Glaucocerinite forming gours in Su Zurfuru Mine (Sardinia, Italy)

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INTRODUCTION

Sulphate minerals are the second group of cave minerals in importance after carbonates (Hill and Forti, 1997). As a general rule, sulphates in limestone caves come from oxidation of sulphide ore bodies placed in the host rock or microbial degradation of hydrocarbons. Stalactites, stalagmites, flowstones, rims, gours, and more usually crusts, powder and patinas made of sulphate minerals have been described in a variety of caves (Hill and Forti, 1997).

Among sulphate minerals, gypsum ($CaSO_4{\cdot}2H_2O$) is the most common, though a broad array of sulphate minerals has been described in caves, including anhydrous minerals such as anhydrite ($CaSO_4$), celestine ($SrSO_4$), barite ($BaSO_4$) and anglesite ($PbSO_4$), as well as some uncommon hydrated sulphates like melanterite ($FeSO_4{\cdot}7H_2O$), fibroferrite [$Fe(OH)SO_4{\cdot}5H_2O$] and halotrichite [$FeAl_2(SO_4)_4{\cdot}22H_2O$], just to name some of up to 100 sulphate minerals reported to date in cave environments (Onac and Forti, 2011).

In the current work, we have studied the mineralogy and the geochemistry of two sets of gour speleothems (also called rimstones) from Su Zurfuru Mine (SW Sardinia, Italy). Our analyses have revealed the presence of a rare sulphate mineral.

GEOLOGICAL SETTING AND MATERIALS

Su Zurfuru Mine is located in the Mining District of Fluminimaggiore in SW Sardinia (Italy). The mine extracted Zn-Pb sulphides and fluorite until the mid 90s, when the mining activities were abandoned. The regional geology comprises low permeability metasandstones and phyllites, dolostone and limestone from Lower Cambrian to Ordovician-Silurian. In Su Zurfuru Mine, flowstones and gours have been found, with colour ranging from white to strong blue, particularly at the site called the "Zinc Fountain" (Forti et al., 2005).

fig 1. Glaucocerinite forming gours in the Su Zurfuru Mine (SW Sardinia, Italy). White gours (A) and sky-blue gours (B) in the mine galleries.

A sampling campaign was carried out in April 2012. ZS-01 sample was collected from a set of white gours, 3 m long and 1.5 m wide, placed in a gallery 500 m far from the mine entrance (Fig. 1A). ZS-02 sample was taken from a set of sky-blue gours, 6 m long and 3 m wide in a gallery 550 m far from the mine entrance (Fig. 1B). Both speleothems were active as revealed by water flowing on their surfaces.

METHODS

SEM microphotographs of samples ZS-01 and ZS-02 were taken using a HITACHI S-3500 instrument in high vacuum mode. The elemental chemistry was determined by micro-EDX (Energy dispersive X-ray spectroscopy) microprobe. Semiquantitative EDX microanalyses used an Oxford INCA 7210 X-ray detector. EDX analyses were performed at the Technical Services Area of the University of Almeria (Spain).

The analyses by Raman spectroscopy used a Laser Research Electro-Optics (REO) working at 632.8 nm coupled to a spectrometer KOSI HoloSpec f/1.8i model from Kaiser. X-Ray diffraction was performed by a diffractometer Philips PW1710, with a Cu anode (CuKα, λ= 0.154 nm). XRD and Raman analyses were carried out at the Department of Crystallography and Mineralogy of the University of Valladolid and the Unidad Asociada al Centro de Astrobiología (UVA-CSIC) (Valladolid, Spain), respectively.

RESULTS

White gours (SZ-01)

Based on the Raman results, the white gours comprise glaucocerinite [$(Zn,Cu)_5Al_3(OH)_{16}(SO_4)_{1.5}{\cdot}9H_2O$], gypsum ($CaSO_4{\cdot}2H_2O$) and fluorite ($CaF_2$). Signals at 450, 544, 615 and 980 cm^{-1} have been assigned to glaucocerinite (Frost et al., 2004), whereas a weak signal at 321 suggests the presence of fluorite. Besides, signals at 1007 and 493 cm^{-1} point to the presence of gypsum. XRD found glaucocerinite and fluorite. EDX microanalyses of pseudo cubic crystals

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found high concentration of F (42 %wt) and Ca (38 %wt), confirming the presence of fluorite (Fig. 2A). Zn (47 %wt), Al (5 %wt), S (3 %wt) and O (42 %wt) have also been detected on intricate laminas of glaucocerinite (Fig. 2A and B). Cu concentration was probably below the detection limit of EDX. In addition, the analyses of fibrous crystals found high levels of Ca (20 %wt), S (18 %wt) and O (52 %wt), confirming the presence of gypsum.

