

Determining gypsum growth temperatures using monophasic fluid inclusions—Application to the giant gypsum crystals of Naica, Mexico

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ABSTRACT

Determining the formation temperature of minerals using fluid inclusions is a crucial step in understanding rock-forming scenarios. Unfortunately, fluid inclusions in minerals formed at low temperature, such as gypsum, are commonly in a metastable monophasic liquid state. To overcome this problem, ultra-short laser pulses can be used to induce vapor bubble nucleation, thus creating a stable two-phase fluid inclusion appropriate for subsequent measurements of the liquid-vapor homogenization temperature, T_h . In this study we evaluate the applicability of T_h data to accurately determine gypsum formation temperatures. We used fluid inclusions in synthetic gypsum crystals grown in the laboratory at different temperatures between 40 °C and 80 °C under atmospheric pressure conditions. We found an asymmetric distribution of the T_h values, which are systematically lower than the actual crystal growth temperatures, T_c ; this is due to (1) the effect of surface tension on liquid-vapor homogenization, and (2) plastic deformation of the inclusion walls due to internal tensile stress occurring in the metastable state of the inclusions. Based on this understanding, we have determined growth temperatures of natural giant gypsum crystals from Naica (Mexico), yielding 47 ± 1.5 °C for crystals grown in the Cave of Swords (120 m below surface) and 54.5 ± 2 °C for giant crystals grown in the Cave of Crystals (290 m below surface). These results support the earlier hypothesis that the population and the size of the Naica crystals were controlled by temperature. In addition, this experimental method opens a door to determining the growth temperature of minerals forming in low-temperature environments.

INTRODUCTION

A common method to obtain information on mineral growth conditions relies on the analysis of the mineral-forming solutions that were trapped during their growth (Roedder, 1984; Bodnar, 2003a). During the formation of a crystal, several processes may provoke the formation of voids, which are filled by the fluid from which the crystal is growing, the so-called primary inclusions. Provided that these inclusions have not been subjected to postentrapment modifications of their composition and/or volume (Bodnar, 2003b), they can be used to assess the pressure-temperature (P - T) conditions of crystal growth. This is done by determining the density of the trapped solution, based on measurements of the liquid-vapor homogenization temperature, T_h , and locating the corresponding fluid isochore using an appropriate equation of state. This technique has been extremely valuable, particularly in the case of hydrothermal mineral deposits (Bodnar et al., 1985; Wilkinson, 2001) and diagenetic environments (Goldstein and Reynolds, 1994); i.e., when the formation temperature of the crystals was high enough to provoke the segregation of the vapor bubble during its cooling history to surface tempera-

ture. However, for most near-surface (i.e., low temperature) crystal formation, most inclusions remain monophasic in the metastable liquid state even after cooling in the laboratory (Roedder, 1967, 1971; Zheng et al., 1991). In all these cases, when cooling, either in nature or in the laboratory, fails to induce the formation of a gas bubble, the fluid inclusion technique cannot provide precise information on mineral growth temperature (Goldstein, 2001). The inability to determine the mineral formation temperature may provide obstacles and limit the applicability of using fluid inclusions to infer past climates.

One mineral that could yield important and decisive thermal information for understanding the history of seas and atmosphere (Orti, 2010), as well as the history of water on Mars in future explorations (McCollom and Hynek, 2005; Tosca et al., 2008), is gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Unfortunately, most gypsum crystals (Sabouraud-Rosset, 1976; García-Guinea et al., 2002; García-Ruiz et al., 2007) contain typically monophasic fluid inclusions or, in the best of the cases, a small percentage of two-phases inclusions that make the microthermometric measurements unreliable. This situation could be changed because femtosecond laser pulses are able to induce vapor bubble nucleation in metastable monophasic inclusions, thus creating a stable two-phase state

