

# First occurrence of the rare mineral slavikite in Spain

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**Abstract** The magnesium and iron sulfate mineral slavikite has been found in Pastora Mine, Aliseda, Cáceres, Spain, in association with a number of other sulfate minerals such as alunogen, fibroferrite and tschermigite. Remarkably, slavikite is the major phase on some walls of Pastora Mine. To the best of our knowledge, this is the first reported occurrence of slavikite in Spain. Here, we present a mineralogical characterisation of the slavikite found in Pastora Mine using X-ray powder diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, electron probe micro-analysis and thermogravimetry. This characterisation also includes an analysis of the morphology of slavikite crystals based on the Bravais-Friedel-Donnay-Harker method, and the determination of the following slavikite formula from microprobe analyses and thermogravimetric

data:  $\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}(\text{OH})_8 \cdot 13(\text{H}_2\text{O})$ . Finally, we discuss the possible formation conditions of slavikite in Pastora Mine on the basis of available geological information and water analyses. We hypothesise that the presence of slavikite as major sulfate phase in some sites of Pastora Mine is partially the result of a process of mineral enrichment in which the moderate solubility of slavikite and wet and dry weathering cycles play a major role.

**Keywords** Hydrated magnesium iron sulphate · Mineralogical characterization · Acid mine drainage · Acid weathering

**Resumen** El mineral eslavikita, sulfato de hierro y magnesio, se ha encontrado en la Mina Pastora, Aliseda, Cáceres, España, asociado con otros sulfatos como alunógeno, fibroferrita y tschermigita. La eslavikita es la fase más abundante en algunas de las paredes de la Mina Pastora. Hasta donde tenemos conocimiento, ésta es la primera vez que se documenta la presencia de eslavikita en España. En este trabajo se presenta la caracterización mineralógica de la eslavikita encontrada en la Mina Pastora utilizando difracción de rayos X por método de polvo, microscopía electrónica de barrido, espectroscopia de rayos X por energía dispersiva, microsonda electrónica y análisis termogravimétrico. Esta caracterización incluye también un análisis de la morfología de los cristales de eslavikita, utilizando el método Bravais-Fiedel-Donnay-Harker, y la determinación de la fórmula de la eslavikita a partir de los análisis químicos y termogravimétricos:  $\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}(\text{OH})_8 \cdot 13(\text{H}_2\text{O})$ . Finalmente, se discuten las posibles condiciones de formación de la eslavikita en la Mina Pastora a partir de los datos geológicos disponibles y de los análisis de aguas locales. El hecho de que la eslavikita sea el sulfato más abundante en algunos lugares de la Mina Pastora indica la actuación de procesos de

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enriquecimiento mineral en los que la moderada solubilidad de la esclavikita y los ciclos de meteorización secos y húmedos juegan un papel importante.

**Palabras clave** Sulfato hidratado de hierro y magnesio · Caracterización mineral · Drenaje ácido de mina · Meteorización ácida

