

# Mineralogy and geochemistry of the Masa Valverde blind massive sulphide deposit, Iberian Pyrite Belt (Spain)

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## Abstract

Masa Valverde is a blind, volcanic-hosted massive sulphide deposit recently discovered in the Spanish sector of the Iberian Pyrite Belt (IPB). The deposit is more than 1 km long and is located at depths between 400 and 850 m, in direct spatial association with a residual gravimetric anomaly. The ore body is concealed beneath Culm sedimentary rocks which cover the western extension of a Hercynian age anticline, a few kilometers west of an area where older massive sulphide workings existed. The Masa Valverde deposit consists of two main ore bodies composed dominantly of massive and banded pyrite which are hosted by a volcano-sedimentary sequence made up of felsic tuffs interlayered with shale, siliceous exhalite and radiolarian chert. The abundance of sedimentary host rocks to the deposit is a feature shared by other large massive sulphide deposits in the eastern sector of the IPB and is interpreted as significant with respect to the origin of the deposit (a break in volcanic activity). The thickness of the upper massive sulphide orebody varies between a few meters and 70 m, and it consists of lenses and blankets of massive sulphides with interbedded tuff and shale and occasionally stockwork zones. The lower orebody is smaller and thinner than the upper one, but this may be due to incomplete drilling. Two types of stockwork occur beneath the massive sulphide bodies, the more common type consists of irregular and anastomosing sulphide veinlets and irregular blebs formed by replacement. Stockwork with cross-cutting, generally straight-sided, sulphide veins is, by contrast, suggestive of formation by hydraulic fracturing. The mineralogy and alteration processes of the ore and host rocks at Masa Valverde are analogous to those of other IPB massive sulphides. The average temperature of formation of the components of the ore zones estimated on the basis of chlorite thermometry are as follows: siliceous exhalites (290 °C), massive sulphides (325 °C) and stockworks (305 °C). Rare earth element measurements indicate that the lowest metal concentrations occur in chloritites, which occasionally host Cu-rich stockwork and are characterised by a strongly negative Eu anomaly. By contrast, rocks hosting the sulphide lenses, where silicification, sericitization and carbonatization are more intense, are enriched in LREE. Two main stages of hydrothermal activity are suggested for the Masa Valverde deposit. During an early stage, ore fluids would have discharged onto the sea floor resulting in the deposition of pyrite with sphalerite and galena. Later on, with continued input of high temperature fluids (290 to 315 °C), chalcopirite precipitated, especially in the stockworks and at the base of the sulphide lenses. At Masa Valverde, this late Cu-rich hydrothermal event would have produced an ascending Cu-front which overpassed the stockwork zone and reached a higher temperature (325 °C) at the base of the massive sulphide lenses. The combination of geological, mineralogical and geochemical features of the Masa Valverde deposit provide guidelines for exploration for new blind orebodies in this part of the IPB, where tuffs and sedimentary rocks

are the dominant host lithologies. The Masa Valverde deposit can be considered as a VHMS subtype transitional to SHMS.

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## 1. Introduction

The Iberian Pyrite Belt (IPB) in south Portugal and southwest Spain is one of the largest mining districts in the world, with massive sulphide reserves in excess of 1700 million tons (Mt), containing 14.6 Mt Cu, 13.0 Mt Pb, 34.9 Mt Zn, 46.1 kt Ag and 880 t Au (Leistel et al., 1998a). The bulk of these reserves, however, correspond to massive pyrite orebodies which are uneconomic because of the low concentration of base- or precious-metals or because of the high cost of producing metal concentrates from the very fine-grained sulphide ore. Nevertheless, since the end of the past century, more than 300 Mt of polymetallic sulphides (Cu, Zn as well as Pb sulphides) and their gossans, which in some cases (e.g., Cerro Colorado, Lomero Poyatos, Aznalcóllar or Filón Sur of Tharsis) contained significant concentrations of Au and Ag (up to 4 and 40 g/t Au and Ag, respectively), have been mined in the IPB (Arribas, 1998).

Renewed exploration in the IPB during the 1980s, following discovery in 1977 of the world-class Neves Corvo deposit in Portugal (Fig. 1), led to the discovery in southwest Spain of four major blind deposits: Migollas (discovered in 1989; Santos et al., 1993), Masa Valverde (discovered in 1986; Ramírez-Copeiro et al., 1988); Aguas Teñidas Este (discovered in 1985; Hopgood, 1994) and Las Cruces (discovered in 1994; Knight et al., 1999). All three deposits were found using geophysical methods at depths of 300 to 500 m within Paleozoic volcanic and sedimentary rocks.

The Masa Valverde massive sulphide deposit, which is the subject of this study, is located 14 km southwest of the town of Valverde del Camino (Huelva Province). The deposit was discovered and explored by a joint venture formed by Empresa Nacional Adaro and Compañía Minera Peñarroya. Exploration drilling was focused on a 1000 × 850 m residual gravimetric anomaly (0.8 mgal of intensity), which was selected following magnetic and electromagnetic (mainly TEM) surveys to help discriminate anomalies due to mafic rocks or shale-related conductors (Maroto et al., 1993).

Exploration of the Masa Valverde deposit involved 25 vertical diamond drill holes whose maximum depth varied between 582 and 1015 m due to the dip of the ore body.

This paper documents the geology of the Masa Valverde orebody with emphasis on its geometry, lithostratigraphic setting, mineralogy and geochemistry. The petrographic and chemical analyses which form the basis of this study were conducted at the School of Mines of the Polytechnical University of Madrid on core samples selected from 21 diamond drill holes. The objectives of the study are (i) to establish a genetic model for the Masa Valverde ore body that may be compared to genetic models for other deposits in the IPB, and (ii) to identify relevant guides for exploration of new blind deposits in the region or elsewhere.

## 2. Regional geology

The Iberian Pyrite Belt extends from near Sevilla in south Spain to the Atlantic Ocean coast in south Portugal, a distance of about 250 km. Geologically, the IPB is located within the South Portuguese Zone, the southernmost tectono-stratigraphic unit of the Iberian Hercynian Massif (Fig. 1). Surface rocks in the South Portuguese Zone consist of Paleozoic submarine volcanic and sedimentary lithologies (Schermerhorn, 1971; Oliveira, 1990).

The geology of the IPB has been studied by numerous authors: notable publications include Strauss et al. (1977), Routhier et al. (1978), Barriga and Carvalho (1983), Sáez et al. (1996, 1999), Quesada (1998) and Leistel et al. (1998a). There is agreement among most workers on the existence of three main geological units in the Spanish part of the IPB, from bottom (older) to top (younger) these are: (1) a detrital platform sequence of Middle Devonian to Late Famennian age, known as the Phyllitic–Quartzite Group, (2) a volcanic and sedimentary formation of Late Famennian to Middle Viséan age (approx. 360 to 340 Ma; Harland et al., 1989), termed the Volcanic–Sedimentary Complex and

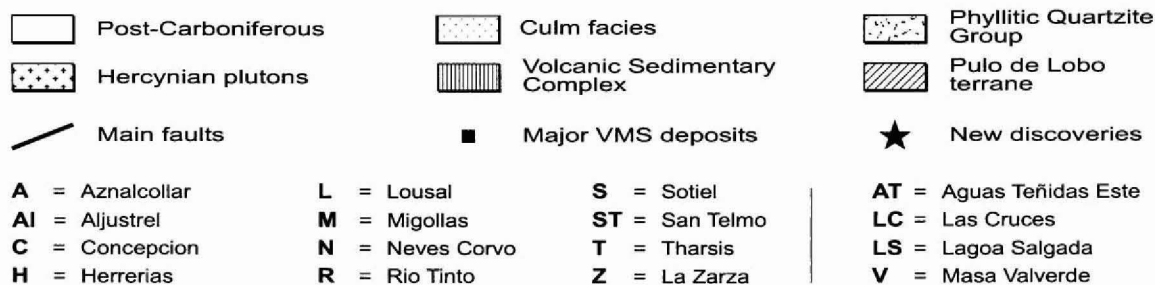
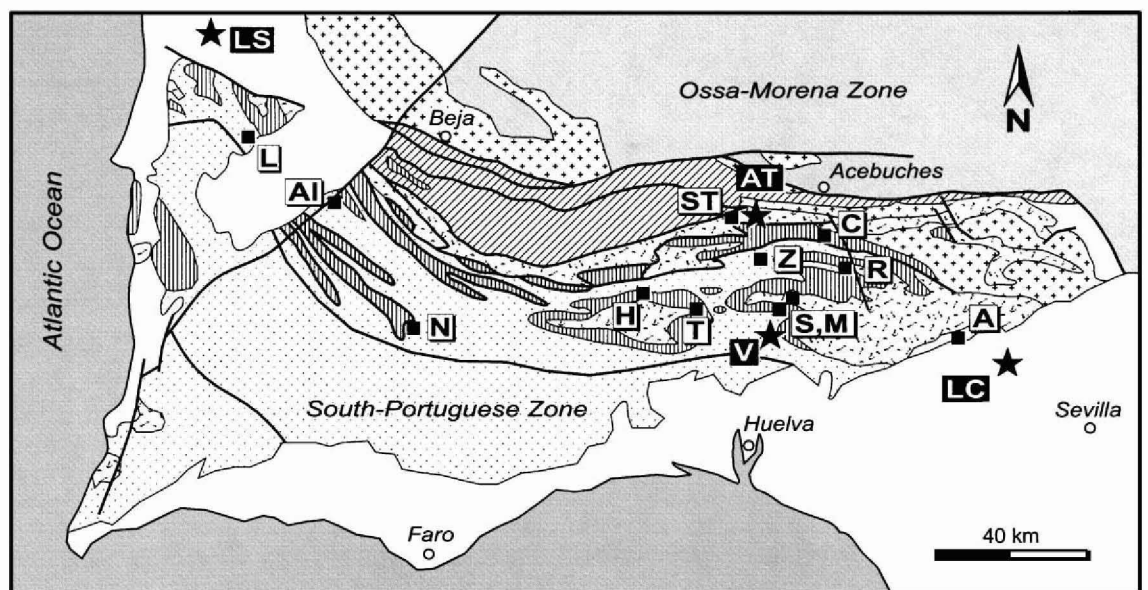


Fig. 1. Map showing the location of the Masa Valverde deposit in the Iberian Pyrite Belt.

host to the massive sulphide orebodies, and (3) a turbidite unit of late Viséan age, known as the Culm facies (Schermerhorn, 1971). The Volcanic-Sedimentary Complex varies in thickness between 50 and 800 m and contains three principal dacitic to rhyolitic volcanic (pyroclastic and lavas) sequences (Thiéblemont et al., 1998), which occur interbedded with mafic lavas and sedimentary rocks. Black shale, sandstone and jasper layers occur within the two lower felsic volcanic sequences; a bed of purple slate separates these from the upper rhyolitic volcanic sequence. The massive sulphide orebodies of the IPB occur within the two lower volcanic units, typically within black shales or lying on top of volcanic rocks.