for subsequent T_h measurements (Krüger et al., 2007). Nevertheless, the technique needs to be carefully tested because gypsum deforms easily and presents perfect cleavage along (010), making inclusions susceptible to postentrapment volume alterations (Bodnar, 2003a). We undertook this study to evaluate the applicability of laser-supported T_h measurements to decode the thermal information contained in fluid inclusions in gypsum. First we tested the method with synthetic gypsum crystals grown in the laboratory at known temperatures under ambient atmospheric pressure conditions. Based on the experimental findings, we then analyzed homogenization temperatures of gypsum crystals grown in a natural environment. For the field test, we chose the giant gypsum crystals of Naica (Chihuahua, México) (García-Ruiz et al., 2007), first because the window of temperatures at which these crystals formed is rather narrow, and second because the geological information suggests that these crystals had a rather simple cooling history.

EXPERIMENTAL METHODS

Synthetic and Natural Gypsum Crystals

Synthetic gypsum crystals were grown in the laboratory from solutions under atmospheric pressure at different temperatures, and natural gypsum crystals were collected at different sites in the Naica mine. (For more details, see the GSA Data Repository¹.)

Liquid-Vapor Homogenization Method

We used an amplified Ti:sapphire femtosecond-laser system (Coherent, Inc.) to induce the vapor bubble in metastable monophasic inclusions (Krüger et al., 2007). Subsequent microthermometric measurements were performed on a Linkam THMSG 600 heating-freezing stage, calibrated by means of synthetic H_2O and H_2O - CO_2 fluid inclusion standards. Based on cross validations, we estimated the precision

¹GSA Data Repository item 2013029, materials and methods, and Figures DR1–DR4, is available online at www.geosociety.org/pubs/ft2013.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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of the T_h measurements to be ± 0.3 °C at 40 °C, and ± 0.8 °C at 80 °C. Repeated nucleation and homogenization cycles on the same inclusions revealed a reproducibility of the T_h measurement within 0.1 °C, confirming that the high-intensity laser pulses did not change the inclusion volume.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the results of T_h measurements from monophase and two-phase inclusions in synthetic gypsum, presented as a probability distribution for each growth temperature, T_g . The diagrams illustrate that T_h of initially monophase inclusions [$T_{h(1ph)}$] are typically lower than T_g . Note that the small number of $T_{h(1ph)}$ values greater than T_g likely results from partial leakage of the inclusions and can be disregarded from further analysis. The variation of $T_{h(1ph)}$ values increases with increasing growth temperature of the host crystal. Within the 10%–90% interval denoted in the diagrams, the variation of $T_{h(1ph)}$ increases from 2.5 °C at a T_g of 40.0 °C, to 8.0 °C at a T_g of 78.9 °C. The same trend can be observed for the deviation of the median value of $T_{h(1ph)}$ from the actual growth temperature T_g ; i.e., an increase of ΔT

[$T_g - T_{h(1ph)(median)}$] from 1.3 °C to 6.0 °C. Figure 1 also shows that homogenization temperatures of two-phase inclusions [$T_{h(2ph)}$] in crystals grown at 78.9 °C are generally higher than the corresponding $T_{h(1ph)}$ values. The variation of $T_{h(2ph)}$ within the 10%–90% interval is only 2.0 °C, compared to 8.0 °C for the monophase inclusions, while $\Delta T [T_g - T_{h(2ph)(median)}]$ is 1.1 °C and 6.0 °C, respectively.

The measured homogenization temperatures of initially monophase and two-phase inclusions are systematically lower than the T_g of the gypsum crystals. The observed deviations are caused by two mechanisms: (1) the effect of surface tension on liquid-vapor homogenization (Fall et al., 2009; Marti et al., 2012), and (2) the postentrapment volume changes by plastic deformation of the inclusion walls due to high internal tension occurring in the metastable state of the inclusions.

