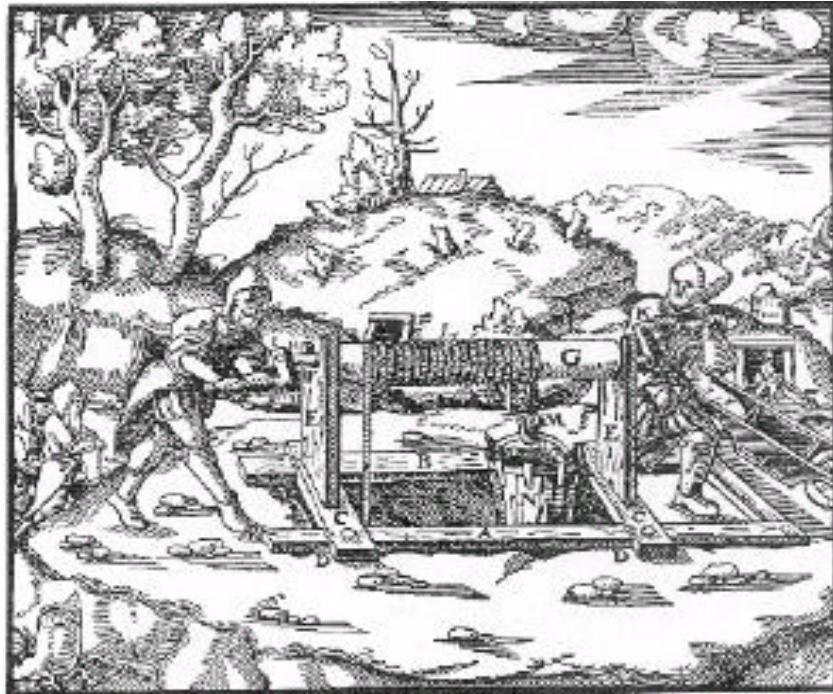


SELECTED TOPICS:
GEOLOGY AND MINERAL RESOURCES
OF THE IBERIAN PENINSULA



A—TIMBER PLACED IN FRONT OF THE SHAFT. B—TIMBER PLACED AT THE BACK OF THE SHAFT. C—POINTED STAKES. D—CROSS-TIMBERS. E—POSTS OR THICK PLANKS. F—IRON SOCKETS. G—BARREL. H—ENDS OF BARREL. I—PIECES OF WOOD. K—HANDLE. L—DRAWING-ROPE. M—ITS HOOK. N—BUCKET. O—BALE OF THE BUCKET.

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Geology of the Iberian Pyrite Belt, southern Portugal and Spain

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Introduction

The Iberian Pyrite Belt (IPB) is the largest volcanic-hosted massive sulfide (VMS) district in the world. The IPB is located in southern Spain and Portugal and forms the main portion of the South Portuguese Zone in the Iberian part of the Variscan Fold Belt (Barriga et al., 1997). The IPB extends eastward from Seville, Spain into southwest Portugal, forming an arcuate belt approximately 250km long and 60km wide of polymetallic deposits (Figure 1). Surface gossans up to 70 m thick commonly mark the position of massive sulfide mineralization. Gossans have been mined for copper, gold, and silver since the Chalcolithic era (4500-3599 B.C.) (Leistel et al., 1998).

VMS deposits are generally stratiform deposits of sulfide minerals that are precipitated from hydrothermal fluids at or below the sea floor, commonly in association with volcanic rocks and syngedimentary-exhalative manganese deposits (Strauss and Madel, 1974). These types of deposits tend to concentrate Fe, Cu, Zn, Pb, Au, and Ag with lesser amounts of Co, Sn, Ba, S, Se, Mn, Cd, In, Bi, Te, Ga, and Ge (Barrie and Hannington, 1999). The IPB represents one of the largest concentrations of S, Fe, Zn, Cu, Pb, and Sn in the world. Average composition of resources and reserves is 1.3% Cu, 2.0% Zn, 0.7% Pb, 0.5 g/t Au, 26 g/t Ag, 45% S, 40% Fe (Barriga et al., 1997).

The most economically important mines in the IPB are Rio Tinto, Tharsis, La Zarza, Perrunal and Sao Domingo (both no longer operational), Aljoustrel, Neves Corvo, and Lousal (Figure 1). Mining operations originally focussed on extraction of S, Cu, and Fe from shallow orebodies, however metallurgical advances since the early 1970's have allowed for increased exploitation of deeper deposits (Strauss and Madel, 1974).

The IPB contains more than 80 known massive sulfide deposits with more than 1700 Mt of ore. Total estimates (mined and reserves) in the IPB VMS include 14.6 Mt Cu, 13.0 Mt Pb, 34.9 Mt Zn, 46100 t Ag and 880 t Au. Surface and near-surface deposits have been mined out so that mining efforts must now be focussed to the deeper orebodies. Six mines are currently active in the IPB, these include La Zarza, Aznocolar-Los Frailes, Rio Tinto, and Tharsis (all in Spain) and Aljustrel (Neves Corvo) in Portugal. Ore grades are ~0.5% to 1.5% Cu (with 6% near Rio Tinto and 14.4% Cu+Sn in Neves Corvo) (Leistel et al., 1998).

Geological Setting

The IPB corresponds to a region of Upper Devonian to Carboniferous volcanic and sedimentary rocks (Figure 1,2) that are covered at the eastward and westward extension of the IPB by Tertiary-Quaternary alluvial and terrace deposits (Leistel et al., 1998). IPB stratigraphy is divided into three main units including the Phyllite-Quartzite Group, the Volcanic Siliceous Complex and the Flysch Group, from oldest to youngest, respectively (Carvalho et al., 1999). During Upper Devonian-Carboniferous time there was a transition from a passive margin sedimentary environment to a foreland basin (Quesada, 1998; Barriga et al., 1997). Basin subsidence in the area of the IPB was from northeast to southwest, and volcanism migrated from southwest to northeast (Barriga et al., 1997).

The Phyllite-Quartzite Group is mostly slate and quartzite with rare quartzitic conglomeratic units and limestone lenses in the upper part of the unit. The total thickness of the Phyllite-Quartzite Group is unknown but greater than 500m (Barriga et al, 1997; Strauss and Madel, 1974).

The Phyllite-Quartzite Group is overlain by the Volcanic Siliceous Complex, primarily submarine felsic to mafic volcanic and sedimentary rocks up to 800m thick. All major stratiform sulfide deposits are contained within the Volcanic Siliceous Complex (Strauss and Madel, 1974). The felsic volcanic rocks are mainly pyroclastic (submarine ashflow tuffs of dacitic-rhyolitic composition) with ignimbrites rare. Pyroclastic felsic rocks are grouped around the eruptive centers that occur along volcanic lineaments. (Barriga et al., 1997; Schermerhorn, 1970). Rhyolite domes are also common near major volcanic centers. Mafic volcanic rocks include diabase and pillow lavas. Radiolarian cherts are interstitial to basalt flows, indicating that mafic volcanism occurred subaqueously. Intermediate composition volcanic rocks are uncommon and concentrated in the north part of the belt (Carvalho et al., 1999; Barriga et al., 1997).

The Volcanic Siliceous Group sedimentary rocks include shale, graywacke, quartzwacke, impure quartzite, jasper, chert, radiolarite, and limestone lenses and nodules. Some of the siliceous units are important in that they are associated with major sulfide and manganese deposits (Carvalho et al., 1999; Barriga et al., 1997). The main host rocks for the polymetallic deposits include felsic tuffs and black shale units while manganese deposits are commonly found in jaspers (Barriga et al., 1997).

The Flysch Group overlies the Volcanic Sedimentary Complex and is extensive over most of the Southern Portuguese Zone, thinning from several kilometers thick in the west to less than 500m thick in the east (Strauss and Madel, 1974). The Flysch Group consists of thick turbidite sequences of graywacke and shale with local lenses of conglomerate that contain clasts of the mafic and felsic volcanic rocks of the Volcanic Siliceous Complex (Barriga et al., 1997; Carvalho et al., 1999).

Tectonic Features and General Structure

The IPB is one of five main structural regions of the Southern Portuguese Zone that are divided from north to south into 1) the Beja-Acebunches Ophiolite, which forms the boundary between the Southern Portuguese Zone and the Ossa Morena Zone 2) the Pulo do Lobo antiform, 3) The Iberian pyrite belt, 4) Baxio Alentejo Flysch Group, and 5) the southwest Portugal domain. The five structural regions that comprise the Southern Portuguese Zone are part of the southwestern portion of the Iberian Variscan fold and thrust belt, an arcuate belt with E-W structural trends in Spain changing to NW-SE in southern Portugal.

The Southern Portuguese Zone consists of a series of imbricate thrust sheets (Figure 3) with southwest-verging fold and thrust displacement (Barriga et al., 1997; Carvalho, et al., 1999; Quesada, 1998). Syn-sedimentary faulting and deformation was common during deposition and there were two main periods of NW directed folding and thrusting during the Hercynian Orogeny that involved oblique collision between the South Portuguese Plate and the Ossa-Morena Zone (Strauss and Madel, 1974; Barriga et al., 1997; Quesada, 1998). The Southern Portuguese Zone represents the southernmost tectonic unit in the Iberian Meseta (Strauss and Madel, 1974). Four main metamorphic zones are recognized in the SPZ with increasing metamorphic grade increasing in a northward direction from a zeolite facies in the south to greenschist facies in the Pulo Formation (Barriga et al., 1997).