The IPB is characterised by at least three phases of Hercynian age deformation (Ribeiro and Silva, 1983). The first phase led to asymmetric isoclinal folding

verging to the S and SW and development of WNW-striking and N-dipping slaty cleavage. During this phase, shearing of the overturned limbs of the asymmetric folds resulted in stacking of normal fold limbs. The second phase of deformation led to undulation of some of the main fold axes and local development of crenulation cleavage. Recently, Quesada (1998) has documented the presence in the IPB of duplex-geometry thrusting with mylonitic foliation associated with flats and ramps.

### 3. The Masa Valverde ore deposit

The Masa Valverde deposit (Ramírez-Copeiro et al., 1988; Ruiz and Arribas, 1993) is located within the southern flank of the Valverde del Camino anticline, a

Hercynian age structure with an average dip of  $20^{\circ}$  to the WNW (Fig. 2). The ore body is concealed beneath Culm sedimentary rocks which cover the western extension of the Valverde del Camino anticline, a few kilometers west of an area where older massive sulphide workings existed (Campanario mines; Fig. 2).

Drilling indicates that the Volcanic-Sedimentary Complex in the Masa Valverde area is more than 425 m thick and consists of alternating shales, tuffites, tuffs and siliceous exhalites (see below). The main footwall lithologies are black and calcareous grey shale and felsic tuffs, the main hangingwall lithologies are shale and, occasionally, tuffite. Lenses of siliceous exhalites are also found both in the footwall and hangingwall of the massive sulphides. The presence of numerous layers

of shale and tuffite in the Masa Valverde area is consistent with its location within the Southern Domain of the IPB, which is characterised by the abundance of sedimentary facies (Quesada, 1996; Leistel et al., 1998a). The volcanic rocks are only pyroclastic, unlike other areas with massive sulphide mineralisation in the IPB, where lavas or domes are present.

The stratigraphic column in the Masa Valverde area is characterised by rapid lateral variations of facies and thickness, both with respect to host rocks and the massive sulphides (Fig. 3). The upper section of the Volcanic-Sedimentary Complex in the Masa Valverde area is missing, and the Culm unit overlies directly the host rocks of the massive sulphides. The Culm has a minimum thickness of 370 m and consists of a seq-

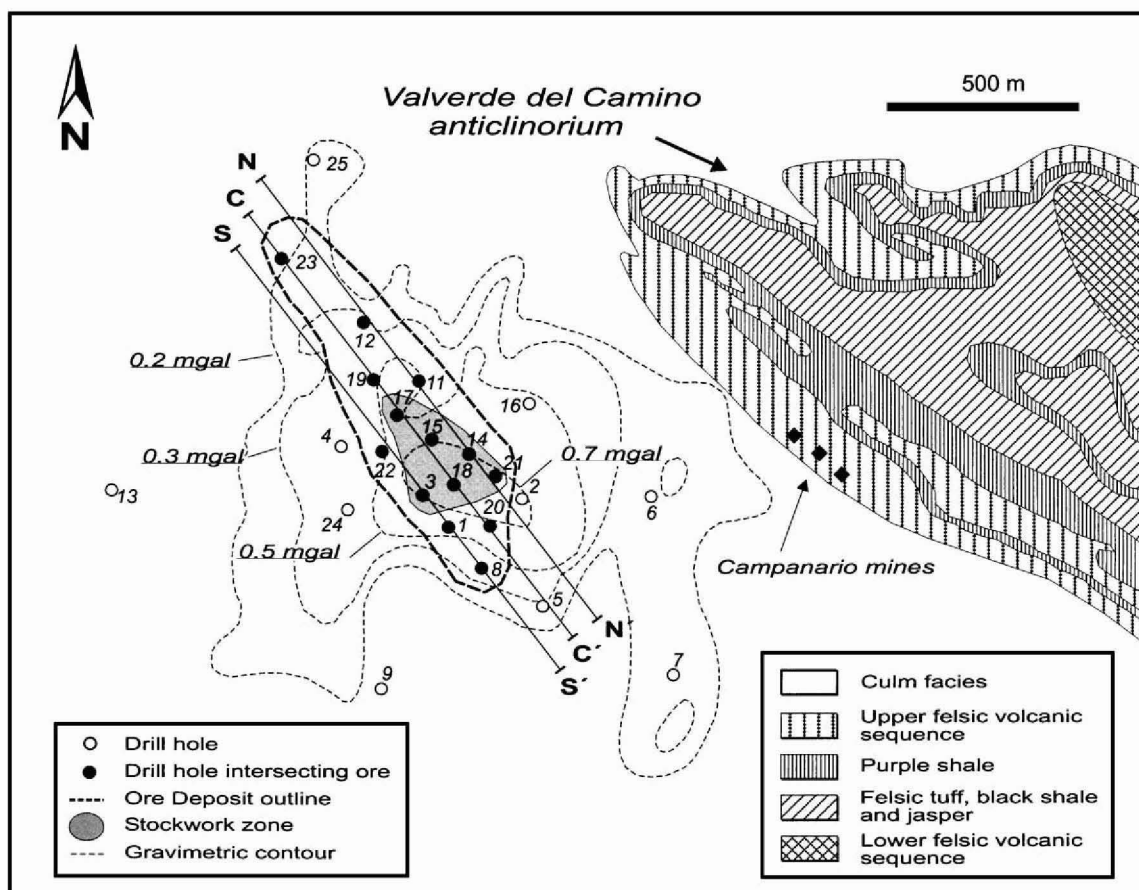


Fig. 2. Location of the Masa Valverde massive sulphide deposit and its associated gravimetric anomaly in the western part of the Valverde del Camino anticlinorium.

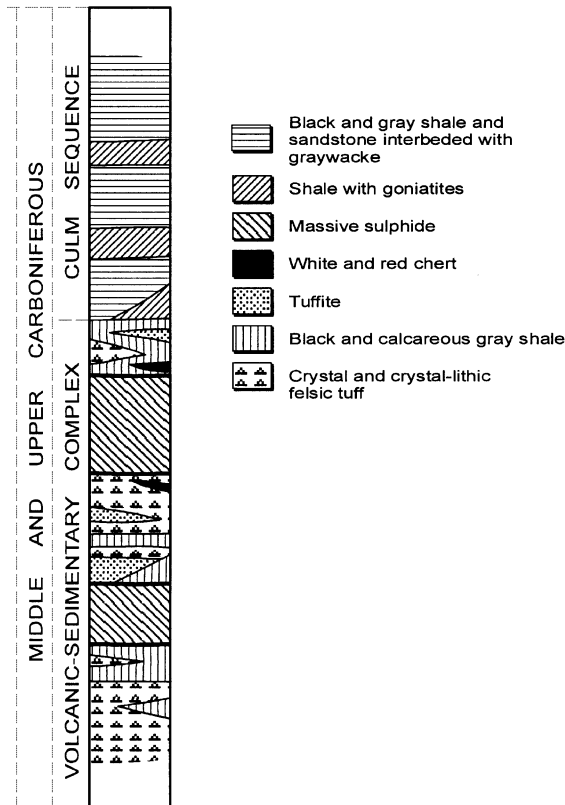


Fig. 3. Generalised stratigraphic column in the Masa Valverde deposit at the contact between the Volcanic Sedimentary Complex and the Culm sequence.

uence of alternating grey and black shale, occasionally containing goniatites, sandstone and graywacke (Ruiz and Arribas, 1993; Castroviejo et al., 1996).

All lithologies within the Masa Valverde region, including the Culm and the massive sulphide ore bodies, underwent tectonic deformation and very low to low grade metamorphism during the Hercynian orogeny (Schermerhorn, 1971; Munhá, 1983, 1990). The effect of the Hercynian metamorphism in the ore bodies is limited to local recrystallization of the sulphides. Multistage tectonic deformation led to tight isoclinal folds verging to the SSW and reverse faults. The massive sulphide orebodies show evidence of faulting and tectonic brecciation, but the evidence available from drill data is limited. The deposit follows the N120E trend of the IPB and is divided into various blocks by late NNE faults. These blocks generally

subside towards the west. Consequently, the western limit of the deposit, which is still open, occurs at a depth of more than 800 m.

The Masa Valverde deposit is more than 1 km long and is located at depths between 400 and 850 m. It is made up of two main orebodies (Fig. 4). The thickness of the upper orebody varies between a few meters and 70 m, and it consists of lenses and blankets of massive sulphides with interbedded tuff and shale occasionally stockwork zones. The lower orebody is smaller and thinner than the upper one, but this may be due to incomplete drilling. Overall, the details of the internal structure of the two ore bodies are poorly understood. The main stockwork zones have been intersected mainly beneath the upper ore body (Fig. 4). A stockwork underneath the upper ore body exceeds 100 m in thickness.

The published ore reserves of the Masa Valverde deposit have been grouped according to three main ore types (Costa and Parrilla, 1992): Complex ore, 11.0 Mt (0.54% Cu, 5.0% Pb+Zn, 0.76 g/t Au); Cupriferous ore, 1.3 Mt (1.91% Cu, 1.7% Pb+Zn, 0.10 g/t Au); Pyrite ore, 80.0 Mt (0.40% Cu, 1.5% Pb+Zn, 0.10 g/t Au).

### 3.1. Host lithologies

#### 3.1.1. Black shale and calcareous grey shale

The black shale is made up of micro- to crypto-crystalline quartz and carbonaceous matter which occurs along a well-developed schistosity. Sericite and chlorite are also present, with some disseminated sulphides, as well as tourmaline and zircon, as accessory minerals. The quartz forms occasionally lenticular aggregates and may be globular and of volcanic origin.

The calcareous grey shale is composed of sericite, carbonates (dolomite and siderite), quartz and chlorite, with tourmaline and zircon as accessory minerals. Quartz occurs as micro- to crypto-crystalline quartz or as globular crystals of volcanic origin. In the latter case, the grey shales are interpreted to have a volcanoclastic origin.