Effect of Surface Tension on T_h

In fluid inclusion research the pressure of the liquid phase is usually regarded as equal to the pressure of the coexisting vapor phase, i.e., the saturation pressure. Under this assumption (that strictly applies only to infinitely large systems), liquid-vapor homogenization proceeds by a

continuous decrease of the vapor bubble volume to zero. The homogenization temperature of such a hypothetical, infinitely large inclusion is defined as the nominal homogenization temperature T_{hso} (Marti et al., 2012) and would equal T_g in our experiments. In real inclusions of finite size, however, the situation is different due to the effect of surface tension. The surface tension at the liquid-gas interface of the vapor bubble results in a pressure difference, ΔP , between the liquid and the vapor phase, and forces the vapor bubble to collapse from a nonzero radius at a temperature below T_{hso} . Thus, T_h is systematically lower than T_{hso} and therefore lower than T_g . The temperature difference, ΔT_h , between T_h and T_{hso} increases with increasing density (i.e., with decreasing T_g) and decreasing volume of the inclusions. In the case of low-temperature inclusions, and particularly for small inclusions, the effect of surface tension on T_h must be taken into account for an accurate determination of mineral growth temperatures (cf. Krüger et al., 2011). The light gray bands in Figure 1 indicate the range of expected T_h values considering only the effect of surface tension and inclusion volumes between 10^2 and 10^4 μm^3 . ΔT_h ranges from -1.5 to -0.5 °C for inclusions formed at 40.0 °C, and from -0.9 to -0.3 °C for inclusions formed at 78.9 °C, assuming a 5 wt% NaCl solution (Fig. DR2 in the Data Repository).

Postentrapment Volume Changes

Upon cooling the inclusions from growth to room temperature, the fluid pressure inside the inclusions becomes negative (tensile stress), following a nearly isochoric P - T path. The inclusions thereby pass from the stable into the metastable liquid state, where the trapped water becomes stretched (cf. Roedder, 1967; Diamond, 2003). This applies not only to monophase inclusions that remain in the metastable state, but also to two-phase inclusions. Recall that spontaneous bubble nucleation in two-phase inclusions was observed ~ 30 – 45 °C below T_g , which implies that the inclusions reached internal negative pressures of as much as -400 bar, though only for a short time. At room temperature (25 °C), the tensile stress acting on the walls of monophase inclusions reaches -120 bar in inclusions formed at 40.0 °C, and as much as -540 bar in inclusions formed at 78.9 °C (see Fig. DR3). This internal tension may cause a decrease of the initial inclusion volume by plastic and viscoelastic deformation of the surrounding gypsum host. As a result, the fluid density increases and T_h decreases. For example, a volume change of -2% results in a decrease of T_h by 7.0 °C for inclusions formed at 40.0 °C, and by 3.7 °C for inclusions formed at 78.9 °C (see Fig. DR4). Note that the reversible viscoelastic volume change of the inclusions was always found to be smaller than the total deformation and

