

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

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Krüger et al. (2013) use a femtosecond-laser system and fluid inclusions to constrain the formation temperature of gypsum speleothems (crystals) formed within the well-studied cave system of Naica, Mexico. The authors focus on two of the several caves documented in that underground mine, namely Cueva de las Espadas (depth: ~120 m) and Cueva de los Cristales (depth: ~290 m).

A fundamental assumption of Krüger et al. (p. 122) is that a cave fluid with close-to-atmospheric pressure generated the gypsum crystals of the shallow Cueva de las Espadas. Based on that assumption, the authors calculate a growth temperature of  $47 \pm 1.5$  °C in that cave, and claim the existence of an ~7 °C temperature difference with the deeper Cueva de los Cristales fluid. We find the assumption of Krüger et al. inconsistent with geological constraints, and their interpretation biased in terms of speleogenetic implications.

A large data set of geological data, cave morphology, cave mineralogy, present-day cave geochemistry, and fluid inclusion data show the Naica caves are hypogenic; i.e., they developed during artesian underground flow (Garofalo et al., 2010, and references therein). Actually, the available data set on Naica fits so well with the characteristics of hypogenic caves (cf. Klimchouk, 2007) that it can be considered today one of the most complete of its kind. The hypothesis of Krüger et al. of near-atmospheric fluid pressure implies essentially no artesian flow at Naica, and would need validation from geological data. Why did the authors completely exclude hypogene speleogenesis at Cueva de las Espadas? Their paper does not offer any discussion on why their growth condition would be preferable, and no mention of previous work is given.

Consistent with hypogene speleogenesis at Cueva de las Espadas, we think that the total homogenization temperatures ( $T_h$ (sub)) of Krüger et al. need the application of a pressure correction. This correction is not straightforward to determine because that cave had a complex phreatic/epiphreatic speleogenesis (Forti, 2010); however, a value of 1 °C is desirable for several reasons. First, that value is equivalent to a hydraulic head of 25–50 m (see Sanna et al., 2011) and a lithostatic load of ~120 m. Second, with their analytical approach, Krüger et al. want to estimate the growth temperature of cave gypsum with a precision of less than 1 °C; thus, the pressure correction we suggest is in line with that approach.

Note that the 1 °C correction brings better agreement between fluid inclusion data and geological constraints at Naica. The 7 °C temperature difference claimed by Krüger et al. would be consistent with a geothermal gradient in the area exceeding 40 °C/km at the time of gypsum growth. That value is higher than what is expected by the 26–30 Ma shallow igneous intrusion present to the southwest of Naica (Alva-Valdivia et al., 2003, and references therein), which drove underground fluid circulation and controlled gypsum growth tens of millions of years after crystallization (i.e., 191–8 ka: Sanna et al., 2011). The pressure-corrected fluid temperature we suggest lowers by one degree the temperature difference

of Krüger et al., but corresponds to a more reasonable geothermal gradient of ~35 °C/km. Thus, pressure-corrected  $T_h$  are not only in agreement with the evidence for hypogene speleogenesis in the caves, but correspond to a more realistic geological evolution of the area. We stress that, irrespective of pressure corrections, the  $T_{hot}$  range of Krüger et al. is very close to the 48–56 °C  $T_h$  range of Garofalo et al. (2010, our figure 4), which was not cited in their paper. That range was made of ~400  $T_h$  determinations from fluid inclusions entrapped in crystals from three caves (Cueva de los Cristales, Ojo de la Reina, and Cueva de las Espadas).

Another important omission we found in their paper deals with the chemical composition of the cave fluid of Naica. Krüger et al. (page 121) claim quite generically that “low-salinity solutions” generated the gypsum crystals, and cite previous calculations of gypsum crystallization from those solutions (García-Ruiz et al., 2007). Krüger et al. omit citing our 71 laser ablation-ICP-MS analyses of individual fluid inclusions (Garofalo et al., 2010), which showed beyond any doubt that, at Naica, two fluids were present in the hypogenic caves at the time of gypsum growth. Garofalo et al. showed evidence for a Mg-rich cave fluid in the shallower Cueva de las Espadas (Mg: 9100 µg/g; Na: 4450 µg/g) and for a moderately saline fluid in the deeper Cueva de los Cristales (Mg: 3000 µg/g; Na: 3500 µg/g). The compositions of these fluids do not identify “low salinity solutions,” but fluids having bulk salinities >7.5 wt% NaCl<sub>eq</sub>, i.e., more than twice the salinity of seawater. Thus, the claim of Krüger et al. is unfounded and superseded by our data. Finally, we stress that Krüger et al. omit also an evaluation of our model of gypsum growth at Naica. Garofalo et al. (2010) suggested that the two chemically distinct cave fluids mixed with each other during their underground flow due to cross-formational hydraulic communication of the caves (which is typical in hypogenic environments, cf. Klimchouk, 2007). That mixing must have controlled gypsum crystallization by determining the supersaturation conditions in which the gigantic crystals formed.

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