

SUPPLEMENTARY DATA

Determining gypsum growth temperatures using monophasic fluid inclusions. Application to the giant gypsum crystals of Naica (Mexico)

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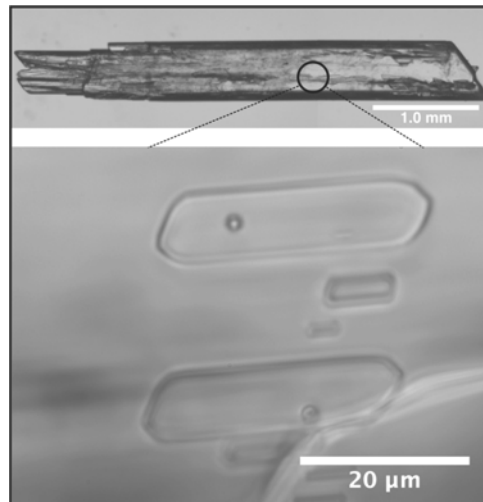


Fig. DR1: (Upper image) Synthetic, needle-like gypsum crystal grown at 60.9°C. (Lower image) Fluid inclusions in the synthetic gypsum crystal. At room temperature, these inclusions were initially in a metastable monophasic state, containing only liquid. To transfer the inclusions into a stable two-phase state (shown on the photograph) we used single femtosecond laser pulses to induce vapor bubble nucleation.

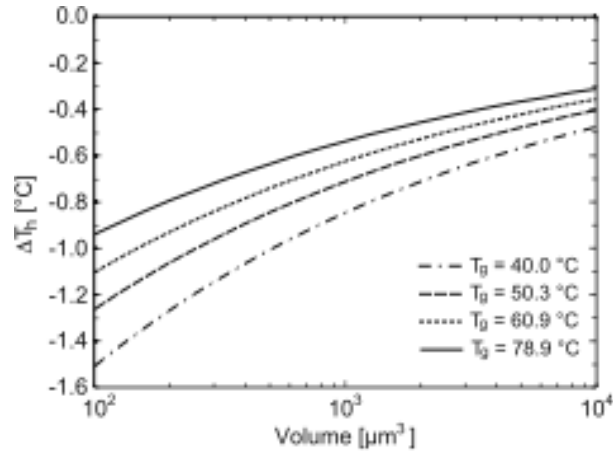


Figure DR2: Effect of surface tension on the liquid-vapor homogenization as a function of the inclusion volume for different gypsum growth temperatures, T_g ; *i.e.*, different fluid densities. ΔT_h denotes the decrease of the observed homogenization temperature with respect to the nominal homogenization temperature, $T_{h\infty}$. The diagram was calculated assuming a 5 wt% NaCl solution. Note: estimated salinities values from measurements of ice melting temperatures range between 4 and 7 wt% NaCl.

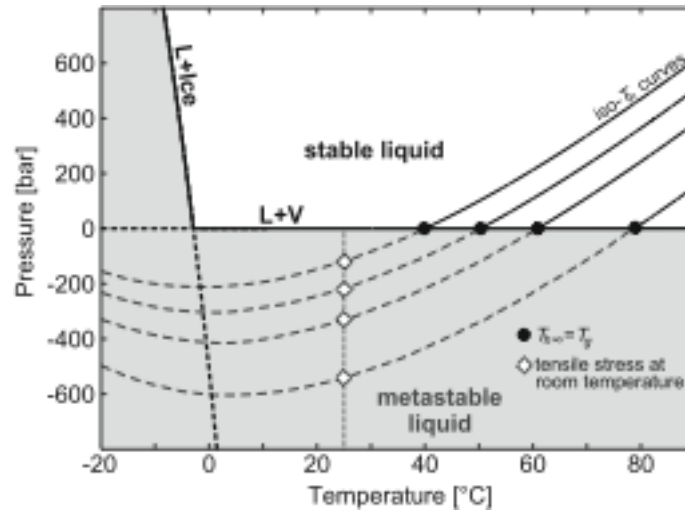


Fig. DR3: Pressure-temperature (P - T) diagram of a 5 wt% NaCl solution displaying the curve of final ice melting (L+ice), the liquid-vapour equilibrium curve (L+V) and the regions of the stable (white) and the metastable liquid (gray), respectively. The diagram illustrates the trend of the fluid pressure inside the monophasic inclusions as a function of temperature, represented by iso- T_h curves. The iso- T_h curves, calculated for different gypsum growth temperatures, T_g , are corrected for the temperature-dependent volume change of the gypsum host and, thus, do not represent isochores. At room temperature, in the metastable liquid state of the inclusions, tensile stress acting on the inclusion walls reaches up to -520 bar depending on the gypsum formation temperature.

