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Mapping Fe-bearing hydrated sulphate minerals with short wave infrared (SWIR) spectral analysis at San Miguel mine environment, Iberian Pyrite Belt (SW Spain)

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Abstract

Short-wave infrared reflectance (SWIR) spectra obtained from a Portable Infrared Mineral Analyser (PIMA) were applied to map acidic mine soils at San Miguel massive sulphide deposit, Iberian Pyrite Belt, Spain. Field spectral measurements and laboratory analysis were performed on samples from 58 stations from two very polluted grounds. These analyses identified secondary and tertiary Fe-rich sulphate–hydrate minerals associated with the alteration of sulphide-bearing mine wastes and other associated infrared active minerals. The spectral absorption features for the pure salt types found in these areas allowed the preparation of a specific reference library for automatic mineral identification.

Using this approach three separate zones around the sources of contamination have been discriminated: a "proximal" zone dominated by rozenite+hexahydrite, a "transitional" zone dominated by copiapite+coquimbite and a "distal" zone of hydro-nium-jarosite. An additional zone of "gypsum" was also recognized locally at the areas, where, last decade the neutralization of the acid soils with limestones was attempted.

In addition to discriminating distinct mineralogical zones quantitative spectral data allowed contoured mineral maps to be produced that are comparable with the estimated mineralogical data obtained from conventional methods, such as XRD and field observations. These maps demonstrate that sulphate minerals were firstly formed by oxidation of the pyrite-rich ores followed by dissolution and precipitation involving a combination of oxidation, dehydration, and neutralization reactions.

The study shows the potential of SWIR spectral analysis to identify and understand the distribution of efflorescent salts and other products of pyrite decomposition and provides a methodology to assist the research and monitoring of sources of environmental contamination.

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Keywords: Short-wave infrared spectroscopy; SWIR; Portable infrared mineral analyser; PIMA; Mapping acidic mine waste; Iron hydrated sulphates; Iberian Pyrite Belt

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1. Introduction

The occurrence of efflorescent sulphate minerals from the weathered sulphide-rich mining environments at the Iberian Pyrite Belt are widely reported (e.g., García García, 1996; Hudson-Edwards et al., 1999; Carrasco, 2000; Buckby et al., 2003) as well as the occurrences of soluble iron salts (Jambor et al., 2000 and references therein). However, little is known about the distribution of minerals around the sources of acid solutions. An understanding of the different sulphates and their distribution however is critical for acid mine drainage control because of the ability of different sulphates to carry harmful trace elements and produce different amounts of acid after dissolution.

In general, source sites of acid rock drainage at past and present mining sites in the massive sulphide deposits of the Iberian Pyrite Belt are easy to identify. However, in order to understand the reason and mechanisms of mineral transformation and to assess



Fig. 1. Sketch map to show the position of the San Miguel mine and the location of the two selected areas ("Open Pit" and "Charcaseca" sites) to develop the SWIR mapping method. The old waste dumps W1 to W7 are partially revegetated whereas W8 and W9 are pyrite-rich wastes.

the degree of acid production of a sulphide-bearing mine waste or sulphated grounds it is necessary to (1) investigate at origin the nature and proportions of all of the salts in the soils; (2) investigate the oxidation progress of hypogene sulphide minerals by reaction with atmospheric oxygen and/or ferric iron-rich solutions; (3) relate the production and abundance of soluble and less soluble ferrous- and ferric-sulphate hydrates in relation to the proximity of the mine waste materials; (4) examine the hydrolysis of ferric iron and subsequent reprecipitation of all the secondary oxydroxides and/or hydroxisulphates; and finally (5) describe the distribution of all the secondary and tertiary minerals formed from removed products after the earlier weathering stages.

Different methods have been used previously to identify the distribution of minerals in areas at the regional and local scale. Particularly useful has been the application of new infrared spectrometers such as airborne spectrometers which combine visible and infrared imaging spectrometry (Baugh et al., 1998; Swayze et al., 2000). Although these spectrometers allow the detection of contaminated sites, they do not provide sufficient information about the mineralogy of the observed sites. At a more detailed scale, field based, short wave infrared (SWIR) spectrometers have been used successfully in exploration of numerous hydrothermal deposits (Thompson et al., 1999; Dennis et al., 1999; Herrmann et al., 2001; Sun et al., 2001).

This study describes a method to characterize, quantify, and map the iron–sulphate salts produced by pyrite oxidation at the abandoned San Miguel mine (Huelva province, Spain), a volcanic massive sulphide deposit from the Iberian Pyrite Belt (Spain). The mine was chosen because it contains several sites with abundant efflorescences, altered waste materials and removed soils. Two sites were studied (Fig. 1): (1) the Open pit ('proximal'), which is full of waste materials and spoils from dredging in close proximity to the sulphide outcrops, and (2) a site "distal" to the ores (referred to as the "Charcaseca"), which is characterised by a shallow and flat excavation on top of shales, that was used to store the pyrite ore prior to roasting.

The study uses SWIR spectral analysis of rock samples and soils, using a Portable Infrared Mineral Analyzer (PIMA) spectrometer. The method is based on detecting the presence of molecular water, OH, and other hydroxyl radicals in the mineral structure, which produce diagnostic vibrational absorptions in the mineral spectra. The technique allows rapid identification of supergene minerals (efflorescences and crusts on the mining soils, associated with prolonged weathering) and delineation of zones exhibiting compositional changes. The PIMA was applied at a local scale to study the sources and characteristics of acid contamination by developing detailed mineralogical information maps of the abandoned mine waste dump and soils, in particular where the first signs of pyrite alteration can be noted and where salt formation and subsequent dissolution develop.

The main objectives of this study were to: (1) document the mineralogies of surface pyrite oxidation and their spectral characteristics; (2) investigate the metal–sulphate paragenesis in the context of a continuous dissolution–precipitation process with time; (3) investigate the possibility of developing a spectral screening method to map the Fe-bearing soluble salts, produced during continuous oxidation of massive pyrite-rich rocks, and (4) develop a framework for both better evaluating acid contamination in sulphide-rich areas and designing remediation programs.

2. Mine geology and study areas

The San Miguel mine started in 1851, although there is evidence of Roman mining and other excavations in the area. From 1859 to 1960 the deposit was exploited for copper, primarily by underground works and later by open pit, after the removal of the thick gossan cover. During that time 1.29 Mt of pyritic ore with an average grade of around 2-3% Cu and 46% S was produced (Pinedo Vara, 1963). The richest parts were located just below the gossan, forming a secondary copper enrichment zone, which has now nearly completely disappeared. The primary ore mainly consists of pyrite with fine inclusions of subordinate chalcopyrite and minor amounts of sphalerite. Galena, tetrahedrite, pvrrhotite, bismuthinite and bornite only appear as trace minerals (García de Miguel, 1990). The major gangue minerals of the deposit are quartz, chlorite, muscovite, plagioclase, and rutile. The mineralization occurs as several stacked massive lenses (of up to 40 m thickness),

that extend about 200 m along strike and dipping around 70°S to subvertical. Sulphides are located between intensely chloritized felsic porphyritic rocks to the north, and volcanoclastic rocks and purple shales to the south. Features of the footwall massive and stockwork ores reveal a strong chloritization and minor shear zones with associated remobilization of the sulphides (Tornos et al., 1999). In general, the San Miguel deposit exhibits similar mineralogical, textural, and geological characteristics to other volcanic-hosted massive sulphide deposits from the northern part of the Iberian Pyrite Belt (Sánchez-España et al., 2000).

Above the massive sulphide mineralization and the stockwork a zone of gossan has formed as a result of the intense weathering, oxidation, and leaching of ores and volcanic rocks that extends down from the surface to a maximum depth of 12 m. Goethite dominates the gossan and is accompanied by quartz, hematite, jarosite, barite, and some clay minerals (kaolinite, illite, montmorillonite, chlorite). In addition secondary minerals, which are products of weathering and alteration of the primary sulphides and occur mainly as efflorescences, are observed on the ground and waste piles, and at the surface of the wall of the open pit.

Several million tonnes of mine-waste consisting of porphyritic volcanic, sedimentary, and epiclastic rocks mixed with coarse fragments of massive pyrite have been deposited at the surface close to the mining area (Fig. 1). In addition, the company Rio Tinto SAL has recently removed many tonnes of oxides from the gossan for assaying, with the aim of recovering gold.

2.1. Study areas: location and features of the waste dump sites mapped

Nine small, mine-waste piles (W1 to W9) were identified in the surroundings of the San Miguel mine (Fig. 1), which contribute different metals (Fe, Al, Mg, Zn, Cu, etc), sulphate, and acidity to the Escalada creek (tributary of the Odiel River), mainly as pulses during periods of rains. Seepage only occurs during rainy periods, demonstrating that the water table lies below the waste dumps. The spoils typically lie next to the Escalada creek, on top of the metamorphosed shales of the Culm Formation (Leistel et al., 1998) and soils that have been moderately developed over the waste dumps and mostly confined to the

upper terrace. Most of these mine-waste piles (W1 to W5) are very old and have been partly vegetated with indigenous scrubland and locally with eucalyptus, so the presence of secondary minerals as transient salts is virtually absent.

W9 was chosen as it represents a pile recently moved during the last attempt at gold recovery from the San Miguel gossan. W8 was selected as it was previously used by the Environmental Office of the Junta de Andalucia Government (between 1993-1996) to apply what turned out to be unsuccessful restoration techniques (Fig. 1). In addition these two areas of the recently removed impoundment, the Open pit and the Chacaseca sites (Figs. 1 and 2), were also chosen as they display abundant "secondary" minerals (as well as tertiary minerals), and have been selected to study the temporary formation of soluble and insoluble minerals. These "secondary" minerals have formed after deposition of the main sulphide association and have been categorized as either secondary, tertiary and quaternary (Jambor, 1994), depending on whether they formed either within the mine impoundment, crystallized by evaporation from pore waters, or, were formed lately by drying of the samples during storage, respectively.