Geotectonic Setting

The tectonic development of the Southern Portuguese Zone remains controversial with opinions ranging from an accretionary prism model related to N-directed subduction, an intracontinental back arc basin model, and NE-directed subduction followed by continental collision (Barriga et al., 1997). In general, massive sulfide deposits are thought to represent ancient mid-ocean ridge environments, bimodal arcs, or mature volcanic or continental arc settings (felsic-sedimentary systems) (Barrie and Hannington, 1999; Leistel et al., 1998). Geochemistry of lavas and sedimentological characteristics suggest that the tectonic setting during IPB emplacement was extensional and epicontinental (Liestel et al., 1998). Reconstruction of the geodynamic and geotectonic setting during emplacement of the IPB remains problematic due to the structural complexity resulting from the Hercynian Orogeny overprint on the southern Iberian Peninsula (Saez et al., 1996).

Sulfide Deposits

The IPB massive sulfide deposits are of Bimodal-Siliciclastic Type according to the volcanic-associated massive sulfide deposit classification scheme of Barrie and Hannington (1999). This type of VMS deposit typically has relatively equal parts of volcanic and siliciclastic rocks with felsic volcanic rocks more predominant than mafic volcanic rocks. The felsic rocks are generally calc-alkaline. Mafic rocks are generally tholeiitic (in the IPB there are alkaline basalts). Bimodal-siliciclastic VMS deposits contain the greatest ore tonnage of the VMS deposits, the largest deposits, lowest Cu and highest Pb contents of the five types of VMS deposits (Barrie and Hannington, 1999).

In the IPB, the main host rocks for polymetallic sulfide deposits are the felsic tuffs, tuffites and black shale units within the Volcanic Siliceous Complex (Barriga et al., 1997; Saez et al., 1996). Most sulfide deposits occur in clusters that may represent several hydrothermal vents associated with a single eruptive center or may be one deposit that has been cut into several pieces as a result of faulting or slumping. Massive sulfide generation in the IPB is thought to confirm the sea water convective model where hydrothermal fluids associated with submarine volcanic centers played an important role in mineral precipitation from sea water at or just below the sea floor (Figure 4) (Barriga et al., 1997).

Regional hydrothermal alteration is notable in igneous rocks of the Volcanic Siliceous Complex and in all host rocks of the massive sulfide deposits. Nearly all volcanic and hypabyssal rocks in the IPB have been metamorphosed (propylitized) by hydrothermal sea water metamorphism. Stockwork alteration zonation associated with interactions between the ore-bearing fluids, country rock and sea water near hydrothermal vents, typically show a central chloritic core with a sericitic halo zone. Individual sulfide-rich stockwork veins are surrounded by chlorite-quartz alteration surrounded by sericite-quartz rock that often grades into rocks affected only by regional alteration. Hanging wall alteration that is mineralogically similar to stockwork alteration is evident in some ore bodies, suggesting that hydrothermal activity continued after deposition of the hanging wall rocks (Barriga et al., 1997; Saez et al., 1996).

Sulfur isotopic studies in the IPB indicate marine sulfate deposits with some bacteriogenic sulfur in generation of massive sulfide deposits. Oxygen and hydrogen isotopic studies suggest that sea water was the main source of mineralizing fluids with magmatic and

metamorphic fluids playing a smaller role (fluid temperatures approx. 200-250°C) (summarized in Barriga et al., 1997). Lead isotopic compositions are fairly homogeneous throughout the IPB (excluding Neves Corvo), and suggest that all IPB deposits were derived on continental crust (Saez et al., 1996; Barriga et al., 1997).

Three types of sulfide concentrations occur in the IPB (Figure 5) including 1) stratiform polymetallic massive sulfide bodies (the best known, 35-51% S or 66-96% pyrite equivalent), 2) disseminated polymetallic pyrite (<35% S) bodies that are, in general, associated with the stratiform deposits, and 3) stockwork and fissure type mineralization (5-25% S with 10-25% pyrite equivalent) (Barriga et al., 1997). Massive sulfide bodies are 4-5km long lensoidal or sheet-like, 80-100 km thick, and are laterally extensive (~1km) with tonnages up to 500 million tons. Stratiform massive sulfide deposits typically overlie basal (footwall) stockworks of varied morphologies (stringers and veins). The contacts between sulfide bodies and host rocks are generally sharp but may have a more disseminated contact (Barriga et al., 1997).

The main structural control for massive sulfide deposits in the IPB are the extensive stockworks (Figure 4,5) that follow a N 120°E trend throughout the IPB (Barriga et al., 1997; Leistel et al., 1998). Stockwork mineralogies are dominantly pyritic with sphalerite, galena, and chalcopyrite with lesser tetrahedrite-tennantite, cassiterite and pyrrhotite, trace minerals, and electrum (Barriga et al., 1997; Leistel et al., 1998). IPB pyritic deposits are fine grained and banded (Schermerhorn, 1970). Rio Tinto, Aznocolar, La Zarza, Aljustrel, and Neves Corvo all have well-developed stockworks. Lousal and Tharsis lack extensive stockworks and associated hydrothermal alteration such that they are considered of allochthonous origin (Barriga et al., 1997)

Manganese Deposits

Many small but economically profitable manganese deposits occur within the Volcanic Siliceous Complex. These deposits are associated primarily with tuffites, siliceous slates, cherts and jaspers (Figure 5). They do not form good markers for the massive sulfide deposits because they occur with ore-bearing and non-ore-bearing volcanic rocks. Manganese deposits, cherts, and jaspers that are associated with felsic volcanic rocks are sea floor chemical hydrothermal precipitates (Barriga et al., 1997; Leistel et al., 1998)

Active IPB Mines

Aznocolar-Los Frailes

The Aznocolar mining district (Figure 6, 7) is located in the southeast part of the IPB about 25km west of Sevilla, Spain. The district contains several deposits totalling >110 million tons (Barriga et al., 1997) with grades approximately 3.6% Zn, 2%Pb, 0.4% Cu and 65 ppm Ag. The open pits at Los Frailes are presently operated by BOLIDEN-APIRISA. Host rocks are mainly restricted to black shales that overlie felsic volcanic rocks with lesser economic stockwork mineralization (Almodovar et al., 1998).

Rio Tinto

The Rio Tinto orebodies are in an E-W trending anticline (Figure 6, 8) interconnected by mineralized stockworks. The Rio Tinto deposits are the largest massive sulfide deposits in the

IPB with >290 tons of deposits (Barriga et al., 1997). Weathering of these deposits has produced a gossan up to 70m thick that is still mined for its gold content. Both the stockwork and the gossan are mined by open pit (Nehlig et al., 1998).

Copper is concentrated at Rio Tinto under the stratiform pyrite deposits as chalcopyrite mineralization in the stockworks. Manganese production has totalled ~3 million tons of manganese oxides (Strauss and Madel, 1974).

La Zarza

La Zarza is located 20km west of the Rio Tinto district. The pyrite orebody (Figure 6, 9) is 2900m long and 100m thick, and is confined to the tuffites and black tuffitic shales in the western end of a west-striking volcanic lineament. The sulfide ores consist of a copper-rich siliceous ore, a massive fine-grained pyrite ore, and stockwork pyritic ore in porphyritic feldspar tuffs (Strauss and Madel, 1974). The La Zarza deposit is estimated as >100 million tons (Barriga et al., 1997).

Tharsis

The Tharsis mines have been worked since 4500 B.C. In the Tharsis district (Figure 6, 10) massive sulfides may be up to 400m thick and total ore tonnage is estimated as >120 million tons (Barriga et al., 1997; Almodovar et al., 1997). Average grades are 46.5% S, 2.7% Zn + Pb, 0.7% Cu, 35 g/t Ag and 0.9 g/t Au. The biggest orebody in the Tharsis district is the Filon Norte deposit and is currently the only actively mined deposit in the Tharsis district (Almodovar et al., 1997). Mineralization is in several stacked sheets (lensoidal shaped) within black shales (stratabound in the Volcanic Sedimentary Complex) (Tornos et al., 1998) that are concentrated along E-W trending volcanic lineaments (Strauss and Madel, 1974).

Aljustrel

Aljustrel is located in the Portuguese portion of the IPB (Figure 6, 11) and contains more than 230 Mt of massive sulfide ore (1% Cu, 3.5% Zn, 1.2% Pb, 1 ppm Au, 35 ppm Ag). The orebodies are concentrated at the boundary between rhyolitic volcanic rocks and overlying chemical sediments in a series of NW-SE trending anticlines and synclines and thrust faults (Silva et al., 1997; Barriga et al., 1997; Barriga and Fyfe, 1998).

Coarse-grained banded ores are rich in chalcopyrite, and bismuth and cobalt – bearing minerals. Massive ore is enriched in chalcopyrite and pyrite. Fine-grained banded ores are rich in sphalerite+galena alternating with pyritic layers (Silva et al., 1997).

Neves Corvo

The Neves Corvo mine is located at the southern end of the NW-SE trending Neves Corvo-Rosario Anticline (Figure 6, 12). Five main orebodies, estimated >270 Mt (Barriga et al., 1997), are lensoidal and typically overlie felsic volcanic rocks of the Volcanic Siliceous Complex. Amphibolite facies hydrothermal metamorphism is evident near volcanic vents and regional lower greenschist facies metamorphism is pervasive (Oliveira et al., 1997).