The carbonates in the calcareous grey shale form fine alternating layers which are sometimes fragmented by the crenulation which deforms  $S_1$ . This has resulted in the formation of carbonate lenses which recrystallized from the nucleus outwards and produced rhombohedral porphyroblasts of Fe-rich carbonate,

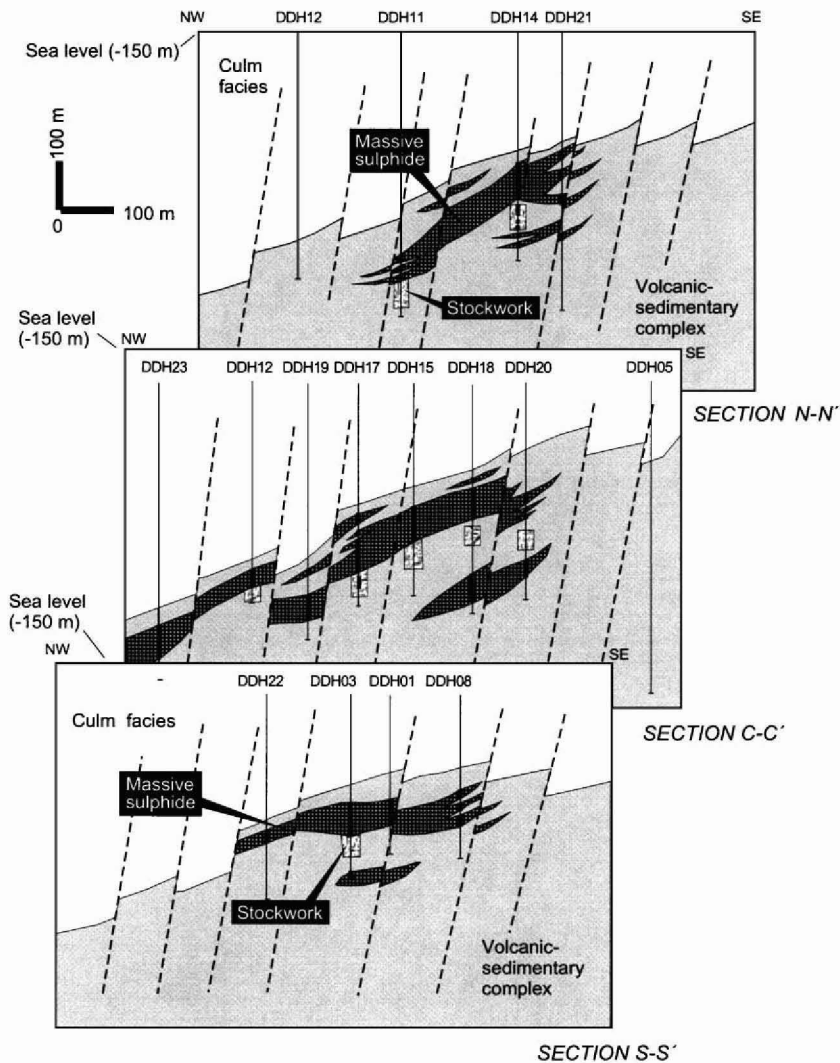


Fig. 4. Longitudinal sections of the Masa Valverde deposit along profiles N–N', C–C' and S–S' shown in Fig. 2.

occasionally zoned according to their Fe content. These porphyroblasts frequently have a core made up of euhedral quartz crystals and are often partially to totally chloritized and silicified. Some of these porphyroblasts exhibit pressure shadows made up of sericite and/or chlorite and/or micro-crystalline quartz.

Occasionally, the calcareous grey shales may be referred to as carbonaceous grey shales because they contain abundant carbonaceous matter disseminated in the form of discontinuous layers roughly parallel to  $S_0$ . This group of rocks also includes greyish-green to

purple shales, the colour of which is due to the abundance of fine-grained chlorite and of Fe oxides that are parallel to the schistosity.

### 3.1.2. *Crystal felsic and crystal-lithic felsic tuff*

The crystal felsic tuff is a rhyolitic pyroclastic rock formed by broken quartz and plagioclase phenocrysts. The quartz crystals are globular with corrosion embayments and reaction rims formed by sericite and quartz. They may have pressure shadows made up of sericite. Twinned plagioclase crystals are less common, and are

frequently carbonatized, sericitized and occasionally silicified. The groundmass is made up of sericite and micro- to crypto-crystalline quartz and, to a lesser degree, chlorite and carbonates. Euhedral zircon and apatite are accessory minerals. In addition to the previous components, the crystal-lithic felsic tuff also contains lithic fragments of felsic tuff, black shale and shards of devitrified, sericitized volcanic glass.

### 3.1.3. Siliceous exhalites

The siliceous exhalites of Masa Valverde form stratiform, lens-shaped bodies of chert in sharp contact with their host rocks. These chert lenses may measure anything from 1 cm to 3 m, although thicknesses of a few centimetres prevail. The siliceous exhalites are located on the hanging wall or footwall of the sulphide bodies, typically a few meters away from them. The footwall chert is generally white, occasionally with a grey or green tone, while the hanging wall chert is commonly red. The radiolarian chert may occur both in the hanging wall and the footwall. The petrography and mineralogy of these chert types are similar to those described by Leistel et al. (1998b) for other deposits in the IPB. It is noteworthy that manganiferous exhalites found elsewhere in the IPB (Leistel et al., 1998a) have not been found associated with Masa Valverde.

*3.1.3.1. White sulphide footwall chert.* The white sulphide footwall chert is composed mainly of two generations of quartz. The first type of quartz consists

of micro-crystalline (<7 µm) quartz irregularly impregnated by powdery carbonate or containing scarce rhombohedral crystals of ankeritic carbonate, as evidenced from chemical analyses (Table 1). This type of quartz is occasionally accompanied by small amounts of ferriferous chlorite which forms light-green or brownish-grey fibrous aggregates of chamosite with radial structure (Table 2; Fig. 5). The second stage of quartz consists of comb-textured, macrocrystalline fracture-filling quartz. The sulphides are euhedral pyrite (avg. size 500 µm) and chalcopyrite (avg. size 70 µm). The white chert was traversed by carbonate veinlets and subsequently brecciated. Breccia fragments, which sometimes contain sponge spicules, are embedded in a sulphide matrix.

*3.1.3.2. Red hematite + magnetite ± carbonate ± chlorite hanging wall chert.* This hematitic chert corresponds to recrystallized silica-rich rocks typically known in the IPB as “jaspes rojos” (red jaspers). Its main component is micro-crystalline quartz containing powdery hematite which forms colloidal textures or gives rise to flakes up to 20 µm across. Magnetite occurs as euhedral crystals measuring about 20 µm across which appear either disseminated or forming aggregates in the micro-crystalline quartz. Exceptionally, the magnetite crystals are altered to hematite (martite) at the edges. The hematite that impregnates the quartz is absent in decoloured zones surrounding the magnetite crystals (Plate 1a). This is interpreted to

Table 1  
Electron microprobe data of carbonates from the Masa Valverde ores and host rocks

Sample <sup>a</sup>	T50	T51	MS36	T52	RE10	RE11	WE20	MS38	MS34	MS35	MS35	S40	S41	S42
CaO	55.79	28.21	0.13	0.28	30.14	30.64	29.92	1.13	30.83	30.45	0.21	1.08	30.22	28.16
MgO	0.00	5.70	6.80	5.83	10.27	8.11	9.31	0.44	14.56	6.91	2.53	3.79	8.42	9.68
FeO	0.16	20.26	52.27	48.35	14.39	15.62	14.99	0.39	7.63	15.76	51.09	53.87	12.74	16.58
MnO	0.59	2.95	1.18	4.43	1.49	1.95	1.58	0.05	1.37	2.70	7.37	1.06	4.31	1.70
BaO	0.00	0.00	0.00	0.68	0.00	0.00	0.33	0.00	0.00	0.00	0.01	0.31	0.42	0.00
SrO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
CO <sub>2</sub>	44.25	42.60	40.27	39.14	44.60	43.68	43.89	2.00	45.61	42.77	38.79	38.73	43.51	43.88
Ca	0.99	1.04	0.00	0.01	1.06	1.10	1.07	1.13	1.06	1.12	0.00	0.02	1.09	1.01
Mg	0.00	0.29	0.18	0.16	0.50	0.41	0.46	0.44	0.70	0.35	0.07	0.11	0.42	0.48
Fe	0.00	0.58	0.80	0.76	0.40	0.44	0.42	0.39	0.21	0.45	0.81	0.85	0.36	0.46
Mn	0.01	0.09	0.02	0.07	0.04	0.06	0.05	0.05	0.04	0.08	0.12	0.02	0.12	0.05
Ba	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
C	1.00	2.00	1.00	1.00	2.00	2.00	2.00	2.00	2.00	2.00	1.00	1.00	2.00	2.00

<sup>a</sup> RE = red exhalite, WE = white exhalite, MS = massive sulphide, S = stockwork, T = tuff.

Table 2  
Electron microprobe data of Masa Valverde chlorites

Ore type	Red exhalites		White exhalites	Massive sulphide	Stockworks			Tuff	
Sample	RE10	RE11	WE20	MS38	S41	S42	S40	T50	T51
SiO <sub>2</sub>	24.41	22.18	23.83	20.92	23.80	24.55	22.83	26.70	23.01
Al <sub>2</sub> O <sub>3</sub>	17.75	19.34	22.15	22.96	21.83	22.20	23.92	19.19	23.34
FeO	38.04	45.80	35.71	36.92	37.73	31.57	38.77	20.69	36.09
MnO	0.09	0.04	0.41	0.43	0.23	0.09	0.38	0.48	0.14
MgO	5.66	0.93	6.64	4.05	6.05	10.03	3.61	20.69	5.29
CaO	0.28	0.00	0.08	0.00	0.01	0.07	0.03	0.06	0.04
TiO <sub>2</sub>	0.03	0.04	0.05	0.04	0.01	0.00	0.00	0.04	0.02
Total	86.26	88.33	88.87	85.32	89.66	88.51	89.54	87.85	87.93
<i>Ions on the basis of 14 oxygens</i>									
Si	2.83	2.62	2.63	2.45	2.62	2.65	2.54	2.75	2.57
Al	2.42	2.70	2.88	3.16	2.84	2.82	3.13	2.33	3.07
Fe	3.68	4.53	3.29	3.61	3.48	2.85	3.60	1.78	3.37
Mn	0.01	0.00	0.04	0.04	0.02	0.01	0.04	0.04	0.01
Mg	0.98	0.16	1.09	0.71	0.99	1.61	0.60	3.17	0.88
Ca	0.03	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00
Total	9.96	10.02	9.93	9.97	9.95	9.94	9.90	10.08	9.90
T (°C) <sup>a</sup>	252.00	317.00	301.00	325.00	305.00	293.00	316.00		

<sup>a</sup> Formation temperatures calculated by following Walshe (1986) for quartz-saturated samples.

indicate that part of the hematite Fe was remobilized during diagenesis or metamorphism, resulting in the formation of magnetite. A similar process was described by Duhig et al. (1992) in iron exhalites of the Mount Windsor Volcanic Belt in Australia.