Both areas are characterized by the presence of different waste products consisting of crushed pyrite from mine extraction, altered rock removed from its original location, blended and contaminated acid soils, and fragments of iron rich oxides from the gossan and on site, open-air, roasted sulphide products, locally referred to as "morrongos". The selected areas can be described as intensely mineimpacted soils, characterized by internal drainage (endorheic drain) and for most of the year numerous patchy zones very rich in efflorescence salts, thin coloured soils, and polygonized muds at the bottom of the ephemeral ponds. Typically the surface of these sites is usually very dry and only contains temporary pools of stagnant water in the open pit (red pools) after rainfall. Most of the ubiquitous salts have been formed during dry periods, after the evaporation of metal-rich solutions and have moved to the surface by capillary action. Typically the area has a temperate climate, with annual precipitation of 770-930 mm per year. When rain occurs, surface water (Escalada and Gitano creeks) forms a torrentlike network flowing to the Odiel river.

The abandoned "Open pit" (Fig. 2A and C), which is approximately 150 m long by 70 m wide by 60 m deep, has been partially filled with about 10,000 m³ of mine-waste rocks and ores. At the northern wall this quarry exhibits subvertical outcrops of pyritic stockwork and chloritized rocks. For sampling purposes the ground at the bottom of the pit has been arbitrarily divided into seven subareas (A to G) based on differences in colour, presence of pyrite, and proximity to the walls and central red pool (Fig. 2C).

The "Charcaseca" site (Fig. 2B and D) is located to the south of the open pit close to the main track for mine access, and consists of a roughly square depression (60×75 m and less 0.20 to 0.60 m depth) with a flat base, excavated in the shale rocks of the Culm formation. This levelled area was used to store the pyrite production prior to roasting the ore in open-air calcination called "teleras".

Typically both sites act as basins and collect water. The deeper parts of the sites often contain large (10-20 m wide) shallow pools. After the water has evaporated the sites are covered by a continuous layer of brown friable and irregularly cemented acid sulphate soil, composed of a mixture of clay and silt size products of weathered rocks including quartz, pyrite, and salts. These highly acidic soils are generally 2 to 10 cm thick, although they can extend up to 30 cm in the central part of the ephemeral pools (Figs. 2 and 3). The soils have similar characteristics to the harmful "cat clay" (Bigham and Nordstrom, 2000). In addition, field observation at the Charcaseca site noted that there are strongly indurated patches of *duricrust* at the surface containing fragments of waste and country rocks (gravel-size up to 3 cm), fine detrital grains of pyrite and quartz (sand- and silt-size), which are cemented by red-brownish materials (Fig. 2B and H).



Fig. 2. (A) View of the San Miguel "Open pit" showing the red pool at the centre, the wall front with the sulphide stockwork (pyritic stringer) covered by a thick gossan; and the ground of acid soils; (B) the Charcaseca mining site partially covered and surrounded by pyrite-rich wastes and sulphate-bearing spoiled soils formerly "restored" by the Regional Environmental Office; (C and D) Sketches from the above respective photographies showing field distribution of the different mine soil zones and an overview of the sampling stations. The bottom of the Open pit is full of waste dumps, whereas the Charcaseca is covered with efflorescences and patches of partially neutralized soils (ferricrusts). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



2.2. Field distribution of the secondary minerals

Field observations were initially carried out to define broad zoning patterns to establish the grid or station sampling. Both sites display fringes of variable colour from least weathered (unchanged pyrite) to fully weathered rocks and brown mine soils. Usually the colour degrades from white, yellowish-palebrown, through to dark-browns. The lighter colours usually occur immediately adjacent to the pyritic-rich rocks sources, or are restricted to walls and surfaces of pyritic stockwork and pyrite piles, where they occur coating the surfaces of the least altered ores, forming a fine-grained crust of dusty and crumbly efflorescences. Yellowish to pale-brown colours occur with the fully altered soils, and particularly dominate the open pit. These altered soils usually have a harder crust (1-5 mm thick) that is easy to crumble with your fingers. The dark brown coloured soils occur at a distance from the pyrite-bearing rocks, and typically dominate around the dry ponds.

Pyrite outcrops are usually coated by powdery efflorescences and dripstone of tertiary sulphates (Fig. 3). Brown silts and dry muds, that are restricted to shore and areas of ephemeral pools, form finely laminated thick layers with desiccated cracks (Fig. 3E and F). These pools usually store the contribution of surface runoff during rainfall. Shrinkage and polygonization occurs by the drying of the wet soils, producing contortion, and mud-crack polygons (with sides up to 30 cm long) with gentle concave surfaces with three to seven sides. Usually the shrinkage is accompanied by massive yellow efflorescences, which have been precipitated quickly during evaporation of the wet muds, and appear as extruded crystals through the cracks (Fig. 3E). Locally the soils are covered by patches of indurated surficial iron rich duricrust layers (Fig. 3H).

Generally a predominantly white fringe of soils occurs that is related to pyrite walls, or pyrite piles ("proximal zone"), followed by a continuous yellowish to pale brown coloured band of soils ("transition zone"), irregularly patched of green to yellowish efflorescences, commonly found in cracked soils and voids of degraded soils. Finally, the pale- to darkbrown zone and areas of crumbly muds and ferricrusts appears located away from the pyrite sources ("distal zone"). These last sediments when completely dried appear as polygonized brown-chocolate muds. This pattern represents the evolution of the alteration, which grades from adjacent areas to the pyrite rich rocks with predominance of ferrous salts, to areas where iron oxidation predominate.

3. Sampling and analytical procedures

3.1. Sampling

The two selected sites were evaluated, mapped, and sampled in detail (in June 2003). Representative samples were selected for field based SWIR spectral analysis and corresponding samples were taken and analysed by binocular microscopy, X-ray diffraction and Scanning Electron Microscopy (SEM)/EDS. The samples from the selected stations were collected at the surface of soils and at depths of 2–10 cm, taking about 50–150 g of dry and crumbly crusts, stored in polypropylene bags and flasks in order to avoid loss of water.

At the open pit site the samples were taken at spacings of 5 to 10 m in order to get the maximum variability of materials, mainly on the basis of colour and texture variation and proximity to the pyrite outcrops. Charcaseca soils were taken on a rectangular surface of 60 by 70 m, taking apart the superficial and inner parts (approximately 10 mm deep) of the thick

Fig. 3. Macroscopic features of efflorescences. A: White powderish efflorescences (rozenite-hexahydrite) in a cavity of the Open pit wall. B: Flowstone-like coatings of hexahydrite with rozenite and halotrichite partially covering the San Miguel pyrite stockwork (Open pit). C: Whitish gray szomolnokite and halotrichite grading into intense yellow copiapite-coquimbite, near fallen gossan blocks (Open pit). D: greenish copiapite mixed with yellow coquimbite in the Open pit dumps; gray dust at top left of the picture is szomolnokite with pyrite remains. E: Polygonized muds made of warped layers of hydronium-jarosite (with very fine sized quartz and muscovite) and green-yellow copiapite extruding through the mud cracks (Charcaseca ephemeral dried ponds). F: Shore of partially dried red pool from the Open pit showing the hydronium-jarosite, butlerite and ferrihydrite polygonized muds (red colour at upper right corner is the residual iron oversaturated waters). G: Hydronium-jarosite and ferrihydrite waxy muds exhibiting the typical "oily" shine. H: Superficial duricrust patches in Charcaseca over a pyrite-rich ground, with hydronium-jarosite, gypsum and calcite (brown coloured crust); note the presence of completely replaced limestone gravels.

layers of evaporative crusts. The overall sampling plan included 29 sampling sites at Charcaseca following a grid of approximately 12×15 m, while sampling at the Open pit was organized to collect representative samples. In addition, a number of relatively pure Fe-bearing salts were obtained from similar altered mine environments (such as from San Telmo mine, Riotinto mine, and others) to complete the reference spectral libraries and to test the effectiveness of the proposed mapping method.

3.2. Analytical methods

3.2.1. Mineralogical characterization

All the collected samples were analysed as bulk sample by X-ray diffraction (XRD) using a Philips PW1710 instrument with Cu–K α radiation (λ = 1.5406 Å) and a graphite monochromator, operating at the following conditions: 40 KV, beam current of 20 mA, in step-scan of 0.01° 2 Θ steps with 1s per step. Samples were gently grounded to a fine particle size to obtain powders suitable for XRD analysis at the Mineralogy Laboratory, Basque Country University. Data were interpreted using the Philips X'Pert High Score software. A rough estimation of the relative abundances of mineral phases was made by comparing the intensities of the main peaks. The presence of ferrihydrite and/or schwertmannite (poorly crystalline ferric oxyhydroxides and hydroxysulphates) was checked out by the use of the differential X-ray diffraction method (DXRD) following the method described by Schulze (1981). Clayey samples were processed differently after the separation by centrifugation of the $<2 \mu m$ fraction to prepare the oriented aggregates on glass slides. In addition, several polished thin sections were prepared from the ferricrete layers and most indurated soil surfaces to determine the mineralogy and texture of the crusts and presence of relicts of previously removed phases.

Scanning electron microscope analysis (SEM) of the representative and principal salts was performed at the Analytical Service Laboratories of the Basque Country University, using a Cameca-BMX and a Jeol JSM 6400 instruments with SEM-EDS systems operating at an accelerating voltage of 15 KV. Metal concentration of these samples is being performed (by X-ray fluorescence and ICP-AES coupled with DXRD) and will be the aim of a separate study.

3.2.2. Spectral analysis

Efflorescence salts were the focus of this study, as they were the principal component of the soils. Their variable abundance of molecular water and variations of cation–O–H vibrations make this group of minerals particularly active in the SWIR. At each grid point from the selected sites, small pieces (2–3 cm diameter) of the efflorescence crusts or soils were measured in situ. All these SWIR analyses were done in a dry state without sample preparation. As a general rule samples were analysed either on flat surfaces, sometimes crushed or flattened with fingers, and or inside a Petri dish when loosely consolidated or crumbly samples split up. All wet samples were collected in plastic flasks and measured in the laboratory after air drying.

