Geology, fluid inclusion and sulphur isotope characteristics of the El Cobre VHMS deposit, Southern Cuba

Xiomara Cazañas · Pura Alfonso · Joan Carles Melgarejo · Joaquín Antonio Proenza · Anthony Edward Fallick

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Abstract  The El Cobre deposit is located in eastern Cuba within the volcanosedimentary sequence of the Sierra Maestra Paleogene arc. The deposit is hosted by tholeiitic basalts, andesites and tuffs and comprises thick stratiform barite and anhydrite bodies, three stratabound disseminated up to massive sulphide bodies produced by silicification and sulphidation of limestones or sulphates, an anhydrite stockwork and a siliceous stockwork, grading downwards to quartz veins. Sulphides are mainly pyrite, chalcopyrite and sphalerite; gold occurs in the stratabound ores. Fluid inclusions measured in sphalerite, quartz, anhydrite and calcite show salinities between 2.3 and 5.7 wt% NaCl eq. and homogenisation temperatures between 177 and 300°C. Sulphides from the stratabound mineralisation display δ34S values of 0‰ to +6.0‰, whilst those from the feeder zone lie between −1.4‰ and +7.3‰. Sulphides show an intragrain sulphur isotope zonation of about 2‰; usually, δ34S values increase towards the rims. Sulphate sulphur has δ34S in the range of +17‰ to +21‰, except two samples with values of +5.9‰ and +7.7‰. Sulphur isotope data indicate that the thermochemical reduction of sulphate from a hydrothermal fluid of seawater origin was the main source of sulphide sulphur and that most of the sulphates precipitated by heating of seawater. The structure of the deposit, mineralogy, fluid inclusion and isotope data suggest that the deposit formed from seawater-derived fluids with probably minor supply of magmatic fluids.

Keywords  VHMS deposit · Sulphides · Fluid inclusions · S isotopes · Cuba

Introduction

The El Cobre deposit, 13 km NW from Santiago de Cuba, is located in the Sierra Maestra Paleogene volcanic arc of the southeastern part of Cuba, (Fig. 1) and is the oldest copper mine in America. The deposit was discovered in 1530 and mined by galleries in 1544 (Ansted 1856). During five centuries of activity, more than one million tons of ore with >14% Cu and more than two million tons of ore with >3% Cu have been extracted. During colonial times (up to 1898), galleries and mine shafts up to 300 m deep were developed on vein-type mineralisation. From the 1970s to the present, open pit mining has operated at the Mina Grande and Mina Blanca sectors, although the Cu vein mineralisation continues more than 1 km eastwards (Gitanilla sector). In the 1960s, a series of deep test drills towards the flanks of the deposit (Barita Occidental, Barita Oriental, Mina Nueva and Melgarejo sectors) led to the
discovery of stratiform and stratabound polymetallic mineralisation (Cazañas et al. 1998), holding gold-bearing polymetallic ores with up to 25 ppm Au. In the 1990s these discoveries prompted foreign mining companies to investigate the new findings; in 1998, however, the copper mine was closed, despite known reserves of more than two million tons of ore with >1% Cu. At present, a new project for the evaluation of the flanks is being carried out by the Empresa Geominera Oriental from Santiago de Cuba. In spite of the economic interest of this deposit, only a few published works are available, and most of them were part of studies of regional metallogeny (Kesler et al. 1990; Russell et al. 2000). Previously, the El Cobre deposit was attributed to a mesothermal origin (Cabrera et al. 1983) and an epithermal origin (Kesler et al. 1990). However, Cazañas et al. (1998), following a detailed structural investigation of the deposit, considered it to be a VHMS deposit; Russell et al. (2000) concurred.

This study presents detailed structural, mineralogical and textural data with a sulphur isotope and fluid inclusion study of the El Cobre deposit; the aim is to characterise the deposit and refine the genetic model of formation proposed in Cazañas et al. (1998).

