THE IBERIAN PYRITE BELT

"Corta Atalaya", Río Tinto Mines (Huelva).
The Iberian Pyrite Belt is located in the SW of the Iberian Peninsula, comprising part of Portugal and of the provinces of Huelva and Seville in Spain. It forms an arch about 240 km long and 35 km wide between Seville and the proximities of Grândola in Portugal. Geologically, it belongs to the South Portuguese Zone, the southernmost of the zones in which the Iberian Massif is divided. The Iberian Pyrite Belt is one of the most important volcanogenic massive sulphide districts in the world, and has been mined during more than 5000 years.

Mining in the Iberian Pyrite Belt was very important in Tartessian and Roman times, working the oxidation and cementation zones of the deposits for gold, silver and copper. After centuries of almost complete inactivity, the mines were again worked during the XIX and XX centuries, focusing the production on copper and sulphuric acid. At the end of the XX century and up to the present day, mining activity has intensively worked the base metals, gold and silver. Between 2005 and 2007 there was no mining in Spain, although the activities are being retaken in Las Cruces (Seville) and Agudas Teñidas (Huelva), and different viability and exploration projects are under development such as those in La Zarza, Rio Tinto, Lomero Poyatos or Masa Valverde. In Portugal, mining continued in Neves Corvo, and Aljustrel has been reopened. Figure 1 shows the geological map of the Iberian Pyrite Belt with the location of the main deposits developed.

The Pyrite Belt also sets a worldwide example of the environmental impact caused by long-lasting and intensive mining development. Continued works for more than 3000 years have modified the landscape and caused a steadily increasing pollution of water resources at a regional scale. The generation of acid waters from the erosion of massive sulphides and mine waste washing, and the drainage of mine waters have originated extremophile ecosystems unique in the world. The natural or anthropogenic character of this phenomenon in the basins of the Tinto and Odiel rivers is still debated, but the prevailing idea is that, in any case, it is an environment to be preserved.

The stratigraphic sequence of the Iberian Pyrite Belt (Figure 2) is relatively simple. It begins with a basal unit (Phyllite-Quartzite Group or PQ Group) with more than 2000 m of slate and sandstone with siliciclastic shelf facies and of Late Devonian age. The PQ Group is overlain by the Volcano-Sedimentary Complex (CVS, Late Devonian-Early Carboniferous), reaching a thickness of 1300 m and deposited in an intrac-ontinental basin during the oblique collision of the South Portuguese Zone (Avalonia?) against the Iberian Massif (Gondwana). The volcanism of the Pyrite Belt shows compositions from basalt to rhyolite. The most felsic terms dominate, as domes and sills associated to volcanoclastic deposits with similar composition, as well as slate and chemical sediments. The Culm Group diachronically lays on the CVS, and consists of a synorogenic flysch with an Early Carboniferous age. The whole series is affected by very low degree metamorphism and a fold and thrust tectonic (“epidermic belt”) within the context of Variscan Orogeny (Silva et al., 1990; Quesada, 1996).

Most of the mineral deposits in this area consist of massive sulphides within the Volcano-Sedimentary Complex (e.g., Leistel et al., 1998; Carvalho et al., 1999). Overall, massive sulphides display the typical structure of volcanogenic massive sulphide deposits: a lens of massive sulphides overlays a wide zone with rocks affected by an important hydrothermal altera-
tion. In its core there is a network (“stockwork”) of sulphide-rich veins considered as the zone which channeled hydrothermal fluids on their way out to exhalation at the sea bottom or a favorable level. The mineral paragenesis is dominated by pyrite, with more accessory proportions of sphalerite, galena and chalcopyrite, together with a wide variety of minerals. There are two main types of mineralization. In the southern zone, large pyrite-rich slate-hosted deposits prevail, considered as exhalative deposits and formed in third order marine basins by brine accumulation and biogenic activity processes. The second mineralization type prevails in the northern zone and is characterized by massive sulphides hosted in pumice-rich volcanoclastic rocks in the marginal areas of domes. These deposits are richer in base metals than the southern ones and are considered to form by replacement of the volcanic rocks (Tornos, 2006). Together with the massive sulphides there are stratabound ore deposits of manganese, and abundant veins of the most diverse metals.