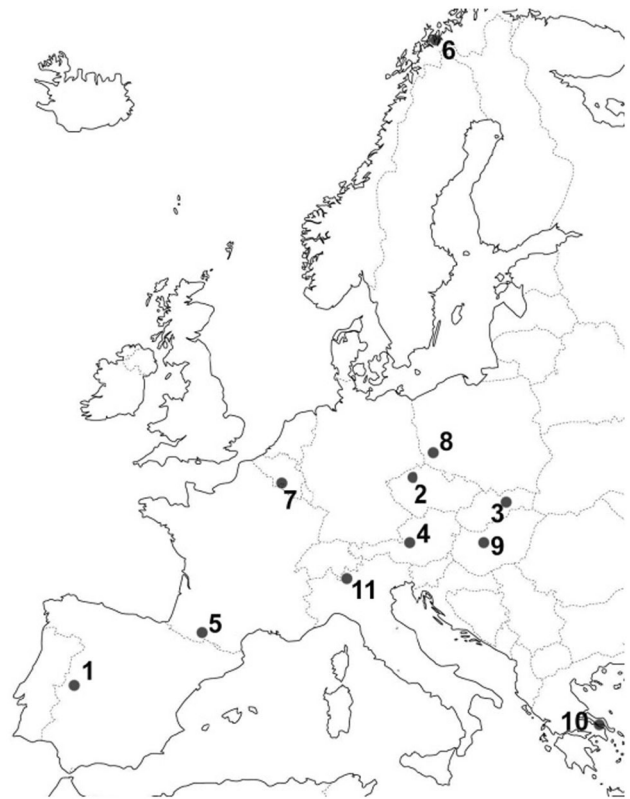
## 1 Introduction

Slavikite is a hydrous magnesium and iron sulfate occasionally formed from the oxidation of pyrites in rocks also containing magnesium minerals. Slavikite crystallizes in the trigonal space group  $R\bar{3}$ , it was named in honour of the mineralogist František Slavík and it was described for the first time by Jirkovský and Ulrich (1926) as the result of the weathering of pyrites found in the locality of Valachov Hill near Skřiváň, Bohemia, Czech Republic. After its discovery, slavikite has been found in various localities in Europe and America (see Van Tassel 1972; Parafiniuk et al. 2010, for reviews on slavikite occurrences). However, the structure and composition of slavikite have been controversial and the following formulas have been reported in the last decades:  $(\text{Na},\text{K})_2\text{Fe}_{10}(\text{SO}_4)_{13}(\text{OH})_6 \cdot 63\text{H}_2\text{O}$  (Jirkovský and Ulrich 1926);  $\text{Fe}(\text{SO}_4,\text{OH}) \cdot 8\text{H}_2\text{O}$  (Rost 1941);  $\text{MgFe}_3(\text{SO}_4)_4(\text{OH})_3 \cdot 18\text{H}_2\text{O}$  (Gordon 1941); and  $\text{NaMg}_2\text{Fe}_5(\text{SO}_4)_7(\text{OH})_6 \cdot 33\text{H}_2\text{O}$  (Süsse 1975). In a recent and detailed study of slavikites from Wieściszowice, SW Poland, Parafiniuk et al. (2010) proposed a new formula:  $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$ .

In this paper we report, to the best of our knowledge, the first occurrence of the mineral slavikite in Spain, the most western locality in Europe (Fig. 1). Furthermore, we propose a new mineral formula for slavikite based on new electron probe micro-analysis and thermogravimetry data. Finally, we discuss the origin of slavikite from Pastora Mine in relation to the weathering of pyrite-bearing slates.

## 2 Geological context

Pastora Mine is an abandoned iron mine located in Aliseda, Cáceres, SW Spain. Goethite and hematite, from a gossan deposit, were the main minerals exploited together with pyrite from pyrite-bearing slates. The mine is situated in the north-western area of the Badajoz-Córdoba fault zone, near the southern edge of Central-Iberian Zone, according to the subdivision of the Hercynian Iberian Massif made by Julivert et al. (1974) (Fig. 2). The Variscan or Hercynian orogeny was mainly responsible for the structure of this zone, which shows wide antiformal structures affecting Neoproterozoic materials (the Schist Greywacke Complex), and narrow synclines where



**Fig. 1** Some localities where slavikite has been found in Europe. 1 Pastora Mine, Aliseda (Spain), 2 Valachov Hill (type locality) (Czech Republic), 3 Smolnik and Medzev (Slovakia), 4 Pöham, Salzburg, Kärnten, and Aigen (Austria), 5 St. Cyprien-sur-Dourdou and Aveyron, Kaymar (France), 6 Nord-Trøndelag, Oppland, Sør-Trøndelag and Troms (Norway), 7 Liège (Belgium), 8 Wieściszowice (Poland), 9 Rudabánya (Hungary), 10 Plaka Mines (Greece), 11 Servette-Chuc mining complex (Italy)