All the spectra were collected using a PIMA SP instrument (Integrated Spectronics, Inc) that measures reflectance in the short wavelength infrared (SWIR) range of 1300 to 2500 nm of the electromagnetic spectrum, with a spectral resolution of 7-10 nm and spectral sampling interval of 2 nm. This spectral range is particularly sensitive for minerals that contain certain molecules and radicals, including H₂O, OH, NH₃, CO₃, SO₄, and cation-OH bonds such as Fe-OH, Al-OH, Mg-OH (Pontual et al., 1997; Thompson et al., 1999), which produce diagnostic absorption features at certain wavelengths in the SWIR spectra (Fig. 4). A description and explanation of the vibrational process in minerals and their signatures in the SWIR region was given by Hunt and Ashley (1979). The features of the spectra, mainly the position, intensity, and widths of the absorption features and the hull (background) shape, are a function of the composition, crystallinity and abundance of minerals in the analysed material (Pontual et al., 1997; Thompson et al., 1999; Crowley et al., 2003a). To ensure the spectra were interpreted correctly spectral interpretations were integrated with field observations (colour, texture, homogeneity, presence of rock fragments), petrography, X-ray diffraction and microprobe analysis.

During the field measurements, field mineral descriptions of the samples, such as colour, texture, homogeneity, presence of rock fragments, were also collected, which can be important in the spectral interpretation as these variables can affect the spectral reflectance of samples (Integrated Spectronics, 1999b; Thompson et al., 1999).



Fig. 4. Stack plot with selected examples (hull quotient) of spectra characteristic of some individual minerals and water found in the San Miguel soils. SWIR spectra show the main wavelength regions (vertical bands) of diagnostic absorption features produced by molecules from the minerals in the target samples. Changes in the reflectance are the result of bending and stretching of principal molecular bonds (OH, H_2O , Al–OH, Mg–OH, Fe–OH, SO_4 , CO_3) found as major components in phyllosilicates, sulphates or carbonates.

The method used was to produce sets of individual spectra that were interpreted using a good spectral library. These spectra were then used for fast identification and estimation of the relative proportion of unknown minerals in each sample, producing an average composition for each sampled station. Finally, the mapping procedure consists in displaying the relative mineral abundances by a system of contouring visualization. These sorts of maps have been performed with the Terrain software (Earthwork Corporation Pty Ltd, 1996).

3.2.3. Processing technique for spectra analysis

All the collected spectra were processed with the PimaView v3.1 software (Integrated Spectronics,

1999a), using the options: auto-scale, normalizing and smoothing the reflectance spectra to enhance the absorption features and reduce the noise in the spectra. As most of the analysed salts have broad spectral absorption and few diagnostic absorption features, to minimize the sources of error all the analyses were made of hull quotient corrected spectra (Integrated Spectronics, 1999a,b; Yang et al., 2000), which allowed the study of the asymmetry, depth, width, and wavelengths of the absorptions as well as enhanced small differences between the spectra. Some of the minerals in the analyzed soils were automatically identified with the PimaView software and its attached reference library, but most of the salts of interest were not identified because their Table 1

Minerals identified by SWIR (quantitative estimate) associated with the sulphide-bearing mine wastes at San Miguel mine, Iberian Pyrite Belt

Station	Zone	n	mel	roz	SZO	hex	cop	coq	h–jar	pick	fer*	gyp	ms	chl	kao
A: "Open pit" site															
A1	prox	20	5	47		35	10			3					
A2	inter	15		10	3		70	10	7						
A3	inter	15		5		5	75	10	5						
A4	inter	20		2	8	2	23	40	5	7	10		3		
B1	prox	13	7	60		12	6		5	10					
B2	prox	17	15	55		3	10	17							
B3	inter	5		3			50	40	5				2		
C1	inter	19	0	10		5	45	15	5	5	10		5		
C2	inter	18			5		44	43	5		3				
C3	distal	24	2	2	0		41	2	25	28					
D1	distal	21					15		55		25		5		
D2	distal	4					45		35				20		
D3	distal	17					20	5	12	50	8		5		
D4	distal	4						5	75	20					
D5	distal	10		4		4	15	15	18		20		17	7	
E1	inter	18				15	45	35			5				
E2	inter	11		2			45	53			-				
E3	inter	6		5			55	15	15		10				
E4	distal	7		-					30				20		50
E5	distal	7					20	10	60				10		•••
F1	distal	9							35		25		30	5	5
F2	distal	3							15		85		20	5	U
F3	distal	2							30		70				
G1	distal	9		2			20	18	25	20	, 0		15		
G2	inter	6		_			90		10						
G3	inter	12					60		15		20		5		
00		312					00		10		20		5		
B: "Chare	caseca" sit	е													
P101	distal	12		3			10	5	27		25	10	20		
P102	inter	27		3			71	16	3		2		5		
P103	inter	12		1			75	24							
P104	inter	21		2			63	10	10		10		5		
P105	distal	24		6			54	17	15		3		5		
P106	distal	23		1			25	9	25		25		15		
P201	inter	13			8		15	44	3		25		5		
P202	crust	25		5				6	15	4	45	25			
P203	crust	21		3		3	37	32	5		10	10			
P204	inter	13		5		5	50	16	10		7		7		
P205	inter	15		5		5	60	25	1		4				
P206	distal	20		2		2	32	16	16		22		10		
P302	crust	14		1		2	3	2	25		32	35			
P303	crust	11		12		10	10	12	10		18	28			
P304	inter	12		3			63	8	15		11				
P305	inter	8					65	10			20		5		
P306	inter	8					50	15			25	5	5		
P401	inter	4					100								
P402	inter	29					15		20		60		5		
P403	crust	11					8	5	15		70		2		
P404	crust	7		5					30		50		15		
P405	inter	6					70	30							
P406	inter	4					25	8	50		12		5		

Table 1 (continued)

Station	Zone	n	mel	roz	szo	hex	cop	coq	h–jar	pick	fer*	gyp	ms	chl	kao
B: "Cha	rcaseca" sit	te													
P501	inter	7					50	50							
P502	inter	10					5	2	40		50	2	1		
P503	crust	18		3			17	10	40			30			
P504	prox	5		27	16	30	20	7							
P505	prox	5		35	17	25	20				3				
P506	distal	10		4			20	27	30		9		10		
		395													

Zone abbreviations: prox=proximal, inter=transitional, distal=distal, crust=duricrust.

n: number of spectra in sampling station.

 $\label{eq:minimized} Mineral abbreviations: mel=melanterite, roz=rozenite, szo=szomolnokite, hex=hexahydrite, cop=copiapite, coq=coquimbite, h-jar=hydronium jarosite, pick=pickeringite, fer*=ferryhidrite+goethite+schwertmannite, gyp=gypsum, ms=muscovite, chl=chlorite, kao=kaolinite.$

empirical spectra are not included in the supplied PimaView database. Consequently, we have developed and verified a specific reference library (Multieflor.los; see explanation below and at the Statistical result section) containing 53 spectra from the most frequent salts and minerals present in the majority of the acid soils.

This reference library was prepared after the selection (by hand picking under binocular microscope) and conventional identification (mainly XRD and microprobe) of a complete collection of pure infrared active minerals, present in each colour fringe of the target soils. The laboratory SWIR spectra were carefully compared with the spectral reflectance properties of secondary Fe-oxide-hydroxide, and Fe-sulphate-hydrate minerals recently published by Crowley et al. (2003b), obtaining a high degree of agreement. The PimaView software, when configured with this custom library, outputs a semi-quantitative percentage of the identified minerals using an algorithm that correlates each raw spectrum with the spectra in the reference library, comparing mainly wavelength position, band absorptions, and taking into account the better score ranges of the correlation. Usually, most of the obtained scores have been around 0.5, which indicates an admissible fit for analysis of mixtures (a good fit for simple minerals is about 0.9 but for mixtures the score may be lower than 0.5). According to Thompson et al. (1999) the estimate accuracy of this method may be within a tolerance of 4%, but will vary depending on the minerals in the mixture and their relative abundances. In any case, these results might be considered as an estimation of the relative abundance of the minerals present in each sample.

3.2.4. Statistical treatment

Several multivariate statistical techniques were applied to evaluate the mineralogy of the mining impacted soils. Interpreted SWIR mineralogy ("virtual" mineralogy) and XRD data must be processed differently because the former contains mineral abundances as percentages of the recognized minerals, whereas XRD data supply mineral abundances represented as categorized variables (absent, minor, major abundances). SWIR "virtual" mineralogy was used as input to perform the Hierarchical Cluster analysis (the average linkage method; after SPSSX statistical package, Norusis, 1992) and to assign each soil sample to a zone and confirm the goodness of fit of the selected mineral associations. In addition, XRD mineralogy was evaluated with Principal non-linear Components Analysis by means of alternating least squares (PRINCALS, De Leeuw and Van Rijckevorsel, 1980), because this method allows simultaneous treatment of different types of variables, such as mixes of nominal, ordinal, and numerical variables. In this statistical technique, the dimensionality of the dataset is reduced after calculating a set of factors (dimensions) which are linear combinations of the original variables. A prior data recodification was needed for adequate treatment using the SPSSX statistical package (PRIN-CALS routine in Norusis, 1992), in order to obtain variables containing positive integer values. In this way, XRD data were categorized in 5 classes ranging

from 1 for absence to 5 for higher mineral proportions of the mineral in the soils.

4. Results and discussion

4.1. SWIR spectra analysis

SWIR spectral investigations of the duplicate samples used for the XRD study were carried out using PIMA. Approximately 707 spectral analyses were obtained from separate minerals and bulk samples: 312 from Open pit and 395 from Charcaseca sites. Table 1 lists the semi-quantitative percentage of the identified minerals at each sampled station. Generally, the bulk samples contain sulphate minerals in sufficient proportion to be easily identified by comparison with the reference spectra. However in some locations, the presence of minerals that are spectrally featureless in the SWIR (such as quartz and some silicates) and certain mixtures hinders the detection of spectrally diagnostic absorption and reduces the recognition of the spectral features of other minerals. To avoid this problem several representative "concentrates" of efflorescences. approximately five samples at each sampling station, were chosen to improve the quality of the spectra. For each station the spectra were subsequently averaged.

Spectral analysis identified a variety of salts including melanterite, rozenite, szomolnokite, halotrichite, pickeringite, copiapite, rhomboclase, as well as brown iron oxides (ochres like ferrihydrite and schwertmannite). The spectra of most of these minerals have recently been described by Crowley et al. (2003a). However, some of the hydrated sulphate reference spectra from minerals found in the San Miguel area have not been reported previously (e.g., hydronium jarosite, hexahydrite). Digital reference spectra from Crowley et al. (2003b) were compared with those obtained from the San Miguel samples, and compared favourably.