Broadly speaking, the massive sulphides are interpreted as precipitates from circulation of deep fluids balanced with the PQ Group, which is also the source of the metals and part of the sulphur. The massive sulphides would have precipitated by mixing these fluids with modified sea water, with most of the sulphate biogenically reduced to sulphur.

At a regional level, the formation of massive sulphides was determined by the Variscan transpressive tectonics. Crustal thinning and fault development facilitated the intrusion of basic magmas into the crust, increasing the geothermal gradient and generating acid magmas. These processes also favored the diagenetic and metamorphic accelerated evolution of the PQ Group with the expulsion of saline water basin fluids rich in metals, which joined the convective cells generated by the intrusion of acid magmas (Figure 3). The time overlap of these processes suited the founding of huge hydrothermal networks capable of washing out big amounts of metals and depositing them in specific environments, normally by mixing them with biogenically-reduced sulphur.

The supergene alteration of these massive sulphides originated cap-rocks or large gossan outcrops, usually enriched in Au-Ag. These gossans covered the massive sulphides and have been systematically developed since ancient times. They are massive and do not show any obvious zoning except for a meter-thick bed at the base, enriched with jarosite, where gold and silver concentrated to 6-30 g/T Au and 100-3000 g/T Ag.

The abundant deposits in the Pyrite Belt can be grouped in three zones according to their location and geological significance:

**Northern Zone:** It is the zone with the highest number of deposits, along a 26 km long and 5-10 km wide band. It includes small to medium size deposits, although it also includes the giant deposit of Aguas Teñidas. Base metal and gold contents make it the most attractive for mine prospecting. From west to east, the most important mines are: San Telmo, Lomero-Poyatos, east Aguas Teñidas, Cueva de la Mora, Monte Romero, Concepción, San Platón and San Miguel.

**Middle Zone:** The middle zone of the Pyrite Belt has the smallest number of massive sulphide deposits. There are only two, although they are the most important ones: La Zarza and Rio Tinto. The massive sulphides in Rio Tinto display intermediate charac-
teristics between those located in the northern and those in the southern zones of the Pyrite Belt.

Southern Zone: It includes most of the giant deposits: Aznalcollar–Los Frailes, Sotiel Migollas, Masa Valverde, Tharsis, and several tens of other smaller deposits. They share a series of common features such as slate host-rock, stratabound ore body, presence of a well defined underlying “stockwork”, lack of zonation of metal contents, and high pyrite content. Its formation corresponds to a single event of Late Famennian (Devonian) age, close to the boundary with the Carboniferous (González et al., 2002).

The San Miguel mine (Figure 4) has been chosen as representative of the Northern Zone. It is the best outcrop example in the Pyrite Belt of a stockwork and massive sulphides replacing volcanic rocks. Besides, it displays one of the most spectacular gossan of the area, with works from Roman times. The recent works began in 1851, and between 1851 and 1960 1,29 million tons of ore were extracted with a 2-3% Cu and 46% S (Pinedo, 1963). Copper content was very irregular, but increased significantly towards the supergene alteration zone. Most of the “gossan” has been recently worked by Minas de Rio Tinto Co.

The mine (Figure 5) worked several lenses of massive sulphides. The biggest one, San Miguel, is 200 m long with an average thickness of 10 m and 40 m maximum, and has been tracked to a depth of 155 m.

Geologically, the massive sulphides replace a volcanoclastic breccia marginal to a dacitic dome. They have coarse grain size with abundant quartz and chlorite inclusions. In detail, there is a gradation from a “stockwork” in chloritized and silicified dacite, to the massive sulfides (Figure 6). The upper contact is a thrust plane with slates and volcanoclastic rocks. In the easternmost part of the mine, the massive sulphides are covered by a thick gossan with a sharp contact with the massive sulphides. There are abundant rests of Roman mining in the gossan and cementation zone.

