

Highlights of Analytical Chemistry in Switzerland

Division of Analytical Chemistry

A Division of the Swiss Chemical Society

Role of Fluid Inclusion Analysis in Understanding Gigantic Selenite Crystal Growth in a Deep Karst Cave (Naica, Mexico)

Mattias B. Fricker^a, Paolo S. Garofalo^b, and Detlef Günther^{*a}

*Correspondence: Prof. Dr. D. Günther^a, Tel.: +41 44 632 46 87, Fax: +41 44 633 10 71, E-mail: guenther@inorg.chem.ethz.ch

^aETH Zurich, Laboratory of Inorganic Chemistry, HCI G113, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich; ^bUniversity of Bologna, Department of Earth and Environmental Sciences, Piazza di Porta S. Donato 1, I-40126 Bologna

Keywords: Fluid inclusion · ICP-MS · Large crystals · Laser ablation · Naica · Selenite

The largest crystals of the world were discovered within deep karst caves of the Ag, Pb and Zn mine of Naica (Chihuahua, Mexico). These selenite crystals (for 'Cristales' up to 11 m in length, corrected U/Th age of 155 ± 47 ka) are as white as the moon when illuminated from the back. Due to the underground mining activities, the ground water is constantly being pumped away, which by chance led to the discovery of the cave crystals at a depth of -290 m (below entrance, b.e.). The caves are accessible for as long as the pumping is maintained for mining, but exploration conditions inside them are lethal due to the high temperature (>50 °C) and close to 100% relative humidity. Thus, special gear has been developed to enter these caves, and



The Naica caves were explored and documented by the Italian non-profit association *La Venta* (photo of 'Cristales', courtesy of *La Venta* and *Speleoresearch and Films*), who developed the protective suit that allows safe working in the cave up to 1 hour, before escaping into the vented and cool mine galleries.

these impressive natural objects have been sampled and studied in detail.

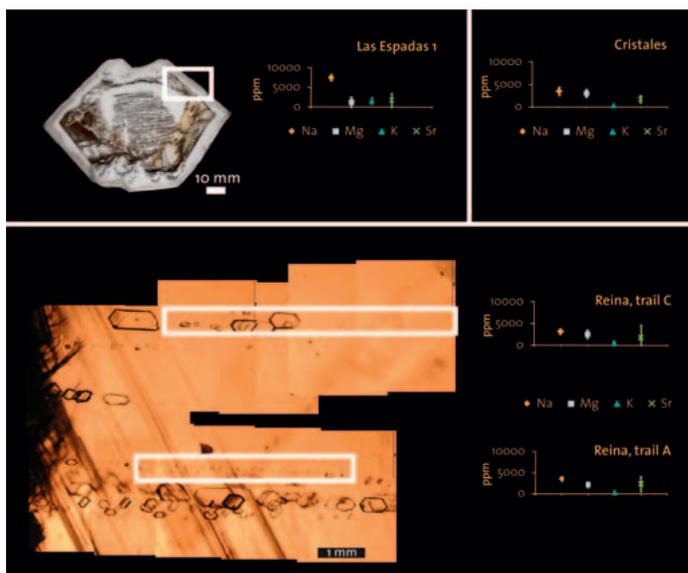
To reconstruct the composition of the cave liquid at the time of crystal growth within the caves, we studied the tiny droplets of aqueous liquid entrapped (fluid inclusions, FI, tens of μm) in the crystals of three caves. These FIs were analyzed using Laser Ablation–Inductively Coupled Plasma–Mass Spectrometry and elements quantified *via* the total salt content of a FI which was obtained prior to ablation by microthermometry. Gypsum samples from the caves named 'Las espadas' (-130 m b.e.), 'Cristales' (-290 m b.e.) and 'Ojo de la reina' (-290 m b.e.) were collected and the bulk composition of the FIs determined. Only Na, Mg, K and Sr were determined, other elements were either not present or below the limits of detection. Results show that major and trace element compositions of deep and shallow cave fluid are different. However, the compositions of contiguous and co-genetic FIs within a crystal are similar.

Our results indicate that the most favorable geological process which controlled the formation of such large crystals was the mixing of two chemically different cave fluids (shallow and deep). Constant mixing of these two fluids created the long-lasting supersaturation conditions necessary to grow these phenomenal crystals.

Received: May 26, 2011

References

- P. S. Garofalo, M. B. Fricker, D. Günther, P. Forti, A.-M. Mercuri, M. Loreti, B. Capaccioni, *Earth Planet. Sci. Lett.* **2010**, 289, 560.
D. Günther, A. Audétat, R. Frischknecht, C. A. Heinrich, *J. Anal. At. Spectrom.* **1998**, 13, 236.



Trace element concentrations of the sample from 'Las espadas' are different from those in 'Cristales' (no photo) and 'Ojo de la reina' (microscope photos of a section), whereas for the latter the concentrations are similar for two different primary FI assemblages as well as to 'Cristales'. Presence of a selection of other elements was not detected in the FIs.

Can you show us your analytical highlight?

Please contact: Dr. Veronika R. Meyer, EMPA St.Gallen, Lerchenfeldstrasse 5, 9014 St.Gallen
Phone: +41 58 765 77 87, Fax: +41 58 765 77 62, Mail to: veronika.meyer@empa.ch