Selected SWIR spectra of ferrous and ferric hydroxisulphates, ferric oxyhydroxides, and related salts were chosen for the reference database (Multieflor.los), Fig. 5, and their wavelength features and sources are listed in Table 2. Most of the spectra show similar H₂O-related absorption features, with defined absorptions at about 1440 and 1950 nm, occasionally the characteristic split of the more intense water-related band is also observed (e.g., rozenite, hexahydrite), as is the typical broad absorption at about 2400 nm. It is noteworthy that the hexahydrite spectra (Fig. 5D) have definite resemblances with the features of the rozenite spectra, but their hulls are continuous and nearly horizontal in the first half of the spectra. This mineral shows the intense feature typical of the water split in a doublet at 1945 and 1978 nm, respectively (similar to that found for rozenite). For the hydronium-jarosite spectra we have identified the two typical deep and broad water-related absorption bands of the hydroxisulphates at 1462 and 1947 nm (this last absorption feature being virtually absent in jarosite and natrojarosite spectra) structure as well as the appearance of two weak diagnostic absorption features at 1845 and 2250 nm (typical of the jarosite group). The water absorption features prove the abundance of hydronium in this mineral. In addition, other features were used in the interpretation of the szomolnokite such as the complete disappearance of the 1448 nm band and the appearance of several weak features in this wide region (at 1339, 1448, and 1518 nm).

For several subordinate hydrated sulphates found at the San Miguel environment (e.g., rhomboclase (HFe'''(SO₄)₂ · 4H₂O) and roemerite (also römerite or romerite) Fe'' Fe'''₂(SO₄)₄ · 14H₂O) we have no spectra because of their relative scarcity at the studied soils and the impossibility of adequately separating them. Consequently, these minerals were not included in the reference library. In any case, the raw spectra are relatively simple being dominated by the main waterrelated absorption bands at about 1940 nm (2002 nm for the rhomboclase) and 1450 nm, and are easily confused with other hydrated sulphates.

Fig. 5. Characteristic SWIR absorption spectra of the main iron-bearing sulphate and related minerals found at San Miguel grounds. Small triangles at all the graphs indicate the wavelength position of the observed absorption bands prior to continuum removal. The plots overlay several spectrum to illustrate the observed reflectance variation and the changes at the feature absorption positions. Reflectance spectra of (A) melanterite, (B) rozenite, (C) szomolnokite, (D) hexahydrite, (E) copiapite, (F) coquimbite, (G) hydronium–jarosite, and (H) pickeringite. General behaviour changes of the spectra could be explained by the continuous trend of dehydration and mixtures (see text for explanation).



,	*			-							
Formula	Shoulder	$_{\rm OH}^{\rm H_2O+}$	Satellite shoulder	Broad shoulder	Broad absorption	Jarosite band	H ₂ O	H ₂ O-split	Shift	FeOH band?	End band
FeSO ₄ · 7H ₂ O		1476		1600			1960				2400
$FeSO_4 \cdot 4H_2O$		1448		1600	1720		1951	1980			2403
$FeSO_4 \cdot H_2O$		1448	1518		1728			1983	2090		2404
$MgSO_4 \cdot 6H_2O$		1442	1585				1945	1978		2172	2427
Fe‴Fe‴4(SO ₄) ₆ (OH) ₂₂ · 20H ₂ O	1335	1451	1487		1786		1940				2410
Fe'''2(SO ₄) ₃ · 9H ₂ O		1446			1729		1960	1984	2080		2410
[H ₃ O]Fe ₃ + 3[SO4] ₂ [OH] ₆		1462				1845	1947		2205	2250	2410
	Formula $FeSO_4 \cdot 7H_2O$ $FeSO_4 \cdot 4H_2O$ $FeSO_4 \cdot 4H_2O$ $MgSO_4 \cdot 6H_2O$ $Fe'''Fe'''4(SO_4)_6(OH)_{22} \cdot 20H_2O$ $Fe''''2(SO_4)_3 \cdot 9H_2O$ $[H_3O]Fe_3+$ $3[SO4]_2[OH]_6$	Formula Shoulder $FeSO_4 \cdot 7H_2O$ $FeSO_4 \cdot 4H_2O$ $FeSO_4 \cdot 4H_2O$ $FeSO_4 \cdot H_2O$ $MgSO_4 \cdot 6H_2O$ $Fe'''Fe'''4(SO_4)_6(OH)_{22} \cdot 1335$ $20H_2O$ $Fe'''2(SO_4)_3 \cdot 9H_2O$ $Fe'''2(SO_4)_3 \cdot 9H_2O$ $[H_3O]Fe_3 + 3[SO4]_2[OH]_6$	$\begin{array}{c ccccc} Formula & Shoulder & H_2O+\\ & OH \\ \hline FeSO_4 \cdot 7H_2O & 1476 \\ FeSO_4 \cdot 4H_2O & 1448 \\ FeSO_4 \cdot 4H_2O & 1448 \\ MgSO_4 \cdot 6H_2O & 1442 \\ Fe'''Fe'''4(SO_4)_6(OH)_{22} \cdot 1335 & 1451 \\ 20H_2O & \\ Fe'''2(SO_4)_3 \cdot 9H_2O & 1446 \\ [H_3O]Fe_3+ & 1462 \\ 3[SO4]_2[OH]_6 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 2 Spectral band positions (in µm) of the main sulphates found at San Miguel area

Bold=main; plain=important; italic=minor.

In summary, during the SWIR analysis the problems with mineral discrimination have been solved in a number of ways. Specifically, the study shows that confident identification and discrimination of the SWIR spectra of hydrated sulphates requires that 1.) samples are always equally dry, 2.) that good separates are used to avoid very complex mixtures, 3.) high integration values are set for the PIMA during measurement to improve the signal to noise of the spectra, and, finally, 4.) the spectra are analysed using algorithms that allow feature extraction, mineral identification, band correlation, and wavelength correlation (Berman et al., 1999; Merry et al., 1999; Integrated Spectronics, 1999a,b).

Significantly, although automatic spectral interpretation provides adequate identification and acceptable quantification when researching terrains with hydrothermal alteration (Pontual et al., 1997) these techniques become more imprecise dealing with ferrous and ferric hydrated sulphates as these minerals are spectrally similar and contain variable proportions of water. In these cases, confident automated identification might not be guaranteed. In this study, for example, automated identification gave wrong results for mixtures of efflorescences, and it was necessary to carry out manual interpretation based on the examination and comparison (loading and plotting spectra of different mixtures) with a wide collection of well known standard spectra.

4.1.1. SWIR mineral distribution

The calculated mineral percentages (Table 1), which are considered to be semiquantitative, have

been grouped according the following class intervals: not detected or trace mineral (<10%), minor (10– 40%), and major (>40%). The tables have been organized in columns of mineral groups taking into account the general trend of observed colour fringes in the field, iron oxidation, progressive dehydration and neutralization of the solid precipitates, and presence of detrital mineral. This procedure facilitates the addition of percentages from prevailing minerals in each zone, minimizing the possible mistakes in the automatic identification.

An R-mode cluster conducted on the correlation matrix between the SWIR "virtual" mineralogy of the acid soils (Fig. 6A, Table 1) displays the principal mineral assemblages of the soils. A close agreement is observed on the classification obtained by the cluster of cases calculated with the 53 samples and the previously assigned zone by on-ground criteria (Fig. 6B). In the dendrogram for the SWIR data, 45 out 53 samples are correctly placed in the four differentiated groups and a closer relationship between soils from groups 3 and 4 is displayed according to the evolution of the oxidation–dehydration processes in the distal soils.

From these results the following spectral association zones have been established:

- "Rozenite zone" for samples displaying spectra matching only secondary minerals (chiefly Fe²⁺ hydrated-sulphate associations), including rozenite and hexahydrite and subordinate melanterite, szomolnokite, and scarce halotrichite.
- 2. "Copiapite zone" for samples in which their spectra belong to the principal Fe²⁺ and Fe³⁺ hydrated

sulphates, including copiapite and coquimbite. The absence of paracoquimbite, ferricopiapite, rhomboclase, and roemerite spectra in this zone has been justified by the scarcity of these minerals in the XRD results and also by the resemblances of their spectra respect to the principal minerals of the zone



Fig. 6. Hierarchical cluster analysis for SWIR "virtual" mineralogy (n=53, 13 variables): (A) dendrogram of the R-mode cluster analysis showing the principal mineral assemblages in the soils; (B) dendrogram of the Q-mode cluster analysis, indicating sample identification and zone as in Table 2; (C) cross tabulation for field coding and cluster grouping.