The ferriferous chlorite (Table 2 and Fig. 5), which is present in small quantities, forms aggregates of small crystals or fibers of strongly pleochroic, emerald-green chamosite associated with the magnetite. Chlorite continued to form after the magnetite had been deposited and filled fissures in which it is accompanied by calcite, sometimes twinned, and quartz. The ankeritic carbonate (Table 1) occurs as abundant euhedral crystals, isolated or in aggregates, within the chert. Pyrite, chalcopyrite, apatite and sericite also occur in limited quantities. The hematite chert is frequently fragmented, presenting a breccia-like texture, and crossed by fractures filled with quartz, chlorite and magnetite, the latter corresponding to a second generation formed from a Fe-rich fluid.

**3.1.3.3. Radiolarian chert.** Both the red and white exhalites may pass laterally to radiolarian-rich zones. The individual radiolaria can measure up to 450 µm in diameter and be completely replaced by micro-crys-

talline quartz and occasionally by chlorite (Plate 1b). Their presence is revealed by the powdery carbonate which impregnates the chert and frequently makes the texture and/or the outline of the radiolarian stand out.

#### 3.1.4. Hydrothermal alteration

Hydrothermal alteration of the host rocks associated with mineralization at Masa Valverde is similar to

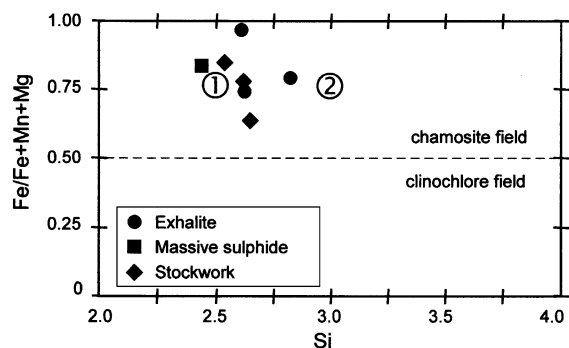


Fig. 5. Composition of chlorites from the Masa Valverde orebody following Foster (1962) and Bayliss (1975). All chlorites lie within the chamosite field, between Mg–Al chamosite (1) and Mg chamosite (2).



other deposits of the IPB and includes chloritization, sericitization, carbonatization and silicification. Silicification represents the most intense alteration type and is found mainly within the sulphide zones; the intensity of silicification is highly variable. Chloritization is observed both within the mineralized zones and their surrounding host rocks. Sericitization is pervasive and typically better developed within the surrounding host rocks, where it extends beyond the reach of chloritic alteration. Carbonatization is less common and accompanies chlorite. Hydrothermal

alteration appears to be more extensive in the footwall zone of the ore body, where it exhibits a roughly concentric zonation, with an inner silicic and chloritic zone and an external sericitic zone. Chloritization has not been observed in the hanging wall.

### 3.2. Massive sulphides

Two types of massive sulphide are recognised at Masa Valverde ore deposit: *massive ore*, with >90% pyrite and *banded ore*, with 50% to 65% pyrite. The mas-

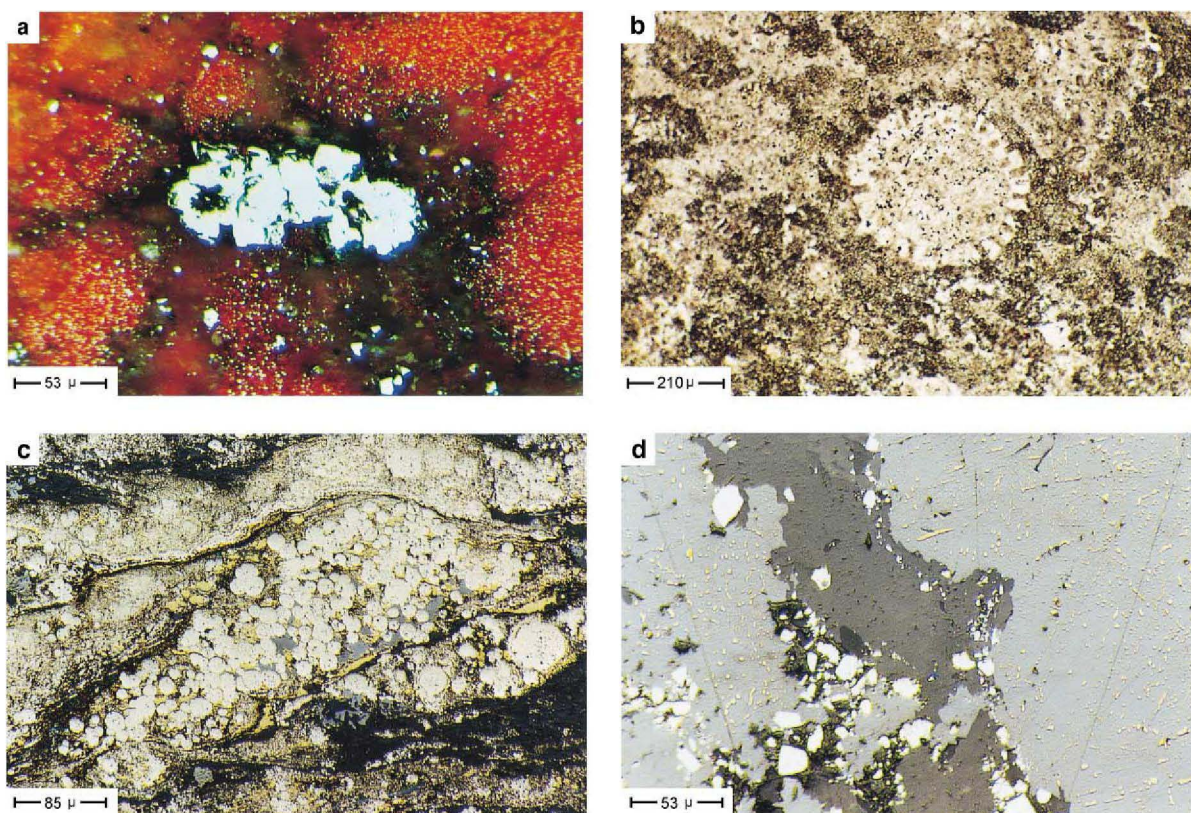


Plate 1. (a) Euhedral magnetite crystals growing at the expense of fine-grained primary hematite in decoloured zones of the red hematite hanging wall chert. Plane-polarised reflected light. (b) The structure of radiolarians in hematitic chert has been preserved after replacement by microcrystalline quartz and chlorite. Plane-polarised transmitted light. (c) Band of framboidal pyrite, with small cavities of sphalerite and chalcopyrite alternating with siliceous–micaceous material in banded sulphide ore. Plane-polarised reflected light. (d) Small pyrite crystals embedded in sphalerite with exsolutions of chalcopyrite in a non-cupriferous massive sulphide ore cross cut by carbonates. Plane-polarised reflected light. (e) Disease texture in the stockwork. The chalcopyrite, which replaced sphalerite along fissures and crystallographic planes, also corroded earlier pyrite and was later replaced by carbonates (centre, dark grey). Plane-polarised reflected light. (f) Stannite crystals within chalcopyrite surrounded by quartz, carbonates and micaceous material. Plane-polarised reflected light. (g) Intergrowth tetrahedrite and of elongated crystals of cosalite embedded in chalcopyrite containing small inclusions of native bismuth. Plane-polarised reflected light. (h) Pleochroic halos surrounding hydrothermal zircons in a chloritite hosting a stockwork located below the upper orebody. Cross-polarised transmitted light.

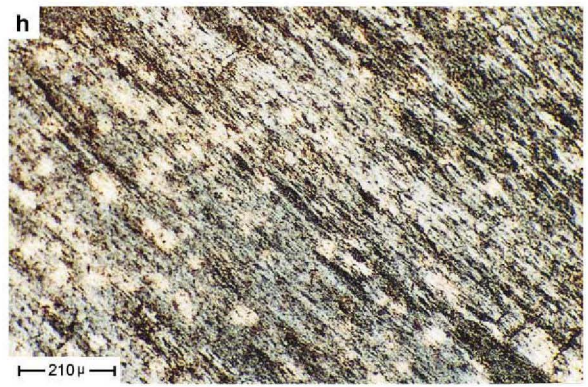
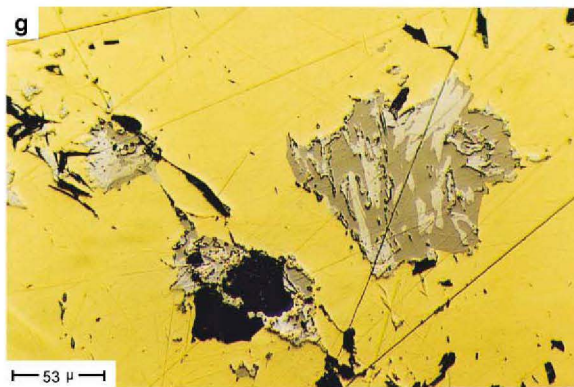
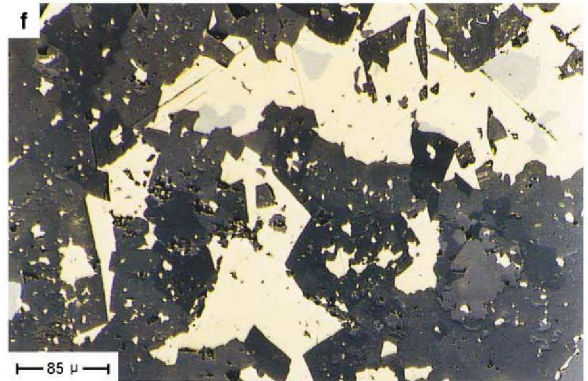
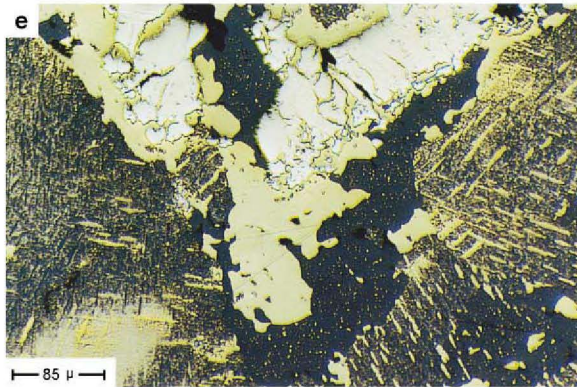


Plate 1. (continued).

sive ore represents about 75% of the massive sulphide mineralization and makes up the bulk of the lower orebody, where banded ore is rare. Banded ore occurs mainly at the top of the upper orebody, and its thickness ranges from some decimetres to 3 m maximum.