Rio Tinto mines (Figure 7) have been proposed as representative of the Middle Zone. It is one of the most famous mining districts in the world for the size of the mineralization and for its intense history: it has been worked discontinuously for about 5000 years by the Tartessians, Phoenicians, Romans, Arabs, British and Spanish.

The high geological interest of this mining district is because it is most probably the biggest sulphur anomaly on the Earth’s crust, with original tonnages around the 2500 million tons of mineralized rock in different degrees. A fifth of it was massive sulphides with an average content of 45% S, 40% Fe, 0.9% Cu, 2.1% Zn, 0.8% Pb, 0.5 g/t Au and 26 g/t Ag (García Palomero, 1992).

From the geological point of view, Rio Tinto district is located on a thrust sequence dipping to the south and folded and overthrust by the Culm Group (Mellado et al., 2006), creating a syncline structure (Rio Tinto Figure 4).
syncline) with an E-W direction. The local stratigraphy consists of:

- Slates and Quartzites of the PQ Group.
- Slates with interbedded basalt flows and volcanoclastic mafic rocks, intruded by rocks with the same composition (Siliciclastic Mafic Unit).
- Acid Unit, consisting of massive felsic rocks (dacities-rhyodacites), hyaloclastites and volcanoclastic rocks, at times rich in pumice, glass and crystals. They are also interbedded with slate.
- Dark slate with conglomerates, dominant in the lower part of the sequence. In the upper part there are purple and green slates, and the massive sulphides are beneath them, covered by a white chert level. This horizon has been dated as Early Tournaisian (Rodrígues et al., 2002) and therefore is more recent than the one over the massive sulphides of the Southern Zone of the Pyrite Belt, which is barren in the Rio Tinto area.

This apparently simple stratigraphy is complicated by the presence of abundant faults and thrusts, together with an overall hydrothermal alteration frequently masking the original structural relationships.

The mineralization is found either as dissemination or small veins in the stockwork areas (Figure 7) within volcanic rocks and slates, or as massive sulphide lenses lying atop or included in the stockwork zones, or in gossan areas representing the supergenic alteration of massive sulphides, sometimes up to 70 m thick.

The massive sulphides form three bands where discontinuous and subvertical lenses are lined up:

- Deposits located in the southern side of the structure, as well as in the so-called Southern Lode which includes the Southern Vein itself, San Dionisio and Atalaya.
- Deposits located north of Cerro Colorado, including the Northern Vein, Salomón, Lago and Quebrantahuesos, which are in the northern side of the structure.
- Deposits located further east (Planes-San Antonio)

There does not seem to be a continuity between the mineralizations of the Northern and Southern Lodes. Actually, what makes Rio Tinto different from other districts in the Pyrite Belt is the fact that the massive sulphides seem to be formed in two different environments. On one side, the mineralizations in Southern Lode and Planes-San Antonio are hosted in slates and have sedimentary structures, suggesting they were formed by exhalative processes in the sea bottom. However, the mineralizations in the Northern Vein hosted by dacite have a coarser grain and always display replacement structures with the hosting dacite.

The stockwork of Cerro Colorado is probably one of the biggest in the world, over a surface around 3 km². Generally, there seems to be a strong lithological control on the type of alteration. Mafic volcanic rocks and slates are only affected by chloritic alteration, whereas felsic volcanic rocks are mainly affected by a sericitic alteration, appearing the chloritic alteration just in the zones of the maximum alteration, commonly near faults. Overall, it seems that the chloritic alteration zones are enriched in copper, whereas those of sericitic alteration are enriched in zinc. The original structure the area has been severely modified by Variscan faults and thrusts.

The mineralization was supergenically altered and eroded during the Cenozoic. Originally, there was a gossan (Cerro Colorado) of 10-70 m deep (average, 30 m) mined between 1974 and 2002 together with the copper of the underlying stockwork (1973-1986). The gossan was rich in Au, Ag, Pb, Sb and Bi, and poor in Cu and Zn. Grades were approximately 79% Fe₂O₃, 1.2% Pb, small amounts of Cu and Zn, 1.8-2.5 g/t Au, and 35-45 g/t Ag. There is a transported gossan

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**Figure 7.** Geological map of the Rio Tinto area.