Table 3

Minerals identified by XRD associated with sulphide-bearing mine wastes, San Miguel mine, Iberian PyriteBelt

Station	Zone	n	mel	roz	SZO	hex	cop	coq	rho	h–jar	pick	fer	gyp	ms	chl	qz	ру	Other minerals
A: "Ope	en pit" si	te																
A1	prox	11	(x)	xx		XX	х		(x)					х	xx	х	XX	halo: x; roe: (x); kao: (x)
A2	inter	9					XXX	XX	(x)	(x)	х				(x)	XX	XX	roe: (x)?; he: (x)?
A3	inter	4					XXX	XX			?							
A4	inter	5	?	х	х		х	XX						(x)		XX	XX	
B1	prox	3	(x)	xx		XX	XX		(x)									halo: xx; roe: x
B2	prox	5		XX		XXX	х											halo: xx; epso: xx
B3	prox	2			XX		XX	х							х	XX		halo: xx
C1	prox	7		xx	(x)		XXX		XX	(x)					xx	XX	XX	halo: (x) ; he: (x)
C2	inter	7			(x)		XXX	XXX									х	
C3a	distal	12				(x)	XX			XXX		х						
C3b	inter	5				xx	XXX	х										epso: xx; halo: xx;
D1	distal	9					(x)			XXX				х	XX	XX	х	but: x; he: (x)
D2	distal	1					x			XX						XX		, ()
D3	distal	7					(x)			х	XXX					XXX		halloy/kao: x
D4	inter	1					x	XXX								XX		2
D5	distal	6					х	XXX		х				х		XX	XX	he: xx
E1	inter	7			х		XX	XXX								XX	XX	
E2	inter	4			(x)		XX	XXX	(x)								х	
E3	inter	4					х	XXX										
E5	distal	2					x			XX		(x)				xxx		
F1	distal	3								xxx		()				x		
F2	distal	2								XXX								
F3	distal	4								xxx		x		xx	x	xx		he: x: but: (x) ?
G1	inter	5					XX	XXX		x				x		XX	х	he: x
G2	inter	4					xx	xx		x						xx	x	he: x
G3	inter	6					XX	x		XX						XXX		he: xx: goe: x
05		135																ner mit, goer n
B: "Cha	ırcaseca	' site																
P101	distal	2								XXX		(x)		х	(x)	XX		illite: x
P102	inter	3					XX	XXX	х	(x)						XX		Butl: ?
P103	inter	2			(x)		х	XXX		(x)						х	х	
P104	inter	2					XXX	XX										cop=ferricop?
P105	distal	3					XX	(x)		XX						XX		
P106	distal	3						х		XXX						XX		roe: ? kao: (x)
P201	distal	3								XX				х		XX	х	he: x
P202	crust	7								XX		(x)	XXX			XX	х	ca: x
P203	inter	2						XX		XX			(x)			XX		
P204	inter	3					XX	х				х				XX		
P205	inter	5			(x)		XX	XXX									XX	
P206	distal	6					XX	XX		XXX				х		XX		
P302	crust	9								XXX			XXX	(x)		XX	х	ca: (x); he: (x)
P303	inter	3					XXX			(x)			х	(x)		(x)	х	goe: (x); ca: x
P304	inter	3					XXX	х						(x)	х	х	х	
P305	inter	4					XX	х		х				(x)		XX	х	he: x
P306	inter	4					XX							x		XX	х	
P401	inter	1					xxx										х	goe: (x)
P402	inter	2					xxx	х							(x)	(x)	х	goe: x
P403	crust	3					(x)	х		xxx			XX		. /	x	х	he: (x)
P404	crust	2					. /			xxx			х			XX	(x)	he: (x)
P405	inter	1					xxx	xx				(x)		х			x	goe: xx
P406	inter	2					XX	XX				. /				XX		hex: xx; cop=ferricop
																		, i F

Table 3 (continued)

Station	Zone	п	mel	roz	szo	hex	cop	coq	rho	h–jar	pick	fer	gyp	ms	chl	qz	ру	Other minerals
B: "Charcaseca" site																		
P501	inter	1					XXX							х			XXX	goe: x
P502	inter	2						х		xx						XX	х	he: (x); butl: (x)
P503	crust	7					х		(x)	xx			XXX			х	х	ca: x; hex: (x)
P504	prox	1		(x)	х		х									XX	XXX	
P505	prox	1			(x)		XX				х					XX	XXX	
P506	distal	3					х	х		xx						XX	х	he: x
		90																

Zone abbreviations: prox=proximal, inter=transitional, distal=distal, crust=duricrust.

n: number of spectra in each sampling station.

Mineral abbreviations: but=butlerite, ca=calcite, chl=chlorite, cop=copiapite, coq=coquimbite, epso=epsomite, fer=ferryhidrite+schwertmannite, ferricop=ferricopiapite, goe=goethite, gyp=gypsum, halloy=halloysite, halo=halotrichite, he=hematite, hex=hexahydrite, h–jar= hydronium–jarosite, kao=kaolinite, mel=melanterite, ms=muscovite, pick=pickeringite, py=pyrite, qz=quartz, rho=rhomboclase, roe=roemerite, roz=rozenite, szo=szomolnokite.

Semiquantitative abundance estimations: xxx=very abundant (>40%); xx=major (>10%); x=minor (<10%); (x)=trace (detected), doubtful.

(copiapite and coquimbite). The progressive oxidation of iron and the loss of hydroxyls during dehydration produce the gradual reduction of the band at 1450 nm, the widening of the main water-related band at about 1960 nm, and the appearance of subordinate new small bands.

3. "Hydronium jarosite zone" for spectra matching the late tertiary minerals like hydronium–jarosite and pickeringite. Whereas the hydronium–jarosite shows broad water-related absorptions features accompanied by starting bands typical of the jarosite group (at 1845 and 2250 nm) that are easily identified, the pickeringite could be confused with the halotrichite and requires manual identification. All the hydronium–jarosite wet varieties (chocolate-coloured "oily samples") have been also counted as a different mineral because of their particular infrared response.

In addition, in this zone other minerals such as goethite and the brown iron oxides (e.g., like ferrihydrite and schwertmannite) have been also added and are included (as fer* in Table 1). These minerals are usually present in the samples from this zone but are difficult to identify with confidence in the SWIR range and consequently introduce serious errors in the estimation of the mineral proportions from the spectra. In any case, their spectra (Clark et al., 1993) have been included in the reference library to try out their identification, although most of the time without success. In contrast, the addition of other infrared active minerals in the reference library, such as gypsum, calcite, muscovite, and chlorite, which are also common in the analysed mineral assemblages from this zone, has resulted in very good results, and it has been possible to identify even the presence of minor quantities of these minerals in the spectra of the mineral mixtures.

4.2. XRD mineral analysis

XRD patterns for all samples were used to identify the primary and secondary minerals present at the Open pit (n=139) and at the Charcaseca (n=90)site (Table 3). Among the primary minerals, which are those that have remained unchanged during the weathering, abundant and ubiquitous quartz, pyrite, and minor muscovite and chlorite were found. Other accessory minerals, such as chalcopyrite, feldspar (plagioclase), and rutile, were identified by optical examination but these appear in amounts below the detection limit of X-ray diffractometry. In addition, some clay minerals that occur both as primary and secondary phases, were recognized. These last minerals typically form part of the deposit host rocks (chlorite, kaolinite, and muscovite) and also appear among the secondary weathering products of the country rocks (halloysite, montmorillonite).

The main identified "secondary" minerals consist of melanterite, rozenite, szomolnokite, copiapite (including aluminiocopiapite, magnesiocopiapite, and ferricopiapite), coquimbite, halotrichite, hexahydrite, pickeringite, and subordinate butlerite, rhomboclase, roemerite, and epsomite. All these secondary minerals (usually categorized as secondary, tertiary and quaternary (Jambor, 1994; Jambor and Blowes, 1998) have been generically and deliberately considered as secondary minerals in this study, as they were formed after deposition of the main sulphide association mainly by chemical weathering and transportation of solutions (dissolution, oxidation, evaporation) from primary minerals and on the surface of the grounds.

Considering the unstable nature of these minerals, several changes might have been promoted during transport and storage of the samples at the laboratory, such as: (a) the nearly complete disappearance of melanterite, to produce rozenite and szomolnokite; (b) the partial transformation of copiapite to coquimbite (given that almost complete transformation was observed after 2 months at the lab); or (c) the probable decrease of the proportions of butlerite by dehydration. In the field these changes develop gradually during the progress of the seasons, and even during the course of days and hours, depending on the relative humidity and prevailing temperature (Hammmarstrom and Smith, 2002). In any case, because the variability of chemical conditions during the transport and laboratory storage, other hydrated iron sulphate minerals could also be found.

From the XRD study we have semi-quantitatively estimated the proportions of these secondary phases by assuming that the intensity of the strongest peak of diffraction of each phase in the multiphase powder pattern with a similar matrix is a function of its relative abundance. The results (Table 3) point out that copiapite and coquimbite are by far the most commonly occurring salts among the investigated efflorescences, whereas hydronium-jarosite predominates in the soils formed by drying and polygonization of wet sediments. It is noteworthy that hydronium-jarosite is normally considered as a relatively rare iron sulphate (Dutrizac and Jambor, 2000). In contrast, the presence of the first products of direct decomposition of pyrite, like melanterite, rozenite and szomolnokite is limited in extent and these minerals always appear located close to the pyrite-bearing sources. Occasionally, the similarity of features among XRD patterns of certain subordinate iron salts and their poor crystallinity made the confident identification of their presence difficult. In these cases it was necessary to carry out inspection by SEM-EDS to confirm the presence or absence of principal cations in order to decide which phase was present. For example, presence of Mg, Al and Fe was used to identify halotrichite, pickeringite, simple copiapite, magnesiocopiapite or Al-bearing ferricopiapite.



Fig. 7. Principal non-linear components (PRINCALS) analysis on XRD data of mining impacted soils from San Miguel mine using 13 mineralogical variables: (A) plot of variables in the factorial plane defined by dimensions 1 (D1) and 2 (D2); (B) sample loadings with indication of zone.

4.2.1. Mineral distribution from XRD

Three principal zones have been distinguished, in agreement with field observations, from the XRD identification, relative abundance estimations (Table 3), and mineral associations described above, which allowed the ground surface mapping: (1) "rozenite zone", comprising all the ferrous hydrated salts (melanterite, rozenite and szomolnokite), halotrichite, hexahydrite, and epsomite; (2) "copiapite zone", including the pure copiapite flowers that appear as efflorescences and the mixtures of copiapite with coquimbite in the soils, in addition of the presence



Fig. 8. The Open pit contoured mineral data from XRD (left pictures) and from PIMA SWIR (right pictures) for the selected mineral assemblages: (A, D) melanterite, rozenite, hexahydrite, szomolnokite, and halotrichite ("Rozenite zone"), (B, E) copiapite, and coquimbite ("Coquimbite zone"), (C, F) hydronium–jarosite, schwertmannite, ferrihydrite, and goethite ("Jarosite zone"). Frame of the picture is the same as Fig. 2.



"Rozenite" zone



"Jarosite" zone



"Gypsum" zone



of subordinate amounts of roemerite, rhomboclase, and some butlerite which are usually mixtured at the soil samples; (3) "jarosite zone", mainly formed by hydronium jarosite accompanied by pickeringite and variable amounts of detrital phyllosilicates (chlorite, muscovite, kaolinite).