The massive ore is formed almost entirely by euhedral or subhedral pyrite aggregates. Occasionally, the pyrite is framboidal, colloform and oolitic, and when this pyrite is located at the base of the upper orebody, it can be accompanied by chalcopyrite and some sphalerite.

The banded ore shows a layered texture due to: (a) alternation of the pyrite with sphalerite, galena and chalcopyrite, occasionally tetrahedrite; (b) disseminated pyrite within silicate- and carbonate-rich layers intercalated in the massive ore or in the country rocks; (c) graded bedding of pyrite grains, which range from 3  $\mu\text{m}$  to 1 mm across, in layers intercalated with the ma-

ssive ore. Slumping and breccia textures are also frequent in the massive sulphides of Masa Valverde, slumping due to syn-sedimentary debris flow and breccia interpreted to be the result of tectonic deformation.

### 3.2.1. Mineralogy

The mineralogy of the Masa Valverde orebody is simple and similar to that of other massive sulphide deposits in the IPB. It consists of pyrite and, to a lesser degree and in order of decreasing abundance, sphalerite, galena, chalcopyrite, tetrahedrite and arsenopyrite. Accessory ore minerals include bournonite, stannite, pyrrhotite, cassiterite, cubanite, native bismuth, cosalite and electrum.

*Pyrite* occurs in aggregates of subhedral and euhedral crystals, occasionally zoned and corroded by later chalcopyrite. Framboidal (Plate 1c), colloform and oolitic textures as well as concentric alternations with

chalcopyrite and tetrahedrite are also common; as it is also the case in other mines (Tharsis, Sotiel y Aznal-cóllar) of the southern zone of the IPB (Velasco et al., 1998).

*Sphalerite* is found within the massive pyrite or filling micro-cavities or micro-fissures. Sometimes it forms isolated zoned crystals and layers alternating with other sulphides, more rarely it is colloformic in texture. The sphalerite colour changes from light- to dark-brown according to its Fe content, which varies from 0.47% to 6.97%, while the Cd content varies from 0.08% to 0.34% (Table 3). These values are consistent with those obtained by Marcoux et al. (1996) for other massive sulphide deposits of the IPB. Less frequently, in non-cupriferous ores, i.e., when the sphalerite is only accompanied by pyrite and galena, the Zn sulphide contains occasionally chalcopyrite exsolutions (Plate 1d). However, the sphalerite normally presents chalcopyrite inclusions in the form of blebs and/or thin plates less than 14 µm in thickness which cause disease texture (Plate 1e). These inclusions are irregularly distributed, or sometimes arranged in a wavy pattern roughly parallel to the crystallographic planes. The disease texture occurs particularly in the stockwork zones and, to a lesser degree, in the interaction or basal zone of the massive sulphide lenses where Bi minerals are also found.

The origin of the disease texture of chalcopyrite in sphalerite at Masa Valverde may be attributed both to replacement as well as coprecipitation processes. The most common case is probably due to the replacement of sphalerite by chalcopyrite (Barton and Bethke, 1987), which at Masa Valverde takes place at the base of the massive sulphide bodies. Here, as indicated by Grenne and Vokes (1990) for the Hoydal deposit in

Table 3  
Electron microprobe data of sphalerite from Masa Valverde

Sample		S	Zn	Fe	Cd
MS-32	Wt.%	32.14	67.32	0.47	0.08
	At.%	1.00	1.03	0.01	
MS-33	Wt.%	31.70	65.60	2.37	0.34
	At.%	1.00	1.02	0.04	
MS-35	Wt.%	32.25	64.84	3.53	0.27
	At.%	1.00	0.99	0.06	
MS-37	Wt.%	34.21	58.82	6.97	
	At.%	1.00	0.84	0.12	

Table 4  
Electron microprobe data of tetrahedrite from the Masa Valverde deposit

Sample <sup>a</sup>		Cu	Ag	Fe	Zn	Sb	As	S
MS-30	Wt.%	34.08	1.22	3.27	3.48	35.12	–	24.49
	At.%	9.13	0.19	1.00	0.91	4.91	–	13.00
MS-31	Wt.%	33.52	2.14	5.08	1.47	31.43	0.67	25.69
	At.%	8.56	0.32	1.48	0.36	4.19	0.15	13.00
MS-32	Wt.%	36.32	2.64	2.20	3.62	30.47	–	24.68
	At.%	9.65	0.41	0.67	0.93	4.23	–	13.00
MS-33	Wt.%	34.15	3.11	4.46	2.68	28.13	2.56	25.71
	At.%	8.71	0.47	1.29	0.66	3.75	0.55	13.00
MS-34	Wt.%	39.26	0.45	2.69	3.18	28.42	–	26.01
	At.%	9.90	0.07	0.77	0.90	3.74	–	13.00
MS-37	Wt.%	18.87	20.13	4.71	2.35	32.01	–	21.10
	At.%	5.87	3.69	1.67	0.71	5.19	–	13.00
BS-60	Wt.%	35.76	2.92	2.23	3.39	31.54	–	24.42
	At.%	9.60	0.46	0.68	0.89	4.42	–	13.00

<sup>a</sup> MS = massive sulphide, BS = banded sulphide.

Norway, later chalcopyrite corrodes and replaces sphalerite through fissures and along its crystallographic planes (Plate 1e). By contrast, the chalcopyrite crystals included within or between sphalerite crystals or crystal aggregates are probably the result of coprecipitation, as proposed by Kojima (1990) for some Kuroko ores and Bortnikov et al. (1991) for the Sharchakmak deposit in Russia. In agreement with the observations of Bortnikov et al. (1991), chalcopyrite inclusions in the sphalerite at Masa Valverde were observed only in the sphalerite with low or high Fe content (0.47% and 6.97%, respectively). Sphalerite with intermediate Fe content (2% to 4%) did not contain chalcopyrite inclusions.

*Galena* and *chalcopyrite* occur within and between pyrite crystals, occasionally forming colloform textures, micro-veinlets and sometimes replacing pyrite. *Tetrahedrite* appears between pyrite crystals, forms micro-veinlets which cross cut chalcopyrite and galena, and is occasionally colloform. Electron microprobe analyses indicate that the Sb/Sb + As and Ag/Ag + Cu ratios of the tetrahedrite (Table 4) vary between 0.87 and 1, and 0.003 and 0.05, respectively, in agreement with those found by Marcoux et al. (1996) in other massive sulphide deposits of the IPB. The Ag content ranges between 0.45% and 3.11% except for a sample that contains 20% Ag and corresponds to freibergite. *Arsenopyrite*, which forms isolated euhedral crystals and

irregular aggregates within the pyrite, contains low concentration of trace elements.

*Bournonite* occurs as an accessory mineral together with tetrahedrite, and its average composition, determined by electron microprobe analyses is: Cu 10.81%, Sb 27.72%, Pb 43.06% and S 18.42%. *Cassiterite* forms typically euhedral crystals, 5 to 15  $\mu\text{m}$  across within sphalerite and occasionally pyrite or gangue minerals. *Stannite* is rare and forms small crystals within chalcopyrite (Plate 1f) and at times, rounded inclusions in sphalerite. A microprobe analysis of a representative sample stannite crystal gives the following chemical composition Sn 27.56%, Cu 27.91%, Fe 9.59%, Zn 3.60% and S 31.24%. The presence of stannite and cassiterite in the Masa Valverde ore indicates an enrichment in Sn, as proposed by Marcoux and Leistel (1996) for large (>20 Mt) massive sulphide deposits. *Pyrrhotite*, scarce but common in the IPB, occurs as rounded inclusions of about 4  $\mu\text{m}$  across in pyrite. This mineral is widely distributed in the Masa Valverde orebody and, in contrast to other massive sulphide deposits in the IPB and, e.g., some Caledonian deposits in the Appalachians (Craig and Vokes, 1992), is not restricted to stockwork zones. *Cubanite* always occurs as small euhedral crystals, sometimes twinned, within the pyrite, chalcopyrite and galena. *Native bismuth* occurs in the form of inclusions in chalcopyrite, the same as *cosalite* (Plate 1g), which is associated with tetrahedrite. The chemical composition determined for cosalite at Masa Valverde is Bi 44.10%, Pb 34.50%, Cu 2.50% and S 18.90%. Native bismuth and cosalite are rare and occur in late, cross-cutting chalcopyrite-carbonate veinlets in the footwall of the massive sulphides, within the "interaction zone" of Marcoux et al. (1996), where Leistel et al. (1998b) and Marcoux and Leistel (1996) also place Bi minerals in other IPB deposits. *Electrum* is very rare and was observed as inclusions in galena at the base of the upper ore body.

Gangue minerals, which make up to 0.5% to 12% of the massive sulphide orebodies, are mainly quartz and carbonates. They occur within the sulphides, or form veinlets or fill cavities in brecciated sulphides. Ankeritic and sideritic carbonates (Table 1) were deposited after the quartz and are replaced by Fe-poor sphalerite along the carbonate cleavage. Sericite and chamosite, which form flakes and radial aggregates between the sulphides, are scarce.

### 3.2.2. Chemical zoning

A longitudinal section of the Masa Valverde orebody along profile C-C' (Figs. 2 and 6), which cuts the massive sulphide lenses approximately along drill holes 23, 19, 17, 15, 18, 20, 2 and 5, shows chemical zoning roughly similar to that observed in other volcanic hosted massive sulphide deposits, including Aznalcóllar in the IPB (Almodóvar et al., 1998). In the Masa Valverde orebody, the Cu content is clearly higher in the lower part of the upper orebody, while the Zn and Pb contents are higher towards the upper part of this zone. However, in the lower orebody, the zoning for Cu and Pb is reversed.

### 3.3. Chloritites and stockworks

The stockwork sulphides, which typically occur directly below the massive sulphide lenses, are formed by anastomosing veinlets and irregular blebs (type A stockwork) and sometimes cross-cutting, clearly defined veins measuring between some millimetres and 5 cm in thickness (type B stockwork). The two types of stockworks are normally hosted by chloritites, although at times they occur within altered felsic tuffs and, exceptionally, black shales.

Pyrite in the stockwork veinlets is euhedral to subhedral, with crystals 5  $\mu\text{m}$  to  $\sim 1.0$  mm across, alone or in aggregates. Among the pyrite crystals there are lesser quantities of chalcopyrite, which sometimes forms thin anastomosing veinlets together with traces of sphalerite and tetrahedrite. Sphalerite frequently exhibits chalcopyrite disease texture, where small blebs and flakes of chalcopyrite are arranged along the crystallographic planes. This disease texture by replacement is more common in the stockwork than in the sphalerite of the base of the massive sulphide lenses. Pyrrhotite, which forms rounded crystals 4  $\mu\text{m}$  across, and arsenopyrite are very scarce in the stockwork sulphides and are present as inclusions in pyrite.