**Figure 8.** Aspect of the Northern Vein massive sulphides, grading to stockwork at the wall and at the back.
(Alto de la Mesa) around 10 m thick with insignificant metal content. It is interpreted as a result of chemical weathering in a river basin controlled by a fracture (Almodóvar et al., 1997).

Together with the geological aspects, Rio Tinto shows abundant archaeological and historical remains from its extended mining history. The ruins of Cerro Salomón are particularly interesting, displaying the rests of a village and a smelting industry of the Iron Age (VIII-VI B.C.) dedicated to the production of silver, either Phoenician or from the natives who supplied them with metals. The Rio Tinto museum hosts many objects from Roman times, and there is also a necropolis and abundant mining industry remains.

Currently, the mining train, the Buenavista mining neighborhood, and the remains of mining facilities are of tourist interest. Because of its importance, Atalaya open pit is noteworthy, as most of the rocks from Rio Tinto can be seen there. The pit began to be worked in 1900, and the works existing inside the area started collapsing. It was under operation until 1994, when the sulphide ore was exhausted, although there are around 45 Mt of massive sulphides at depth, and an undetermined volume of copper-rich stockwork which has been tracked down to a 450 m depth.

The mining district of Tharsis, in the Southern zone, is especially remarkable and another of the big districts of the Pyrite Belt (Figures 9 and 11). This mining district comprises 16 massive sulphide lenses with original reserves around 133 million tons. The massive sulphides are distributed along three E-W lines. The northern one includes the big masses of Northern Vein, San Guillermo and Sierra Bullones, as well as the small deposit of Poca Pringue. The central line includes Central Vein and Los Silillos, and the southern line includes the Southern Lode and Esperanza.

The biggest deposit is the one comprising the masses of Northern Vein (Figure 9), San Guillermo and Sierra Bullones, worked in the open pits of Filon Norte and Sierra Bullones, and from which 40 tons of massive sulphides, mainly pyrite, have been extracted. As a whole the minimum original tonnage is of 88 million tons with 46.5% sulphur, 2.7% zinc and lead, and 0.7% copper, although it is open in depth. The minimum orebody dimensions are approximately 1500 m long, 400 m wide and an average thickness of 80 m. These lenses which today appear separated were probably a single original mass which has been tectonically dismembered.

The structure of the area is defined by four major south-dipping tectonic units limited by thrusts. Each tectonic unit presents its own lithological and hydrothermal features, and the thrusts are marked by vein swarms rich in quartz veins. The more competent lithologies within each unit define tectonic lenses surrounded by slates and vein swarms in a ramp and flat structure. The tectonic reconstruction suggests that, except for the PQ Group, the sequence was inverted, so that the units currently lying on top of the massive sulphide were previously lateral to them.

From south to north, the structure is defined by: (a) slate and sandstone of the PQ Group, interpreted as a parautochthonous unit in contact with the overlying series by an out of sequence thrust; (b) the Lower...
Unit, which includes the massive sulphides and the host slate. Here, there are no volcanic rocks beneath the massive sulphides, except in the eastern part of the pit, where there are small volcanoclastic levels immediately underneath them; (c) the Intermediate Unit, overthrusting the previous unit, and made by slate intruded by basalt, completely espilitzed and ankeritized, and with bodies of hydrothermal breccias, and (d) the Upper Unit, made of rhyodacite sills intruding slate. The hydrothermal alteration here is accessory and consists of a sericitization and irregular silicification of the volcanic rocks.

The stockwork beneath the massive sulphides is included in a single zone of chloritic alteration of the slate. Included in the stockwork there are some replacement areas where the slate has been replaced by semimassive sulphides rich in coarse-grained pyrite. Besides the pyrite, there are also abundant minerals of As-Co-S, tellurides and gold (Marcoux et al., 1996; Tornos et al., 1998).