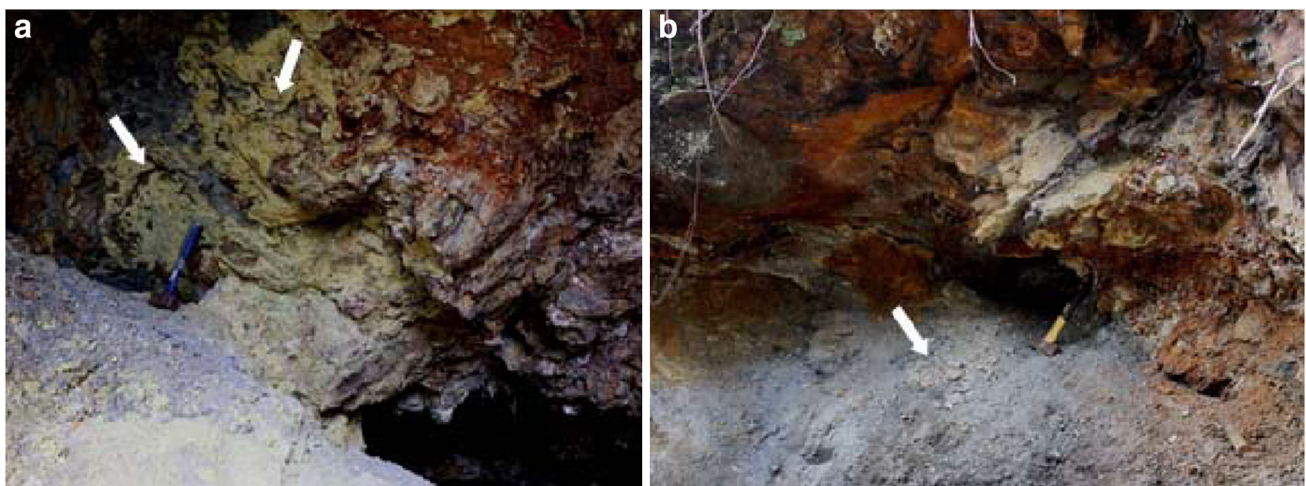
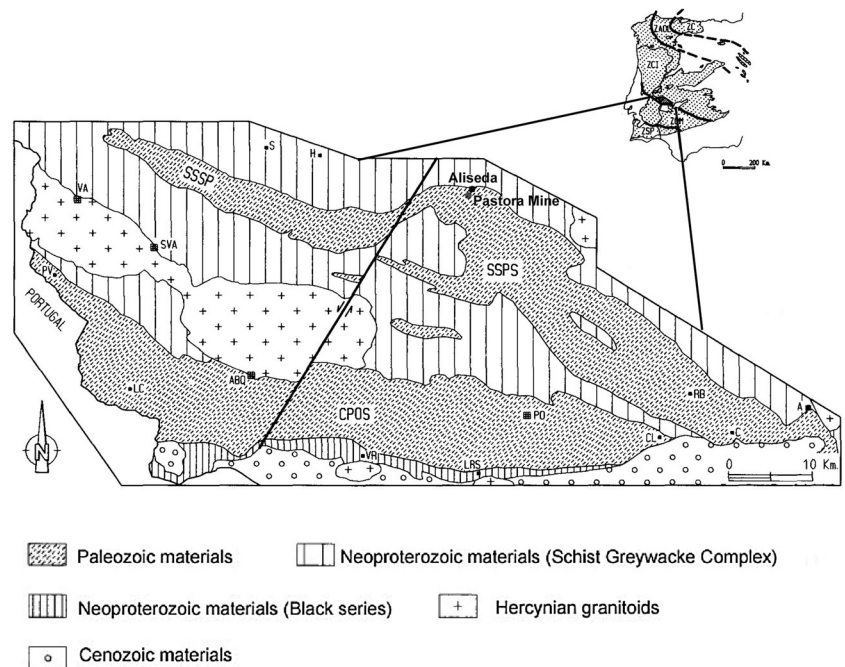
an almost complete sequence of the Paleozoic age, partially buried by Neogene and Quaternary deposits, can be observed (Soldevila 1991).

Several abandoned mine-sites such as Pastora Mine can be found in the North flank of Sierra de San Pedro syncline structure. Outcropping rocks are formed by a Paleozoic detrital sedimentary sequence of quartzites, sandstones and slates (Crespo 2015; Soldevila 1992), ranging from Ordovician to Permian ages (Soldevila 1992). In particular, Pastora Mine is situated in Devonian quartzites and slates. In this area, mining took place intermittently by means of underground galleries, pits and open pits. Mines were active from 1910 until 1958 when all mines in the region closed down.

## 3 Occurrence of slavikite in Pastora Mine

Slavikite occurs in Pastora Mine, as crusts and efflorescences on the weathered walls of the mine, which also contains other secondary sulfates in variable amounts

**Fig. 2** Schematic geological map showing the location of Pastora Mine within the Sierra de San Pedro syncline structure. The *inset* shows a geological scheme of the Central-Iberian Zone and the area where Pastora Mine is situated. The two main geological structures are indicated: Sierra de San Pedro Syncline (SSPS), and La Codosera-Puebla de Obando Syncline (CPOS). Figure modified from Soldevila (1992)



**Fig. 3** **a** Yellow crusts of slavikite (and other sulfates in minor amounts) at site 1 and **b** ground containing slavikite and other sulfates in variable amounts at site 2 in Pastora Mine. White arrows indicate the places where slavikite was found

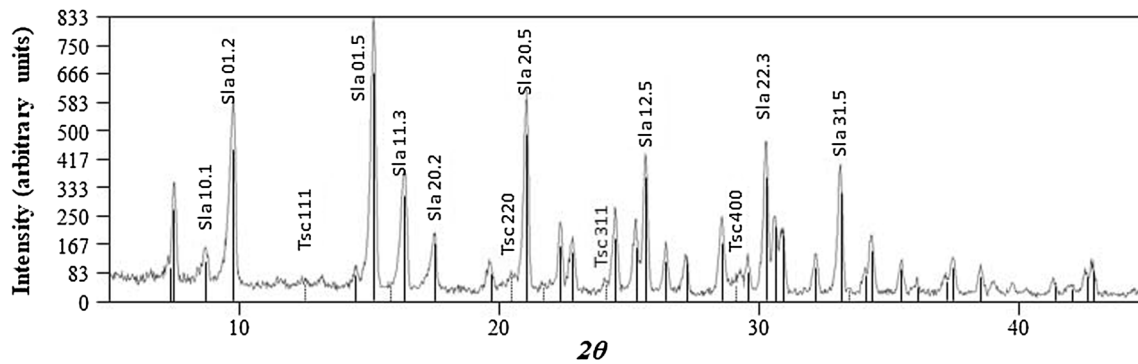
(Crespo 2015). In Pastora Mine, slavikite is found in two representative sites with different environmental conditions (see map in Supporting Information). While site 1 is currently more protected and sulfates are persistent all along the year, site 2 is more exposed to meteoric waters and consequently sulfates alternately dissolve and reprecipitate (Fig. 3).