Regional geology

The Sierra Maestra range formed as a result of the collision of the eastern Cuban microplate with the North American plate, with the development and activation of the North Caribbean transform fault, during the Oligocene. The North Caribbean transform fault was reactivated during the Miocene, modifying the overall structure of Sierra Maestra by wrenching and determining the present southern slope of the range (Rojas-Agramonte et al. 2005, 2006).

The Sierra Maestra is composed of a Cretaceous basement of arc-related rocks, unconformably overlain by widespread Paleogene volcanic arc rocks, which are overlain by Middle to Upper Eocene sedimentary rocks of the Puerto Boniato and San Luis Formation (Iturralde-Vinent 1996; Cazañas et al. 1998; Kysar 2001; Rojas-Agramonte et al. 2004, 2005, 2006) (Fig. 2). The Paleogene volcanic island arc, developed between the Paleocene (Thanetian) and the Early Middle Eocene, is represented by the El Cobre Group, a sequence of volcanic rocks more than 4,000 m thick (Iturralde-Vinent 1996, 1998; Cazañas et al. 1998; Rojas-Agramonte et al. 2006).

The El Cobre Group consists of volcanic and volcaniclastic rocks with intercalations of epiclastic material and fossiliferous limestones. The volcanic sequence is comprised of lavas, pyroclastic flows, subvolcanic sills and their feeder dykes (Iturralde-Vinent 1996; Cazañas et al. 1998; Kysar 2001; Rojas-Agramonte et al. 2006). The volcanic rocks in the lower and middle sequence of the El Cobre Group, in the Sierra Maestra range, are low-K island arc tholeiites (IAT), similar to those of the Kermadec arc in the SW Pacific (Cazañas et al. 1998; Kysar 2001; Rojas-Agramonte et al. 2006).

The Paleogene volcanic arc successions were intruded by calc-alkaline, low- to medium-K tonalites and trondhjemites during the final stages of subduction. These rocks have geochemical characteristics similar to subduction-related granitic rocks as found worldwide in intra-oceanic arcs (Kysar 2001; Rojas-Agramonte et al. 2004). Iturralde-Vinent (1996, 1998) considers that the El Cobre Group formed in the axial zone of the volcanic arc.

The El Cobre Group gives way by lateral facies change to the Pilón and Caney formations. It is divided into three sequences: lower, middle and upper (Méndez 1997) (Fig. 2). The lower sequence consists mainly of thick andesite–basalt flows, interbedded with several hundreds of metres-thick intermediate to basic tuffs. The middle sequence begins with andesite–dacite and conglomerates, giving way to several overlying cycles of explosive volcanism. Each cycle consists of pyroclastic deposits of coarse to very coarse grain size, indicating a proximal source. These deposits are followed by limestone olistostromes, which may be coeval with the emplacement of intermediate to acid lavas. The most important volcanic episode, 300 m thick, occurs close to the base of the sequence and consists of very coarse-grained pyroclastic rocks with fragments of more than 15 mm in diameter. This cycle is followed by another, 300 m thick, composed of finer-grained pyroclastic rocks with fragments up to 15 mm in diameter. At the top of this unit, limestone olistostromes...
occur, and a stratiform mineralisation of anhydrite, barite and Mn oxides can be present. Most of the El Cobre deposit is hosted by rocks of the second cycle.

The contact between the upper and middle sequences is an unconformity. Thick conglomerate beds occur at the base of this sequence and vertically give way to other distal explosive volcanic cycles. In the El Cobre stratigraphic column, explosive cycles of the upper sequence consist of several tens of metres-thick beds of fine-grained breccias, followed by similarly thick beds of tuffs and ash tuffs located at the top. Epiclastic components and olistostromic limestones increase towards the top of the series, suggesting the progressive extinction of Paleogene volcanism and the subsequent dismantling of the volcanic structures.

Geology of the deposit

The ore deposit is hosted by volcanoclastic rocks of the Middle Sequence of the El Cobre Group, near the unconformity with the Upper Sequence, which consist of marine conglomerates and sandstones (Fig. 2).

