INTRODUCTION

Hemimorphite (Zn₄Si₅O₁₉(OH)₀.₅H₂O), previously called calamine together with smithsonite (ZnCO₃) 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 metasediments and phylmites, dolostone and limestone from Lower Cambrian to Ordovician 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 mining activities. This cave is associated with silicilastic 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 quartzite 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).

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 (PbAl₂(CO₃)₃(OH)₆H₂O) and plancheite (Cu₉(Si₄O₁₃)₂(OH)₁₂H₂O), 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 (RED) working at 632.8 nm coupled to a spectrometer KOSI HoloSpect 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
% 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 SiO₂. 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).

**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 (Bonì 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 quartzitic 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 quartzite (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 H₄SiO₄⁻(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 quartzitic materials and metal mobilization from ore minerals in subaerial conditions. This controlled both dissolution of quartz and later precipitation of hemimorphite.

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