The Neves-Corvo mine is the most important European copper-tin mine, with uniquely high copper and tin contents when compared to other massive sulfide deposits in the IPB. All deposits have stockwork mineralization in a footwall host rock. Original resource estimates are >42 Mt copper ores (7.6% Cu) with 4.3 Mt of tin ores (2.5% Sn), 47 Mt of zinc ore (6.2% Zn) and 180 Mt of pyrite (0.5% Cu and 0.2% Zn) (Oliveira et al., 1997).

Lousal

The Lousal mining district is located in the westernmost part of the IPB. Tertiary basin cover has limited mining and exploration north, east, and south of the district so that the main area of focus is in the southwest area of the district in the ore-bearing Volcanic Sedimentary Complex. There are 18 orebodies (from 100,000 to 3 million tons each) that include pyrite, chalcopyrite, sphalerite, galena and gangue minerals. Lousal orebodies are aligned along the flanks of the southeast-trending Lousal anticline (Figure 6, 13) that incorporates the tuffs, tuff-breccias, and lava flows of four volcanic centers. The primary sulfide ore-bearing horizon consists of black and gray shale with dolomitic lenses. Manganese ore is mainly rhodochrosite and rhodonite which occurs interbedded with pillow lavas. Disseminated copper ore is concentrated in ash flow tuffs and tuff shales with the principal minerals pyrite, pyrrhotite, chalcopyrite, sphalerite, and galena (Strauss and Madel, 1974).

Conclusions

The Iberian Pyrite Belt is one of the oldest mining districts on earth and represents giant and supergiant massive sulfide deposits including those of Rio Tinto, Tharsis, Neves Corvo, Aljustrel, La Zarza, and Aznocolar. The most widely accepted genetic model for formation of these VMS deposits is the sea water convective model in which massive ore formation results from exhalative-sedimentary processes whereby stockworks were the hydrothermal feeders to the system. Bacteriogenesis, sea water and connate waters also played an important role in ore mineralization. The fact that terrigenous and marine rocks and bimodal volcanic rocks are associated with massive sulfide deposits rather than andesitic arc-type rocks suggests that mineralization was in an extensional setting (Saez, et al., 1996). Notable differences between the IPB VMS deposits and other VMS deposits include their large size, the fact that they were formed on continental crust rather than on oceanic crust, and volcanics are bimodal and mostly felsic.

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The Tectonic Development of the Iberian Peninsula

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Introduction

The Iberian Peninsula contains complex tectonic and structural regimes resulting in the development of an orocline. As with other oroclines, or curved deformation belts, structural cross sections, physical modeling, and paleomagnetic interpretation are tools available to geologists interested in determining the tectonics, structure and timing of development of the orocline. In the case of the Iberian Peninsula, the formation of the orocline was pivotal for the formation of mineral deposits throughout Iberia.

The Ibero-Armorican orocline extends across the Iberian Peninsula and Central Europe (Figure 1). Exposures of the complex pre-Mesozoic geology of Iberia are mainly concentrated in the western Iberian Massif with minor outcrops in the Alpine ranges and the southern Betic Cordillera (Dallmeyer and Martínez García, 1990), while sediments derived from later events have covered the pre-Mesozoic exposures in the interstices.

Five discrete deformation zones based on stratigraphic, structural and metamorphic characteristics divide the Iberian Massif (Figure 2) - the Cantabrian Zone (Figure 3), the West Asturian-Leonese Zone (Figure 4), the Central Iberian Zone (Figure 5), the Ossa-Morena Zone (Figure 6), and the South Portuguese Zone (Figure 7). Each zone progressively wraps around the Cantabrian Zone at the heart of the Ibero-Armorican Arc. Understanding the tectonic development and structural complexity of these zones is essential to understanding the development of one of the world's most prolific volcanic massive sulfide districts.

Plate Tectonic Models Affecting the Iberian Peninsula

Multiple events of formation and destruction created in succession Gondwana, Laurussia, and Pangaea from Precambrian through late Eocene time. Each major tectonic event contributed to the shaping of the Iberian Peninsula, incorporating exotic terranes, oceanic ophiolite deposits, and episodic magmatism and metamorphism.

Gondwana and Laurussia

During the Precambrian and Cambrian, the Cadomian Orogeny (650-550 Ma) set the stage for the Hercynian Variscan deformation front. The Caledonian Orogen, the initial phase of plate suturing of Laurussia, consolidated the Armorican craton of France with the Irish Sea Horst, the London Platform, the Bohemian Craton, the East Silesian Block and the Maloploska Massif (Ziegler, 1990) creating the core of the Laurussian mega-continent. Concomitantly, the breakup of Gondwana to the south liberated terranes to be joined to the southern margin of Laurussia in the creation of the Iberian Peninsula (Figure 8) and the Ibero-Armorican Arc.

The presence of ephemeral oceanic basins between the terranes was as important as the amalgamation of exotic terranes in the formation of the orocline. The rifting of Gondwana created oceanic basins, whereas oceanic basins were subducted in the formation of Laurussia. Several oceanic basins, the Iapetus, Tornquist and Rheic Oceans to the north of the Armorican and Iberian micro-continents and the Massif Central Ocean and Proto Tethys to the south, were interspersed between Gondwana, Armorica, Iberia and Laurussia. As Gondwanan terranes accreted onto Laurussia, oceanic ophiolites were incorporated into the land, plate sutures locked, and plate margins shifted successively to the south (Ziegler, 1990), building the base of Pangaea.

Pangaea

The Hercynian Orogeny, spanning the Carboniferous to Permian, completed the amalgamation of Laurussia and Gondwana into the supercontinent Pangaea. The macro-scale deformation producing the Ibero-Armorican Orocline connected present-day eastern North America with northwest Africa and Europe, uniting the Marathon-Ouachita-Appalachian fold belt, with the Mauretides and Variscan fold belt in the core of Pangaea (Ziegler, 1990). The Variscan deformation ended in the Late Westphalian completing the Ibero-Armorican Orocline with the final amalgamation of Pangaea.

Collisional Events Shaping Iberia

Variscan Deformation

Two stages of European Variscan deformation ensued during the amalgamation of Pangaea – a Variscan geosynclinal stage, and a subsequent Variscan Orogen spanning the late Viséan to late Westphalian of the Carboniferous.

The Variscan geosynclinal system followed the collapse of the Caledonides in a tensional setting in the Early Devonian (Ziegler, 1990) allowing the formation of multiple marine depositional basins across western and central Europe. Continental highs separated the basins, thus supplying sediment sources to the basins. Within the Variscan geosynclinal stage, the Ligerian Orogeny of the Late Silurian to Early Devonian amalgamated the pieces of Iberia – the Avalon-Meguma-South Portuguese and the Aquitaine-Cantabrian terranes derived from Gondwana with a proposed third terrane, the Intra-Alpine (Ziegler, 1990, Figure 9). In addition to shaping the morphology of the peninsula, the amalgamation of the rafted terranes incorporated substantial ophiolite deposits between the docked cratonic pieces. Structurally, the collision of the South-Portuguese and Aquitaine-Cantabrian terranes produced east-verging ophiolite nappes in Galicia, while the newly created east-verging nappes of the Ossa-Morena Zone underwent dextral wrenching (Ziegler, 1990).

The eventual collision of the Variscan geosynclinal system with Africa in the Viséan produced the Himalayan-type Variscan Orogeny, which encompassed the arcuate Appalachian-Central Iberian-Ligerian-Moldanubian system (Ziegler, 1990). The orogeny spread across Europe, incorporating the Alpine-Mediterranean fold belt. Shortening of the Cantabrian platform during the orogen is estimated at about 50% (Ziegler, 1990) as oceanic basins were destroyed. Additionally, the orogen created multiple events of igneous intrusion across Europe as subduction ensued.

Pyrenean Orogeny

Ultimately, the breakup of Pangaea – the separation of Laurussia and Gondwana – in the Jurassic after a union of 100 m.y., propelled the Iberian Peninsula to its present day position. Initial separation of the supercontinent created new oceanic basins – in the Central Atlantic, Caribbean and Mediterranean, while sending the amalgamated Iberian Peninsula into isolation from both Laurussia and the Armorican margin with the creation of the Bay of Biscay (Ziegler, 1990). After a relatively brief separation from the Armorican margin, tectonic gears changed during the Santonian and Campanian, sending the Iberian micro-continent crashing into southern Europe, subducting the Bay of Biscay between Armorica and Iberia and creating the Pyrenean Orogeny coeval with the Alpine Orogeny. Structural evidence indicates that Iberia docked onto Europe with a dextral transpressive motion, similar to a clockwise rotation. By the Late Tertiary, the Pyrenean Orogeny completely sutured the Iberian Peninsula to the European continent.

Altogether, these successive plate tectonic events in the Paleozoic created and reworked the Iberian Peninsula, contributing to the development of the Ibero-Armorican Orocline.

Development of the Iberian Orocline

Intrigue surrounding oroclinal development focuses on the dynamics and kinematics of development, timing of curvature relative to structural deformation and the style of deformation, itself. The scale of both the Ibero-Armorican Arc and the Cantabrian-Asturian Arc reflects the importance of the plate tectonic history of the area in the curvature of both thin- and thick-skinned deformation.