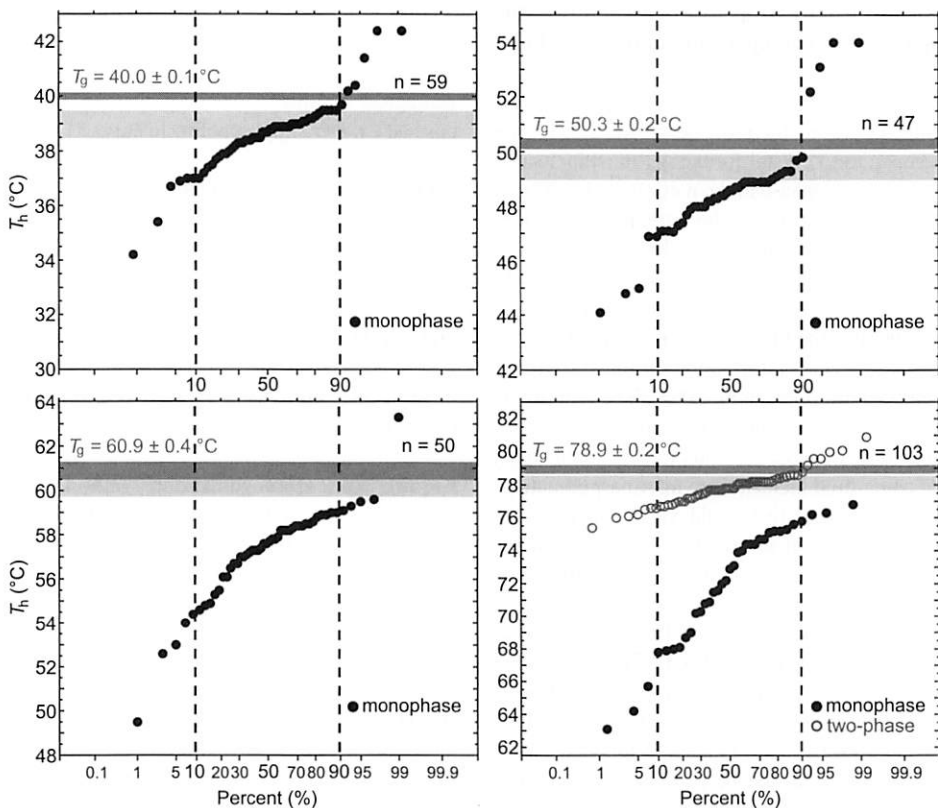


Figure 1. Probability distribution of homogenization temperature (T_h) values measured from initially monophase (dots) and two-phase (circles) inclusions in synthetic gypsum crystals. Dark gray bands denote gypsum growth temperature, T_g . Light gray bands denote expected range of T_h values considering only the effect of surface tension and inclusion volumes between 10^2 and 10^4 μm^3 (see text). Large variation of T_h results from post-entrapment volume changes of inclusions caused by internal tensile stress (see text).

manifests by a slow increase of T_h over several days and weeks after relaxation of the internal tensile stress, i.e., when the inclusions were in the stable two-phase state.

The results of T_h measurements from initially monophasic inclusions shown in Figure 1 indicate a clear increase of both the variation of $T_{h(1ph)}$ and ΔT with increasing gypsum T_g , i.e., with increasing internal tension. Burnley and Davis (2004) showed that additional factors may influence the resulting deformation, such as size and shape of the inclusions, the thickness of inclusion walls, and the orientation of inclusions within an anisotropic crystal. The interaction of all these parameters causes the large variation of the $T_{h(1ph)}$ values. Furthermore, the comparatively small variation of $T_{h(2ph)}$ values indicates that the duration of the metastable state in the inclusions has a major influence on the resulting volume change.

In summary, we have shown that the effect of surface tension on T_h is comparatively small in our experiments, but increases with decreasing volume and formation temperature of the inclusions, whereas the reduction of T_h due to deformation increases with increasing tensile stress. Our results indicate that T_h measurements from two-phase inclusions allow for a close approximation of the gypsum formation temperature, while T_h data from monophasic inclusions can be affected strongly by postentrapment volume changes. However, monophasic inclusions that formed below 50 °C, and thus underwent only low tensile stress, can still provide an accurate determination of T_g based on the characteristic distribution pattern of $T_{h(1ph)}$ data.

APPLICATION TO GIANT GYPSUM CRYSTALS FROM NAICA

Gypsum also occurs at the later stages of hydrothermal systems, and in very odd cases forms colossal single and twinned crystals, up to 11 m in length, the explanation of which is a challenge (García-Ruiz et al., 2008). The most outstanding site for these gigantic crystals is the underground mine of Naica, México. According to the proposed model (García-Ruiz et al., 2007; Van Driessche et al., 2011), Naica's gypsum crystals have grown from calcium sulfate-rich solutions that formed by dissolution of sedimentary and hydrothermal anhydrite when the system cooled below ~58 °C, i.e., the temperature at which the solubilities of anhydrite and gypsum become equal. Two-phase fluid inclusions in a large twin crystal from the Cave of Crystals (290 m below surface) indicate that the crystal precipitated from low-salinity solutions at a temperature of ~54 °C. Based on calculations derived from the classical nucleation theory, it was postulated (García-Ruiz et al., 2007) that gypsum crystals from the Cave of Swords (120 m below surface) have grown at lower temperatures than crystals from the deeper Cave

of Crystals, but the low frequency of two-phase inclusions in these crystals did not allow confirmation of this.

