El presente trabajo pretende dar un breve repaso sobre la problemática de la generación de aguas ácidas de mina en la Faja Pirítica Ibérica, incluyendo algunos aspectos teóricos básicos sobre los mecanismos de oxidación y disolución de los sulfuros y la lixiviación de metales que tiene lugar en los huecos mineros (pozos, galerías, cortas) tras su abandono, y otros aspectos importantes como la composición química de las aguas ácidas resultantes de esta oxidación disolutiva (incluyendo lixiviados de escombreras y balsas, y lagos formados en cortas), o las fases minerales más relevantes que se generan en estos ambientes, y su papel como control de la composición química de los drenajes ácidos. Las aguas ácidas de la Faja Pirítica presentan importantes variaciones químicas tanto espaciales (composiciones muy distintas en función del foco generador y de la geología local de la mina) como temporales (con marcadas variaciones hidrológicas estacionales), y entre las numerosas aguas analizadas hasta la fecha se incluyen casos con valores de pH extremadamente bajos (cercanos a cero en algunas zonas) y contenidos muy altos en sulfato, metales y metaloides disueltos (p.ej., concentraciones de centenares de gramos por litro de sulfato, y de decenas de g/L de Fe, Al, Cu y Zn). También se comentan diversos aspectos sobre la mineralogía y quimismo de los precipitados de Fe(III) (schwertmanita, jarosita, goetita, ferrihidrita), Al (hidrobasaluminita, alunita) y sales eflorescentes de Fe(II)-Fe(III)-Mg-Al (melanterita, rozenita, epsomita, hexahidrita, copiapita, halotriquita, coquimbita) presentes en estos ambientes, así como su solubilidad y capacidad de retención y absorción de metales y metaloides traza como Cu, Zn, As o Pb. Finalmente, se proporcionan varios ejemplos de evolución hidrogeoquímica y transporte de metales para ilustrar el tipo y grado de impacto ambiental que generan este tipo de aguas.

This work provides a brief overview about the generation of Acid Mine Drainage (AMD) in the Iberian Pyrite Belt (IPB), including some theoretical considerations about the mechanisms of sulphide oxidation and metal leaching that occur in the mining areas, the water chemistry of the resultant AMD discharges and acidic mine pit lakes, and the most relevant mineral phases associated to the acidic mine waters. These acidic solutions vary largely in chemical composition, either spatially (between different mine sites) and seasonally (due to marked hydrologic variations), and include cases with very low pH and very high sulphate and metal contents. The mineralogy and chemistry of the Fe precipitates (e.g., schwertmannite, jarosite, goethite, ferrihydrite), Al phases (e.g., hydrobasaluminite, alunite) and Fe(II)-Fe(III)-Mg-Al efflorescent sulphates (e.g., melanterite, rozenite, epsomite, hexahydrite, copiapite, halotrichite, coquimbite) present in the AMD-generating mine sites, as well as their solubility and trace metal retention capacity, is also discussed. Finally, some examples of hydrogeochemical evolution and metal transport and precipitation are provided to illustrate the environmental impact of AMD in the IPB.

Acid Mine Drainage in the Iberian Pyrite Belt: an Overview with Special Emphasis on Generation Mechanisms, Aqueous Composition and Associated Mineral Phases

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INTRODUCTION

A long history of metalliferous mining in the IPB mining district has left a legacy of abandoned mines, mainly in the province of Huelva (SW Spain), and a big number of waste piles (n=57, total volume of 107 Hm^3), tailings impoundments (n=10, total volume of 42 Hm^3) and flooded pits (n=22, total volume of acidic water of 25 Hm^3), which represents one of the World´s largest accumulations of mine wastes and AMD.

The mineralogical and textural characteristics of the IPB ores (with a dominantly pyritic, fine-grained, usually brecciated and fractured, and highly reactive mineralization, and a considerable lack of carbonates to neutralize acidity), has favoured the oxidation and dissolution of pyrite, and the subsequent formation of AMD. These acid mine waters have caused severe pollution of acidity and dissolved metals (Fe, Al, Mn, Cu, Zn, Cd, Pb), As and SO_4 to the Odiel and Tinto river systems (Van Geen et al., 1991; Nelson and Lamothe, 1993; Elbaz-Poulichet et al., 1999; Davis et al., 2000; Cossa et al., 2001; Braungardt et al., 2003; Olías et al., 2004; Sánchez-España et al., 2005a, 2006a). This acidity and metal pollution has caused the loss of most forms of aquatic life, with the exception of acidophilic microorganisms which inhabit these extreme environments (e.g., López-Archilla and Amils, 1999; López-Archilla et al., 2001; González-Toril et al., 2003; Aguilera et al., 2006).

This paper provides an overview about the AMD problem in the IPB district, mainly from a geochemical and mineralogical perspective. It firstly reports some basic features about the oxidation of pyrite, the main geochemical process responsible for the generation of AMD, and about the microorganisms that catalyze this process in shafts, galleries, piles, tailings and pits. Secondly, the composition of AMD typically found in the IPB, as well as the mineralogy and chemistry of mineral phases associated to the acid mine waters, are also discussed.
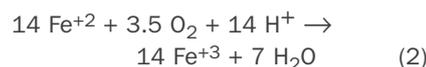
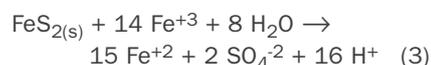## THEORETICAL CONSIDERATIONS

Fundamentals of pyrite oxidation

The oxidative dissolution of pyrite is one of the most extensively studied geochemical processes on the Earth surface, although it is not yet fully understood (e.g., Nordstrom and Alpers, 1999a; Ehrlich, 2002). The reaction which classically describes the oxidation of pyrite in the presence of oxygen and water is (Singer and Stumm, 1970):

$$FeS_{2(s)} + 3.5\ O_2 + H_2O \rightarrow$$
$$Fe^{+2} + 2\ SO_4^{-2} + 2\ H^+ \quad (1)$$

The formed ferrous iron is then usually oxidized to Fe^{+3} by the reaction:

$$14\ Fe^{+2} + 3.5\ O_2 + 14\ H^+ \rightarrow$$
$$14\ Fe^{+3} + 7\ H_2O \quad (2)$$

A critical factor in the oxidation of pyrite and the generation of acid mine waters is that Fe^{+3} is able to oxidize pyrite under anoxic subaqueous conditions at a much faster rate than does molecular oxygen, according to the reaction (Garrels and Thompson, 1960; McKibben and Barnes, 1986):

$$FeS_{2(s)} + 14\ Fe^{+3} + 8\ H_2O \rightarrow$$
$$15\ Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+ \quad (3)$$