The Middle Sequence in the El Cobre deposit consists of coarse-grained pyroclastic rocks. Metre-sized fragments are common at the base of the sequence, whilst the upper part consists of an interbedding of several decimetres-thick beds of ash tuffs, lapilli tuffs and fine- to medium-grained epiclastic rocks. The composition of the pyroclasts is variable, from andesite-dacitic at the base to rhyolitic at the top. Two discontinuous, olistostromic
reefal limestones, up to several tens of metres in thickness, occur interbedded with the pyroclastic rocks at the top of the sequence and could represent episodes of tectonic instability in the Eocene basin. Volcanic dykes of different sizes and compositions, ranging from andesite–basalt to rhyolite, crosscut the previous units.

The ore bodies are located along the El Cobre fault (Fig. 3). This fault, more than 40 km long, is linked with an E–W fault system that generated two sets of associated joints trending SW and NW. Rocks in the fault zone show cataclastic textures. Quartz veins, hydrothermal alteration of host rocks and a copper vein mineralisation are associated with the fault zone; a late andesite–basalt dyke also intruded along the fault and cuts the vein mineralisation. To the east, Middle Eocene limestones from Sierra de Boniato preserve this fault. Hence, the El Cobre fault and the accompanying systems formed during the early stages in the development of the volcanic arc (Pérez and García 1997) and facilitated the development of fissure volcanoes in later stages.

A late Eocene strike–slip N–S system (Pérez and García 1997; Rojas-Agramonte et al. 2005) produced movements...
of several tens of metres, developing a block structure to the deposit and tilting the blocks. Consequently, the present topographic height of the various outcrops differs from the original. These movements affected the thickness and concentration of ore bodies. The central sectors of the deposit, Mina Blanca and Mina Grande (Figs. 4 and 5), located in a raised block, display the maximum width, up to 24 m.

Mineralisation styles

Based on detailed drilling and the existing outcrops (Fig. 5), three main styles of mineralisation are distinguished in the El Cobre deposit: (1) stratiform (manganese, anhydrite and Au-bearing barite bodies); (2) disseminated, stratabound (polymetallic with Zn–Cu–Au); and (3) vein mineralisation, copper-rich with parallel veins at depth and stockwork development in surficial sectors.

Stratiform mineralisation

Stratiform lenses of manganese oxides, barite and anhydrite are located north of the El Cobre fault within an E–W trending belt. The lenses are typically about 1.7 km long and 100 m wide.

Stratiform Mn oxides These form a 4-m thick body which outcrops along more than 1 km in the north block of the El Cobre fault at a distal position. The base comprises an

Fig. 4 Geological 3-D diagram compiled after drilling in the El Cobre deposit (see direction of the profiles in Fig. 3). Modified after Cazañas et al. (1998)
interbedding of red jaspers with scarce botryoidal cryptomelane and hematite beds up to 1.5 m thick in total, followed by a celadonite–hematite bed up to 1 m thick. A Mn-rich unit overlies this Fe-rich unit and consists of an interbedding of strata rich in Mn-silicates, mainly macfaltite, chert and pyroclastic rocks cemented by cryptomelane. The top of the unit consists of 20 cm of massive cryptomelane.

Stratiform barite Two lenses of barite occur in the Barita and Melgarejo sectors. One, 4 m thick, is found at the footwall of the deposit and has nodular texture; it is crosscut by quartz–sericite–pyrite veins. The other, a 3-m thick lens, occurs at the hanging wall of the deposit and has massive or banded structure and foliated texture (Fig. 6a). These textures are similar to those reported in the Kuroko deposits in Japan (Shikazono 1994). Sphalerite, chalcopyrite and minor galena occur in the uppermost body, although euhedral or framboidal pyrite is the most abundant sulphide in this unit (Fig. 6b).