Structural Styles and Metallogeny within the Ibero-Armorican Arc

While it is commonly accepted that the Iberian Peninsula is an amalgamation of exotic terranes and interstitial ocean crust, the exact kinematics of the formation of the orocline is still in question. Matte (1986) proposed that a rigid Iberian block indented into the Hercynian Orogen forming the Ibero-Armorican Arc; the indenter acted to push Armorica to the north, imparting a dextral sense of motion, while producing a sinistral sense of motion in Iberia (Figure 10). However, others recognized that the shear belts reveal the nature of docking between the peninsula and Pangaea and that the docking was more complicated than simple compression. Work by Dias and Ribeiro (1994) built upon the indenter model by proposing a transpressive nature to the indentation, with lateral escape of material (Figure 11) generating the Ossa-Morena Zone and South Portuguese Zone during the Variscan Orogeny (Figure 12). This theory emphasized the importance of shearing to the development of the orocline as indentation progressed, taking into account the shear belts that separate the five zones of the Iberian Peninsula. Most recently, Shelley and Bossière (2000) proposed, “The Ibero-Armorican Arc was formed by wrapping the mobile dextral shear belts about a rigid Iberian basement block.” All recent models agree that an indenter of terranes created the orocline.

Cantabrian Zone

The structures produced during the formation of the Cantabrian Zone of the Iberian Peninsula are thin-skinned fold-thrust belts that display both radial and longitudinal orientation

with respect to the Ibero-Armorican Arc (Pérez-Estaún, 1990). There are several thrust décollement levels within the two major thrust units making up the Cantabrian-Asturian Arc. Overall, the nappes of this region display a forward type deformation sequence of ramp and flat thrusts, which developed from west to east. The units curve clockwise (Figure 13), widening to the north and are typically referred to as similar to the “iris of a photographic camera.” Their arrangement indicates multiple directions of emplacement and a progressive formation and tightening of fold structures (Pérez-Estaún and Bastida, 1990). Several important thrusts exist in the southern part of the zone. These thrusts record strike-slip and reverse movement across the region, critical to the orocline development (Pérez-Estaún *et al.*, 1988).

The Cantabrian Zone is rich in copper, cobalt, nickel, lead, zinc, mercury, arsenic, antimony, gold, iron and manganese, as well as fluorite, talc, magnesite, kaolin and gypsum. The many, small mineral deposits within the Cantabrian Zone are located mainly in strongly folded and faulted Carboniferous carbonate rocks and are of hydrothermal origin (Lugue *et al.*, 1990). Most deposits are considered to have been formed by fluids of moderate to high salinity (10% - 23% eq. NaCl) and low pressures (200 – 600 bars). Other deposits are metasomatic, with complex skarn type mineralizations formed around Hercynian granodioritic stocks.

West Asturian-Leonese Zone

The structures of the West Asturian-Leonese Zone contain both autochthonous and allochthonous units that display “originally recumbent folds with E vergence, thrust faults and large open folds with steep axial surfaces, superimposed in that order.” (Martínez Catalán *et al.*, 1990) This zone also has radial and longitudinal sets of folds, but unlike the structures of the Cantabrian Zone, synkinematic metamorphism is commonly seen. Due to the sediment thickness and concomitant thinning of the basement rocks beneath, the fold structures within the zone are typical of thick-skinned tectonics induced by shearing. The change in style between the Cantabrian Zone and WALZ reflects a transition from an external to an internal zone of Variscan deformation from east to west across the peninsula.

The West Asturian-Leonese Zone also contains many, small mineral deposits of iron, lead, zinc, copper, silver, gold, molybdenum, antimony, manganese, tungsten, uranium, mercury, arsenic and cobalt, as well as barite, kaolin, magnesite and andalucite. Structural control on the development of each mineral is evident with vein deposits or in association with both contact and regional metamorphism.

Central Iberian Zone

While the Central Iberian Zone is also considered an internal Variscan deformation zone, the geology becomes much more complicated than that of the West Asturian-Leonese Zone. Dominant to the zone is the presence of allochthonous sequences, autochthonous sequences, ophiolites and low- to high-grade metamorphic rocks. The zone contains three dominant regions from NE to SW – the domain of recumbent folds, verging NE, the domain of vertical folds and the Badajoz-Córdoba shear zone (Díez Balda *et al.*, 1990). The rocks of this zone underwent deformation during the Precambrian, with subsequent Paleozoic shearing, and both non-rotational and rotational deformation superimposed on older events.

The Central Iberian Zone contains widespread granitic plutonism and metamorphism (Martínez *et al.*, 1990) created both before and during the formation of Iberia and important to

the development of the famous Almaden mercury deposit, the antimony deposit of San Antonio (Badajoz), the old Pb-District of Linares-La Carolina (Jaen), and some important Sn, W, U, Cu, P, Li, Pb, Zn, Sb and Au mineralizations. (Gumiel, P. and Arribas, A., 1990) Two stages of mineral development are evident in the Central Iberian Zone, exhalative deposits related to preorogenic volcanism, and Cadomian synorogenic sequences, including regional metamorphism, collisional magmatism and postorogenic volcanism. The most important regional deposits, antimony and mercury, are known to be of pre-orogenic origin associated with volcanism.

Ossa-Morena Zone

The most complex and most controversial geology of the Iberian Massif lies in the Ossa-Morena Zone. The zone has been divided into six regions from south to north based on the deformation induced during the Hercynian - the Southern crystalline massifs, the Ossa-Morena south-central belt, the Ossa-Morena north-central belt, the Sierra Albarrana domain, the Badajoz-Córdoba shear zone and the Obejo-Valsequillo-Puebla de la Reina domain.

The Ossa-Morena Zone contains Precambrian basement with imprints of tectonic events from that era. Superimposed are three distinct phases of Paleozoic tectonics – rifting in the Cambrian, passive margin in the Ordovician-Devonian, and a synorogenic phase in the Mid-Devonian to Early Permian (Liñán and Quesada, 1990).

The complexity of tectonic development of the Ossa-Morena Zone is richly revealed in the density and diversity of mineral deposits across the region. Evolutionary complexity of the zinc, lead, silver and iron deposits depend upon successive tectonosedimentary cycles (Locutura *et al.*, 1990) spanning the Cadomian through the Hercynian. The most significant deposits of the region are the “Pb-Zn (Cu) mineralizations at the NE of the Monesterio thrust zone, while at the SW, Fe (Cu) ore deposits predominate.” These Hercynian deposits are indicative of an active marginal setting with late collision producing Cu-Pb-Zn lodes, with epithermal ores deposited during tensional tectonics. Plutonism, metamorphism and thrust and shear-related zones, coeval with the Hercynian tectonics, contributed to mineral development. However, iron-copper skarns provide economically important reserves, on the order of 100 million metric tons (Locutura *et al.*, 1990).

South Portuguese Zone

The curvature in the South Portuguese Zone involved both thin-skinned transpressive deformation producing thrust faults, as well as extension-induced volcanism. Five structural domains from west to east - the Beja-Acebuches ophiolite, the Pulo do Lobo antiform, the Pyrite Belt, the Baixo Alentejo flysch group and Southwest Portugal - form a succession of anticlines and synclines across the South Portuguese Zone (Silva *et al.*, 1990). The intensity of deformation emanating from the transpressive collision of the South Portuguese Zone with the Ossa-Morena Zone decreases outward from the southwest.

Volcanism is common across the South Portuguese Zone, comprised of both MORB and calc-alkaline volcanic rocks. The combination of tectonic transpression and volcanism contributed to an environment rich in massive sulfide mineral deposits, commonly referred to as the Iberian Pyrite Belt and containing Aljustrel, Neves Corvo, Lousal, Tharsis, the Rio Tinto deposit and Aznalcóllar. Geologic studies have deduced that the development of sulfide

orebodies are 1) syngenetic; 2) volcanogenetic 3) exhalative; and 4) submarine in nature, thus the deposits in the Iberian Pyrite Belt reveal autochthonous and allochthonous characteristics (Barriga, 1990). The minerals of the zone show younger ages than the transpression, but are dependent upon the transtensional regime for volcanic development.

Physical Models

Several models for the kinematics and dynamics of oroclinal folds have been proposed in recent years. Popular theories for oroclinal fold development in fold and thrust belts are the presence of buttresses, lateral sediment thickness changes, the presence of an evaporitic decollement layer, or the action of a rigid indenter. Physical modeling isolates key parameters, such as boundary conditions, in the development of curvature to examine their role in both space and time.

The most probable and most supported cause for the oroclinal shape of the Ibero-Armorican Arc was the action of a rigid indenter as plate movements formed Laurussia and Pangaea, followed by subsequent fold tightening during the fixation of the Iberian Peninsula at its present-day location. Physical modeling carried out by Marshak *et al.* (1992) showed that the development of an oroclinal shape could be concurrent with indentation and fold-thrust development, rather than just a secondary event that re-shapes the fold belt. In the formation of the Ibero-Armorican Arc, each micro-terrane contributed both to the growth of the Iberian Peninsula and acted as an indenter to the foreland terrane, creating and modifying the orocline in a piecewise fashion (Dias and Ribeiro, 1995). As sequential events modified the curvature, folds tightened and new directions of fold fronts developed.