Non-metallic minerals in the stockwork are chlorite, carbonates and quartz. Chlorite appears as micro- to crypto-crystalline aggregates and occasionally as well developed isolated crystals with shredded borders. Carbonates (ankerite or siderite; Table 1) occur interstitially between the sulphides which they sometimes traverse in veinlets, and their texture varies from micro- to macro-crystalline with well developed, sometimes

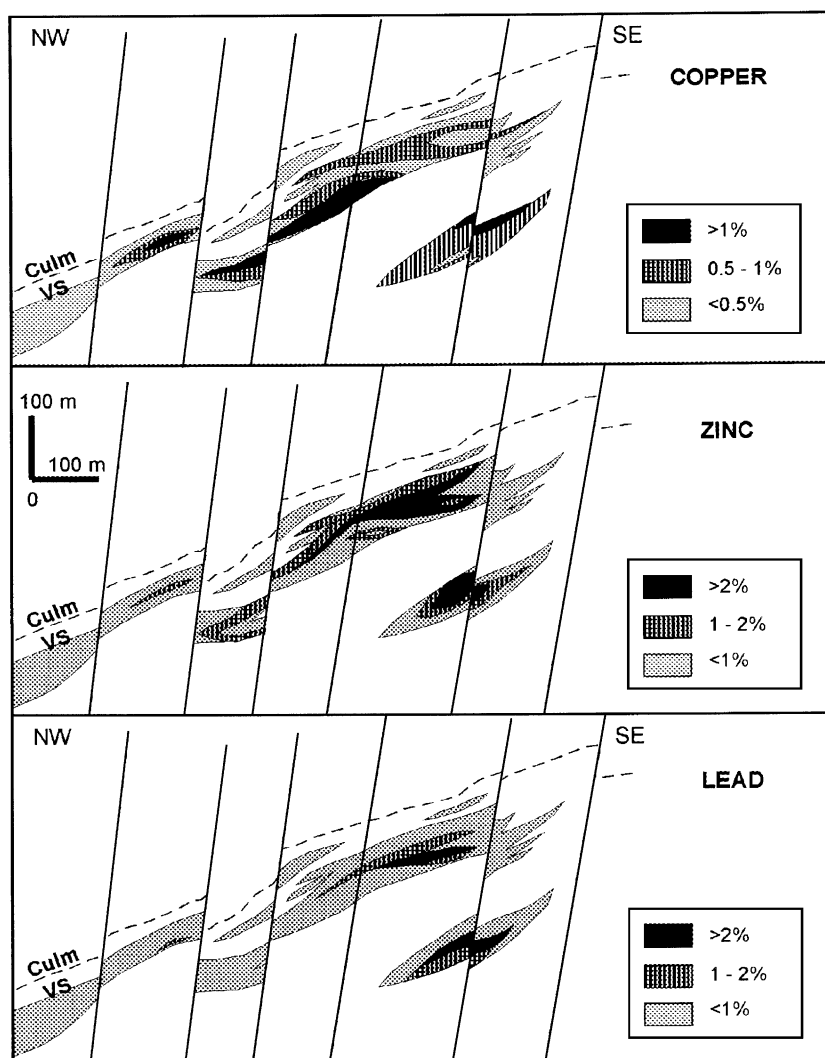


Fig. 6. Distribution of Cu, Pb and Zn along the massive sulphide bodies in C–C' longitudinal section of Figs. 2 and 4. Values in drill holes reflect 5-m samples. Dashed line indicates contact between the Culm facies and the volcano-sedimentary (VS) sequence.

euhedral crystals. Quartz is frequently feathery and sometimes forms pressure shadows on the sulphide crystals.

Schermerhorn (1978) introduced the term chloritites to describe IPB rocks essentially made up of chlorite and directly related to massive sulphides mineralisation. In Masa Valverde, the chloritites are common beneath the massive sulphide bodies (Fig. 4) and are typically spatially associated with the stockworks. They vary in colour from greyish-green to

dark green and consist of chlorite, minor quartz and small euhedral zircon, with rutile and apatite as accessory minerals. Based on chlorite electron microprobe analyses (Table 2), the chloritites closer to the sulphide lenses are enriched in Fe and Mn, and depleted in Mg, relative to chloritites at lower stratigraphic levels.

Under the microscope, the chlorite is dark green and corresponds chemically to a chamosite (Fig. 5). In the chloritites that host the stockwork, the chamosite forms

compact aggregates of flakes, sometimes submicroscopic, which occasionally have a radial structure. The Fe content of the chamosite ( $\text{Fe}/\text{Fe} + \text{Mg} = 0.64$  to  $0.86$ ) is consistent with the values obtained by Toscano et al. (1993).

The zircons are relatively abundant and are surrounded by pleochroic halos. There are two kinds of zircons: one formed by small, uniformly distributed euhedral crystals, in which only the halo is often seen, and the other consisting of thicker, irregularly distributed anhedral crystals similar to those occurring in the volcanic host rocks (Plate 1h). The euhedral zircons were interpreted by Ruiz and Arribas (1993) as being of hydrothermal origin and formed during the alteration process associated with the genesis of the stockwork. They were subsequently described in the chloritic alteration zone hosting the stockwork of the Los Frailes-Aznalcóllar orebody (Nesbitt et al., 1999) where they were observed to contain, among other inclusions, pyrite, galena, rutile, sericite and apatite. The existence of hydrothermal zircons associated with the Masa Valverde stockwork chloritites, equivalent to the presence of monazite cited in chloritite bodies in other massive sulphide deposits (Gustin, 1990; Schandl and Gorton, 1991), provides evidence of the hydrothermal remobilization of Zr and REE during alteration.

From the genetic point of view, the stockworks of Masa Valverde belong to types 1, 2 and 3 of Large (1992). Type 3, which is apparently formed by replacement, is the most abundant and occurs commonly as irregular blebs and anastomosing veinlets of sulphides within the chlorite- and sericite-rich tuffs of the foot-wall. Frequently, the veinlets and blebs are aligned approximately parallel to cleavage. Type 1, which consists of cross-cutting sulphide veins, is sometimes present, mostly in the shales. The Type 2 of Large has not been observed in the drill holes studied.

The chloritites, whose development was fracture-controlled and preceded formation of the stockwork, are interpreted to represent the channel-ways for the mineralising fluids. The stockwork was formed in two stages: the first included chloritization, incipient carbonitization and sulphide deposition, while the second, which took place after hydrothermal brecciation of the early-stage stockwork, involved the formation of new quartz, chlorite and carbonate veinlets. Furthermore, as a consequence of the tectonic processes affecting the orebody after its formation, the chlor-

itites exhibit tectonic banding and, like the stockwork, may be refolded, brecciated and sheared.

## 4. Geochemistry

### 4.1. Chlorite geochemistry

The presence of chlorite in the siliceous exhalites, massive sulphides and stockworks has enabled, with the aid of electron microprobe analyses of representative chlorite samples (Table 2), to calculate the chlorite formation temperature using the six-component solid-solution model of Walshe (1986) for quartz-saturated samples. This calculation shows that the highest estimated formation temperature ( $325\text{ }^{\circ}\text{C}$ ) corresponds to chlorite associated with the massive sulphide in the basal part of upper orebody, while the average temperature of the chlorite present in the stockwork sulphides is  $305\text{ }^{\circ}\text{C}$  (three samples,  $293\text{--}316\text{ }^{\circ}\text{C}$ ). These temperatures are higher than the average temperature ( $290\text{ }^{\circ}\text{C}$ ) of the chlorite formed with the overlying exhalites (three samples,  $252\text{--}317\text{ }^{\circ}\text{C}$ ).

The temperatures obtained for the two types of sulphide mineralisation (massive sulphides and stockwork,  $325$  and  $305\text{ }^{\circ}\text{C}$ , respectively) are within those suggested by Toscano et al. (1997) for the Masa Valverde stockwork ( $139\text{--}387\text{ }^{\circ}\text{C}$ ) and broadly consistent with those proposed by Large (1992) for this type of deposit and with the temperatures estimated by Barton and Bethke (1987) for the disease texture formation ( $200\text{--}400\text{ }^{\circ}\text{C}$ ). The temperature range ( $252\text{--}325\text{ }^{\circ}\text{C}$ ) calculated for chlorites produced by the hydrothermal system which led to the formation of the Masa Valverde orebody (Table 2) is also consistent with the temperature range suggested by Almodóvar et al. (1998) for the chlorite chemistry-based temperatures in the Aznalcóllar deposit.

Using the quartz-chlorite fractionation of oxygen isotopes, Barriga and Kerrich (1984) calculated the formation temperature of the chlorite associated with the stockwork, massive sulphide and overlying chert for the Aljustrel orebody, located in the Portuguese part of the IPB. The respective temperatures for the above-mentioned chlorites varied from  $270\text{ }^{\circ}\text{C}$  to  $220\text{--}240\text{ }^{\circ}\text{C}$ , to  $110\text{--}130\text{ }^{\circ}\text{C}$ . These temperatures, lower than those obtained at Masa Valverde with the chlorite geothermometer, show a similar decreasing

trend, with the lower temperature corresponding to the hydrothermal chert.

#### 4.2. Rare earth element geochemistry

Twenty nine drill core samples representing the most significant lithologic units of the Masa Valverde ore deposit, namely the shales, felsic tuffs, siliceous exhalites, massive sulphides and the chloritites which hosts the stockworks, were selected for REE geochemical analysis. The samples were analyzed by induced neutron-activation analysis (INAA) at the Activation Laboratories in Ancaster, Ontario (Canada). Table 5 contains the results of the REE analyses and Table 6 the average chondrite-normalized  $La_N/Yb_N$  and  $Eu/Sm$  ratios for the main rock types, the latter having been used to express the Eu anomalies following Fyffe (1995).

