.

To avoid artificially induced volume changes and to preserve potential information on natural temperatures variations, crystals like gypsum or halite must be maintained close to the present–day site temperature during transport, storage and preparation. During microthermometric measurements, finally, tensile stress can be minimised by stimulating vapour bubble nucleation a few degrees below Th using femtosecond laser pulses. Thus, the application of femtosecond laser pulses makes Th measurements independent of two-phase inclusions forming by spontaneous bubble nucleation.

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