The cited mineral distribution in the soils and the grouping of samples by zones has also been statistically interpreted by principal non-linear components analysis. In the light of on-ground information some PRIN-CALS analysis were run for 13 XRD variables (the minerals in Table 3), which yielded two dimensions that explain the 28.1% and 19.8% of the total inertia, respectively (Fig. 7A and B). The first axis (D1) reflects the variation of the first products of pyrite alteration (e.g., melanterite, rozenite and hexahydrite) with the highest negative loadings, whereas in the D2 axis it is possible to identify a continuous variation between copiapite-coquimbite rich mineral associations and those minerals deposited in the final stages of alteration. In the view of these mineralogical associations, the previously established four principal zones have also been distinguished for soil mapping purposes, which agrees with the described fringe soil zones : "proximal", "transitional", "distal", and ferricrust.

This kind of mineral distribution, from ferrous-, to ferrous-ferric-, to ferric-salts, may also be outlined as roughly concentric colour bands (Figs. 8 and 9), moving from areas adjacent to the primary pyrite focus (proximal zones) to more distal parts, located away from the main zones of pyrite alteration. This arrangement agrees with the mineral composition, progress of oxidation and the distance from the sulphide-bearing sources. The distribution of the accounted salts at the studied Open pit and the Charcaseca sites seems to be crudely related to the distance from the primary ore sulphides (outcrops of pyrite and pyrite-rich waste dumps) and consequently with the advance of iron oxidation and dehydration of the unstable products.

4.2.2. XRD and SWIR data comparison

Checking the virtual SWIR mineralogy of each spectral zone against the zones obtained from the

XRD analyses, yielded an acceptable agreement with some discrepancies. On the whole, the measures of the copiapite and jarosite zones supply the best results providing high and tolerable consistency between the two techniques, whereas the rozenite zone displays poorer results, sharing tolerable and high scores with some bad results.

In particular, at the proximal zones, the analysis of samples with minor amounts of melanterite display the strongest disagreement, while those samples dominated by rozenite and hexahydrite contribute with the best results. In the distal sediments, the presence of small quantities of muscovite in the dried and polygonized muds, is frequently underevaluated in the spectral data if totally automated identification procedures are used, although the assessment is easily correctable with manual analysis. Other problems in the analysis of the distal zone samples, are associated with the estimation of the main iron oxyhydroxides (ferrihydrite, ochre, goethite and hematite), because of their relative chemical similarity and simplicity of their spectra. Finally, the silicate minerals and sulphides, such as quartz and pyrite recognized by visual observation and XRD analysis, which produce noisy spectra with notable absence of absorption features, have been omitted in this comparison.

4.3. Development of the SWIR maps

Using the SWIR results (Table 1) all the identified minerals have been grouped into different batches according to the previously proposed spectral zones. Using these groups three efflorescence maps (Figs. 8 and 9) have been generated: (1) "rozenite map", comprising rozenite+szomolnokite+melanterite+hexahydrite, as secondary minerals released in the initial stage of pyrite decomposition; (2) "copiapite map", including copiapite+coquimbite, as tertiary minerals typically precipitated from oxidized acid sulphate pore waters; and, (3) "hydronium jarosite map", containing hydronium–jarosite+pickeringite+ferrihydrite+ goethite, as tertiary minerals precipitated from acid waters at the bottom of the pools and spillways. At

Fig. 9. The Charcaseca contoured mineral data from XRD (left pictures) and from SWIR (right pictures) for the selected mineral assemblages: (A, E) melanterite, rozenite, hexahydrite, szomolnokite, and halotrichite ("Rozenite zone"), (B, F) copiapite, and coquimbite ("Coquimbite zone"), (C, G) hydronium–jarosite, schwertmannite, ferrihydrite, and goethite ("Jarosite zone"), and (D, H) gypsum and calcite ("Gypsum zone"). Frame of the picture is the same as Fig. 2.

the Charcaseca site an additional map, "gypsum" map, was constructed to include the minerals forming the superficial gypsum-rich ferricrusts. These groupings agree with the paragenesis, relative stability and natural evolution during progressive oxidation-dehydrationneutralization process of the acid waters. Importantly, the clear spatial associations between the mineral assemblages that characterise each zone help to reduce the inherent errors in the SWIR identifications when these data are plotted.

Contour maps showing the quantitative spatial distribution of the dominant mineral assemblages in both study areas are shown in Figs. 8 and 9. The described zones form roughly circular bull's eye patterns that resemble those described at the Leadville waste rock piles and other environmental impacted regions (Swayze et al., 2000; Jerz and Rimstidt, 2003).

These maps provide important information that impact on environmental considerations and remedial processes. Specifically:

(a) The "rozenite maps" show the predominance of rozenite \pm hexahydrite in areas with abundant pyrite ores (proximal zones). These minerals are located directly on the roof of sulphide wastes or linked to the pyritic outcrops. Hexahydrite, which is relatively abundant at the Open pit, could have been derived from early weathering of Mg-rich minerals (chlorite) by the mine water drainage. All these sulphates are usually accompanied by minor amounts of copiapite and coquimbite just close to the areas where the pyrite-rich waste piles and rocks appear, mainly at the stockwork outcrops (vertical walls). Consequently, it is suggested that the distribution of semidehydrated products from melanterite, such as rozenite and szomolnokite, may be used as indicators of proximity to hypogene pyrite or as a vector towards massive ore lenses.

In these areas the first step of the oxidation of pyrite occurs, creating melanterite and sulphuric acid. While the sulphuric acid is taken into the pore solution or reacts with the surrounding minerals to release cations (e.g., Mg^{2+} , Al^{3+} , Cu^{2+} , Zn^{2+}), the melanterite is quickly dehydrated to rozenite and szo-molnokite, changing from green to whitish powder (Alpers et al., 1994). These salts are predominantly formed from ferrous sulphate solutions, and are frequently associated with hexahydrite. They are probably evidence for the dramatic change in magnesium

concentration in the first solutions after the acid attack and dissolution of the primary chlorite. In contrast to the relative abundance of hexahydrite, epsomite was only identified at the Open pit (C3 sample; Table 1) and was not found at the Charcaseca grounds, probably because epsomite shows preference for relatively higher humidity (Jambor et al., 2000) and less acidic environments. In addition, the shortage of halotrichite at both studied sites confirms the existence of local environments preserving relatively high humidity and pore waters with high activity of aluminium (Jerz and Rimstidt, 2003).

(b) The "copiapite maps" show the presence of abundant copiapite largely associated with coquimbite, and are by far the most extensive salts mapped at the studied sites. These minerals are particularly abundant in the cracks of the corrugated and polygonized soils and dried muds of the grounds. The percentages of the copiapite (usually above 60%) are balanced by the relative proportions of coquimbite as result of progressive oxidation. The presence of hydronium jarosite \pm muscovite and even rozenite \pm szomolnokite in these areas clearly indicates the mixture of mineral associations grading to distal or proximal zones, respectively, and evidence for the relative instability of the secondary and tertiary mineral associations. In any case, neither copiapite nor ferric iron oxyhydroxides have been observed as formed directly on the surface of pyrite grains (Frau, 2000).

The main changes of soil colour at these transitional zones are caused by changes in the relative proportion of ferrous and ferric iron precipitates mixed with minerals from the neighboring zones (copiapite or transition zones). According to the SWIR results the yellow greenish colours of the early efflorescences are dominated by copiapite (the ferrous-bearing copiapite), while the yellow-orange colours are dominated by the transformation of ferricopiapite to coquimbite and demonstrate the progress of the oxidation and changes of hydration. The limited appearance of butlerite (interpreted as a typical product of oxidation-dehydration, Jambor et al., 2000), could indicate relative low humidity, presumably because butlerite requires higher humidity to be stable (Jerz and Rimstidt, 2003). Although hydronium-jarosite is generally below 20% in the "copiapite zones" its presence causes an incipient cementation of the upper part of the soils, and brittle hardened crusts. This kind of crumbly ferricrusts sometimes survives the weathering because of the comparatively low solubility of the hydronium jarosite.

The presence of these slightly hardened crumbly ferricrusts suggests that salts were precipitated from solutions evaporated by capillary action and reprecipitated through the action of recurrent infiltrated waters. As a rule, these salts were formed from the intraporous acid aqueous solutions (as tertiary minerals according to Jambor, 1994) during a second stage of efflorescence generation. The drying of the soils causes the fast growth of yellow to orange coloured salts, emerging 2 to 10 cm from the ground as efflorescent blooms, which usually appear at the same time as the shrinkage of the contorted and polygonized soils develops. Generally copiapite is the first mineral formed in these "extruded" efflorescences firstly located at the soil-cracks, but with time the progress of air oxidation transforms the copiapite to coquimbite and, less frequently, to ferricopiapite and rhomboclase. In either case the presence of abundant copiapite on the ground, the most stable of the ferric hydrated sulphates (Zodrow, 1980; Alpers et al., 1994; Buckby et al., 2003), indicates a relatively high degree of oxidation and relative high humidity during the time of formation and conservation (second stage).

Near the ephemeral pools these copiapite-rich zones usually have sharp edges next to the hydronium–jarosite mud-layers. In addition to the detrital quartz and pyrite, these soils also contain some phyllosilicates (chiefly muscovite and chlorite coming from the altered country rocks).

(c) The "jarosite maps": Distal to the pyritic acid sources of contamination, the soils are mostly composed by hydronium jarosite with subordinate pickeringite, and traces of some detrital minerals such as chlorite, muscovite and (rarely) kaolinite. These minerals are usually accompanied by ferrihydrite and some poorly crystalline brown ochres, also found along the Escalada creek, cited as "yellowboy" (Bigham et al., 1996; Schwertmann et al., 1995). These ochres were investigated by DXRD and were interpreted as ferrihydrite (2-lines) and possible schwertmannite+ferrihydrite aggregates (Jambor and Dutriziac, 1998; Dold, 2003). Also identified in these distal zones are butlerite (Fe³⁺SO₄OH · 2H₂O) as well as minor chlorite and muscovite detritus transported from the country rocks.