Because at pH<3.5, reaction (2) is orders of magnitude slower than reaction (1), the oxidation of Fe^{+2} by oxygen is usually considered the rate-limiting step in pyrite oxidation (Singer and Stumm, 1970). However, the presence of acidophilic bacteria such as *Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans* greatly accelerate (by a factor of around 106) the abiotic oxidation rate (Singer and Stumm, 1970; Nordstrom and Alpers, 1999a), thus maintaining a high concentration of ferric iron in the system.
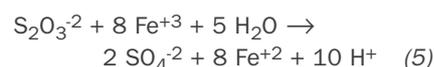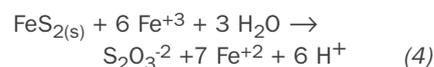
The overall process resulting from the combination of reactions *(2)* and *(3)* is traditionally known as the "propagation cycle" (Singer and Stumm, 1970), and along with reaction *(1)* depicts a model by which pyrite oxidation initially starts by reaction *(1)* with oxygen as the oxidant at near-neutral pH conditions, and as pH decreases to about 4 the oxidation of pyrite proceeds through reaction *(3)*. Oxygen will always be required to replenish the supply of ferric iron according to reaction *(2)*, so that the overall rate of pyrite oxidation in a tailings or waste pile or in a mine will largely depend on the overall rate of oxygen transport by advection and diffusion (Nordstrom and Alpers, 1999a; Ritchie, 2003).
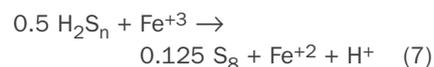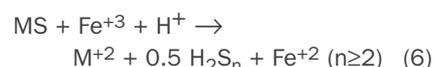
The concept of bioleaching: direct vs. indirect mechanism

The mechanisms by which acidophilic chemolithotrophic microorganisms obtain energy by oxidizing sulphidic minerals have been controversial for many years (Ehrlich, 2002). Two basic mechanisms, concerning the relative relationship between the mineral substrate and the microbial catalyst, the direct and the indirect attack, have been considered (Sand et al., 2001; Schippers et al., 1996; Schippers and Sand, 1999). In the direct attack, microorganisms solubilize mineral sulphides by attaching to their surface, facilitating an enzymatic oxidation by channelling electrons from the mineral to an appropriate electron acceptor (respiration). In the indirect attack, microorganisms are mainly involved in the regeneration of ferric iron, a strong oxidant, in the solution. This soluble ferric iron is responsible for the oxidation of exposed sulphidic minerals and other reduced compounds. The demonstration that ferric iron present in the cell envelop and/or the exopolymers of bioleaching microorganisms is responsible for the electron transfer from the sulphidic minerals to the electron transport chain (Gehrke et al., 1995), has clarified the situation. Based on this observation, Sand and coworkers proposed that because ferric iron is ultimately responsible for the oxidation of metal sulphides in both the direct and the indirect attack, there is no basic difference between these mechanisms. The difference seems to exist at the level of the chemical attack, which is dependent on the structure of the mineral substrates (Schippers et al., 1996; Schippers and Sand, 1999; Sand et al., 2001). Some metal sulphides, like pyrite (and also MoS_2 and WS_2), which can only be oxidized by ferric iron, undergo oxidation through the so-called thiosulfate mechanism,
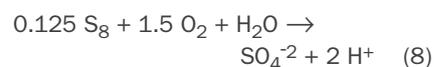
with sulphate as the main product (Schippers and Sand, 1999; Sand et al., 2001):

$$FeS_{2(s)} + 6\ Fe^{+3} + 3\ H_2O \rightarrow$$
$$S_2O_3^{-2} + 7\ Fe^{+2} + 6\ H^+ \quad (4)$$

$$S_2O_3^{-2} + 8\ Fe^{+3} + 5\ H_2O \rightarrow$$
$$2\ SO_4^{-2} + 8\ Fe^{+2} + 10\ H^+ \quad (5)$$

Most metal sulphides (including ZnS, $CuFeS_2$ and PbS) are susceptible to a proton acid attack as well as to ferric iron oxidation. They are oxidized through the so-called polysulphide mechanism (Schippers and Sand, 1999; Sand et al, 2001):

$$MS + Fe^{+3} + H^+ \rightarrow$$
$$M^{+2} + 0.5\ H_2S_n + Fe^{+2}\ (n{\geq}2) \quad (6)$$

$$0.5\ H_2S_n + Fe^{+3} \rightarrow$$
$$0.125\ S_8 + Fe^{+2} + H^+ \quad (7)$$

The produced elemental sulfur can be further oxidized to sulfuric acid:

$$0.125\ S_8 + 1.5\ O_2 + H_2O \rightarrow$$
$$SO_4^{-2} + 2\ H^+ \quad (8)$$

Although microbes do attach to sulphide mineral surfaces and can oxidize them (e.g., Edwards et al., 1998), it is generally accepted that the soluble ferric iron produced by microbial oxidation is responsible for the oxidation of other sulphides common in waste piles or tailings.

Thus, this model proposes that the principal microbial function in AMD systems during sulphide bioleaching is to keep the FeIII ions in an oxidized state and to generate sulphuric acid biologically to supply protons for hydrolysis attack. Based on laboratory experiments, Schippers and Sand (1999) estimated that up to 16% of the total sulphur released during pyrite oxidation was elemental sulphur (the rest being mainly SO_4^{-2}), whereas the oxidation of other sulphides like sphalerite, chalcopyrite or galena can result in the production of between a 92% and nearly a 100% of native sulphur, and only trace amounts of sulphate and polythionates ($S_4O_6^{-2}$, $S_5O_6^{-2}$).

Finally, Schippers et al. (1996) have demonstrated that the bacterial species involved in pyrite oxidation is a determining factor as regards to the sulphur species generated during the cyclic (indirect) leaching mechanism. Thus, in the case of pyrite bioleaching by Leptospirillum ferrooxidans, an organism without sulphur-oxidizing capicity,

besides the production of tetra- and pentathionate, a detectable accumulation of elemental sulphur may occur, whereas in the case of *Acidithiobacillus ferrooxidans*, only small amounts of elemental sulphur are detectable because of the microorganism's capacity to oxidize sulphur compounds.

"Iberian" microbes involved in pyrite and Fe(II) oxidation

The microbiological findings carried out until now in the acidic mine waters of the Iberian Pyrite Belt (e.g., López-Archilla and Amils, 1999; López-Archilla et al., 2001; González-Toril et al., 2003; Aguilera et al., 2006) have been mainly centered on the microbial (prokaryotic and eukaryotic) communities of the Tinto and (in a lesser extent) the Odiel river systems, which are both highly acidic (average pH values of around 2 and 3.5, respectively) and present metal contents in the order of hundreds to a few thousands mg/L. The iron-oxidixing, acidophilic, prokaryotic community of these waters is dominated by *Acidithiobacillus ferrooxidans and Leptospirillum ferroxidans*, two microorganisms that have been extensively studied in mine drainage environments, along with a minor presence of *Acidiphilium* spp. These microorganisms have been also found in pit lakes of the IPB such as San Telmo (Sánchez-España et al., 2007c) or Corta Atalaya (D.B. Johnson, University of Bangor, pers. com.). A study conducted in acidic effluents draining several mines (Sánchez-España et al., 2007) has revealed that these acidophilic microbes oxidize Fe(II) at field rates of about 10^{-7} mol L^{-1} s^{-1}.