Sulfate mineral assemblages are quite different for sites 1 and 2. In site 1 slavikite is predominant and it is associated with tschermigite,  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , whereas in site 2, slavikite appears together with fibroferrite,  $\text{Fe}^{3+}\text{SO}_4\text{OH} \cdot 5\text{H}_2\text{O}$ , which is predominant, and minor amounts of alunogen,  $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$  (see Fig S1 in the

Supplementary Information). Since slavikite is more abundant and purer in site 1 of Pastora Mine, the study of its characterisation was conducted on samples collected from that site.

#### 4 Experimental methods

Ten samples (eight from site 1 and two from site 2) containing slavikite were taken from selected places at Pastora Mine using a stainless steel spatula, collected in plastic vessels with hermetic lids, and stored at room temperature. Aliquots of the samples were grounded and sieved to a



**Fig. 4** Typical diffractogram of a sample collected at site 1 in Pastora Mine. *Vertical solid lines* indicate the positions and relative intensities of slavikite (Slav) diffraction peaks (PDF number 20-0679).

*Vertical dotted lines* indicate the positions of the peaks of tschermigite (Tsc) (PDF number 07-0022)

particle size  $<53 \mu\text{m}$  and subsequently analysed by X-ray powder diffraction (XRPD) at the Crystallography and Mineralogy Department of the Complutense University of Madrid (UCM) using a Siemens D-500 diffractometer with a  $\text{CuK}\alpha$  source. Mineral phases present in the samples were identified by comparing the collected diffractograms with the PDF2 database using the XPowder software. A selected number of samples, previously coated with gold, were also examined at the ICTS Centro Nacional de Microscopia Electrónica of UCM with a scanning electron microscopy (SEM, JEOL JSM 6400–40 kV) equipped with a Link-analytical Energy Dispersive X-ray Analysis (EDX) system.

Mineral compositions were determined by electron probe microanalysis (EPMA) at the ICTS Centro Nacional de Microscopia Electrónica of UCM with a JEOL Superprobe JXA-8900M instrument. Selected slavikite samples were mounted in epoxy and then polished. The microprobe, equipped with five wavelength-dispersion spectrometers, was operated at 15 kV with a beam current of 10 nA, and a beam diameter ranging from 5 to 10  $\mu\text{m}$ . Counting times on peak and background positions were 10 s. Microprobe standards included galena for S, dolomite for Mg and siderite for Fe. ZAF was the matrix correction used.

A thermogravimetric analysis (TGA) of the samples was carried out in a thermobalance Q-500 (TA Instruments) using initial sample weights of around 2 mg. Prior to perform the thermogravimetric measurements, samples were washed with deionized water and filtered to remove impurities as much as possible. The temperature ramp was done from 50 to 1000  $^{\circ}\text{C}$  in nitrogen atmosphere at 10  $^{\circ}\text{C}/\text{min}$ . An isotherm was performed before the ramp for 1 min at 50  $^{\circ}\text{C}$  in order to stabilize the temperature. As samples are highly hygroscopic, previous to the collection of thermograms, they were pretreated by drying them in vacuum ( $\sim 1 \text{ mbar}$ ) in an oven (VT6130M, Thermo Fisher Scientific) at 80  $^{\circ}\text{C}$  overnight.

A volume of 120  $\text{cm}^3$  of acid mine drainage (AMD) water from Pastora Mine was collected in June 2015 in a sealed plastic tube and stored at room temperature. The sampling of water was conducted in the underground galleries of the mine and subsequently analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES),  $\text{IT}^{-1} = 04345\text{J0 3701}$ . Before analysis, the water sample was filtered below 0.2  $\mu\text{m}$  and acidified with nitric acid to a pH below 2. Measurements of the water pH were performed in situ using a portable pH-meter (Eutech Instruments, Eoscan).