Note: At present, we do not have an appropriate equation of state for H₂O-NaCl solutions that can be extrapolated into the metastable region. Therefore, we used a simple approximation based on the IAPWS-95 formulation for pure water (Wagner and Pruß, 2002). To calculate the slope of the iso- T_h curves for a 5 wt% NaCl solution we applied a correction that accounts for the decrease of the temperature of maximum density with increasing salinity. In the stable-liquid region, our approximation is in good agreement with the results derived from the equation of state for aqueous salt solutions proposed by Mao and Duan (2008).

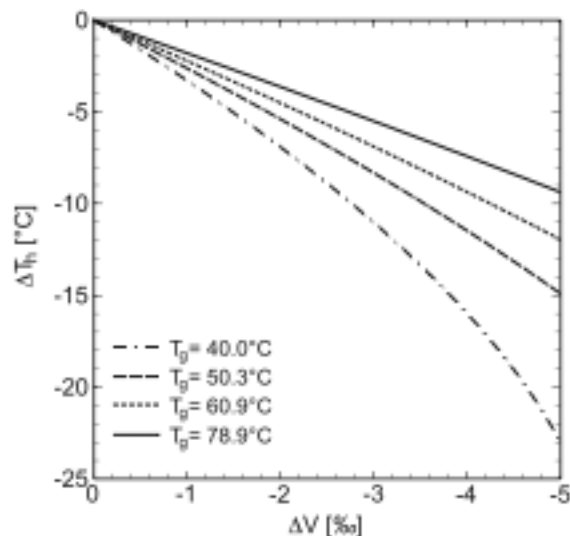


Fig. DR4: Decrease of the homogenization temperature ΔT_h due to decreasing inclusion volumes ΔV , calculated for different gypsum formation temperature T_g ; *i.e.*, different initial fluid densities.

SYNTHETIC GYPSUM CRYSTALS

Synthetic isothermal gypsum crystals, of up to 10 mm length, were grown at four different nominal temperatures: 40.0°, 50.3°, 60.9°, and 78.9°C. Batch crystallization, consisted in mixing equal amounts of equimolar solutions of CaCl₂ and NaSO₄, and storing these crystallization solutions in sealed containers at a fixed temperature inside a temperature controlled chamber (Mettmert). Temperature variations inside these chambers were monitored *in situ*. The deviation from the nominal temperature never exceeded 0.2 °C. Once nucleation had occurred and crystals ceased to grow, the rate of evaporation of the solution, and thus the rate of supersaturation, was controlled by introducing small openings in the top lid of the crystallization containers. This allowed the crystals to grow and reach an appropriate size (>5mm) for T_h measurements. The continued growth after nucleation also promoted the formation of fluid inclusions inside of the crystals.

Under these specific formation conditions, the measured T_h of the trapped fluid is commonly assumed to be equal to the crystal T_g . The needle-like gypsum crystals were used as grown for microthermometric measurements; *i.e.*, without any additional preparation (cleaving, grinding or polishing). The typical size of the fluid inclusions ranged between 10^2 and $10^4 \mu\text{m}^3$. The salinity of the trapped solutions was between 4 and 7wt% NaCl, determined from ice melting temperatures. In crystals grown at temperatures equal or below 60.9°C , the majority of the inclusions were found to be monophasic at room temperature, except for a few two-phase inclusions with different vapor bubble volume ratios which indicated leakage. In crystals grown at 78.9°C both monophasic and two-phase inclusions were found which allowed us to measure homogenization temperatures in the two types of inclusions. In the two-phase inclusions, spontaneous vapor bubble nucleation occurred around 30° to 45°C below the homogenization temperature.

NATURAL GYPSUM CRYSTAL FROM NAICA

The crystals were collected at different sites in the Naica mine (Chihuahua, Mexico), from the Cave of Crystals (290 m below surface) and the Cave of Swords (120 m below surface). The crystals contained both monophasic and two-phase inclusions ranging in size from 10^3 to $10^6 \mu\text{m}^3$. We have measured T_h values of monophasic and two-phase inclusions in a gypsum crystal from the Cave of Swords and we have complemented the available fluid inclusion data from the Cave of Crystals (García-Ruiz et al., 2007) by additional measurements of monophasic inclusions. For the measurements, the crystals were prepared as slices of approximately 0.5 to 1.0 mm thickness by splitting along the {010} cleavage plane.

REFERENCES

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