Johnson (2006) studied the microbiology of an acidic and thixotrophic mine pond in Sao Domingos (Portugal) and reported an ecosystem composed of *L. ferrooxidans, Ferrimicrobium spp.* and *At. Ferrooxidans*. Rowe et al. (2007) have studied the microbiology of an acidic effluent (pH 2.5-2.7) draining an old cementation channel in Tharsis mine and found a complex community dominated by *Acidithiobacillus ferrooxidans* in the mine water, and by the heterotrophic acidophilic bacteria *Acidobacteriacae* and *Acidiphilium spp.* in the streamer growths, along with sulfidogenic bacteria in the lowest depths of the streamers.

More recently, Sánchez-España et al. (in press) have described the microbiological composition of an extremely acidic (pH 0.61-0.82) and hypersaline (e.g., 134 g/L SO_4^{-2}, 74 g/L Fe, 7.5 g/L Al, 3 g/L Mg, 2 g/L Cu, 1 g/L Zn) leachate which seeps from a pyrite pile in San Telmo mine (Huelva, SW Spain). This ultra-concentrated water accumulated in

fig 1. Examples of acid mine drainage generation in mines sites of the Iberian Pyrite Belt: (a) Esperanza mine portal (pH 2.6); (b) Lomero mine portal (pH 2.9); (c) Seepage from a waste pile in Aznalcóllar; (d) The acidic Tintillo river (pH 2.7-2.9) after collecting a number of different acidic leachates draining various waste piles near Corta Atalaya (Riotinto mines); (e) Precipitation of iron hydroxysulphates (red) and aluminum hydroxysulphates (white) in the confluence of the Tintillo acidic river and the Odiel river (pH 7-8); (f) Filón Norte pit lake (pH 2.4) in Tharsis mine. Photographs by Enrique López Pamo and Javier Sánchez España.

evaporative pools and formed crystals of Zn-rich melanterite ($Fe^{+2}SO_4 \cdot 7H_2O$). The microbiological investigation has revealed a surprisingly high biomass ($1.4x10^6$ cells mL^{-1}) and an exotic ecosystem composed of acidophilic, Fe-oxidizing archaea (mainly *Ferroplasma spp.*, representing 52% of the microbial population), and minor numbers of acidophilic bacteria (including *Leptospirillum spp.* (3.2%), *Acidithiobacillus spp.* (1.6%), and *Alfaproteobacteria* (2.8%), which is only comparable to those reported in similar waters with pH 0.5-1.0 from Iron Mountain, California (Edwards et al., 1999, 2000; Druschel et al., 2004).

AQUEOUS CHEMISTRY OF ACID MINE DRAINAGE IN THE IBERIAN PYRITE BELT

Effluents from piles, tailings and mine portals

In a previous paper, Sánchez-España et al. (2005a) studied 64 AMD discharges from 25 different mines of the IPB. These AMD-generating mine sites included waste rock piles (50%), mine adits (30%), tailings impoundments (10%), mine holes (7%), and mine pit lakes (3%) located in some of the largest and most important deposits of the IPB (Río Tinto, Tharsis, La Zarza, San Telmo, Sotiel-Almagrera) and many others of medium size (Lomero-Poyatos, San Miguel, Cueva de la Mora, Aguas Teñidas, Concepción, San Platón, Poderosa, Tinto-Sta Rosa). Some examples of mine drainage systems of the Iberian Pyrite Belt are illustrated in *Figure 1*.

The physico-chemical data reported for these acidic effluents suggested a highly variable nature as regards to seasonal continuity (permanent, seasonal or ephemeral drainage), water volume (0.1-220 L/s), acidity (200-30000 mg/L $CaCO_3$ eq.), redox conditions (Eh=400-800 mV), electric conductivity (EC=1000-24000 mS/cm), dissolved O_2 content (anoxic to O_2-saturated), or dissolved Fe(II) to total iron ratio (Fe(II)/Fe$_{tot}$=0.1-1).

Parameter	Units	Acid mine drainage		Acidic mine pit lakes	
		Average [a]	Extreme case [b]	Average [c]	Extreme case [d]
pH	S.U.	2.7	0.82	2,6	1.2
T	ºC	21	16.5	23	24
EC	mS/cm	7.9	-	5.3	55.6
Eh	m	627	625	782	584
DO	mg/L	3.8	-	7,6	0
DO	% sat.	42	-	93	0
SO_4	mg/L	7.460	134.200	4.000	41.900
Na	mg/L	32	37	31	78
K	mg/L	3	130	2	12
Mg	mg/L	414	3.036	357	1.957
Ca	mg/L	162	137	180	286
Fet	mg/L	1.494	74,215 [1]	332	36.675
Fe(II)	mg/L	801	40,600 [2]	15	32.500
Fe(III)	mg/L	476	28,630 [2]	312	3.950
Al	mg/L	386	7.556	123	1.919
Mn	mg/L	37	38	34	128
Cu	mg/L	64	1.945	20	1.350
Zn	mg/L	169	1.096	31	6.670
As	µg/L	2.123	303	91	158.730
Cd	µg/L	490	13.759	102	18.020
Co	µg/L	3.413	2.447	1.100	18.689
Cr	µg/L	118	52	38	1.295
Ni	µg/L	1.063	3.220	656	5.214
Pb	µg/L	61	108	122	5.402
Th	µg/L	23	376	6	-
Tl	µg/L	27	2.683	4	-
U	µg/L	64	981	7	-
V	µg/L	65	6.756	27	-

(a) Average chemical composition of 62 AMD waters from 25 mines of the Iberian Pyrite Belt (from Sánchez-España et al., 2005a); (b) Chemical composition of a pyrite leachate in San Telmo mine (taken from Sánchez-España et al., in press); (c) Average chemical composition of 22 acidic mine pit lakes (AML) from the IPB (excluding CA; Sánchez-España et al., 2008); (d) Chemical composition of the Corta Atalaya pit lake (Sánchez-España et al., 2008)
(1) Total iron measured by Atomic Absorption Spectrometry (AAS)
(2) Ferrous and Ferric iron measured on site by reflectance photometry

table 1. Chemical composition of acidic mine drainage and acidic mine pit lakes of the Iberian Pyrite Belt (the average value and an extreme case is provided in both cases).

The chemical composition of these waters is extremely variable, and may include extreme concentrations of dissolved SO_4 (up to 44 g/L) and metals (up to 7.7 g/L Fe, 2.6 g/L Al, 2.9 g/L Mg, 1.4 g/L Zn, 435 mg/L Cu and 440 mg/L Mn). Trace elements are also found to be significantly enriched in these acid waters (for example, maximum values of 17 mg/L As, 8 mg/L Cd, 48 mg/L Co, 17 mg/L Ni, and 725 µg/L Pb). Also, U and Th, with peak values around 1100 and 400 µg/L, respectively, in a waste pile near Corta Atalaya (Riotinto), were unusually concentrated. An average composition of typical AMD from the IPB is given in Table 1.

In general, these compositions are comprised within the range normally reported for AMD from VMS-type deposits (see Plumlee et al., 1999). The higher SO_4 and metal concentrations were usually found in the acid leachates from the waste piles of Corta Atalaya (Riotinto) and Filón Norte (Tharsis), and suggested an important oxidation and subsequent dissolution of pyrite and other sulphides (chalcopyrite, sphalerite, galena, arsenopyrite).