Subsequent to the complete evaporation of the red ponds, a nearly continuous layer (thickness up to 20 cm) of hydronium jarosite was deposited. This finegrained sediment is usually characterized by the presence of thick upper crusts, like puff pastry with very dry and strongly polygonized covers, dominated by hydronium jarosite (up to 75%). Locally, the layer exhibits an oily shine at the surface showing a darkbrown colour. At the edges of the red pools, particularly when they are full of very acid solutions, the brown zone passes sharply (at the scale of few centimetres) to the adjacent "copiapite zone". Finally, after the complete evaporation of water the center of the dry ponds remains covered by a film-layer of delicate pickeringite as the final precipitate of the evaporative cycle.

The predominance of the hydronium–jarosite and ferrihydrite in these distal dry muds is evidence that the products of pyrite alteration have reached the highest stage of oxidation in agreement with that indicated by the intense red colour of the remaining brine pool (Fig. 2A,C). It also stresses the alkali-deficient character of the solutions (Ripmeester et al., 1986) at the San Miguel pore waters, in connection with the high concentration reached by the hydronium. Finally, the thin superficial layers of pickeringite found at the central part of the dried ponds, reveal that iron was exhausted by crystallization of hydronium jarosite just before the end of the evaporative cycle.

(d) The "gypsum maps" show that gypsum is an abundant constituent of the ferricrete crusts at the Charcaseca, where it is mixed with variable proportions of hydronium jarosite and ferrihydrite and, occasionally, with calcite. These crusts are crossed by the typical efflorescences found at the intermediate zone and, consequently, some copiapite and coquimbite have also been identified in them. The presence of calcite and gypsum in these soils is clearly related to the addition of limestone gravels and blocks to some parts of the contaminated sulphide-bearing mine wastes, in an effort to remediate the site. Calcite always appears as a very subordinate mineral, as unstable relicts associated with gypsum, providing evidence that the remediation treatment performed during the eighties was inadequate, especially considering the permanence and abundance of efflorescence salts at the area. Specifically, the association of hydronium jarosite, ferrihydrite and gypsum proves that

imbalanced reactions were produced during the neutralization treatment, while the residue of calcite is evidence that only in restricted areas was the neutralization of the system properly achieved.

4.4. Schematic model of mineral formation

A model of mineral formation can be established from the field mineral examinations and the mapping



Fig. 10. (A) Diagram showing the evolution paths of iron sulphate minerals during the process of pyrite alteration at the surface of the acid mine soils. First stage reactions are mainly oxidation and dehydration, producing ferrous hydrated sulphates as decomposition products of melanterite. Second stage reactions develop ferrous–ferric sulphate hydrate salts variably oxidized and dehydrated from acid ground solutions. Third stage reactions are usually of neutralization and generate the final products as ferric hydroxysulphates and hydroxides (adapted from Jerz and Rimstidt, 2003). Mineral abbreviations are the same of Tables 1 and 3. (B) Paragenetic sequence of iron sulphate minerals from pyrite alteration observed at San Miguel mine grounds. The dashed lines divide the diagram according to the stages, the proximal to distal zones, and the secondary or tertiary character of the minerals.

of the acid soils. First, the process of pyrite alteration starts forming sulfuric acid, and in acidic conditions melanterite is formed (Fig. 8). This mineral quickly and progressively loses water in open air to produce rozenite and then recrystallizes slowly to szomolnokite (Jambor et al., 2000). As rozenite appears to be metastable in aqueous solutions (Reardon and Beckie, 1987), the occurrence of the relatively abundant rozenite at the "proximal zones" suggests a process of formation by dehydration of first formed melanterite or, less probably, by the rehydration of szomolnokite in absence of a solution phase.

In addition, from the evaporation of pore acidic solutions retained by the soils, the following sequence of "secondary" minerals was precipitated from early to late stages: melanterite \rightarrow rozenite \rightarrow halotrichite \rightarrow szomolnokite \rightarrow copiapite \rightarrow coquimbite \rightarrow rhombo $clase \rightarrow butlerite \rightarrow hydronium jarosite \rightarrow pickeringite$ (Fig. 8). This is in good agreement with the trends commonly observed in other sulphide mine wastes elsewhere (Bandy, 1938; Buurman, 1975; Nordstrom and Alpers, 1999; Jambor et al., 2000). Despite data on solubility, acid concentration, and temperature from the literature (Mitchell, 1984; Reardon and Beckie, 1987) precise relationships of stability conditions among the cited salts are not well known. However transition temperatures below 45 °C, a dry climate with relative humidity down 65%, and duration of less than 4-6 weeks seem to have been sufficient at San Miguel to have allowed the development of the observed minerals. This conclusion is consistent with temperature, pH measurements, and relative humidity records in the region (López-Pamo et al., 1999; Sánchez-España et al., 2005).

This study suggests that sulphide weathering develops in three stages (Fig. 10): firstly the pyrite oxidation produces melanterite and/or their dehydration products together with sulphuric acid (first stage), secondly from the acid solutions tertiary minerals precipitate as hydrated salts (second stage), which are successively dissolved and reprecipitated by the rain and by the pore waters, and finally they discharge as hydronium jarosite and pickingerite (third stage). The process of natural neutralization of these acid soils begins with the formation of the classical neutralized ferrihydrite (Bigham et al., 1996) and with the formation of gypsum when the neutralization of acid soils was

locally carried out with limestones. Examination of the remains of the weathered rocks demonstrates that primary pyrite and chalcopyrite have almost completely dissolved, however, locally when pyrite alteration is partially neutralized by mafic silicate minerals (e.g., chlorite-rich rocks of the pyrite stockwork) the result is the pseudomorphism of the pyrite cubes by an amorphous red oxihydroxide of the type of ferrihydrite. It is interesting to note that goethite and/or lepidocrocite have not been found as *today's* product of sulphide oxidation. However, the goethite and hematite were the almost only products of the massive sulphide alteration during the gossan formation.

5. Concluding remarks

This study has demonstrated that at the San Miguel Mine supergene processes include the leaching, dissolution of the primary minerals, and precipitation of abundant sulphates as secondary and tertiary minerals. Iron-, magnesium-, calcium-, and aluminum-hydroxysulphate minerals such as melanterite, rozenite, szomolnokite. halotrichite, copiapite, coquimbite. rhomboclase, roemerite, butlerite, hydronium-jarosite, pickeringite, and (locally) gypsum have been identified. Based on field and laboratory analysis, from proximal to distal areas, these minerals occur as three distinct zones containing rozenite+hexahydrite, copiapite+coquimbite and hydronium jarosite, respectively. These zones appear to be generally concentric and onlapped around the acidic sources. An additional zone with gypsum and calcite appears only at the remediated areas.

All the supergene sulphates are hydroxyl- and/or water-bearing, which allow the identification and calculation of their characteristics and relative distribution on the basis of their diagnostic SWIR spectral reflectance signatures. A comparison between XRD mineral identification and SWIR data shows that analysis with PIMA can allow quantitative mapping of the concentration of iron sulphate minerals and their distribution in acidic mine waste environments. Furthermore the results of the SWIR analysis also agree with visual and field observations.

Quantitative maps of mineral distribution were created by producing an estimation of the percentage of minerals, after the grouping of the salts in three main associations according to field occurrence, stability, and progress of oxidation–dehydration–neutralization reactions. Importantly, these contoured mineral maps are consistent with the estimated mineralogical data obtained from conventional methods (such as XRD).

The method described in this paper could be applicable to mapping iron hydrated sulphate minerals and other infrared active minerals at other environmental impacted sites. However, it may be necessary to develop a new reference library for contaminated regions in different geological environments to include different mineral assemblages to those observed in this study.

In summary, this work has shown that weathering of sulphide minerals has produced hydrogen ions during oxidation which have contributed to the production of toxic acid water which has dissolved and precipitated the relatively complex suite of soluble and insoluble secondary minerals. As acid waters result in mineral destruction, dissolving and transporting metals a long way from the polluted areas, these acid effluents have impacted on the quality of the environment and make restoration of the ecosystem difficult at the San Miguel Mine. The study shows the potential of SWIR spectral analysis to identify and understand the distribution of efflorescent salts and other products of pyrite decomposition and provides a methodology to assist the research and monitoring of other sources of environmental contamination.

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References

- Alpers, C.N., Blowes, D.W., Norstrom, D.K., Jambor, J.L., 1994. Secondary minerals and acid-mine water chemistry. In: Jambor, J.L., Blowes, D.W. (Eds.), Short Course Handbook of Sulfide Mine Wastes. Mineralogical Association of Canada, Waterloo, Ontario, pp. 247–270.
- Bandy, M.C., 1938. Mineralogy of three sulphate deposits at northern Chile. American Mineralogist 23, 669–760.
- Baugh, W.M., Kruse, F.A., Atkinson, W.W., 1998. Quantitative geochemical mapping of ammonium minerals in the southern Cedar Mountains, Nevada, using the airborne visible/infrared imaging spectrometer (AVIRIS). Remote Sensing of Environment 65, 292–308.
- Berman, M., Bischof, L., Huntington, J., 1999. Algorithms and software for the automated identification of minerals using field spectra or hyperspectral imagery. 13th International Conference on applied Geologic Remote Sensing, Vancouver, BC, Canada, Ann Arbor, Environmental Research Institute of Michigan, Proceedings, pp. 222–232.
- Bigham, J.M., Nordstrom, D.K., 2000. Iron and aluminium hydroxysulfates from acid sulphate waters. In: Alpers, C.N., Jampor, J.L., Nordstrom, D.K. (Eds.), Sulfate Minerals, Reviews in Mineralogy and Geochemistry, vol. 40, pp. 351–403.
- Bigham, J.M., Schwertmann, U., Pfab, G., 1996. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. Applied Geochemistry 11, 845–852.
- Buckby, T., Black, S., Coleman, M.L., Hodson, M.E., 2003. Fe-sulphate-rich evaporative mineral precipitates from the Rio Tinto, southwest Spain. Mineralogical Magazine 67 (2), 263–278.
- Buurman, P., 1975. In vitro weathering products of pyrite. Geologie en Mijnbouw 54, 101–105.
- Carrasco, I., 2000. Historia de la Faja Pirítica. Bocamina 5, 10-49.
- Clark, R.N., Swayze, G.A., Gallagher, A.J., King, T.V., Calvin, W.M., 1993. The U.S. Geological Survey, Digital Spectral Library: Version 1 (0.2 to 3.0 μm), Open File Report, vol. 93-592. U.S. Geological Survey. 1326 pp.
- Crowley, J.K., Williams, D.E., Hammarstrom, J.M., Piatak, N., Chou, I., Mars, J.C., 2003a. Spectral reflectance properties (0.4–2.5 μm) of secondary Fe-oxide, Fe-hydroxide, and Fesulphate–hydrate minerals associated with sulphide-bearing mine wastes. Geochemistry: Exploration, Environment, Analysis 3, 219–228.
- Crowley, J.K., Williams, D.E., Hammarstrom, J.M., Piatak, N., Mars, J.C., Chou, I., 2003b. Digital Spectra Reflectance Data of Fe-Oxide, and Fe-Sulphate Minerals Associated with Sulfide-Bearing Mine Wastes, Open File Report, vol. 03-196. U.S. Geological Survey.
- De Leeuw, J., Van Rijckevorsel, J., 1980. HOMALS and PRIN-CALS: some generalizations of principal components analysis. In: Diday, E., et al., (Eds.), Data Analysis and Informatics. North-Holland, Amsterdam, pp. 231–242.
- Dold, B., 2003. Dissolution kinetics of schwertmannite and ferrihydrite in oxidized mine samples and their detection by differential X-ray diffraction (DXRD). Applied Geochemistry 18, 1531–1540.

