Microprobe and Micro-Raman Determination of Hemimorphite Speleothems in Mine Caves of SW Sardinia (Italy)

/ FERNANDO GAZQUEZ (1*), JOSE MARIA CALAFORRA (2), FERNANDO RULL (3), JESUS MEDINA (3), AURELIO SANZ –ARRANZ (3), JO DE WAELE (4) AND PAOLO FORTI (4)

(1) Godwin Laboratory, Department of Earth Sciences, University of Cambridge, Downing Street, CB2 3EQ, Cambridge (United Kingdom)
(2) Water Resources and Environmental Geology Research Group. University of Almería. Ctra. Sacramento s/n, 04120. (Spain)
(3) Unidad Asociada UVA-CSIC al Centro de Astrobiología (ERICA), University of Valladolid, Parque Tecnológico Boecillo, 47151, Valladolid (Spain)
(4) Italian Institute of Speleology, Department of Biological, Geological and Environmental Sciences, University of Bologna. Via Zamboni, 67, 40126. Bologna (Italy)

INTRODUCTION

Hemimorphite ($Zn_4Si_2O_7(OH)_2{\cdot}H_2O$), previously called calamine together with smithsonite ($ZnCO_3$) and other Zn-bearing minerals, is one of the most common mined Zn ores worldwide. This sorosilicate usually occurs as an oxidation product at the upper parts of sphalerite [(Zn, Fe) S] bearing ore bodies, accompanied by other secondary minerals, which form the so-called iron cap or "*gossan*". The presence of hemimorphite in natural caves is rare and almost restricted to mine caves, normally of hypogenic origin and associated with the oxidation front of polysulfide deposits. Here we present mineralogical (Raman spectroscopy) and geochemical data (SEM-EDX) of several hemimorphite speleothems from two mine caves of the Iglesiente mining district in the SW Sardinia, Italy. These results have enabled us to envisage a genetic model for these speleothems.

GEOLOGICAL SETTING AND MATERIALS DESCRIPTION

The regional geology of the Carbonia-Iglesias mining district comprises low permeability metasandstones and phyllites, dolostone and limestone from Lower Cambrian to Ordovician-Silurian age. The Variscan deformation phase is responsible for low-grade metamorphism and several phases of magmatic intrusion, some of which produced skarn deposits as a result of the interactions between the igneous intrusive bodies and the carbonate rock. (Boni et al., 1992). Some caves in this region are developed in these skarn deposits.

Crovassa Quarziti Cave is located in Mt. San Giovanni, in which more than 50 caves were accidentally discovered as a result of the mining activities. This cave is associated with siliciclastic intrusions and oxidation of polymetallic ores that gave rise to Sulfuric Acid Speleogenesis (SAS) (De Waele et al., 2013). Evidences of hydrothermal activity in the Mt. San Giovanni Caves are the presence of calcite spars in some of its cavities, bell-shaped chambers and widespread subaqueous and subaerial corrosion forms. In Crovassa Quarziti Cave, hemimorphite appears in the form of 10-m-high flowstones made of submillimetric whitish to greenish laminae of this mineral. In cases, hemimorphite occurs directly on quarzitic materials. Occasionally, it appears deposited on blackish layers of oxides (sample GQ-01; Fig. 1) or forming part of stalactites (De Waele et al., 2013)

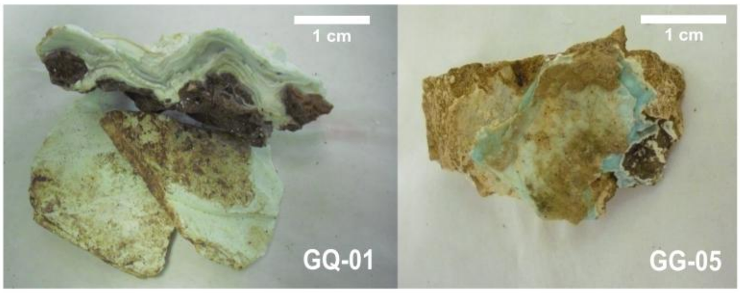

fig 1. *Hemimorphite flowstones from Grotta Quarziti Cave (GQ-01) and Monte Guisi Cave (GG-05).*

Monte Guisi Cave is carved in calcitic skarn, in which rich Pb-Zn (±Ba) mineralizations occur as veins, breccia cements, void-filling, and diagenetic replacements (Moldovan et al., 2013). Its speleothems comprise rare Pb-Zn-Cu-bearing minerals, such as dundasite ($PbAl_2(CO_3)_2(OH)_4{\cdot}H_2O$) and plancheite ($Cu_8(Si_4O_{11})2(OH)_4{\cdot}H_2O$), which have never been reported in other cave environments (Moldovan et al., 2013). In this cave, hemimorphite appears as 1-cm-thick bluish flowstones deposited on quartzite and oxides (GG-05; Fig. 1).