Some anomalous exceptions to the reported sulphate and metal concentrations can be eventually found in evaporative pools of ultra-concentrated water seeping from pyrite piles, as described recently in San Telmo mine (Sánchez-España et al., in press). A liquor found in this mine site showed a pH of 0.6 and extreme sulphate (134 g/L) and metal concentrations (e.g., 74 g/L Fe, 7.5 g/L Al, 3 g/L Mg, 1.9 g/L Cu, 1 g/L Zn; Table 1).

Pit lakes

The water chemistry of twenty-two pit lakes of the IPB has been recently reported in Sánchez-España et al. (2008). These pit lakes show surface areas ranging from less than 1 ha (e.g. Angostura, Herrerías) up to 28 ha (e.g., Aznalcóllar), and maximum depths from around 15 m (e.g., Concepción) to more than 100 m (e.g., San Telmo, Los Frailes). The pit lakes of the IPB show a large variety of water compositions, ranging from circumneutral and relatively low metal contents (e.g., Los Frailes pit lake, with pH 7.2, 0.07 mg/L Fe, 1 mg/L Al, 0.01 mg/L Cu, and 30 mg/L Zn) to extremely acidic and metal-enriched solutions (e.g., Corta Atalaya pit lake, with pH 1.2, 36.7 g/L Fe, 1.9 g/L Al, 1.3 g/L Cu and 6.7 g/L Zn; Table 1), with a general pattern of increasing dissolved solids content at decreasing pH. However, with the cited exceptions of Corta Atalaya and Los Frailes, a "typical" pit lake of the IPB shows a pH value around 2.6 (2.2-4.7), total Fe chiefly composed of Fe(III), average values of dissolved SO_4^{-2} around 4 g/L, and metal contents (average values) in

the order of 265 mg/L Fe, 123 mg/L Al, 34 mg/L Mn, 20 mg/L Cu, and 31 mg/L Zn, in addition to around 90 µg/L As, 100 µg/L Cd, 1100 µg/L Co, 650 µg/L Ni, and 120 µg/L Pb (Table 1).

The lithology of the rock substrate, with abundance of massive sulphide (especially pyrite) and aluminosilicates, and scarcity of carbonates, is undoubtedly determining the water chemistry of the IPB mine pit lakes. The high contents of Fe and SO_4^{-2} dissolved in the waters result from the oxidative dissolution of pyrite, whereas the rest of metals are thought to be the result of the subsequent dissolution of sphalerite (source of Zn, and minor Cd), chalcopyrite (source of Cu and Fe), galena (Pb), arsenopyrite (As, Fe), tetrahedrite-tenantite (Fe, Cu, Zn, As, Sb), rhodocrosite (Ca, Mn) and gangue aluminosilicates like feldspars (Al, K, Na, Ca), chlorite (Al, Fe, Mg, Co, Ni) and sericite-muscovite (Al, Na, K). In addition to these primary sources, the dissolution of secondary sulphate salts (see below) must have been another control of the pit lake water chemistry, especially during the initial flooding phases.

MINERAL PHASES ASSOCIATED TO AMD: ENVIRONMENTAL SIGNIFICANCE

As can be deduced from the above stated chemical compositions, iron, aluminum, magnesium and calcium are, by far, the most abundant metals dissolved in AMD (with Fe>Mg≈Al>Ca>>Zn>Cu>Mn), so that the minerals that are commonly formed in these AMD environments are chiefly Fe(II), Fe(III), Al, Mg and Ca sulphates and (oxy)hydroxysulphates. Some
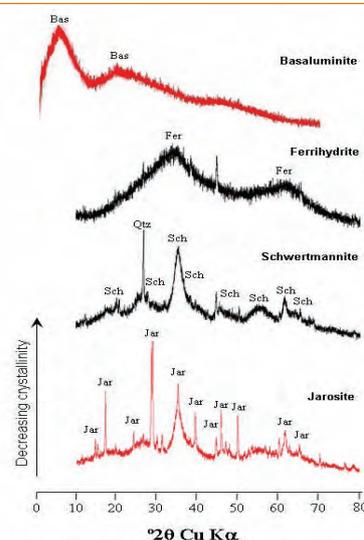
fig 2. XRD patterns of selected Fe(III) and Al precipitates found in AMD of the IPB (compiled from Sánchez-España et al., 2006a,b, with kind permission of Springer Science and Business Media).

Mineral	Formula	pH range*	Occurrence	Location	Abundance
Soluble iron sulphate salts					
Melanterite	$Fe^{+2}SO_4 \cdot 7H_2O$	<1-1.5	Efflorescences	Near pyrite sources	Very common
Rozenite	$Fe^{+2}SO_4 \cdot 4H_2O$	-	Efflorescences	Near pyrite sources	Very common
Szomolnokite	$Fe^{+2}SO_4 \cdot H_2O$	-	Efflorescences	Near pyrite sources	Very common
Copiapite	$Fe^{+2}Fe^{+3}_4(SO_4)_6(OH)_2 \cdot 20H_2O$	1.5-2.5	Efflorescences	Mining areas and margins of streams	Very common
Coquimbite	$Fe^{+3}_2(SO_4)_3 \cdot 9H_2O$	1.5-2.5	Efflorescences	Mining areas and margins of streams	Common
Rhomboclase	$(H_3O)Fe^{+3}(SO_4)_2 \cdot 3H_2O$	<1	Efflorescences	Mining areas, evaporative pools	Rare
Halotrichite	$Fe^{+2}Al_2(SO_4)_4 \cdot 22H_2O$	1.5-2.5	Efflorescences	Mining areas and margins of streams	Very common
Other soluble sulphate salts					
Epsomite	$MgSO_4 \cdot 7H_2O$	2-3	Efflorescences	Mining areas, margins of streams, pools	Very common
Hexahydrite	$MgSO_4 \cdot 6H_2O$	-	Efflorescences	Mining areas, margins of streams, pools	Very common
Gypsum	$CaSO_4 \cdot 2H_2O$	1-5	Efflorescences	Mining areas, margins of streams, pools	Ubiquitous
Iron hydroxides/hydroxysulphates					
Jarosite	$KFe^{+3}_3(SO_4)_2(OH)_6$	<2	Efflorescences, precipitates	Highly acidic effluents, pools and pit lakes	Very common
Natrojarosite	$NaFe^{+3}_3(SO_4)_2(OH)_6$	<2	Efflorescences, precipitates	Highly acidic effluents, pools and pit lakes	Common
Hydronium jarosite	$(H_3O)Fe^{+3}_3(SO_4)_2(OH)_6$	<2	Efflorescences	Mining areas	Rare
Schwertmannite	$Fe^{+3}_8O_8(SO_4)(OH)_6$	2.5-4	Fine-grained precipitates	AMD, AMD-impacted streams, pit lakes	Ubiquitous
Goethite	$\alpha\text{-}Fe^{+3}O(OH)$	2.5-7	Hard crusts	AMD, AMD-impacted streams, pit lakes	Very common
Ferrihydrite	$Fe^{+3}_5HO_8 \cdot 4H_2O$	5-8	Fine-grained precipitates	Confluences between AMD and streams	Common
Aluminum hydroxides/hydroxysulphates					
Gibbsite	$\gamma\text{-}Al(OH)_3$	>4.5-5.0	Fine-grained precipitates	Pit lakes, AMD-impacted rivers	Rare
Alunite	$KAl_3(SO_4)_2(OH)_6$	3.5-5.5	Efflorescences, precipitates	Mining areas and margins of streams	Common
Alunogen	$Al_2(SO_4)_3 \cdot 17H_2O$	<1	Efflorescences, precipitates	Mining areas	Rare
Jurbanite	$Al(SO_4)(OH) \cdot 5H_2O$	<4	Efflorescences, precipitates	Mining areas and margins of streams	Rare
Basaluminite	$Al_4(SO_4)(OH)_{10} \cdot 5H_2O$	>4.5-5.0	Fine-grained precipitates	Confluences between AMD and streams	Very common
Hydro-basaluminite	$Al_4(SO_4)(OH)_{10} \cdot 12\text{-}36H_2O$	>4.5-5.0	Fine-grained precipitates	Confluences between AMD and streams	Very common