Paleomagnetic Interpretation

To validate the results of physical modeling, paleomagnetic data can be obtained from geologic strata in an attempt to constrain crustal movement and structural timing. Several studies have been carried out on the Cantabrian-Asturian Arc, the most obviously curved strata in Iberia with an arc of almost 180°, to determine curvature development. Paleomagnetic results from Parés *et al.* (1994) identified an initial horizontal folding event in the Late Carboniferous followed by vertical folding in the Permian. Paleomagnetic results from Weil *et al.* (2000) suggested three major oroclinal shaping events spanning the Late Carboniferous to Permian. Their interpretations concluded that two earlier deformation events were later tightened, rotated and tilted through a regionally compressive/transpressive event possibly related to the amalgamation of Pangaea. Clearly, understanding of the complexity of the orocline in the Iberian Peninsula is evolving.

Conclusions

The formation of the Iberian Peninsula involved multiple episodes of plate tectonic movements ultimately producing an orocline shaped by subduction and rifting, folding and thrusting, volcanism, and metamorphism. Additional geologic complexity within the Iberian Orocline is exemplified by the presence and diversity of mineral deposits formed in conjunction with the tectonic development of the Iberian orocline. The tectonism forming the peninsula provided the geologic setting needed for the development of the many minerals across the region. The unique geologic and tectonic setting of the Iberian Peninsula and the development of the mineral deposits of the peninsula combined to create a rich environment for geologic study.

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Seafloor hydrothermal systems and volcanic massive sulfide deposits

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Introduction

Massive sulfide deposits, while found in many different host rocks and different tectonic environments have one thing in common: they are formed by hydrothermal fluids at or just below the seafloor (Barrie and Hannington, 1999). Thus, understanding the hydrothermal systems are of utmost importance when studying massive sulfide deposits. This paper presents a brief overview of the major components of oceanic crust and their hydrothermal seafloor systems and finishes with a case study from the Aljustrel region in Portugal within the Iberian Pyrite Belt.

Structure of oceanic crust

In general, a layered structure is assumed for the ocean crust, based on seismic surveys, direct sampling of the seafloor, as well as the structure observed in ophiolites-sections of ocean crust exposed at the surface (Alt, 1995). These layers are, from shallow to deep: sediments, pillow basalts, breccias and massive basalt flows; sheeted dikes (the conduits that feed the volcanics); gabbro and other plutonic rocks; and finally peridotite, which is thought to represent the mantle (fig. 1).

This model is further complicated by different tectonic settings. While it describes the sequence that is expected to form at mid ocean ridges, other submarine environments (various arcs and associated basins, sedimented continental margin rifts (Barrie and Hannington, 1999)) contribute other types of rocks to the section, such as silicic igneous rocks and siliciclastic rocks. However, for the purposes of this paper, all of the marine hydrothermal systems experience similar evolutionary and alteration paths, and connections can be made between ordinary ocean crust and crust that has been modified by multiple tectonic events and different tectonic environments.

Heat sources and convection

Circulating seawater is the dominant cooling mechanism in submarine rocks. These convective regimes may be divided into two groups: active and passive (Alt, 1995), which occur on and off-axis respectively, in a spreading environment (fig. 2).

Active convection occurs at ridge axes over an active magma chamber or areas where cooling plutonic rocks contract and fracture, increasing the flow of fluids and heat. Temperatures are high ($>250^{\circ}$), circulation is fast, and discharge zones (zones where hot fluids are expelled from the rock) are more focused than recharge zones (zones where water is drawn into the rock) (Alt, 1995). Seafloor vents where these hot ($250-400^{\circ}\text{C}$) fluids are expelled are restricted to a narrow zone above the magma chamber. For example, on the East Pacific Rise, this zone is ~ 100 meters wide. However, in some places faults will control the locations of the vents, with the faults acting as pathways for hydrothermal fluids, and have been found as much as a kilometer off-axis (Alt, 1995).

The penetration depth of fluids in active convection zones is limited by the depth of the top of the magma chamber itself, generally 1 to 2 km (Alt, 1995). Where there is no discrete

magma chamber, these fluids may penetrate deeper, facilitated by faults or fractures formed during cooling of the rock (Alt, 1995).

Passive convection occurs off-axis, with heat supplied by the cooling crust. Temperatures are lower ($<200^{\circ}\text{C}$), and circulation slower than in active convection zones. Like the active convective cells, discharge zones are more focused than recharge zones, but the passive circulation cells move with the moving crust, whereas the active circulation cells are fixed over the heat source (Alt, 1995). Fluids circulating through passive convective cells appear to penetrate to greater depths, up to several kilometers, but this is controlled by the permeability of the rock and can vary greatly, and is generally poorly constrained (Alt, 1995).

Hydrothermal Alteration

Hydrothermal alteration in oceanic crust occurs in 3 distinct zones: recharge, reaction and discharge (fig. 3). Recharge zones, where seawater is drawn into the rock, are diffuse and widespread. Seawater is heated and drawn downward, causing alteration on the journey to the reaction zone where the highest temperature ($>350^{\circ}\text{C}$) reactions occur, generally in the sheeted dikes and upper gabbros. In the reaction zone the hydrothermal fluids acquire their chemical signatures. They are then discharged, rising rapidly to the surface, driven by their greater buoyancy at high temperatures, until they are expelled on the ocean floor (Alt, 1995). The following describes the processes that occur at each step along the way.

Recharge Zones

Recharge zones are those diffuse zones where seawater is drawn into the rock. The largest volumes circulate through the more porous volcanic section; smaller volumes will penetrate into the deeper rocks such as the dikes and gabbros. The main processes that occur during recharge are low temperature ($<40^{\circ}\text{C}$) oxidation, low temperature alkali fixation, magnesium fixation, anhydrite formation, and finally alkali loss at higher temperatures ($>150^{\circ}\text{C}$) (fig. 4) (Alt, 1995).

Low temperature oxidation and alkali fixation (also known as “seafloor weathering”) occur during initial penetration of water into the rock. These processes are most pronounced in the upper volcanics, where the $\text{Fe}^{3+}/\text{Fe}^{\text{total}}$ and K_2O contents of altered rocks are highest. During oxidation, Fe-oxyhydroxides (goethite, amorphous material and hematite) replace olivine and primary sulfides, fill veins and pores, and generally give the rocks a reddish color. These oxyhydroxides are rarely pure, typically intergrown with smectite and commonly containing Mn (Alt, 1995).

The alkalis K, Rb, Cs and B are predominately fixed as celadonite and nontronite (ferric mica and smectite) or combinations of the two (Alt, 1995). These replace olivine and fill pores and veins, typically in the volcanic section (Alt, 1995). This replacement appears as black halos around the olivine and veins and appears to precede the reddish alteration of oxidation. The formation of celadonite and nontronite appears to occur at temperatures up to 40°C (Kastner and Gieskes, 1976) in seafloor basalts. In addition, these black zones are enriched in Fe relative to unaltered rocks, suggesting another source for the iron, which may be either breakdown of volcanic glass or from a deeper source. The latter may indicate formation near the axis during mixing of cool seawater with distal upwelling fluids. However, it is often difficult to determine the differences between reactions that have occurred during oxidation and those that have

occurred during alkali fixation, as the chemical effects are similar and commonly combined. In general, rocks are enriched in Fe^{T} , H_2O , P, K, Li, Rb, Cs, B, REE and U, have lost Mg (which is gained in Mg fixation, the next reaction described), Si, S, Ca, Co, and Ni, and have increased $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^{18}O and ^{11}B .

Deeper in the crust, the alteration becomes more restricted and more reducing at depths below 300m. This change is evidenced by only slightly increased $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ and alkali contents, which reflect both the decrease in water volume reaching these depths as well as the reacted nature of the fluids (alkali and oxygen depleted) (fig. 4) (Alt, 1995).

The fixation of seawater Mg in the crust is the third major reaction that occurs during the recharge cycle (fig. 4). Mg^{2+} and $(\text{OH})^-$ from seawater combine to form a component of smectite (saponite) at low temperatures ($<200^\circ\text{C}$) and chlorite at higher temperatures ($>200^\circ\text{C}$) (Alt, 1995). This Mg enrichment tends to be concentrated in fractures and pores, while bulk rocks with relatively low water-rock interactions will have lower Mg uptake. Porosity and crystallinity of the rocks will dictate the extent to which Mg will be enriched, i.e., glassy pillow rims may be totally replaced with chlorite \pm albite whereas adjacent crystalline rock may only be partially altered (Alt, 1995). In addition, experimental reactions indicate that Mg uptake should be balanced by Ca release (Alt, 1995).

The fourth main reaction during the recharge cycle is the formation of anhydrite (fig. 4). Heating of seawater ($150\text{--}200^\circ\text{C}$) as it descends through the crust will precipitate the Ca and most of the sulfate as anhydrite. This reaction in turn limits the formation of calc-silicates by removing Ca from the fluids. Anhydrite is generally found in veins and to a lesser extent, replacing plagioclase. Note that studies indicate that anhydrite may be formed both due to the penetration of fluids into hot rock (deep sheeted dike levels) and by the interaction of down-going fluids with hot upwelling fluids at shallower depths (rocks in the pillow-dike transition) (Sleep, 1991).