## 5 Results and discussion

### 5.1 Identification and characterisation of slavikite from Pastora Mine

Slavikite was firstly identified in the diffractograms performed on samples taken from site 1. Figure 4 shows a characteristic diffractogram in which slavikite peaks listed in the reference file (PDF number 20-0679) appeared as the main peaks. In addition, a few peaks with low intensities and corresponding to the minor phase tschermigite were also detected in the diffractograms. Table 1 shows the values of  $d$  and intensities of the main diffractograms peaks of slavikite collected in site 1. From analysis of a number of diffractograms, we can conclude that slavikite usually constitutes up to  $\sim 88$  weight % of the crystalline material of the samples (calculated using the reference intensity ratio (RIR) tool of the XPowder software for X-ray diffraction data analysis; Hubbard and Snyder 1988; Martín 2008).

SEM images of samples from site 1 show aggregates of randomly oriented slavikite crystals very similar to those previously reported by Parafiniuk et al. (2010) (Fig. 5a). The single crystals which form the aggregates have a tabular habit and sizes typically ranging from 10 to 30  $\mu\text{m}$ .

**Table 1** X-ray powder diffraction data for slavikite from site 1

PDF number 20-0679		Slavikite from Pastora Mine	
d (Å)	% (I/I <sub>0</sub> )	d (Å)	% (I/I <sub>0</sub> )
12.100	40	–	–
11.700	80	11.65	95.1
10.1	60	10.13	13.19
9.04	100	9.04	73.6
6.11	20	–	–
5.83	80	5.82	94.7
5.41	80	5.40	43.7
5.07	50	5.05	22.8
4.55	60	4.51	9.6
4.21	80	4.21	62.9
3.97	50	3.96	18.1
3.89	40	3.88	23.3
3.63	50	3.63	29.8
3.52	60	3.52	18.2
3.47	80	3.46	41.4
3.37	40	3.36	17.0
3.35	20	–	–
3.28	20	3.27	18.9
3.12	50	3.11	34.6
3.02	20	–	–
2.947	80	2.946	50
2.917	50	2.912	31.8
2.888	60	–	–
2.776	40	2.774	12.4
2.701	80	2.70	35.2
2.631	20	–	–
2.606	40	2.607	24.3
2.526	40	2.526	11.2
2.416	20	–	–
2.396	20	2.395	15.8
2.33	20	2.33	12.3
2.1050	20	2.1055	10.5
1.98	30	1.98	17.5
1.9408	40	1.942	32.2

EDX analyses of crystals are consistent with the chemical composition of slavikite (see inset in Fig. 5a). Slavikite crystal morphologies seem to be characteristically defined by a combination of the {00.1} pinacoid and the {10.1} and {01.2} trigonal bipyramids. These three forms are the morphologically most important forms of slavikite crystals according to the Bravais-Friedel-Donnay-Harker (BFDH) method for calculating theoretical crystal morphologies (Bravais 1866; Friedel 1907; Donnay and Harker 1937) (Fig. 5b).

EPMA analyses were performed on ten slavikite crystals. In all of them only iron, magnesium and sulphur

appear above the detection limit of the apparatus used (~2 atomic %). Table 2 shows the ten analyses. Calculated Fe:Mg, S:Mg, and S:Fe ratios from average values of the ten analysis are 2.45, 3.79 and 1.55, respectively. These ratios are comparable to those calculated from averaged data for slavikites from Wieściszowice (Poland) by Parafiniuk et al. (2010), which are: Fe:Mg = 2.84, S:Mg = 3.83 and S:Fe = 1.34.

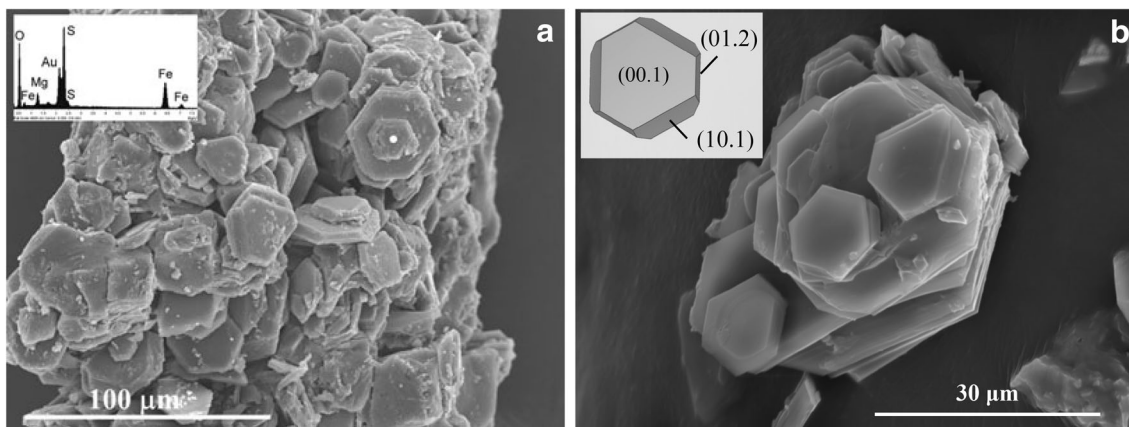
It is interesting to note that we have not found sodium in any of our ten slavikite analyses (or it is below the detection limit). This result agrees with Gordon (1941), Coskren and Lauf (2000) and Parafiniuk et al. (2010), whose analyses also discarded the presence of sodium in the slavikite formula.