* Common pH range of the acidic waters associated with these mineral phases

table 2. Relevant secondary minerals precipitating from acidic mine drainage and acidic mine pit lakes of the Iberian Pyrite Belt.

common Fe, Al, Mg and Ca minerals associated to, and precipitating from AMD of the IPB, along with their respective formulae and usual pH ranges of occurrence, are given in *Table 2*. This table includes highly crystalline sulphate salts (e.g., melanterite, rozenite, copiapite, halotrichite) formed by evaporative processes from very acidic brines in small pools or in the margins of AMD-impacted streams, as well as nearly amorphous compounds of Fe(III) (schwertmannite, ferrihydrite) and Al (hydrobasaluminite, basaluminite, gibbsite). Some examples of typical XRD patterns for some of these minerals are provided in *Figure 2*, and the occurrence of several efflorescent sulphates and (oxy)hydroxysulphates is illustrated in *Figure 3*. For a more comprehensive review about the metal oxides, hydroxides, sulphates and (oxy)hydroxysulphates precipitating in AMD environments, the reader is referred to the works of Nordstrom and Alpers (1999a), Jambor et al. (2000), or Bigham and Nordstrom (2000). A compilation of secondary sulphate salts found in the Riotinto mines and river was reported by Buckby et al. (2003), and a list of sulphates and (oxy)hydroxysulphates found in mines and AMD-affected streams of the Odiel fluvial system is given in Sánchez-España et al. (2005a).

Formation of evaporative sulphate salts near the pyrite sources

The formation of efflorescent sulphates from AMD waters occurs throughout all the year, although it is especially abundant during spring and summer. The mineralogy of these soluble sulphates is clo-

sely associated with their spatial distribution and the pH of the brines from which these salts are precipitated (Nordstrom and Alpers, 1999a,b; Nordstrom et al., 2000; Jambor et al., 2000; Buckby et al., 2003; Velasco et al., 2005; Sánchez-España et al., 2005a; Romero et al., 2006). Thus, the Fe(II)-sulphates like melanterite, rozenite or szomolnokite are dominant in isolated and highly concentrated pools near the pyrite sources, under conditions typical of green, ferrous AMD with very low pH (melanterite is commonly found in close association with waters with pH below 1, whereas rozenite and szomolnokite form by partial dehydration of the former). On the other hand, mixed Fe(II)-Fe(III), and/or Fe(III)-Al sulphates like copiapite, coquimbite or halotrichite, are common in the margins of rivers impacted by AMD, where iron has been partially oxidized and the pH is slightly higher (typically between 1.5 and 3). These sulphates have been observed to follow a paragenetic sequence of dehydration and mineralogical maturation, with *melanterite > rozenite > szomolnokite > copiapite > coquimbite > rhomboclase > halotrichite (Nordstrom and Alpers, 1999a,b; Jambor et al., 2000; Nordstrom et al., 2000; Buckby et al., 2003; Velasco et al., 2005).*

In the Iberian Pyrite Belt mining district, many evaporative sulphate salts have been reported from mine sites and from the margins of rivers severely affected by AMD pollution such as the Tinto and Odiel rivers (e.g., García García, 1996; Hudson-Edwards et al., 1999; Buckby et al., 2003; Velasco et al., 2005; Romero et al., 2005; Sánchez-España et al., 2005a, and in press). In the margins of

acidic effluents, these soluble metal sulphates are usually found as botryiodal (colliform-like) efflorescences of variable colour (turquoise blue to emerald green in the case of melanterite, white in the case of szomolnokite, orange to yellow in the case of the epsomite-hexahydrite series; *Figure 3a-c*), being normally zoned from the inner to the outer zones, and suggesting a paragenetic sequence of sulphates with distinct solubilities and degrees of dehydration. They are rarely found as monomineralic phases, and most commonly consist in mixtures of Fe(II)-Fe(III)-Al-Mg hydrated sulphates. Gypsum is also very frequent as acicular crystals and efflorescences in mine adits and waste piles (Figure 3d). Stalactites composed of gypsum±copiapite±jarosite have been observed at some AMD discharge points.

Chemical analyses of mixtures of these sulphates have revealed very high metal contents (e.g., average values of 2,800 ppm Cu and 9,000 ppm Zn, with Zn values eventually reaching percent units; Sánchez-España et al., 2005a). On the other hand, As contents of the sulphates are very low (195 ppm on average), whereas Co, Ni and Cd show average values of 240, 155 and 30 ppm, respectively.