- Dennis, A.M., Colman, T.B., Cooper, D.C., Hatton, W.A., Shaw, M.H., 1999. The combined use of PIMA and VULCAN technology for mineral deposit evaluation at the Parys Mountain mine, Anglesey, UK. 13th International Conference on Applied Geologic Remote Sensing, Vancouver, BC, Canada, Ann Arbor, Environmental Research Institute of Michigan, Proceedings, pp. 25–32.
- Dutrizac, J.E., Jambor, J.L., 2000. Jarosites and their application in hydrometallurgy. In: Alpers, C.N., Jambor, J.L., Norstrom, D.K. (Eds.), Sulphate Minerals, Reviews in Mineralogy and Geochemistry, Mineralogical Society of America and Geochemical Society, vol. 40, pp. 405–452.
- Earthwork Corporation Pty Ltd., 1996. Terrain. Software, Downhole Explorer, 3.0 Earthworks Corporation.
- Frau, F., 2000. The formation–dissolution–precipitation cycle of melanterite at the abandoned pyrite mine of Genna Luas in Sardinia, Italy: environmental implications. Mineralogical Magazine 64 (6), 995–1006.
- García de Miguel, J.M., 1990. Mineralogía, paragénesis y sucesión de los sulfuros masivos de la Faja Pirítica en el suroeste de la Península Ibérica. Boletín Geológico y Minero 101-1, 73–105.
- García García, G., 1996. Famous mineral localities: The Rio Tinto mines, Huelva, Spain. The Mineralogical Record 27, 275–285.
- Hammmarstrom, J.M., Smith, K.S., 2002. Geochemical and mineralogic characterization of solids and their effects on waters in metal-mining environments. In: Seal II, R.R., Foley, N.K. (Eds.), Progress on Geoenvironmental Models for Selected Mineral Deposit Types, Chapter B: U.S. Geological Survey Open-File Report 02-0195 (on-line Version 1.0), pp. 8–52.
- Herrmann, W., Blake, M., Doyle, M., Huston, D., Kamprad, J., Merry, N., Pontual, S., 2001. Short wavelength infrared (SWIR) spectral analysis of hydrothermal alteration zones associated with base metal sulfide deposits at Rosebery and Western Tharsis, Tasmania, and Haighway-Reward, Queensland. Economic Geology 96-5, 939–956.
- Hudson-Edwards, K.A., Schell, C., Macklin, M.G., 1999. Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. Applied Geochemistry 14, 1015–1030.
- Hunt, G.R., Ashley, R.P., 1979. Spectra and altered rocks in the visible and near infrared. Economic Geology 74, 1613–1629.
- Integrated Spectronics, 1999a. Pima View v3.1 User Manual. Integrated Spectronics Pty Ltd. Document Ref. No. ISPL-PV-3.1-01, Baulkan Hills, NSW, Australia, p. 102.
- Integrated Spectronics, 1999b. Short Wave Infrared Spectroscopy for Geological Mapping and Mineral Exploration Using the Pima Field Portable Spectrometer 6th edition of Pima SP and Pima View User Manual, Baulkan Hills, NSW, Australia, p. 72.
- Jerz, J.K., Rimstidt, J.D., 2003. Efflorescent iron sulfate minerals: paragenesis, relative stability, and environmental impact. American Mineralogist 88, 1919–1932.
- Jambor, J.L., 1994. Mineralogy of sulfide-rich tailings and their oxidation products. In: Jambor, J.L., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Mineral Wastes, Short Course, vol. 22. Mineralogical Association of Canada, pp. 59–102.
- Jambor, J.L., Blowes, D.W., 1998. Theory and applications of mineralogy in environmental studies of sulfide-bearing mine wastes.

In: Cabri, L.J., Vaughan, D.J. (Eds.), Modern Approaches to Ore and Environmental Mineralogy, Short Course, vol. 27. Mineralogical Association of Canada, pp. 367–401.

- Jambor, J.L., Dutriziac, J.E., 1998. Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. Chemical Reviews 98, 2549–2585.
- Jambor, J.L., Nordstrom, D.K., Alpers, C.N., 2000. Metal-sulfate salts from sulfide mineral oxidation. In: Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (Eds.), Sulfate Minerals, Reviews in Mineralogy and Geochemistry, vol. 40. Mineralogical Society of America and Geochemical Society, Washington, D.C., pp. 303–350.
- Leistel, J.M., Marcoux, E., Thiéblemont, D., Quesada, C., Sánchez, A., Almodóvar, G.R., Pascual, E., Sáez, R., 1998. The volcanichosted massive sulphide deposits of the Iberian Pyrite Belt. Mineralium Deposita 33, 2–30.
- López-Pamo, E., Barettino, D., Anton-Pacheco, C., Ortiz, G., Arranz, J.C., Gumiel, J.C., Martínez-Pledel, B., Aparicio, M., Montouto, O., 1999. The extent of the Aznalcollar pyritic sludge spill and its effects on soils. Science of the Total Environment 242, 57–88.
- Merry, N., Pontual, S., Gamson, P., 1999. The Spectral Geologist 'TSG' v2.0 User Manual. AusSpecInternational Pty Ltd. Commonwealth Scientific and Industrial Research Organisation (CSIRO), p. 136.
- Mitchell, A.G., 1984. The preparation and characterization of ferrous sulfate hydrates. Journal of Pharmacy and Pharmacology 36, 506–510.
- Nordstrom, D.K., Alpers, C.N., 1999. Geochemistry of acid mine waters. In: Plumlee, G.S., Logsdon, M.J. (Eds.), The Environmental Geochemistry of Mineral Deposits: Part A Processes, Methods, and Health Issues, Reviews in Economic Geology, vol. 6A, pp. 133–160.
- Norusis, M.J., 1992. SPSS/PC+: Professional Statistics. 5.0. Ed. SPSS Inc., Chicago. 236 pp.
- Pinedo Vara, I., 1963. Piritas de Huelva (su Historia, Mineria y Aprovechamiento). Editorial Summa, Madrid. 1003 pp.
- Pontual, S., Merry, N., Gamson, P., 1997. G-Mex Vol 1: Spectral Interpretation Field Manual: AusSpec International Pty Ltd.
- Reardon, E.J., Beckie, R.D., 1987. Modelling chemical equilibria of acid-drainage: the FeSO₄–H₂SO₄–H₂O system. Ceochemica Cosmochemica Acta 51, 2355–2368.
- Ripmeester, J.A., Ratcliffe, C.I., Dutriziac, J.E., Jambor, J.L., 1986. Hydronium ion in the alunite–jarosite group. Canadian Mineralogist 24, 435–447.
- Sánchez-España, J., Velasco, F., Yusta, I., 2000. Hydrothermal alteration of felsic volcanic rocks associated with massive sulphide deposition in the northern Iberian Pyrite Belt (SW Spain). Applied Geochemistry 15, 1265–1290.
- Sánchez-España, J., López Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., Barettino, D., 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): geochemistry, mineralogy and environmental implications, Applied Geochemistry 20, 1320–1356.
- Schwertmann, U., Bigham, J.M., Murad, E., 1995. The first occurrence of Schwertmannite in a natural stream environment. European Journal of Mineralogy 7, 547–552.

- Schulze, D.G., 1981. Identification of soils iron oxide minerals by differential X-ray diffraction. Soil Science Society of America Journal 45, 437–440.
- Sun, Y., Seccombe, P.K., Yang, K., 2001. Application of short-wave infrared spectroscopy to define alteration zones associated with the Elura zinc–lead–silver deposit, NSW, Australia. Journal of Geochemical Exploration 73, 11–26.
- Swayze, G.A., Smith, K.M., Clark, R.N., Sutley, S.J., Pearson, R.M., Vance, J.S., Hageman, P.L., Briggs, P.H., Meier, A.L., Singleton, M.J., Roth, S., 2000. Using imaging spectroscopy to map acidic mine waste. Environmental Science and Technology 34, 47–54.
- Thompson, A.J.B., Hauff, P.L., Robitaille, A., 1999. Alteration mapping in exploration: application of short-wave infrared (SWIR) spectroscopy. SEG Newsletter 39 (p. 1), 16–27.
- Tornos, F., Locutura, J., Martins, L., 1999. The Iberian Pyrite Belt. Field Trip Guide. Joint SGA IAGOD International Meeting, Field trip B4, 28 August to 3 September, ITGE-IGM. 49 pp.
- Yang, K., Huntinton, J.F., Browne, P.R.L., Ma, C., 2000. An infrared spectral reflectance study of hydrothermal alteration minerals from the Te Mihi sector of the Wairakei geothermal system, New Zealand. Geothermics 29, 377–392.
- Zodrow, E.L., 1980. Hydrated sulfates from Sydney Coalfield, Cape Breton Island Nova Scotia, Canada: the copiapite group. American Mineralogist 65, 961–967.