Stratiform anhydrite This unit, up to 100 m thick, consists of anhydrite beds interbedded with altered pyroclastic rocks. Anhydrite is bluish and has nodular texture (Fig. 6c). Nodules are regular or elongated, some millimetres to several centimetres in diameter. Near the base of the deposit, they are rimmed by euhedral quartz aggregates with montmorillonite and euhedral pyrite (Fig. 6d). In addition, a second replacement generation of fine-grained anhydrite occurs. All textural types of anhydrite are replaced by several generations of gypsum. Quartz and pyrite veins crosscut this unit; these veins are more frequent in the lower part.

Stratabound mineralisation

Three stratabound units can be distinguished according to depth: lower, intermediate and upper (Cazañas et al. 1998). The ores do not outcrop and were recognised by drilling. Quartz veins of variable thickness crosscut the stratabound mineralisation in the vicinity of the El Cobre fault; these veins can contain pyrite and chalcopyrite.

Lower stratabound mineralisation Five ore bodies, several tens of metres long and 4–8 m thick, occur in an area of 700×400 m in the west of the Mina Blanca sector. The mineralisation replaces olistostromic limestone bodies. There is a horizontal zoning related to the El Cobre fault. Highly recrystallised carbonate beds occur in the most distal zones, although micritic textures may also be preserved. Primary calcite is strongly replaced by bladed calcite, followed by sparitic calcite, sometimes with a phanerocrystalline talc+pyrite+chalcopyrite+quartz association.

In a more internal zone, anhydrite and quartz replace calcite. Anhydrite is, in turn, replaced by hematite, which is pseudomorphed by magnetite and, this, eventually, by pyrite. Quartz–chlorite–pyrite associations can pseudomorph anhydrite crystals.

Close to the El Cobre fault, the lower stratabound mineralisation consists of massive micro- to phanerocrystalline quartz aggregates associated with chalcopyrite, pyrite, minor amounts of sphalerite and Fe-rich chlorite. Kaolinite commonly occurs as inclusions within quartz. Minor amounts of hessite (Ag2Te), tetradymite (Bi2Te2S) and tellurobismuthite (Bi2Te3) are associated with chalcopyrite.

Intermediate stratabound mineralisation This mineralisation is located several metres above the previous unit and comprises a partly silicified, discontinuous carbonate layer of tens of metres in thickness. Zn–Pb sulphide mineralisation occurs in some areas.

Upper stratabound mineralisation This mineralisation comprises a polymetallic Zn–Cu–(Pb) layer, 1.7 km in length and...
90 m thick with low Cu/Zn ratio. This layer is located at the north of the El Cobre fault. It occurs directly below the anhydrite deposit near to the surface, but outcrops are scarce. According to texture, three zones can be distinguished within the body: (1) basal zone, (2) silicification zone and (3) contact zone with the upper anhydrite stratiform deposit.

In the contact zone with the host rock, microcrystalline quartz, montmorillonite, anatase, pyrite and other sulphides replace anhydrite. Pyrite is the most abundant sulphide; it becomes almost massive. Pyrite is usually corroded by sphalerite (I) and chalcopyrite. Sphalerite I is replaced by chalcopyrite and a late sphalerite generation (sphalerite II). Chalcopyrite locally co-crystallises with bornite and chalcocite, suggesting a high fugacity of sulphur.

The silicified zone consists of quartz with disseminations of chalcopyrite, sphalerite, pyrite and gold (Fig. 6e and f). Quartz, pyrite and sphalerite crystals contain remains of strongly corroded anhydrite crystals. Gold occurs interstitially among quartz grains or overgrowing early-formed pyrite crystals, and it is sometimes associated with hessite (Ag₂Te) and chalcopyrite in small veins that crosscut pyrite.

Therefore, this mineralisation can be interpreted as the replacement of the basal anhydrite bodies and volcanosedimentary rocks at the base of the stratiform deposit by a silicification process. The basal zone, roughly tabular and several metres thick, consists of strongly kaolinitised, sericitised and silicified volcanosedimentary rocks. It contains sphalerite, pyrite and chalcopyrite.