After validating the laser-induced method in the lab, we measured T_h values of monophasic and two-phase inclusions in a gypsum crystal from the Cave of Swords (upper left photo, Fig. 2), and we complemented the fluid inclusion data for the Cave of Crystals (upper right photo, Fig. 2) by additional measurements of monophasic inclusions. Figures 2A and 2C display

the probability distributions of $T_{h(1ph)}$ and $T_{h(2ph)}$ values from the two caves. As in the case of synthetic samples, $T_{h(1ph)}$ values of initially monophasic inclusions are generally lower than $T_{h(2ph)}$ values of two-phase inclusions. However, in comparison to synthetic inclusions formed at 50.3 °C, the variation of $T_{h(1ph)}$ is significantly larger. Furthermore, Figures 2B and 2D display a clear inverse correlation between $T_{h(1ph)}$ and the volume of the inclusions, particularly for large volumes. In synthetic gypsum samples

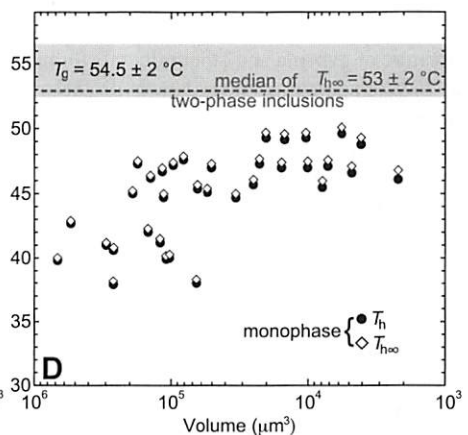
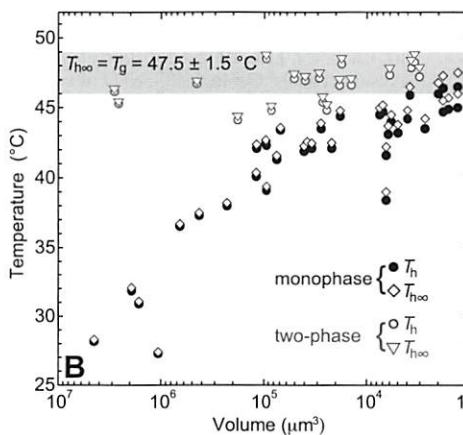
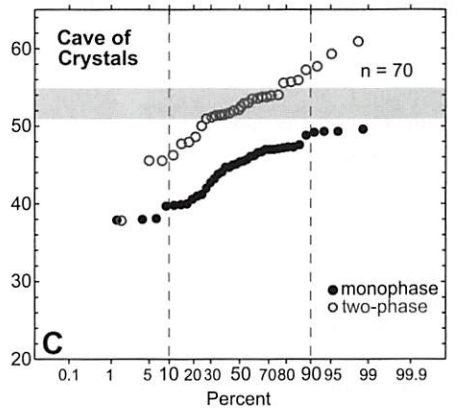
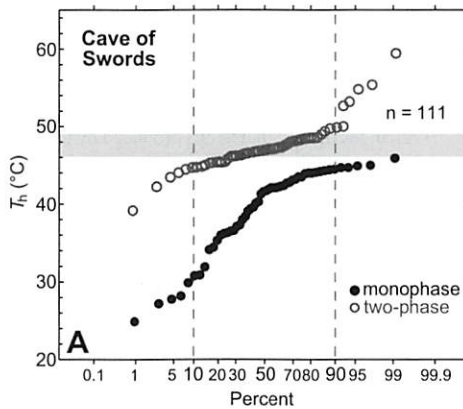
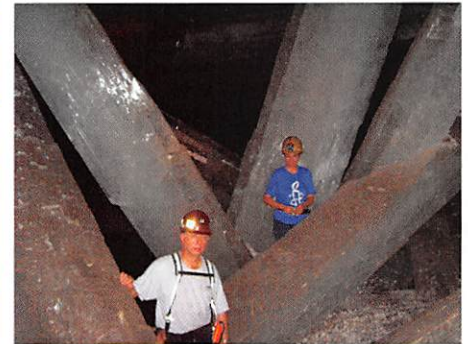