We have obtained further crystallochemical information on slavikite from thermogravimetric analysis of washed samples. X-ray diffractograms have shown that washed samples are highly enriched in slavikite (>97 wt% of the crystalline material in the samples), containing much smaller amounts of tschermigite than those found in the original samples (see Fig S2 in the supplementary information). Figure 6 shows typical thermogravimetric (TG) and differential thermogravimetric (DTG) curves of a washed slavikite sample from Pastora Mine.

TG and DTG curves shown in Fig. 6 are very similar to those previously reported for slavikite (Parafiniuk 1991; Smykatz-Kloss and Warne 1991; Parafiniuk et al. 2010). However, we have found that the weight loss of our sample occurs more continuously with temperature than in the TG and DTG curves reported to date. This can be partially due to the fact that samples of slavikite analyzed by different authors are not pure slavikite but they contain different amounts of impurities.

The dehydration of slavikite from Pastora Mine starts at room temperature in dry air and it occurs up to 270 °C with the most intense peak in the DTG at around 126 °C, in good agreement with observations by Parafiniuk (1991). The corresponding weight loss in this temperature range is 9.71 wt%. This percentage is far below the typical values previously reported (Parafiniuk 1991; Smykatz-Kloss and Warne 1991; Parafiniuk et al. 2010). This disagreement can be attributed to our previous overnight drying pre-treatment, which completely removes ambient humidity.

Above 270 °C the dehydroxylation of slavikite starts. Such a dehydroxylation is a two-stage process consistent with the presence of the iron and magnesium cations (Fe<sup>3+</sup> and Mg<sup>2+</sup>) in the slavikite structure (Smykatz-Kloss and Warne 1991). However, these two dehydroxylation steps appear overlapped generating a broad peak in the DTG at around 420 °C. In the range from 350 to 480 °C, dehydroxylation results in a weight loss of 5.63 wt%, in good agreement with previous studies (Smykatz-Kloss and Warne 1991; Parafiniuk et al. 2010).



**Fig. 5** SEM images of aggregates of slavikite crystals from Pastora Mine (site 1). **a** The inset shows a EDX spectrum at the position marked with a white point (see explanation in the main text), **b** group of slavikite crystals showing their typical tabular habit. In the upper

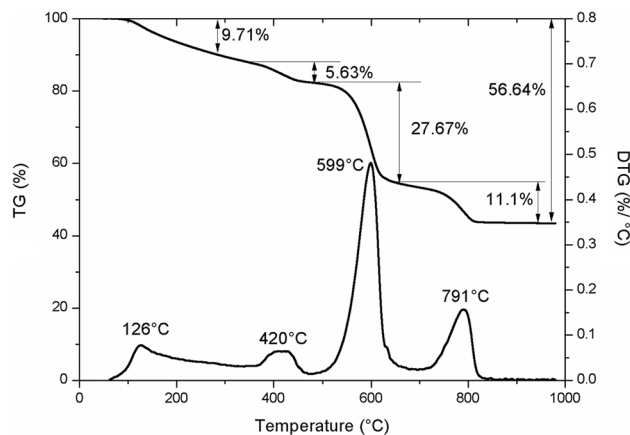
left corner of the figure a model of a slavikite crystal is depicted. This model has been constructed by slightly modifying the theoretical BFDH morphology of slavikite using VESTA software (Momma and Izummi 2011)

**Table 2** EPMA of slavikite from Pastora Mine (site 1)

Element <sup>a</sup>	S	Fe	Mg
Spec-1	25.63	16.50	6.63
Spec-2	25.83	16.26	6.26
Spec-3	25.24	16.55	7.73
Spec-4	25.71	15.87	7.01
Spec-5	25.44	16.87	6.82
Spec-6	25.79	16.48	6.15
Spec-7	25.52	16.95	6.51
Spec-8	25.52	17.05	6.39
Spec-9	25.64	16.16	6.93
Spec-10	25.51	16.45	7.03
Average	25.58	16.51	6.74
STDEV	0.175	0.368	0.465
Fe:Mg		2.45	
S:Mg	3.79		
S:Fe	1.55		