A mesh of veins, each up to several centimetres thick, cuts all the above-mentioned units. They are composed of vuggy quartz+chalcopyrite+sphalerite. Two types of sphalerite are present: a first generation (sphalerite I), strongly replaced by chalcopyrite, and a second generation (sphalerite II), that co-crystallises with chalcopyrite. Microcrystalline quartz constitutes a first generation of vein infilling; it is followed by a second generation of phanerocristalline quartz, which contains abundant sericite inclusions. Radial kaolinite crystals coat the rhombohedral faces of these quartz crystals. On them, passive growths of pyrite and sphalerite II occur. This stage of mineralisation is rich in gold. Gold grains, more than 100 μm in size, occur associated with quartz or pyrite. Sphalerite II is sometimes slightly replaced by chalcopyrite. Galena, small native gold grains up to 10 μm in diameter, and calaverite (AuTe₂)
rimmed by hessite, occur as inclusions in sphalerite II. A late vein stage consists of quartz, calcite and anhydrite, and they occur either as late discrete veins crosscutting the above-mentioned associations or as infillings of the vuggy porosity.

Vein mineralisation

Vein mineralisation in the Mina Blanca, Mina Grande, Mina Alta and Gitanilla sectors occurs along the El Cobre fault in an area about 1,200×140 m. Minimum known depths are 500 m in Mina Grande and Mina Blanca sectors and 200 m in the Gitanilla sector. In Mina Alta, 800 m SW of Mina Blanca, veins up to 2 m wide are located in an area 270 m long and 130 m deep. Mina Alta is located on a satellite fracture. All of them have Cu >0.7% ore.

Four subtypes of veining can be established according to structural and mineralogical criteria: siliceous stockwork, anhydrite stockwork, siliceous subparallel veins and anhydrite–epidote veins. Subparallel vein mineralisation has an approximate E–W or ENE–SSW trend and 80–85° S dip. It is from one to several tens of centimetres in thickness and several hundreds of metres in length. The mineralisation follows the fault trend, suggesting a strong structural control for these veins. The veins can be siliceous near the El Cobre fault and of anhydrite–epidote composition towards the flanks of the deposit. Subparallel veins grade upward to a siliceous stockwork with chalcopyrite and pyrite; in the transition zone, very wide high-grade veins are found. The stockwork extends several hundreds of metres and consists of veins, up to 1 m wide, of variable orientation, although the prevailing direction is the same as the fault.

**Siliceous subparallel veins** These veins comprise vuggy infillings of fine-grained quartz which grades to larger crystals rich in sericite or chlorite inclusions associated with sulphides. Quartz crystals are coated by sericite. The remaining porosity is filled by anhydrite or late-formed calcite. Towards the top of the subparallel veins, chalcopyrite occurs associated with small amounts of hessite (Ag₂Te), coloradoite (HgTe), tellurobismuthite (Te₂Bi₃) and tetradymite (Bi₂Te₂S).

**Anhydrite–epidote veins** The mineralogy of these veins consists of cryptocrystalline quartz, followed by microcrystalline quartz with chlorite, calcite and zoned epidote in radial aggregates. Epidote is occasionally found associated with pyrite, chalcopyrite and sphalerite. Anhydrite or a late generation of calcite fills the remaining vein porosity (Fig. 7a). Contacts among these minerals do not show evidence of replacement.

**Siliceous stockwork** Veins are composed of quartz accompanied by pyrite and chalcopyrite. Sulphide-rich quartz veins show a symmetric, some centimetres thick, banding of vuggy quartz growths associated with interstitial pyrite and chalcopyrite (Fig. 7b and c). At the top of the deposit, sericite growths on quartz crystals include remains of anhydrite, calcite, hematite and rutile. Sericite is corroded by kaolinite. At the innermost part of the vein, chalcopyrite and pyrite occur, and sometimes no vuggy porosity is present.