Another important seafloor process at higher temperatures ($\sim 150^\circ\text{C}$) is the mobilization of alkalis. High temperature vent fluids ($\sim 350^\circ\text{C}$) sampled at mid-ocean ridges commonly are enriched in alkalis- Li, K, Rb, Cs, and B, which is counter-intuitive since alkalis are fixed in the rocks in the previously described reactions. At higher temperatures, many alkalis are remobilized, which appears to coincide with the uptake of Mg by the rocks, and may account for the enrichment. For example, experimental results indicate that K is taken up by basalts at temperatures of 70°C , but is released from the rocks at temperatures of 150°C and above (Seyfried and Bischoff, 1979).

Reaction Zones

High temperature ($\sim 350^\circ\text{C}$) fluids that are sampled at mid-ocean ridges have chemical signatures that are thought to be acquired at depths of 1 to 2 km, in what are called “reaction zones” (fig. 5). It is here that fluids are heated to high temperatures by a hydrothermal heat source, metals and S are leached from the rocks, and high temperature reactions occur (fig. 5). In addition, the fluid temperatures increase to the point that the fluids become buoyant, and begin to rise back toward the seafloor through discharge zones (Alt, 1995). This is the hottest point in the journey of the hydrothermal fluids, estimated as high as $400\text{--}600^\circ\text{C}$.

Experimental data and analyses of fluids sampled from discharging vents suggest that vent fluid compositions are controlled by mineral assemblages in the subsurface reaction zones. Seafloor subsurface information provided by drill holes also supports these data (Alt, 1995) as do

lower sheeted dikes in ophiolites (Harper, 1999). Specifically, Ca-plagioclase and epidote (though rare) are present, as well as fresh rock that is available for reaction (Alt, 1995). Amphibole compositions change from mainly actinolite to Mg-hornblende, with increases in Al and Ti in amphibole. Secondary Ca-plagioclase may replace igneous plagioclase along veins and in patchy areas, in contrast to the shallower albitization of plagioclase. Zn, Cu and S are depleted, the Zn due to replacement of FeTi oxides by titanite (Fe oxides can be important accumulators of Zn, Scott and Taylor, 1987) and the Cu and S due to breakdown of magmatic sulfide minerals. Reaction zone rocks show little or no enrichment in Mg, some Na enrichment and some Ca depletion (both vary) (Alt, 1995).

Discharge

Fluids in subsurface reaction zones approach the critical point for seawater, causing changes in the physical properties of the fluids. Density decreases, the coefficient of thermal expansion and the heat capacity reach their maximum limits, and the viscosity reaches a minimum (Alt, 1995). These properties cause the fluids to ascend to the surface at high speeds (estimated at 0.5 to 1 m/s from black smoker discharge on the seafloor) in either “focused” zones or “diffuse” zones (fig. 6) (Alt, 1995). In focused zones, fluids are sufficiently channeled along faults and fractures to reach the seafloor, while in diffuse zones, hydrothermal fluids do not reach the seafloor, mixing with seawater in the subsurface. Evidence for diffuse upflow comes from the presence of lower temperature, diffuse fluid flow in discharge zones, and from subsurface rocks on the seafloor and in ophiolites (Alt, 1995). Evidence for focused upflow zones is found in black smoker vents and sulfide deposits on the seafloor. Stockworks that form beneath these deposits are commonly exposed in sub aerial exposures of ocean crust, but are rarely exposed on the seafloor by faulting (some submarine localities have been sampled, but not many.) The deeper sections beneath this have not been sampled from the ocean crust (Alt, 1995) but have been studied by analogy in ophiolites and other submarine rocks exposed above the seas, although this connection has not been proven (Alt, 1995). Discharge alteration is recognized by distinctive mineral assemblages that will be described in the following sections.

Focused discharge

Focused upflow zones in ophiolites are characterized by a progression of mineralization; from epidiosites at the base that transition to zones of mineralized veins (epidote + quartz, epidote + prehnite, quartz + prehnite, quartz + pyrite) with argillic alteration to massive sulfides at the shallowest depths (fig. 6). The basal epidiosites are rocks replaced almost entirely by granular epidote + quartz + titanite found within altered diabase. In ophiolites, these epidiosite zones may be 100's of meters wide, are often elongate parallel to sheeted dikes and inferred paleo-spreading axes, and have been suggested to form the deep upwelling feeder zones for massive sulfide deposits. Relative to fresh diabase, the epidiosites are enriched in Ca, Sr, and ^{34}S , have increased $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, and are depleted in Mg, Na, Zr, K, Cu, Zn, and S (Alt, 1995). Fluid inclusion data and the losses of metals indicate temperatures of 350 to 440°C (Alt, 1995), and all of these effects are interpreted to reflect interactions of rock with Mg-depleted, Ca-enriched acidic fluids (Harper, 1999) like those sampled from black smoker seafloor vents.

Epidiosites have been interpreted to be the deep reaction zones supplying metals and sulfur to overlying massive sulfide deposits. However, while epidiosites form large percentages of the sheeted dikes in massive sulfide-bearing ophiolites, only one sample has been described

that was recovered from the seafloor, which may reflect either a sampling problem or a fundamental difference between oceanic crust and ophiolites (Alt, 1995).

In some ophiolites, focused upflow zones are seen to extend from epidiosites to zones of quartz + epidote and/or quartz + prehnite which can be then traced to veins of quartz + sulfide ± epidote and argillic alteration that underlie the stockwork feeder zones for seafloor massive sulfide deposits (Alt, 1995).

The stockwork pipes are on the scale of 100m in diameter, and exhibit chloritic or illitic alteration. They are commonly zoned with Mg-enriched chloritic regions in the outer zones (enriched in Mg, Na, depleted in Ca, K, Rb and Ba) and illitic or Fe-enriched chloritic regions in the more intensely mineralized inner zones (enriched in K, Rb, Ba, Fe, Si, S). This zoning is thought to reflect mixing of the upwelling fluids with seawater. The inner, Mg-poor zones exhibit alteration expected from metal- and K-rich, Mg poor hydrothermal fluids at temperatures of 300-370°C, while the outer Mg-rich zones seem to indicate mixing of these fluids with Mg-rich seawater around the edges of the upwelling zone (Alt, 1995). Zoning is different in other pipes, due to different temperatures and degrees of mixing of fluids during alteration. Some pipes exhibit Mg-enrichment and K depletion in their chloritic cores, which reflects the greater stability of Mg-chlorite at higher temperatures. Other phases may also affect the Mg/Fe ratio of chlorite as well, such as pyrite. Precipitation of chlorite and pyrite simultaneously tends to push the chlorite toward more magnesian compositions.

Other effects seen in the shallow upflow zones in ophiolites are: silicification caused by cooling and mixing of hydrothermal fluids and seawater, formation of albite-bearing epidiosites at shallower depths with true epidiosites deeper, formation of prehnitites and pumpellyosites, (granoblastic rocks similar to epidiosites with different mineralogy) (Harper, 1999), and K and ¹⁸O enrichment of the volcanic section (Alt, 1995).

On the seafloor, upflow zones are seen as discharging fluids that form massive sulfide deposits and the associated high temperature hydrothermal vents. Although very few descriptions of the deeper parts of the upflow zones exist, limited seafloor data support the processes documented in ophiolites.

Diffuse discharge

Diffuse upflow zones occur when faulting and fracturing are not extensive enough to directly channel hydrothermal fluids to the seafloor, and the fluids instead mix with seawater in the subsurface (fig.6). Most evidence for diffuse upflow in ophiolites resides in the uppermost sheeted dikes and the transition to volcanics. Here, alteration is more patchy than in the focused upflow zones, with the highest mineralization occurring in a stockwork zone just below the volcanics, indicating mixing of ~300°C hydrothermal fluids with cool seawater circulating throughout the more permeable volcanics (Alt, 1995; Harper, 1999). The rocks are pervasively altered to chlorite; albite, titanite and sulfides are abundant. Generally, chlorites are Mg-rich, again showing interaction with seawater. In contrast to the focused zones, sulfides are deposited in the subsurface, and the fluids that discharge on the seafloor are much cooler (3-13°C) than those in focused upflow zones (250-400°C).

Aljustrel Volcanics- a case study

The Mississippian Aljustrel volcanics in the Aljustrel, Portugal region of the Iberian Pyrite Belt (figs. 7, 8) bear mineralization and depletion that is similar in style to that in the

recharge and reaction zones of seafloor hydrothermal systems. Within the Aljustrel area reside more than 200 Mt of massive sulfide ore in a cluster of several orebodies that overlie (and are hosted by) the Aljustrel volcanics and are in turn overlain by metalliferous sediments (Barriga, 1998). Petrography, mineral chemistry, whole rock geochemistry and isotope data indicate that the Aljustrel volcanics are a suitable source for the seawater that precipitated the massive sulfides in the region.