<sup>a</sup> Analyses in atomic %

From 480 to 650 °C, the most intense endothermic peak in the DTG curve is observed. This peak corresponds to the thermal dissociation of  $\text{Fe}_2(\text{SO}_4)_3$  (Coombes and Munir 1989; Siriwardane et al. 1999; Hammerschmidt 2009). Such a thermal dissociation is accompanied by a weight loss of 27.67 wt%, a value slightly larger than those reported by Parafiniuk (1991) and Parafiniuk et al. (2010). The second most intense endothermic peak at higher temperatures is related to the thermal dissociation of  $\text{Mg}(\text{SO}_4)$ . Usually,  $\text{Mg}(\text{SO}_4)$  decomposes in air at temperatures ranging from 880 to 1100 °C. However, such a decomposition is strongly affected by the atmosphere. Therefore, when reducing agents (i.e. sulfur) are present, thermal dissociation of  $\text{Mg}(\text{SO}_4)$  starts at lower temperatures



**Fig. 6** TG and DTG of slavikite sample from Pastora Mine. Measured weight losses are indicated. Sample weight: 2 mg, heating rate: 10 °C/min. Atmosphere: nitrogen

(Scheidema and Taskinen 2011). In the DTG shown in Fig. 6, the peak related to the decomposition of  $\text{Mg}(\text{SO}_4)$  occurs at 791 °C with an associated weight loss of 11.1 wt%, again in good agreement with previous studies (Parafiniuk 1991; Smykatz-Kloss and Warne 1991; Parafiniuk et al. 2010).

Interestingly, during the thermal decomposition of slavikite from Pastora Mine up to 1000 °C, the total weight loss is 56.64 wt%, a value slightly lower than those previously reported, i.e. 60 wt% (Smykatz-Kloss and Warne 1991), and about 66 wt% (Parafiniuk 1991). This disagreement can be related to differences in the initial loss of water molecules as a consequence of variations in the drying pre-treatment (see Fig S3 in the Supplementary Information).

From EPMA and the information provided by the TG and DTG curves, we have calculated a new chemical formula for slavikite from Pastora Mine. From the Fe:Mg,

S:Mg and S:Fe ratios listed in Table 2, we have first calculated two possible approximate stoichiometries:  $\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}$  and  $\text{Mg}_5\text{Fe}_{12}(\text{SO}_4)_{19}$ . However, the second formula resulted inconsistent with the subsequent assignment of  $\text{H}_2\text{O}$  and  $\text{OH}^-$  groups from TG and DTG weight losses and, therefore, it was discarded. Taking into account that the molar weight of  $\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}$  is 2096.50 g/mol, calculations from the loss of weight attributed to water molecules (9.71 wt%) and hydroxyl groups (5.63 wt%) allow us to propose the following formula for slavikite:  $\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}(\text{OH})_8 \cdot 13(\text{H}_2\text{O})$ . Even though this formula is similar to the slavikite formula recently proposed by Parafiniuk et al. (2010),  $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$ , and the Mg:Fe ratios are comparable, some differences become apparent. First, our formula has a slightly higher S:Mg and S:Fe ratios than those reported by Parafiniuk et al. (2010). Such differences can be partially due to the chemical analysis technique and the subsequent data treatment performed by Parafiniuk et al. (2010). These authors, conducted bulk ICP-OES chemical analysis of samples initially containing admixtures of slavikite, gypsum and pickeringite. The subsequent correction of the chemical analysis by extracting both sulfates, gypsum and pickeringite, could easily result in an underestimation of the S in the slavikite formula. In contrast, our EPMA were performed on single and relatively large slavikite crystals ( $\sim 30 \mu\text{m}$ ) and, consequently,

significant contamination from other minor mineral phases present in the samples can be excluded.

The second main difference between the two slavikite formulas is the  $\text{OH}^-$  and  $\text{H}_2\text{O}$  content. Since dehydration of slavikite starts at room temperature, the determination of the number of  $\text{OH}^-$  groups and  $\text{H}_2\text{O}$  molecules in slavikite formula is difficult. To minimise the overestimation of water content in slavikite formula due to the presence of non-structural water molecules, our samples were pre-treated by keeping them at  $80^\circ\text{C}$  during several hours before conducting TG analysis. Thermograms of these samples show a clear plateau, which approximately extends up to the first  $100^\circ\text{C}$  of heating. This indicates that the continuous loss of water at room temperature was avoided by our pre-treatment of the samples. Then, the loss of weight starts. Differently, the loss of weight of non-pre-heated samples occurred even before starting the temperature ramp. In such a case, the determination of water content of slavikite is unreliable. In the study by Parafiniuk et al. (2010), the loss of water was measured from a temperature as low as  $20^\circ\text{C}$  and apparently without any pre-treatment. This could be the reason why the numbers of  $\text{OH}^-$  and  $\text{H}_2\text{O}$  molecules in the slavikite formula proposed by these researchers are much larger than those reported in the present and previous studies (e.g. Gordon 1941; Süss 1975). Finally, unlike the slavikite formula by Parafiniuk et al. (2010), our formula does not require the ad hoc