Because these sulphates are highly soluble, the first rainstorm events taking place in the early autumn usually imply the re-dissolution of large amounts of these salts accumulated during the spring-summer, and the subsequent incorporation of toxic metals to the rivers. Therefore, seasonal cycles of
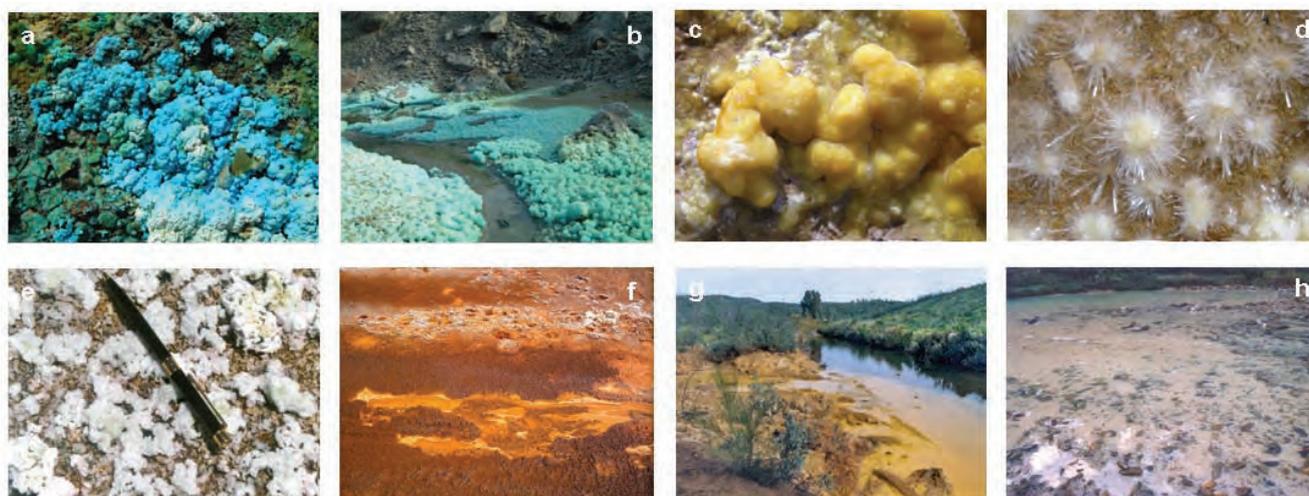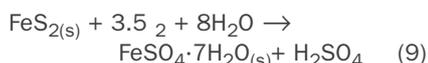
fig 3. *Efflorescent sulphates and iron-aluminum (oxy)hydroxysulphates precipitating from AMD systems of the IPB: (a) Cu-rich melanterite, rozenite and szomolnokite forming from an acidic discharge in the Cantareras mine (Tharsis); (b) Zn-rich melanterite formed by evaporation of extremely acidic (pH 0.6) seepage emerging from a pyrite pile in San Telmo mine; (c) Colliform-like epsomite and hexahydrite near the Lomero mine portal; (d) acicular crystals of gypsum formed in a Ca-rich acidic effluent in Lomero mine; (e) hexahydrite and halotriquite in San Telmo mine; (f) Jarosite deposit (light orange) which is partly transformed into goethite (dark orange to brown); (g) Schwertmannite precipitates in the confluence of an acidic effluent with a pristine stream (Lomero mine); (h) Hydrobasaluminite precipitates deposited on the streambed of the AMD-impacted El Escorial creek (pH 4.5) near Riotinto mines. All photographs by Enrique López Pamo and Javier Sánchez España except (b) which is courtesy of Francisco Velasco Roldán.*

precipitation/re-dissolution of salts can seriously determine the water quality of AMD-impacted rivers. As an example, a seasonal pattern of background Cu and Zn values during the summer, followed by sharp increases in their concentrations during the first rainfalls in autumn, has been reported in rivers draining the IPB province (e.g., Tinto and Odiel rivers; Olías et al., 2004) and in many other mine districts (e.g., Alpers et al., 1994).

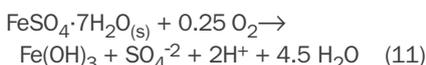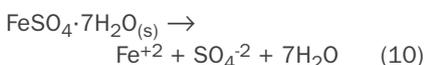*The formation-dissolution-precipitation cycle of melanterite in pyrite piles*

The formation-dissolution-precipitation cycle of melanterite represents an important control of the aqueous composition of the acidic leachates draining pyrite piles. When oxygen and moisture are available, melanterite can be directly formed on the pyrite grain surfaces by the reaction:

$$FeS_{2(s)} + 3.5\ _2 + 8H_2O \rightarrow$$
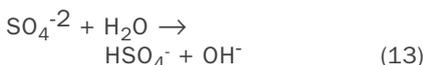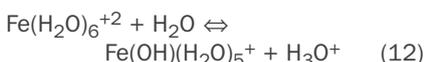$$FeSO_4 \cdot 7H_2O_{(s)} + H_2SO_4 \quad (9)$$

This mineral can either persist if the ambient humidity conditions are appropriate, or be transformed to less hydrated forms of ferrous sulphate such as rozenite ($FeSO_4 \cdot 4H_2O$) or szomolnokite ($FeSO_4 \cdot H_2O$) or even mixed Fe^{+2}-Fe^{+3} salts like copiapite (Fe^{+2}-$Fe^{+3}(SO_4)(OH)_2 \cdot 20H_2O$) (Nordstrom and Alpers, 1999a,b; Frau, 2000), but regardless of the final mineral phase considered, these solids always store large amounts of $Fe^{+2}(\pm Zn \pm Cu)$, SO_4 and acidity in solid form, which are readily released during flushing, thus originating very acidic and ferrous

iron-rich water in the piles.

Apparently, the simple dissolution of melanterite through reaction (10) does not produce acid, unless coupled with oxidation of Fe(II) and hydrolysis/precipitation of a ferric iron hydroxide (11):

$$FeSO_4 \cdot 7H_2O_{(s)} \rightarrow$$
$$Fe^{+2} + SO_4^{-2} + 7H_2O \quad (10)$$

$$FeSO_4 \cdot 7H_2O_{(s)} + 0.25\ O_2 \rightarrow$$
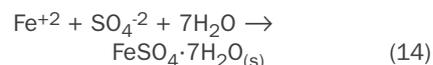$$Fe(OH)_3 + SO_4^{-2} + 2H^+ + 4.5\ H_2O \quad (11)$$

However, laboratory experiments carried out by Frau (2000) have demonstrated that the simple dissolution of melanterite is a fast acidity-producing mechanism without the participation of Fe^{+2} oxidation. This author explained the production of acidity by the coupled reactions of Fe^{+2} hydrolysis (12) and the SO_4^{-2}/HSO_c^- buffer system (13):

$$Fe(H_2O)_6^{+2} + H_2O \Leftrightarrow$$
$$Fe(OH)(H_2O)_5^+ + H_3O^+ \quad (12)$$

$$SO_4^{-2} + H_2O \rightarrow$$
$$HSO_4^- + OH^- \quad (13)$$

The acid $Fe(H_2O)_6^{+2}$ ($K_a=10^{-9.5}$) is stronger than the base SO_4^{-2} ($K_b=10^{-12.1}$; Stumm and Morgan, 1996), so that the dissolution of melanterite is an acidity-generating process.

Once the acidic solutions emerge from the piles to the surface, flow downstream and accumulate in pools, the water is partly evaporated and therefore all solutes (including H^+) are re-concentrated. If the Fe^{2+} and SO_4^{-2} concentra-

tions reach the solubility product constant for melanterite, this mineral may precipitate from the solution through reaction (14) until chemical equilibrium is attained:

$$Fe^{+2} + SO_4^{-2} + 7H_2O \rightarrow$$
$$FeSO_4 \cdot 7H_2O_{(s)} \quad (14)$$

The presence and environmental significance of melanterite has been widely reported in the IPB mining district. For example, Buckby et al. (2003) reported the presence of melanterite in the banks of the Tinto river which had apparently precipitated from a highly acidic water (pH≈0.4) draining a pyritic waste pile. Velasco et al. (2005) have also reported melanterite and rozenite forming directly from pyrite oxidation in a dried pool adjacent to a pyrite pile in the San Miguel mine, although these authors did not include water analyses in their study. The role of these sulphate efflorescences in the storage and transport of trace elements in stream waters polluted by acid mine drainage in Peña del Hierro mine, has been also reported by Romero et al. (2006). More recently, Sánchez-España et al. (in press) have reported the occurrence of melanterite crystals directly formed in green pools of extremely acidic water (pH≈0.6) in San Telmo mine (*Figure 3b; Table 1*). This acidic liquour was close to saturation with respect to melanterite, and its composition was found to be influenced by dissolution of this mineral.
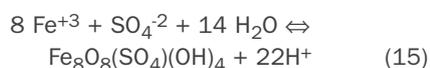
Mineral phases controlling the solubility of Fe(III) and Al