METHODS

The micro-Raman spectroscopy analysis used a Laser Research Electro-Optics (REO) working at 632.8 nm coupled to a spectrometer KOSI HoloSpec f/1.8i model from Kaiser. Microanalyses up to a 40 µm diameter spot were undertaken with a Nikon Eclipse E600 microscope using 50x magnification. The RUFF database was utilized for minerals identification. SEM microphotographs were taken using a HITACHI S-3500 instrument in high vacuum mode. The elemental chemistry was determined by Energy dispersive X-ray spectroscopy (micro-EDX microprobe). Semi-quantitative EDX microanalyses used an Oxford INCA 7210 X-ray detector. Results are given in weight %. 5 microanalyses were performed on each sample.

RESULTS

The Raman spectrum of the greenish laminae in sample GQ-01 shows the typical signal of hemimorphite (928, 673, 450, 396 and 329 cm^{-1}) (Fig. 2), whereas the dark materials on which this mineral precipitated are poorly crystalline Fe-Mn oxides (672 and 606 cm^{-1}). The EDX microanalyses found ~53

palabras clave: Hemimorfita, Espeleotemas, Cuevas en Minas | ***key words:*** Hemimorphite, Speleothems, Mine Caves

* corresponding author: **f.gazquez@ual.es**

% of Zn, ~29 % of O and ~14 % of Si in the hemimorphite layers, in addition to traces of Mg, Cl, Ca, Al, Ni, Fe and K (all below 1%). No significant compositional differences were detected between different laminae. The SEM images showed compact microcrystalline layers, 20-100 μm in width (Fig. 3A).

The bluish coatings in sample GG-05 were also identified as hemimorphite by Raman (Fig. 2). High Zn concentrations, up to 72 %, in addition to O (~20 %) and Si (~10 %) were detected, whereas the presence of minor elements was below the detection limit of the instrument (Fig. 2). The hemimorphite layers are deposited on quartzite, as revealed by the intense Raman signal centred in 462 cm^{-1} observed in the underlying material, which is assigned to the presence of SiO_2. In cases, between the quartz and hemimorphite layers there is a lamina of poorly crystalline oxides of Zn (21 %), Fe (19 %), Mn (6%), Cu (6 %) and Pb (2 %). The SEM images revealed tabular crystals forming "boxwork" morphologies in this hemimorphite flowstone (Fig. 3B).