**Table 3** Chemical analyses of AMD of Pastora Mine compared to those of Tinto, Odiel and Pantones river

	Pastora Mine <sup>a</sup> (Aliseda)	Tinto River <sup>b</sup> (Niebla)	Odiel River <sup>b</sup> (Gibraleón)	Pantones River <sup>c</sup> (Arroyo de la Luz)
Temperature ( $^\circ\text{C}$ )	15	19	18	–
pH	3.5	2.8	3.6	8.9
Aluminum	4	77	37	<0.2
Arsenic	0.007	0.202	0.013	<0.02
Sulphur	66	224	712	<10
Calcium	4.8	73	50	<5.0
Cobalt	0.048	0.558	288	<0.01
Copper	0.011	19	5.4	<0.01
Iron	6	157	7.5	<0.05
Lithium	0.032	0.137	79	–
Magnesium	9.6	76	72	<5.0
Manganese	1.8	7.8	8.5	<0.01
Nickel	0.039	0.175	152	<2.0
Potassium	7.0	3.9	2.8	<2.5
Sodium	12	38	21	8.5
Silicon	5.2	15	14	–
Zinc	0.063	24	13	<0.02

Concentrations in mg/l

<sup>a</sup> Crespo (2015)

<sup>b</sup> Olías et al. (2010)

<sup>c</sup> Data (2014.05.28) from Tajo Hydrographic Confederation

inclusion of  $\text{H}_3\text{O}^+$  clusters to balance the excess of negative charge because its stoichiometry ensures electrical neutrality.

## 5.2 Origin and formation conditions of slavikite from Pastora Mine

The formation of slavikite from Pastora Mine can be interpreted as the result of the alteration and weathering of pyrite-bearing Paleozoic slates by the action of meteoric waters (e.g. Joeckel et al. 2007; Parafiniuk et al. 2010). The acid weathering of these pyrite-bearing slates is the main source of AMD waters in Pastora Mine and surroundings.

Although sulphur and metal concentrations are far above typical values of local drinking waters (see Pantones River in Table 3), they are much lower than those measured in Tinto and Odiel rivers (Table 3). Nevertheless, Pastora Mine AMD waters are able to promote an intense chemical weathering of slates and associated gossan minerals. As a consequence, a large variety of secondary sulfates are produced. Since most of these sulfates are hydrated and highly soluble in water, they partially or completely dissolve during wet seasons (autumn, winter and spring) and re-precipitate in the summer. Only in sheltered places of the pits and in relatively dry places in mine galleries these secondary sulfates remain relatively unaltered throughout the year. Remarkably, slavikite is relatively abundant in Pastora Mine and in some places this mineral is even the major secondary sulfate (i.e. in site 1 analyzed here).

Following the recent ideas by Hazen et al. (2015), slavikite can be considered as a rare mineral with a quite limited “habitability zone”, i.e., it only appears in certain mineralogical niches where other “competing” salts (e.g. tschermigite) are total or partially removed after a number of wet and dry cycles. Therefore, taking into account the moderate solubility of slavikite (Parafiniuk 1991; Coskren and Lauf 2000), the enrichment and distribution of slavikite (and other minerals) within Pastora Mine is presumably determined by the interplay between an internal factor (solubility) and an external factor (local climatic conditions). This suggests that the concepts of mineralogical habitability and habitable zones proposed by Hazen et al. (2015) are not only applicable to a planetary level but also to microenvironments such as those found in gossans and abandoned mines.

## 6 Conclusions

In this paper we have presented a characterization of the mineral slavikite found in Pastora Mine, Aliseda, Cáceres (Spain), the most western European locality reported to date. In Pastora Mine, slavikite appears as aggregates of

micrometric tabular crystals associated with variable amounts of other secondary sulfate minerals (e.g. alunogen, fibroferrite and tschermigite). Chemical and thermogravimetric analyses of samples from Pastora Mine allowed us to calculate the following slavikite formula:  $\text{Mg}_4\text{Fe}_{10}(\text{SO}_4)_{15}(\text{OH})_8 \cdot 13(\text{H}_2\text{O})$ . The finding of slavikite in Pastora Mine further confirms the origin of slavikite as the result of complex weathering and crystallization processes from pre-existent pyrite-bearing rocks. Future accurate determinations of the solubilities of the mineral phases found in Pastora Mine, together with a detailed study of the effect of wet-dry cycles on sulfate assemblages, will contribute to a better understanding of the mineralogical evolution of similar old mining areas where the formation of rare or even new mineral species is frequent.

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