Geology of the Aljustrel region

The Iberian pyrite belt contains an ore-hosting Volcanic-Sedimentary complex that is generally underlain and overlain by 2 sedimentary units: the Phyllite-Quartzite group (PQ) and the Baixo Alentejo Flysh group, though regional variances are common (Barriga, 1998). At Aljustrel, the base of the Volcanic-Sedimentary group (locally known as the Aljustrel Group) is not seen, nor is the underlying PQ. In this area, the Volcanic-Sedimentary group is composed of a thick (>250m) submarine felsic pyroclastic unit (Aljustrel Volcanics) overlain by an ~50m thick unit of siliceous sediments, tuffites and tuffs. The volcanics are divided into two groups- a high iron rhyolite tuff (Quartz-eye tuff) and a high silica rhyolite tuff (Mine tuff). At or near the contact between the volcanics and the sediments are several massive sulfide deposits. The Aljustrel Group is found in an extensively folded, elongate 1.5 by 5-km area, and is conformably surrounded by turbidite deposits, and bounded to the north by a major fault (Barriga and Fyfe, 1998).

The Aljustrel Group rocks are found in a series of northwest trending anticlines separated by synclines and/or thrust faults (fig. 8). Among these, the Feitais anticline is the least deformed, and because of this was selected as the location for the detailed work of Barriga and Fyfe (1998).

Alteration of the Aljustrel Volcanics

The Aljustrel Volcanics exhibit alteration that is consistent with that seen in ophiolite recharge and reaction zones, and postulated in sub-seafloor recharge zones (Barriga and Fyfe, 1998). In the following sections, the petrography as it relates to this alteration will be described. The effects are summarized in table 1.

The volcanics are mostly composed of granular tuffs characterized by a matrix of felsic fragments and silicic fragments encased in sub-microscopic felsic, sericitic, and local chloritic matrix. Felsic fragments vary in shape, size and composition, and may be packed close together with minor sericitic-felsic matrix may be dominated by matrix, the latter indicating considerable silica leaching (recharge) (Barriga and Fyfe, 1998). All exhibit elevated ^{18}O levels as seen in recharge and reaction zones.

The uppermost 50m of each of the tuffs are characterized by an abundant phyllitic matrix, composed primarily of chlorite with lesser sericite and rare Ti-hematite flakes (Barriga and Fyfe, 1998). These effects are characteristic of the hydration, oxidation and Mg-fixation seen in recharge zones, with chlorite forming at temperatures around 200°C (Alt, 1995).

Both magmatic and metasomatic feldspars are present in the tuffs, displaying events of both alkali depletion and alkali fixation, which are common, given the alkali mobility dependence on temperature.

Fe varies progressively downward through the tuffs, becoming more leached with depth. Leaching primarily affects magmatic Fe-Ti oxides, with the Ti remaining as leucoxene and titanite (Barriga and Fyfe, 1998). In addition, Zn and Cu are leached from both of the tuffs,

although not with a consistent stratigraphic pattern as seen with the Fe. However, Zn and Cu both decrease with increasing alteration in the rock (Barriga and Fyfe, 1998). This mobilization of metals occurs within the reaction zones, and presumably this effect would be progressive as the fluids passed down through the rock, becoming heated and more acidic.

Aljustrel Volcanics and sulfide deposits

It is evident that the Aljustrel Volcanics experienced considerable post-eruption hydrothermal alteration. The patterns of alteration indicate the formation of a Fe-Mn-Cu-Zn-Pb-Si -bearing fluid, which is an excellent candidate for an ore forming fluid (Barriga and Fyfe, 1998). The evolution of these fluids as they pass downward through the rock from cool, oxidizing, Mg-bearing, to hot, reducing, Mg-free and enriched in Si, Fe, Cu and Zn is evident, and fits well with hydrothermal models. Chemical analyses indicate that 1% of all Fe was removed from the Aljustrel volcanics in this process, which is enough to account for all of the iron in the overlying orebodies and metalliferous sediments. In addition, a minimum of 30ppm Cu and 100ppm Zn were removed. This would require about 20km³ of rock to supply the 2Mt Cu and 6Mt contained in the Aljustrel massive sulfides, which exceeds the known volume of the Aljustrel Volcanics. However, as the base is not exposed, it is not known what the actual thickness of the unit is, and it may be that the thrust that underlies the units has truncated a portion of the package (Barriga and Fyfe, 1998)

Conclusions

Volcanic hosted massive sulfide deposits are intimately linked with oceanic hydrothermal systems. The structure of the oceanic crust and the varying rock types present due to different tectonic settings will effect the progression of the hydrothermal fluids and the final precipitation of the massive sulfide deposit. However, regardless of the exact rock types, the hydrothermal alteration seen in the recharge, reaction and discharge portions of the cycle remain constant. This is illustrated in the Aljustrel volcanics, the proposed source for several deposits in the Portuguese Iberian Pyrite Belt that displays alteration consistent with down-going and reacting fluids on the seafloor. An analogy can be drawn from alteration seen in ophiolites and in ocean crust to what is seen in the Aljustrel Volcanics, even though the Aljustrel volcanic composition is quite different to that seen in ophiolites or in typical mid-ocean crust.

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Almaden: An Overview of the World's Largest Mercury Deposit

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Introduction

Almaden, the location of the world's largest concentration of mercury, is 120 km north of Cordoba in central Spain's Castilla de Nueva province. The Almaden deposits have accounted for one third of historical production of mercury and have been producing for 2,000 years. Though ore grades have steadily decreased through the life of the mine, quite a bit of recoverable ore remains. Saupe (1990) reported grades were 7.6% Hg in 1796, 6.9% Hg in the period from 1881-1885, 5.8% Hg in 1944, 3.0% Hg in 1970, and 1.0% in 1980, with early figures being significantly lower than the actual grade due to inefficient Hg recovery techniques. Total Hg content of the Almaden deposits has been estimated at approximately 250,000 tons, with peak production occurring during the Renaissance and World War II (Hernandez et al. 1999).

The name "Almaden" is, like so many names in Spain, derived from the Arabic word *Al-maaden*, meaning "the ore." Almaden was also the site of the Almaden School of Mines, the world's fourth oldest school dedicated to mining and related topics, founded in conjunction with German mining engineers from Freiberg in 1777 (Hernandez et al. 1999)

Geological Setting

The Almaden district is located within an E-trending Paleozoic synclinorium that is approximately 30 km by 15 km (**figure 1**). The Almaden synclinorium formed as a result of folding that occurred during the Hercynian (lower Carboniferous) phase (Saupe 1990). The mercury deposits themselves are largely constrained to the Criadero quartzite, one of four Lower Silurian quartzites that are exposed as ridges contouring the synclinorium (Saupe 1990).

Stratigraphy

The Almaden synclinorium stratigraphy comprises a Precambrian and a middle Paleozoic (Silurian to Devonian) group, separated by an angular unconformity. The middle Paleozoic sequence ranges from 2,700 to 3,000 m thick, and consists primarily of rhythmically alternating sandstones and black shales with minor limestone and dolomite (**figure 2**), which Saupe (1990) interpreted as submarine deltaic deposits on an

epicontinental shelf. This Paleozoic group also contains Almaden's stratabound mercury deposits in the Criadero quartzite. The Precambrian group, 6,000 to 7,000 meters thick, is composed of alternating graywackes and slate (Saupe 1990).

Volcanics

Hydraulically brecciated diatremes crosscut the Paleozoic sequence, and they are concentrated primarily in the Silurian, though similar structures are found scattered throughout the Paleozoic sequence (**figure 2**). These diatremes contain altered mafic volcanic and sedimentary clasts, and the diatremes display a typical cone-shape, widening towards stratigraphic up (Hernandez et al. 1999). The volcanic hydraulic breccia found in the Silurian is called *frailesca*, named for its grayish color, which mimicked that of robes worn by Franciscan monks, or *frailes* (Ransome 1921). The *frailesca* is important because nearly everywhere ore is found at Almaden, *frailesca* is found nearby. Jebrak and Hernandez (1995) argue that deformation is more extensive than previously thought, so these *frailesca* diatremes are not present throughout the Silurian as proposed by Saupe (1990) and many others, but represent a single phase of volcanism in the Lower Silurian.

Ransome (1921), one of the first to study *frailesca* in detail, was first to recognize that a portion of the *frailesca* was composed of altered local sandstone, darkly-colored due to hydrothermal activity, and was partially volcanogenic. Van der Veen (1924) tried to work out a timeline for the emplacement of the *frailesca*. He concluded that an altered "diabase tuff" was volcanically emplaced, and that the *frailesca* itself represented an even later stage of fault brecciation. Van der Veen also attributes the volcanic activity to nearby Tertiary volcanics that were visible in outcrop near Almaden, while today it is accepted that these are not genetically related (Saupe 1990).

de Boorder and Westerhof (1994) have proposed that an exposure of alkali basalt near the town of Almadenejos is the feeder pipe, though the tectonic control is unknown. Saupe (1990) interpreted incipient rifting in the Paleozoic sequence of submarine deltaic sediments, allowing for concurrent alkali basalt volcanism.

Today it is widely accepted that the *frailesca* is Paleozoic in age, but the exact timing is still debatable. Saupe (1990) argued that the *frailesca* "fills a crater," because there is no apparent disruption in overlying sediments, and no thinning in the local Criadero quartzite towards the contact with *frailesca*. Saupe (1990) proposed that some lithification must have taken place, however, in order to allow for adequate buildup of pressure and subsequent diatreme emplacement and brecciation. Clasts of mafic volcanics and Criadero quartzite are present in the *frailesca*. Saupe (1990) notes that there is no known root zone for *frailesca* diatremes, with one possible exception that has been drilled at El Entredicho deposit in the Almaden district.