Figure 2. Probability distribution of measured homogenization temperature (T_h) values of initially monophasic (dots) and two-phase (circles) inclusions in natural gypsum crystals. A,B: Cave of Swords (upper left photo). Gray bar in A indicates range of T_h values of inclusions that are supposed to have preserved their original fluid density. Relation between T_h and inclusion volume is shown in B. C,D: Cave of Crystals (upper right photo). Relation between T_h and inclusion volume is shown in D. Gray bar in C indicates range of T_h values of inclusions that are supposed to have preserved their original fluid density. Diamonds and triangles denote calculated nominal homogenization temperatures, $T_{h\infty}$. Note that B and D display only data from inclusions, where both T_h and vapor bubble radius have been measured. Gray bars denote estimated gypsum growth temperature, T_g .

this correlation was not observed, because of the smaller size of the inclusions (10^2 to 10^4 μm^3). Our measurements confirm that the relative decrease of the inclusion volume due to deformation depends also on the inclusion volume (cf. Burnley and Davis, 2004), and we conclude that small monophasic inclusions are less affected by postentrapment volume alterations than large ones. The volume and the T_{hom} of the inclusions have been calculated based on the measured T_{h} values and measurements of the vapor bubble radius at known temperatures (cf. Marti et al., 2012). The temperature difference between T_{hom} and the measured T_{h} value never exceeds 0.8 $^{\circ}\text{C}$, and is therefore of little importance for the interpretation of the data.

We assume that gypsum crystals from the Cave of Swords formed close to the ground-water table, i.e., close to atmospheric pressure; we therefore expect that the T_{hom} equals the gypsum T_{g} . Based on the distribution of the measured T_{h} data, we estimate T_{g} to be 47 ± 1.5 $^{\circ}\text{C}$. However, for gypsum crystals from the Cave of Crystals, we assumed crystal growth under a hydrostatic pressure of ~ 16.7 bar, corresponding to a water column of 170 m. In this case, the T_{g} does not equal T_{hom} but is ~ 1.5 $^{\circ}\text{C}$ higher, due to the pressure correction. We determined a gypsum T_{g} of 54.5 ± 2 $^{\circ}\text{C}$ ($T_{\text{hom}} = 53 \pm 2$ $^{\circ}\text{C}$) for the Cave of Crystals. These results demonstrate that the gypsum growth temperatures in the Cave of Swords were ~ 7 $^{\circ}\text{C}$ lower than in the Cave of Crystals; this supports the idea that the larger number and smaller size of crystals in the Cave of Swords are due to an increase of supersaturation upon faster cooling of the solution (García-Ruiz et al., 2007).

CONCLUSIONS

The use of monophasic fluid inclusions opens the possibility of determining the growth temperature of gypsum and other minerals forming at low temperature under late hydrothermal, diagenetic, or even evaporitic environments. However, differential stress (internal tension or fluid overpressure) may result from natural temperature variations during uplift or burial processes, or can be artificially induced during sampling, when collected crystals are not preserved at their actual temperature on site. Therefore, the crystals should be maintained close to their present-day ambient temperature during transport, storage, and sample preparation. We also recommend choosing fluid inclusions as small as possible in order to reduce

plastic deformation. In those cases, however, when the fluid inclusions have been naturally exposed to a very complex postcrystallization thermal history with large fluctuations, and/or have been deformed by external tectonic stress, the high accuracy demonstrated here probably cannot be assured.

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