Table 5  
INAA-REE data of representative lithologies from the Masa Valverde deposit

Sample	Type <sup>a</sup>	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	$La_N/Yb_N$	Eu/Sm
A-1-4	2	51.90	103.00	39.00	6.60	1.50	0.80	2.80	0.42	12.30	0.23
A-1-5	2	41.00	92.00	43.00	9.00	2.10	1.50	3.30	0.45	8.24	0.23
A-1-6	2	98.00	173.00	60.00	8.90	2.10	1.00	3.80	0.55	17.11	0.24
A-1-7	2	43.50	67.00	25.00	4.10	0.90	0.50	3.00	0.49	9.62	0.22
A-1-8	1	47.50	93.00	36.00	6.30	1.10	0.80	3.70	0.58	8.52	0.17
A-1-9	2	33.00	73.00	29.00	5.30	1.00	0.60	2.00	0.31	10.95	0.19
A-3-5	5	8.60	23.00	5.00	0.80	0.20	0.50	1.90	0.33	3.00	0.25
A-3-6	5	11.10	23.00	10.00	2.00	0.70	1.00	2.20	0.34	3.35	0.35
A-3-7	5	2.70	7.00	5.00	1.60	0.30	0.50	5.40	0.85	0.33	0.19
A-3-112	5	7.20	15.00	8.00	1.80	0.05	0.40	2.20	0.35	2.17	0.03
A-3-8	5	13.50	27.00	12.00	2.60	0.60	0.50	2.80	0.41	3.20	0.23
A-3-121	5	5.10	12.00	6.00	1.50	0.23	0.40	2.11	0.34	1.60	0.15
A-3-9	5	6.20	15.00	8.00	2.00	0.20	0.50	2.30	0.35	1.79	0.10
A-3-639	5	3.00	9.00	5.00	1.48	0.10	0.10	1.36	0.21	1.46	0.07
A-11-1 <sup>b</sup>	3	9.00	22.00	14.00	4.10	1.60	0.90	5.30	0.78	1.13	0.39
A-12-1	1	50.30	87.00	38.00	7.10	1.50	1.20	4.00	0.55	8.34	0.21
A-14-1	4	12.70	30.00	13.00	2.30	0.70	0.50	1.50	0.22	5.62	0.30
A-15-1	3	38.10	71.00	26.00	4.40	0.80	0.50	2.10	0.30	12.04	0.18
A-15-2	6	1.80	4.00	5.00	0.40	0.20	0.50	0.30	0.05	3.98	0.50
A-15-3	7	7.70	16.00	8.00	1.60	1.10	0.50	1.30	0.15	3.93	0.69
A-17-111	4	11.00	20.00	7.00	1.60	0.45	0.40	1.54	0.28	4.74	0.28
A-17-115	4	6.00	11.00	5.00	0.98	0.40	0.20	0.74	0.09	5.38	0.41
A-17-124	4	8.20	16.00	7.00	1.00	0.30	0.20	0.57	0.09	9.54	0.30
A-17-128	4	7.70	15.00	6.00	0.84	0.33	0.10	0.50	0.09	10.22	0.39
A-18-119	4	9.40	20.00	9.00	2.10	0.71	0.40	1.30	0.22	4.80	0.34
A-18-128	4	12.90	25.00	11.00	2.00	0.45	0.30	0.93	0.14	9.20	0.23

<sup>a</sup> 1: black shale, 2: calcareous black shale, 3: tuff; 4: massive sulphide; 5: chloritite.

<sup>b</sup> Sample A-11-1 = weakly altered rock; 6: red exhalite; 7: white exhalite.

Table 6  
REE data for representative samples of the Masa Valverde deposit

Rock type	$La_N/Yb_N$	Eu/Sm
Host rocks	10.89	0.20
Massive sulphides	7.07	0.32
Chloritites	2.11	0.17
Sample A-11-1 <sup>a</sup>	1.13	0.39

<sup>a</sup> Sample A-11-1 = weakly altered rock.

#### 4.2.1. Wall rocks, massive sulphide and chloritites

Figs. 7–9 represent the chondrite-normalized REE profiles of the wall rocks, the massive sulphides and the chloritites hosting the stockworks of the Masa Valverde orebody, respectively. Fig. 10 shows chondrite-normalized REE profiles of samples representative of the different sample types. For comparison, the REE profile of a sample of felsic tuff from one of the

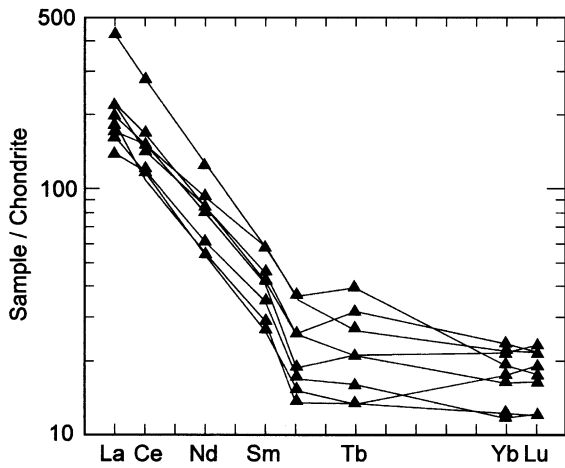


Fig. 7. Chondrite-normalized REE profiles of selected host rocks from Masa Valverde.

least altered drill holes in the Masa Valverde area (sample A-11-1) is also shown in Fig. 10.

The comparative REE profiles (Fig. 10) provide evidence for remobilization of REE during formation of the Masa Valverde orebody. Compared to the profile of the weakly altered sample, the chloritites associated with the footwall stockwork show a significant negative Eu anomaly and a slight depletion of REE elements (Figs. 9 and 10). Both observations suggest remobilization (leaching) of REE during hydrothermal alteration at relatively high temperatures (McLean and Barret, 1993). Similar depletion of REE in zones of chloritic alteration located below massive

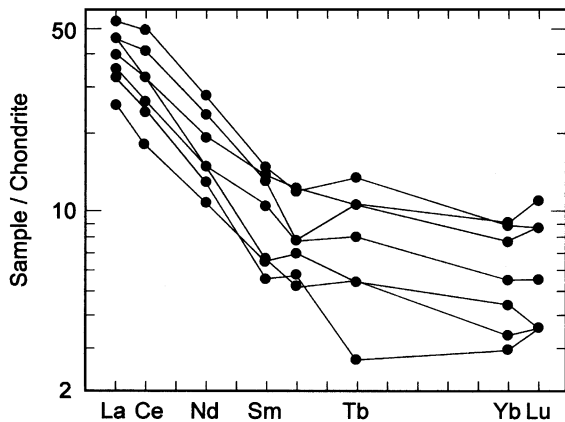


Fig. 8. Chondrite-normalized REE profiles of selected massive sulphide samples from Masa Valverde.

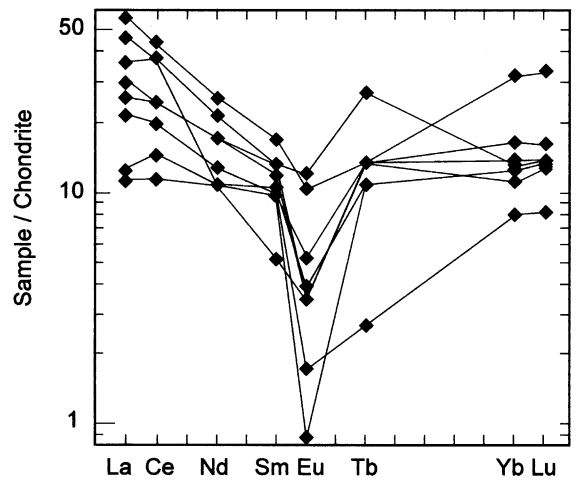


Fig. 9. Chondrite-normalized REE profiles of chloritite hosting the stockwork of Masa Valverde.

sulphide ore lenses were documented by Campbell et al. (1984), McLean (1988) and Barret et al. (1992). The strong negative Eu anomaly may be due to reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  during hydrothermal activity (Sverjensky, 1984; Bau, 1991) and leaching (Bence and Taylor, 1985).

The depletion of REE in massive sulphide samples is more apparent in the heavy REE (Figs. 8 and 10).

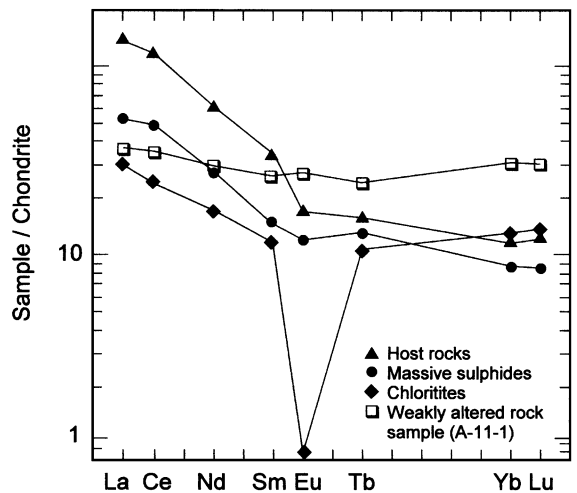


Fig. 10. Chondrite-normalized REE profiles of representative samples of host rocks (A-1-9), massive sulphides (A-14-1), chloritites associated with stockworks (A-3-112) and weakly altered tuff (A-11-1).



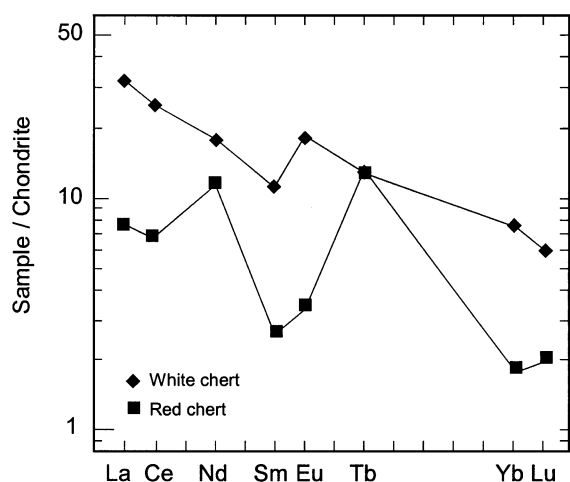


Fig. 11. Chondrite-normalized REE profiles of Masa Valverde cherts.

For its part, Eu shows a small or insignificant negative anomaly, which contrasts with other volcanogenic massive sulphide deposits where positive Eu anomalies are observed (e.g., Brunswick no. 6 deposits, Graf, 1977; also Gale et al., 1997). The absence of a positive Eu anomaly at Masa Valverde could be explained both to the possible modification of the REE content due to metamorphic processes and by the scarcity of complexing agents, such as  $\text{CO}_2$  (Gale et al., 1997), which could have facilitated the mobility of Eu.

The chondrite-normalized REE patterns of the altered host rocks are similar for different rock types (Fig. 7), and show a strong enrichment of the light REE compared to the sample of weakly altered rock (Fig. 10). The enrichment of LREE may be due to redeposition of REE leached elsewhere within the hydrothermal system. Europium in the samples of altered rock shows a weak negative anomaly, in marked contrast with the strongly negative Eu anomaly of the chloritites. Given the higher temperature of formation of the chloritites, on the basis of chlorite composition, a relation may exist between temperature and intensity of Eu anomaly.