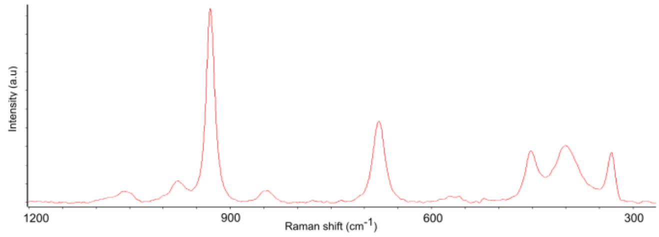

***fig 2.** Raman spectrum of hemimorphite in the analysed samples. Both samples showed similar spectra*

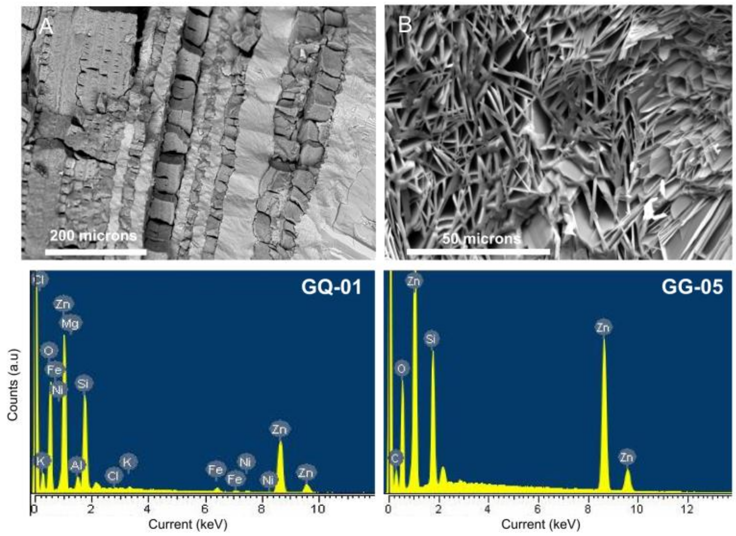

***fig 3.** SEM images of samples GQ-01 (A) and GG-05 (B), and their corresponding EDX spectra.*

DISCUSSION

Hemimorphite precipitation in the studied caves was associated with alteration of quartzitic materials, which form part of the calcitic skarn generated during earlier geological stages. Tectonic-hydrothermal events were responsible for this silicification processes affecting the upper part of the Cambrian dolostones (Boni et al., 1992). Afterwards, sulphuric acid speleogenesis took place. This mechanism generated most of the cavities in Mt. San Giovanni (De Waele et al., 2013).

Previous investigations suggests that quartz dissolution rate gets reduced under acid and neutral conditions, whereas it exponentially increases under high pH (Sauro et al., 2014, and references therein). Therefore, quartzite alteration may be impeded during these earlier hydrothermal phases, resulting in diminished concentration of different species of siliceous acids in solution. Once the water table fell and hydrothermal water abandoned the cave level during the Late Quaternary (De Waele et al., 2013), SAS stopped and acidic conditions were neutralized by the carbonate materials of the bedrock. During this stage, precipitation of oxides on quartzite could be favoured due to reduced solubility of metals in neutral-basic and oxygenic conditions occurred in the cave.

The precipitation of zinc silicates became an important process at this post-oxidation stage. We propose that a water lamina flowing on the quarzitic substrate produced hemimorphite precipitation in the form of flowstones. The presence of alkali cations has been demonstrated to increase the solubility of quartz, and could be responsible for the speleogenesis in quarzite (Sauro et al., 2014). We hypothesize that high metals content in water supplied by mineralization in the host rock favored quartz dissolution and gave rise to relatively high concentration of H_4SiO_4 (aq) even under neutral or slightly basic conditions. This produced subaerial hemimorphite precipitation during the Late Quaternary in these caves.

CONCLUSIONS

Hemimorphite in the studied speleothems formed as a result of neutral or slightly basic pH of the water lamina flowing on quarzitic materials and metal mobilization from ore minerals in subaerial conditions. This controlled both dissolution of quartz and later precipitation of hemimorphite.

ACKNOWLEDGEMENTS

Financial support was made available through the ESP2013-48427-C3-2-R Project of MINECO (Ministerio de Economía y Competitividad, Secretaría de Estado de Investigación, Desarrollo e Innovación). The authors are grateful for the support of Angelo Naseddu of the Speleo Club Domusnovas. Esmeralda Urea performed the SEM-EDX analyses at the Technical Services Area of the University of Almeria (Spain).

REFERENCES

Boni, M., Iannace, A., Köppel, V., Früh-Green, G., Hansmann, W. (1992): Late to Post-Hercynian hydrothermal activity and mineralization in Southwest Sardinia (Italy). Econ. Geol. ***87****, 2113–2137.*

De Waele, J., Forti, P., Naseddu, A. (2013): Speleogenesis of a complex example of an exhumed sulphuric acid karst in Cambrian carbonates (Mount San Giovanni, Sardinia). Earth Surf. Proc. Landf., ***38****, 1369–1379.*

Moldovan, C., Calugar, M.I., Onac, B., De Waele, J., Naseddu, A., Fornos, J.J. (2013): A contribution to the mineralogy of Monte Guisi cave (SW Sardinia, Italy). Proceedings of the 16th International Congress of Speleology, ***3****, 486-489.*

Sauro, F., De Waele, J., Onac, B.P., Galli, E., Dublyansky, Y., Baldoni, E., Sanna, L. (2014): Hypogenic speleogenesis in quartzite: The case of Corona 'e Sa Craba Cave (SW Sardinia, Italy). Geomorphology, ***211****, 77–88.*