Tharsis mines were extensively worked by the Romans, leaving around 3.5 million tons of slag. They were rediscovered in 1853 by Ernesto Deligny and sold in 1867 to The Tharsis Sulphur and Copper Co. In the last years, mining activities were carried out by Nueva Tharsis, during which around half a million tons/year of pyrite were extracted to make sulphuric acid. Despite relatively high contents (2-10 g/t gold and 0.04-0.16% cobalt), the mineralization is irregular and the definition of a mineable body has not been possible. The Filon Norte open pit was the last pyrite mine to close in the Iberian Pyrite Belt, in December 2000.

In the southern strip, the gossan of Southern Lode was recently worked, developed upon almost completely oxidized massive sulphides. It had around 8 million tons with a content of 1.4 g/t gold and 27 g/t silver.

The mine of Soloviejo has been selected as the last representative example. Located in the northern sector (Ramírez Copeiro and Maroto, 1985), it was the biggest of a high number of small manganese deposits. Currently, none of them is worked. But in the end of the XIX century, Spain was the largest producer of manganese in the world, with more than 2/3 of the global production. Most of this production came from the lenses of manganese and jasper oxides (Figure 12) interbedded within the upper part of the purple slate of the Volcano-Sedimentary Complex. These stratabound manganese deposits are related to oxidizing environments and low-temperature exhalites, spatially and genetically independent from the massive sulphides.

The mineralization and associated jasper are hosted by purple slate underneath felsic volcanoclastic rocks and slates below the Culm Group. This level has channeled an important shear deformation, so deformation structures, breccias and quartz veins are very common. This deposit includes a primary mineralization dominant in depth, consisting of fine-grained rhodonite and rhodocrosite, with abundant sericite and chlorite replacing or interbedded within the jasper. The supergene alteration is economically more interesting and includes variable proportions of pyrolusite, romanechite, lithiophorite, vernadite, cryptomelane, todorokite and hematites (Jorge, 2000), which are especially abundant in the later fractures (Figure 13).
The oxidation and erosion, both natural and human-induced, of the massive sulphides and debris has meant an important environmental modification of the area. Water draining these orebodies is characterized by extremely acid pH, and carries important amounts of metals (Fe, Al, Zn, Cu, Mn, Cd, Co, Ni, etc.) leading to a very unusual trophic chain compared to what is common on the Earth’s crust (López-Archilla and Amils, 1999). The evolution of these waters, or the interaction with other kinds of water or underlying rocks, has led to a complex geochemistry currently under study (Sánchez España et al., 2005, 2006, 2007). As an example, we hereby select one of the many pollution cases related to acid water circulation: the Odiel river basin and its tributary the Tintillo or Agrio river (Figure 14).

The Odiel river (Figure 15) is a good example of the progressive pollution of an originally alkaline and clean river by the acid drainage from several middle-sized mines (Concepción, San Plató, Esperanza and Poderosa) and from the Tintillo or Agrio river. It is possible to see the formation of Fe$^{3+}$ (schwertmannite, ferrihydrite) and Al (basaluminite, gibbsite) precipitates.

The Agrio or Tintillo river (Figure 16) is a tributary to the Odiel and the best example of a river exclusively made of acid waters coming from mine waste lixiviation, mud ponds and mining galleries around the Atalaya open pit (Rio Tinto Mines). The river has a consistent pH around 2.8 in its 10 km course down to the confluence with the Odiel, where a series of geochemical processes take place, representing the

Figure 13. Aspect of the fault zone, with the oxidized mineralization at the Soloviejo Mine.

Figure 14. Distribution of the fluvial network in relation to some mining works. Marked in red are some of the most affected areas.

Figure 15. Odiel river after the confluence with the drainage from the Poderosa and El Soldado mines.
critical and irreversible pollution of the latter. The different geochemical behavior of the different metals can be seen (Fe, Al, Cu, Zn, Mn, Cd, Co, Ni), as well as the presence of spectacular travertine terraces of schwertmannite.