Although magnesium and calcium are

usually very abundant in most acidic effluents and pit lakes of the IPB, these elements are highly soluble and commonly behave conservatively, only precipitating as efflorescent sulphates (mostly as epsomite and gypsum, respectively) in evaporative pools or margins of acidic effluents and AMD-impacted rivers. Conversely, iron and aluminum are much less soluble and precipitate as the pH of the acidic discharges is increased. At pH values below 2, both iron and aluminum are chiefly dissolved, and these metals may only precipitate from highly concentrated brines from evaporative pools, where oversaturation of secondary sulphates (e.g., melanterite, copiapite, halotrichite, jarosite, alunogen) is eventually reached. As pH increases (for example, by partial neutralization during mixing with pristine streams), iron is hydrolyzed and precipitates at pH>2.2, whereas Al tends to be hydrolyzed at pH~4.5-5.0 (Nordstrom and Alpers, 1999a; Bigham and Nordstrom, 2000; Figure 3f-h). The formation of these mineral phases plays an important role in the geochemical evolution of the AMD and pit lakes, as discussed below.

Iron (oxy)hydroxysulphates

The solid formed by precipitation of Fe(III) at pH 2.5-3.5 during mixing and neutralization of the AMD solutions of the IPB is usually schwertmannite (Sánchez-España et al., 2005a, 2006a,b, 2007b, 2008). This mineral is a poorly crystallized iron oxyhydroxysulphate whose formation from acid-sulphate waters is described as follows (Bigham et al., 1994, 1996; Bigham and Nordstrom, 2000):

$$8\ Fe^{+3} + SO_4^{-2} + 14\ H_2O \Leftrightarrow$$
$$Fe_8O_8(SO_4)(OH)_4 + 22H^+ \qquad (15)$$

In addition to schwertmannite, some other minerals of Fe(III) have been recognized, with a close relation between their occurrence and the water pH *(Table 2)*. Jarosite is usually favoured to precipitate from very acidic solutions *(Figure 3f)*, normally at pH<2. Schwertmannite precipitates near the discharge points at pH 2.5-3.5 *(Figure 3g)*, whereas ferrihydrite usually forms in fluvial environments (as in the confluences between AMD and unpolluted rivers) at pH>5. These three minerals are meta-stable with respect to goethite, which is the most stable form of Fe(III) at low temperature (Bigham et al., 1996; Bigham and Nordstrom, 2000). Goethite can also precipitate from AMD, although its presence in the particulate fraction of AMD-impacted waters is very

fig 4. Examples of iron terraces formed in mine drainage systems of the IPB: (a) Tintillo river (near Corta Atalaya, Riotinto mines); (b) Perrunal creek (near La Zarza mine); (c) acidic effluent in the Filón Norte pit lake (Tharsis mine); (d) Acidic effluent in the Lomero mine portal. These terraced iron deposits are mineralogically dominated by schwertmannite, also containing minor amounts of other iron minerals (jarosite, goethite), gypsum, as well as algal and bacterial biofilms and plant debris (modified from Sánchez-España et al., 2007b). Photographs by Enrique López Pamo.

minor in relation to schwertmannite or ferrihydrite.

The chemical composition of schwertmannites analyzed in the IPB district includes minor amounts of SiO_2 (0.4-3.8 wt.%) and Al_2O_3 (0.7-3.0 wt.%), which suggests either (1) some silicate (clay) contamination of samples, and/or (2) some degree of sorption/coprecipitation of Si and Al onto the schwertmannite particles. Samples formed by titration of acid solutions in the laboratory have shown SiO_2 contents of 0.4-1.5%, which strengthens the second possibility. Average compositions of the analyzed Fe minerals also include significant trace element contents (e.g., 23-12770 ppm As, 80-4800 ppm Cu, 5-6230 ppm Zn, Sánchez-España et al., 2005a, 2006b). This suggests variable sorption of dissolved trace metals onto the schwertmannite, ferrihydrite and jarosite mineral surfaces.

Iron terraces forming in AMD effluents

An outstanding example of iron precipitation in AMD systems is the case of the iron terraces, which are unique geomicrobiological systems which can provide highly relevant information about the interaction between microbes and their surrounding aqueous environments *(Figure 4)*. These singular systems can represent, additionally, potential models for the study of ancient geological formations (e.g., banded iron formations, stromatoli-

tes; Brake et al., 2002, 2004), having been also proposed as models for the cycling of iron on Mars (e.g., Fernández-Remolar et al., 2004). Geochemical, mineralogical, morphological and microbiological evidences obtained in the highly acidic and Fe-rich Tintillo river (Riotinto mines, Huelva; Sánchez-España et al., 2007b; Figures 1d and 4a) suggest that a number of organic and inorganic processes appear to control the formation and internal arrangement of these iron terraces *(Figure 4a)*. The photosyntetic production of dissolved oxygen by eukaryotic microorganisms (green algae, euglenophites and diatoms), and the iron-oxidising metabolism of acidophilic prokaryotes are critical factors for the formation of TIFs, whereas abiotic parameters such as water composition, flow rate and velocity, or stream channel geometry, also appear to be essential variables.
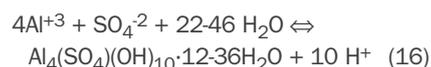
Aluminum (oxy)hydroxysulphates

If compared with the Fe(III) solids, the aluminum minerals formed at pH~4.5-5.0 in the IPB mine sites are not so well characterized. These solids are nearly amorphous to XRD, although two broad reflections (near 7 and 20 $^o2\theta$) are usually recognized by XRD *(Figure 2)*.

This diffraction pattern, along with their chemical composition, suggest that these waite Al precipitates probably consist of poorly ordered hydroxysulpha-

tes with composition intermediate between hydrobasaluminite and basaluminite (Figure 3h; see Bigham and Nordstrom (2000) and Sánchez-España et al. (2006b), and references cited therein). Alunite and aluminite have been also suggested to precipitate from waters with high concentrations of Al and sulphate (0.1M and 0.4M, respectively), although both minerals are rarely found as direct precipitates).

Hydrobasaluminite is metastable with respect to basaluminite, which forms by dehydration of the former. Basaluminite is a common Al hydroxysulphate in mine drainage environments, although it also tends to be transformed to alunite during maturation or heating (Bigham and Nordstrom, 2000). The hydrolysis of Al^{+3} to form hydrobasaluminite may be written as follows:

$$4Al^{+3} + SO_4^{-2} + 22\text{-}46\ H_2O \Leftrightarrow$$
$$Al_4(SO_4)(OH)_{10}\cdot12\text{-}36H_2O + 10\ H^+ \quad (16)$$

The formation of this mineral during neutralization of AMD can also imply a significant removal (by sorption) of toxic trace elements (e.g., Cu, Cr, Zn, U, etc.) from the aqueous phase (Sánchez-España et al., 2006b).