Ore Occurrence

Ore Types

Most of the ore in the Almaden district is contained in stratabound orebodies within the Criadero quartzite. Of the many deposits in the district, one notable exception, Las Cuevas, differs considerably. Hernandez et al. (1999) divide Almaden ore into two main types:

Type 1: stratabound ore characterized by cinnabar (HgS) concentrations in lower Silurian (Criadero) quartzites (e.g. Almaden deposit proper and El Entredicho deposit)

Type 2: discordant orebodies hosted by or related to fraileasca diatremes (e.g. Las Cuevas deposit, **figure 3a and b**)

Mercury occurs in the quartz arenites (Type 1 deposits) principally as cinnabar, but native mercury and metacinnabar are also present. Cinnabar appears in several facies described by Saupe (1990): reticulate (used by Saupe to replace previous term of “stockwork ore”), massive, impregnation in healed cracks, between and within quartz grains, and in pyrite grains, and as euhedral and botryoidal crystals filling cavities. Fraileasca sometimes contains significant mercury mineralization, but this is the exception (Hernandez et al. 1999).

In the Las Cuevas deposit (Type 2 deposits), cinnabar is the major sulfide with minor pyrite present. Secondary native mercury is also common. Most of the Las Cuevas ore is hosted in actual volcanics. Cinnabar and minor pyrite occur as massive replacements, infillings in tension cracks, and as “mylonitic cinnabar” in association with thrust shears (Higueras et al. 1999).

Type 2 deposits have been identified in the Lower Silurian (Nueva Concepcion), Upper Silurian-Lower Devonian (Las Cuevas), Lower Devonian (El Burcio), and Upper Devonian (Guadalperal and Corchuelo) (Hernandez et al. 1999). These stratigraphic positions vary more widely than Type 1 deposits, but these determined positions have varying degrees of certainty (see Jebrak and Hernandez 1995).

Though the Almaden district is monometallic, there are some occurrences of antimony, a common accessory to mercury, known locally. Three stibnite occurrences within 20 km are the known extent of antimony within the Almaden district, those these are very small in extent and have not been adequately described (Saupe 1990).

Old Almaden Mine

The old Almaden mine is the deposit after which the district is named, and consists of several stratabound Hg lenses in the Criadero quartzite. Of the four Criadero quartzite members, two are significantly mineralized. The lowest member is a pure white quartzite and hosts the San Pedro and San Diego orebodies, while the uppermost member is black and hosts the San Nicolas and San Francisco orebodies (Jebrak and Hernandez 1995).

Las Cuevas Deposit

The Las Cuevas deposit, the only one on the northern flank of the Almaden synclinorium, is estimated to contain 135,000 flasks of mercury (at 76 pounds of mercury per flask) at an average ore grade of 5% Hg, with local grades up to 40% (Higuera et al. 1999). Las Cuevas is worthy of mention because unlike other deposits in the Almaden district, it displays distinctly epigenetic features. Ore occurs in both volcanics and as stratabound lenses in black sandstone (Jebrak and Hernandez 1995). The volcanics in Las Cuevas differ from the frailesca because they are not simply a mega-brecciated diatreme, but are diatremes of what is described as a “lapilli tuff” (Jebrak and Hernandez 1995).

Though it has long been thought that the Las Cuevas deposit is in Devonian sediments, there are few paleontological indicators. This assumption is based on a theory that the Almaden synclinorium is a fairly simple structure, but Jebrak and Hernandez (1995) have found that tight folding is common and that deformation is more penetrative than previously thought. Based on this model and stratigraphic similarities, Jebrak and Hernandez (1995) hypothesized that Las Cuevas is actually hosted by the same lower Silurian sediments that host the old Almaden deposits, though this is not widely accepted (see Ortega 1997).

Ore Genesis

Early reports by Ransome (1921) and van der Veen (1924) focused on the connection between the Almaden ores and igneous rocks as a possible source of mercury. Ransome (1921) put forth the early theory that cinnabar was a replacement in the Criadero quartzite. Today, geologists are still trying to determine the source of mercury, how the mercury was deposited, and relative timing of deposition.

Timing of Ore Deposition

Cinnabar in the old Almaden deposit impregnates the Criadero quartzite, and is thought to be syn- or diagenetic because it does not mineralize faults, and therefore must date to sometime before lower Carboniferous regional folding and faulting that created the Almaden synclinorium (Saupe 1990). Saupe (1990) noted textures in cinnabar from the Almaden mine that is interpreted to show mechanical reworking of cinnabar grains and load casts in cinnabar mud, though this has yet to be substantiated by others. Saupe (1990) preferred a syngenetic deposition with hydrothermal ore fluids based on these observations, with frailesca diatremes as possible channeling mechanisms for Almaden Type 1 deposits.

The discordant nature and epigenetic characteristics of the Las Cuevas deposit can lead to the quick assumption that perhaps Almaden ores might also be epigenetic. Cinnabar fills tension gashes and fold hinges, and horizontal tension cracks at the contact of black shale and the volcanics, presumed to be the hinge of a drag fold, are mineralized into stockwork ore (Jebrak and Hernandez 1995). These are clearly mineralized post-

sedimentary structural features. $^{40}\text{Ar}/^{39}\text{Ar}$ dates on Las Cuevas illites in proximal alteration date from 363.2 ± 0.8 Ma, during the Hercynian compressions (Hall et al. 1997). Higuera et al. (1999) and Jebrak and Hernandez (1995) agreed that discordant Type 2 ore is a result of deep orogenic activity and remobilization of mercury. Jebrak and Hernandez (1995) identified reticulate, stratabound ore in black quartzite in Las Cuevas as the possible source of remobilized ore fluids. If Jebrak and Hernandez (1995) are correct in their hypothesis that this black quartzite is actually Criadero quartzite, then it is easy to visualize syn- or diagenetic deposition of ore with later remobilization with some control being exerted by the Las Cuevas Fault (**figure 4**).

Sources of Mercury

Almaden is far and away the largest mercury anomaly known in the Earth's crust, so it is obvious to wonder where all this mercury came from. Early associations with the volcanics that created the frailesca are still valid due to their proximity to Almaden orebodies, though their role as fluid channeling mechanisms and sources of mercury are not well understood. Because the orebodies seem to be associated so intimately with frailesca diatremes, all theories of ore deposition implicate them somehow, although it is unclear exactly what their role in ore deposition is.

Saupe (1990) presented the somewhat unpopular view that the source of mercury is not the alkali basalts that formed the frailesca, but Ordovician black shales that contain 2 ppm Hg. At Almaden, these shales are 500 m thick, and the mercury budget for the entire Almaden district could be accounted for by 100 km^3 of the black shale (Saupe 1990). However, de Boorder and Westerhof (1994) point out that these shales have a wide distribution in Europe, but nowhere else has mercury deposits approaching the magnitude of Almaden. Saupe's (1990) explanation is that the Criadero quartzite is a unique porous stratum above the Ordovician black shale, and does not occur elsewhere in Europe, though this is not entirely satisfactory.

de Boorder and Westerhof (1994) find a sedimentary origin unsatisfactory because ultimately mercury is not a rock-forming constituent of sediments, so it must have come from somewhere, even if it was from minerals in the basement rocks. They, like most others, prefer a mantle source, where mercury originated from the Paleozoic alkali basalt volcanism. Alkali basalt volcanism is rare in Iberia but also associated with mercury and antimony mineralization in Cantabria (de Boorder and Westerhof 1994). They also note that Sb-W-Hg deposits tend to have genetic relationships with mafic and ultramafic volcanism (e.g. New Almaden, California), whether it is direct or in formation of sediments in basins where sedimentary exhalation takes place. This certainly does not exclude the Ordovician black shales as a source, but does add the qualifier that the ultimate source was the mantle.

Hernandez et al. (1999) find that many mercury deposits have a connection with mantle metasomatism, and the presence of ultramafic xenoliths and other geochemical data for volcanics at Almaden suggest that mercury deposition may have taken place as a result of rifting and mantle pluming. Hg-enrichment of the black shales may have occurred through hydrothermal processes during the deposition of stratabound bodies in the Criadero quartzite.

Conclusions

The Almaden region is unique for the very large nature of its monometallic mercury deposits. Among the questions still to be studied by geologists are: the source of mercury, whether primary ore deposition was epi-, syn-, or diagenetic, and why Almaden is the only mercury deposit of such magnitude.

- 1) Most geologists agree that the mercury source is mantle derived and was channeled through the volcanic diatremes that today are expressed as frailesca. Because the frailesca is so intimately related to ore zones, and mercury is thought to be mantle-derived in this case, it is logical to assume that hydrothermal circulation transported mercury and impregnated the Criadero quartzite. Saupe (1990) even envisioned so-called “black smokers” spewing cinnabar onto the ocean floor, and reticulate cinnabar may represent a stringer zone in this system.
- 2) Under those circumstances, ore deposition would be undeniably syngenetic. Clasts of lower Silurian sedimentary units are present in the breccia, so some degree of lithification must have taken place before ore deposition. Once the Criadero sediments had undergone some degree of diagenesis, then diatreme formation and subsequent ore deposition could take place.
- 3) The magnitude of the Almaden has yet to be adequately addressed. Because of its anomalous size, unique characteristics such as frailesca must be considered as a possible conduit in the development of such large orebodies, and may also be of use in exploration for other Paleozoic mercury deposits in Iberia.

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