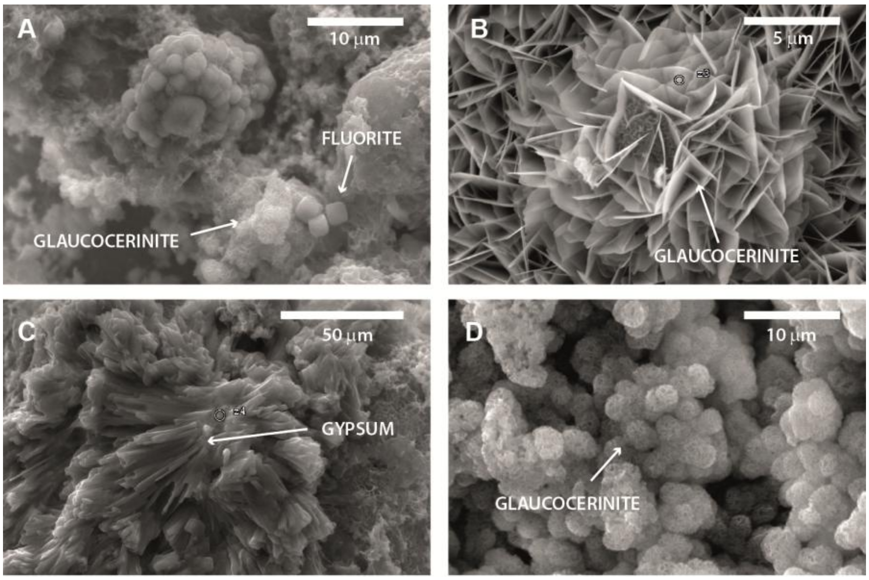

fig 2. Secondary electron images (SEM) of glaucocerinite (A and B), fluorite (B) and gypsum (C) in the white gours (SZ-01) and glaucocerinite (D) in the sky-blue gours (SZ-02) of Su Zurfuru Mine.

Sky-blue gours (SZ-02)

Both Raman spectroscopy and XRD have revealed the presence of glaucocerinite in the sky-blue gours (Fig. 1B). The Raman spectra show broad signals at 455, 568 and 618 cm^{-1}, a shaped peak at 980 cm^{-1}, and a minor signal at 1092 cm^{-1}, in addition to a broad peak around 3430 cm^{-1}, which is assigned to the OH-bending of water, in concordance with earlier vibrational studies on this mineral (Frost et al., 2004). EDX detected Zn (38 %wt.), Cu (2 %wt.), Al (14 %wt.), S (5 %wt.) and O (37 %wt.), as well as traces of Si, F and Ca, so corroborating its mineralogical nature. At microscopic scale, this mineral displays as spherulitic aggregates, 3 nm wide, composed of intricate laminas (Fig. 2D).

DISCUSSION

In Su Zurfuru Mine, glaucocerinite occurs as gour-type formations on the floor and walls of the mine galleries, and precipitates from a small spring. In places, the gours form close to fissures of the carbonate host rock from which water springs up. Previous works of Forti et al. (2005) also suggested the presence of hydrated Zn-sulphate minerals in this mine, but the exact mineralogy of these speleothems could not be identify by these authors.

Glaucocerinite is an uncommon polymetallic sulphate which has been identified just in one natural cave worldwide to date (Kiinyugawa-dam Cave, Japan, Kashima and Hisatomi, 2005). However, these authors erroneously described this mineral as $CuAl_2SO_4(OH)_{12}{\cdot}3H_2O$, rather than $[(Zn,Cu)_5Al_3(OH)_{16}(SO_4)_{1.5}{\cdot}9H_2O]$ (Raade et al. 1985), so its occurrence in natural subterraneous environments has not yet been confirmed.

In spite the fact that the two gours formations studied in this work mainly comprise glaucocerinite, they are totally different in colour. The EDX analyses suggest that the sky-blue colour in sample SZ-02 comes from small amounts of Cu^{2+}, not detected in sample SZ-01. Conversely, white colour in SZ-01 could also be related to the presence of gypsum and fluorite.

The origin of glaucocerinite in Su Zurfuru Mine, so far seems to be linked to oxidation and/or hydrolysis of ore deposit, mainly Zn-Cu-bearing minerals (sphalerite, and chalcopyrite). Sulphide-bearing water emerging from the bedrock cracks generated sulphate as a result of sulphide oxidation in oxygenic conditions when the solution reached the subterraneous voids. In addition, hydrolysis of clay minerals present in the substrate under the gours (coming from hydrothermal alterations or residues from corrosion of the host rock) supplies aluminium for the glaucocerinite precipitation.

CONCLUSIONS

The gours of Su Zurfuru Mine represent the first reliable evidence of glaucocerinite forming gour speleothems in a subterraneous environment. The concentration of Cu, which is in solid solution with Zn, is the determinant factor of blue color in some of these speleothems.

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