Natural attenuation of metal concentrations due to metal precipitation and sorption

Downstream from the sources, the geochemical evolution of AMD is usually controlled by *(1)* oxidation of Fe(II) to Fe(III), *(2)* progressive pH increase and dilution of metal concentrations by mixing with pristine waters, *(3)* hydrolysis and precipitation of different metal cations (e.g., Fe^{+3}, Al^{+3}) as pH increases, and *(4)* sorption of different trace elements (As, Pb, Cr, Cu, Zn, Mn, Cd) onto the solid surfaces of precipitated metal hydroxides/hydroxysulphates. The pH-dependent sequences of precipitation and sorption are very similar and follow the order:
Fe(III) > Pb > Al > Cu > Zn > Fe(II) > Cd (Dzombak and Morel, 1990; Nordstrom and Alpers, 1999a). The overall result of these processes represents a mechanism of natural attenuation, as has been shown in AMD-impacted rivers of the IPB (Sánchez-España et al., 2005b, 2006a, 2007a, 2008).

As an example of this self-mitigating capacity, the graphs provided in *Figure 5* show the spatial evolution of metal loadings in an acidic effluent emerging from a waste-pile in Tharsis mine (Sánchez-España et al., 2005b). This

effluent emerged with a pH of 2.2, and subsequently converged with a number of small creeks of unpolluted water, thus provoking a slight but progressive pH increase from around 2 to values close to 5. This pH increase allowed the precipitation of Fe(III) (mostly schwertmannite) during the first 11 km of the AMD course (pH<3), and of Fe(III) and Al compounds (Al as amorphous hydro-basaluminite) during the next 9 kms of the stream course (pH 3-5). The evolution shows that the precipitation of Fe(III) resulted in a strong decrease of the total iron loading to around a tenth of its initial content at only 10 km from the source. The precipitation of Al compounds in the last reach also accounted for an important loss of the Al loading. Interestingly, both the Fe and Al solids acted as efficient sorbents for a number of trace elements. Arsenic (present mainly as $HAsO_4^{-2}$ species, as suggested by geochemical modelling with PHREEQC) showed a strong tendency to be adsorbed by the ferric iron colloids at low pH (<3), having been totally removed from the water at less than 10 km from the discharge point. Other trace metals such as Cr(VI) (mainly present as $HCrO_4^-$), was significantly sorted onto the Al compounds formed at pH~4.5-5, also implying a total scavenging of this toxic element at 20 km from the source. Finally, divalent metal cations like Cu^{+2}, Zn^{+2} and Mn^{+2} behaved conservatively until pH~5, and then, they were only slightly removed by sorption onto the Al minerals during the final reach.

Such metal scavenging may imply important water quality improvements at a basin scale. For example, it has been estimated that only 1% of the total Fe and As dissolved load and around 20-40% of the total Al, Mn, Cu, Zn, Cd, Pb and SO_4 dissolved load initially released from the mine sites, was transferred from the Odiel river basin (including more than 25 studied mines) to the Huelva estuary in 2003 (although this still represented very high metal fluxes; Sánchez-España et al., 2005a). Most of the iron and arsenic load seems to remain in solid form near the pyrite sources within the mines, mainly in ochreous Fe(III) precipitates covering the stream channel, whereas the rest of metal cations (Al, Cu, Zn, Mn) migrate further downstream.
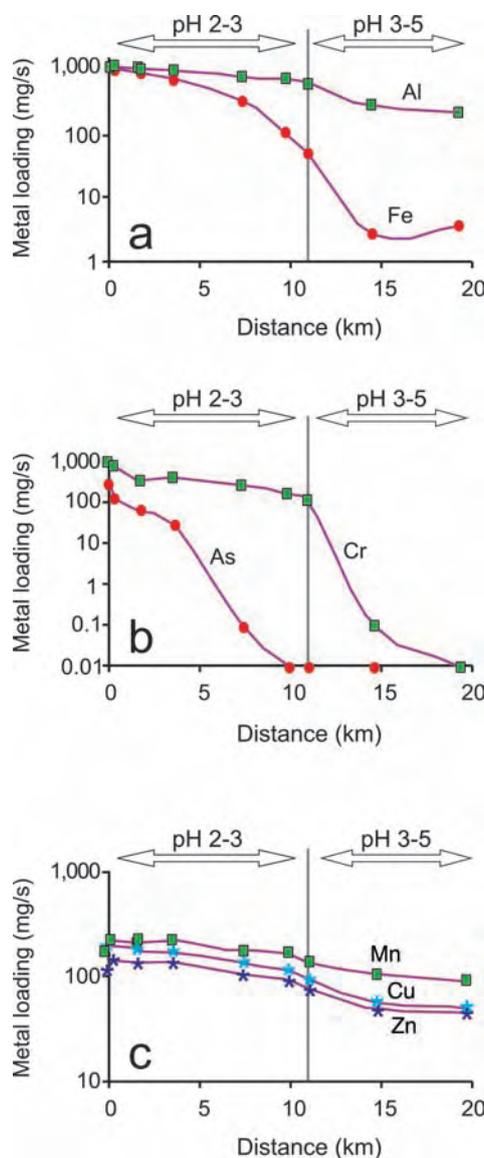

fig 5. *Spatial evolution of metal loadings of an acidic mine effluent in Tharsis mine: (a) Fe and Al; (b) As and Cr; (c) Cu, Zn, and Mn. Metal loadings calculated from analyzed aqueous metal concentrations and measured flow rates at distinct sampling stations downstream from the source point (modified from Sánchez-España et al., 2005b, with kind permission of Springer Science and Business Media).*

CONCLUSIONS

The microbially-catalyzed oxidation of pyrite and other sulphides present in piles, tailings, pits, shafts and galleries of the presently abandoned mines of the Iberian Pyrite Belt, generates an important volume of highly acidic and metal-polluted water which drains the mining areas and transport this acidity and metal content to streams, rivers and dumps, thus provoking and important environmental damage as regards to the water quality of the water resources. The singular chemical composition of the acidic mine waters, dominated by a low pH and high concentrations of sulphate and metals (especially Fe and Al), gives rise to a number of

characteristic mineral phases that precipitate downstream from the discharge points as the acidic waters are neutralized by mixing with pristine waters (e.g., schwertmannite at pH>2.5, hydrobasaluminite at pH>4.5) and/or by evaporation in the margins of streams or in pools (e.g., eflorescent sulphate salts like melanterite, rozenite, epsomite, hexahydrite, coquimbite, halotrichite, copiapite, etc.). The iron and aluminum precipitates usually sorb trace metals and are thus responsible for a certain degree of natural attenuation, although this self-mitigating mechanism can be reversible and the trace metals may be released to the solution phase as the mineral phases are mineralogically matured (e.g., transformed to more stable phases). The sulphate salts are also temporal sinks of acidity and metals (especially Fe, Al, Cu and Zn), but these elements are readily re-incorporated to the aqueous phase due to redissolution of these sulphates during rainstorm events. The problem of acid mine drainage in the IPB is of regional scale, and any attempt to mitigate or attenuate its environmental impact should be afforded by all the government authorities involved in decision making and environmental quality regulation.

ACKNOWLEDGEMENT

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