The value of REE data for exploration in the IPB or elsewhere is uncertain; it may be argued, however, that two observations provide positive exploration criteria: finding areas of hydrothermally altered rocks enriched in LREE (evidence of redeposition within a hydrothermal system) and finding chlorite-rich altered

areas with strong negative Eu anomalies (evidence of channel-ways used by high temperature mineralising fluids).

#### 4.2.2. Siliceous exhalites

Two samples of the Masa Valverde red and white cherts were analyzed for REE content. Both samples were located in the hanging wall of the deposit, about 1 to 3 m from the upper orebody, respectively.

The sample of white sulphide chert presents higher REE concentrations than the sample of red oxide chert (Table 5; Fig. 11). Both siliceous exhalites show a relative enrichment in LREE and a depletion in HREE. The REE profile and REE content of the Masa Valverde red hematite+magnetite chert is roughly similar to the average REE profile of the upper oxide cherts studied by Leistel et al. (1998b). By contrast, the REE profile of the Masa Valverde white sulphide chert shows a higher REE content and a positive Eu anomaly. The petrography, REE content, low LREE to HREE ratio and the very weak Ce anomaly of the Masa Valverde red chert are also similar to those of the silica iron exhalites of the Mount Windsor volcanic belt in Australia (Duhig et al., 1992). The formation temperature of the Masa Valverde siliceous exhalites (252–317 °C) estimated with the chlorite geothermometer are unusually high when compared with the deposition temperatures (110–130°) of the Aljustrel jaspers, as estimated by Barriga and Kerrich (1984) using the fractionation of oxygen isotopes in quartz and chlorite. Compared to the Aljustrel jaspers, in addition to higher apparent temperatures of formation, the Masa Valverde cherts show a positive Eu anomaly and undepleted Ce concentrations. The positive Eu anomaly may reflect higher concentration in this element in hotter hydrothermal fluids, as suggested by Lottermoser (1992).

Table 7  
Pb isotopic composition of representative ore samples from Masa Valverde

Sample	Ore type	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	Model age (Ma)
A21-502	Stockwork (stringer)	18.160	15.633	38.250	411
A3-519	Massive-pyritic	18.154	15.628	38.246	406
A14-432	Banded polymetallic	18.157	15.631	38.256	409

The lack of a negative Ce anomaly in Masa Valverde cherts, as well as in other deposits of the IPB (Leistel et al., 1998b) may be due to precipitation from meteoric water-dominated hydrothermal fluids, since low Ce contents are generally considered to be a characteristic feature of sea water-dominated fluids (Hogdahl et al., 1968).

#### 4.3. Lead isotope geochemistry

Lead isotope data were obtained from three samples representative of the main types of ore at Masa Valverde: massive pyrite sulphide, banded polymetallic sulphide and stockwork. The results (Table 7; Fig. 12) show identical isotopic composition for the three ore Pb samples, suggestive of a mineralising event

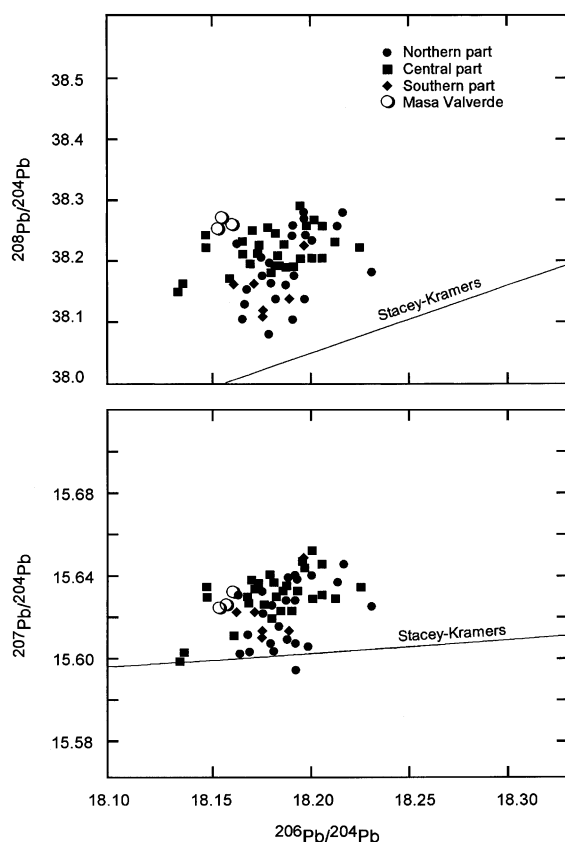


Fig. 12. Pb isotopic composition of three representative ore samples from Masa Valverde. For comparison, Pb isotopic composition of numerous IPB massive sulphide deposits, excluding Neves Corvo (Marcoux 1998), are also shown.

with Pb thoroughly homogenised from a crustal source or, more likely, a variety of crustal sources. The isotopic composition of the Masa Valverde Pb is similar to that documented earlier by Marcoux et al. (1992) and Marcoux (1998) for other 26 deposits of the IPB. With the exception of the Neves Corvo deposit, these authors concluded that Pb in stockwork or in pyrite or polymetallic massive sulphide bodies has an identical composition for each given deposit.

## 5. Discussion and conclusions

Masa Valverde is a recently discovered giant (>90 Mt), blind Zn–Pb–Cu massive sulphide deposit hosted by felsic tuffs and shale. The deposit is formed by two large lenses of massive and banded pyrite ore, with the banded ore predominantly located at the top of the upper massive sulphide lens. Two types of stockwork occur beneath the massive sulphide bodies. Type A is more common and consists of irregular and anastomosing sulphide veinlets and irregular blebs interpreted to have been formed by replacement. Type B is formed by cross-cutting, generally straight-sided, sulphide veins which are suggestive of hydraulic fracturing. The presence of these two types of stockwork suggests that pressures within the hydrothermal system exceeded lithostatic during the formation of type B stockwork. In turn, the origin of the two types of stockwork may reflect variations in the nature and permeability of the footwall host rocks, as suggested by Green (1983). For example, type A stockwork occurs mainly in relatively permeable tuffs, whereas the second type is present mostly in comparatively less permeable shales. Thus fluid flow was better focused in the shales, favouring open-space filling, and more poorly focused in the tuffs, where it gave place to replacement processes (e.g., Morton and Franklin, 1987).

The red hematite + magnetite chert of Masa Valverde has petrographic characteristics and REE profiles and concentrations similar to those of the silica iron exhalites of Mount Windsor in Australia (Duhig et al., 1992) and the upper oxide cherts of the IPB (Leistel et al., 1998b). The temperature of deposition of the Masa Valverde red chert, (252 to 317 °C), calculated with the chlorite geothermometer, is unusually high. This high temperature may be consistent with the docu-

mented lack of a negative Eu anomaly. In addition, the lack of a negative Ce anomaly may reflect precipitation of the cherts from meteoric water dominated hydrothermal fluids. As mentioned above, this feature may be common to other deposits in the IPB (Leistel et al., 1998b), with the notable exception of the deposits in the Aljustrel, where sea-water dominated hydrothermal fluids might be more important and temperatures of formation of the associated cherts are lower (Barriga and Kerrich, 1984).

With respect to the REE content in other rocks of Masa Valverde, the minimum values occur in the chloritites associated with the Cu-rich stockworks, which are the locus of relatively high hydrothermal temperatures (about 305 °C). The zones enriched in LREE correspond to the host rocks of the sulphide lenses where silicification, sericitization and carbonatization took place together with the mineralising process. The LREE content of massive sulphides is intermediate between that of chloritites and host rocks.

From the mineralogical and chlorite-thermometry studies carried out at Masa Valverde, it can be assumed that the massive sulphide lenses and underlying stockwork originated during at least two main stages of hydrothermal activity. The temperature evolution of the submarine hydrothermal system through time could have followed a trend consistent with the temperatures estimated for stages 2 and 3 in the model of Large (1992) for the Australian mound-shape deposits. In Masa Valverde, the earlier ore fluids would have discharged onto the sea floor resulting in the deposition of pyrite with sphalerite and galena. Later on, with continued input of high temperature fluids (293 to 316 °C), chalcopirite precipitated, especially in the stockworks and at the base of the sulphide lenses. At Masa Valverde, this late Cu-rich hydrothermal event would have produced an ascending Cu-front which overpassed the stockwork zone and reached a higher temperature (325 °C) at the base of the massive sulphide lenses.

In common with other giant massive sulphide deposits in the IPB, such as Sotiel, Aznalcóllar and Tharsis (Sáez et al., 1999), the Masa Valverde deposit is characterized by the abundance of sedimentary host lithologies. For example, the massive sulfide lens and stockwork in the Lower Unit of the Tharsis deposit are hosted entirely within shales (Tornos et al., 1998), in

contrast with the spilitic flows and rhyolites that outcrop in the upper sections of the Tharsis open pit, where mineralization is not present. At Sotiel, the main massive sulphide bodies and the footwall and hanging wall stockworks (Santos et al., 1996) are also hosted by shales and tuffs. The giant massive sulphide blankets and limited stockwork of the Aznalcóllar mine (Almodóvar et al., 1998) are also hosted by black shale, as well as tuffites and tuffs.

The combination of the geologic, petrographic and geochemical data obtained so far with the study of the Masa Valverde core samples allows us to propose the following metallogenic facts, some of which could be used as an exploration tool in the search for new blind ore deposits in this part of the IPB where tuffs and sedimentary rocks are the dominant host lithologies: (a) the existence of a close relationship between the massive sulphide lenses and some characteristic pyroclastic and sedimentary horizons, namely tuffs in the footwall of the deposit and black shales in the hanging wall; (b) lead isotopes indicative of a single mineralising event, with Pb homogenised from a sole metal source, or, more likely, a variety of crustal sources, among them the Carboniferous volcanic rocks and the underlying Devonian sediments; (c) light REE enrichment of the altered host rocks; (d) a roughly zoned hydrothermal alteration of the chloritites hosting the Cu-rich stockwork, where there is a significant remobilization of Zr and REE, and a strongly negative Eu anomaly.

Although having many points in common with classic volcanic-hosted massive sulphide type deposits (VHMS), the Masa Valverde deposit originated during a break in volcanic activity. Due to this and other features described in this report, the environment of formation of Masa Valverde presents characteristics that are similar to those prevailing in the sediment-hosted massive sulphide type (SHMS). In our view, the Masa Valverde deposit can be assigned to the Iberian model of massive sulphide deposits proposed by Sáez et al. (1999), and thus be considered as a VHMS subtype transitional to SHMS.

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