**Anhydrite stockwork** This outcrops only in the uppermost section of Mina Blanca and consists of a dense mesh of anhydrite veins (Fig. 7d), many being subhorizontal. The
sequence of crystallisation in the veins starts with the development of calcite and anhydrite, together with lower contents of sphalerite and pyrite. These minerals infill all the vein cavity. A second silicification stage produces the replacement of anhydrite and calcite by quartz associated with small amounts of chlorite, apatite and pyrite.

Hydrothermal alteration

Significant hydrothermal alteration of the host rocks occurs in the proximity of the El Cobre fault; the distribution of the different alteration types is shown in Fig. 8.

The uppermost part of the deposit is strongly kaolinised. This alteration develops around the anhydrite stockwork and especially inside the stratiform anhydrite and barite bodies. The replacement products consist of cryptocrystalline kaolinite and minor smectite.

Chloritisation, silicification and pyritisation are extensive close to the siliceous veins wherever they occur; similar hydrothermal alterations are found around the lower and intermediate stratabound bodies. Fine-grained chloritisation (Mg-rich chlorite) produces a complete replacement of the host rock. In turn, Mg-chlorite is replaced by Fe-rich chlorite, which is dominant in the uppermost part of the vein system. Pyritisation can be intense, and coarse pyrite crystals are formed in the replaced rocks. Silicification produces the development of small quartz veins and fine-grained quartz aggregates that can pseudomorph preexisting minerals in the volcanic host rocks. Sericitisation is poorly developed, and it only occurs around the uppermost part of the siliceous vein system. It is also accompanied by pyritisation and silicification.

A detailed study of these alterations in thin section identified the next stages of alteration, ordered from older to younger: kaolinisation, chloritisation (Mg-rich)+pyritisation+silicification, chloritisation (Fe-rich)+pyritisation+silicification, sericitisation. By contrast, the volcanic rocks at the wall of the Mn stratiform mineralisation have green colour due to celadonite alterations.

Analytical methods

Based on the structural patterns described above, extensive sampling was undertaken to determine the conditions of formation of the deposit as elucidated by study of fluid inclusions and S isotopes.

Microthermometry of fluid inclusions was performed on 16 doubly polished thin sections using a Linkam THMSG 600 heating and freezing stage at the University of Barcelona. Calibration was made with standard compounds between −56.6°C and 263°C. The accuracy was ±0.2 for the final ice melting temperature and ±2.0 for the homogenisation temperature.
The presence of CO₂, H₂S, N₂ and CH₄ was determined by Raman scanning spectrometer, operating with a 488-nm exciting frequency at a laser beam power of 600 mW. The results are given as δ³⁴S values relative to the V-CDT standard. The analytical precision is within ±0.2‰.

Fluid inclusions

Fluid inclusions are abundant in minerals from the different mineralisation units. All of them are two-phase, liquid–vapour. Only those classified as primary, according to the criteria of Roedder (1984) and Goldstein and Reynolds (1994), have been measured. Minerals used were quartz (stockwork and upper stratabound mineralisation), sphalerite (upper stratabound mineralisation and siliceous subparallel veins), anhydrite (upper, middle and lower stratabound mineralisation and anhydrite–epidote veins) and calcite (middle and lower stratabound mineralisation). The samples are representative of the different types of mineralisation except for the vein mineralisation where they belong to the most surficial parts because fluid inclusions from minerals of the lower zones are scarce and exhibit post-entrapment changes presumably acquired during recrystallisation.

Fluid inclusions occur isolated, following the crystal growth or in clusters located in the core of the crystal. The inclusions, up to 40 μm in size, are usually between 5 and 20 μm. The bubble occupies 10–20% of the total volume of the inclusion. Occasionally, trapped solids have been observed in quartz from the siliceous veins. Fluid inclusions with trails or necking down phenomena are common but only regular shape inclusions have been measured.

### Table 1 Summary of microthermometric results of fluid inclusions from the different mineralisation styles of the El Cobre deposit

<table>
<thead>
<tr>
<th>Style</th>
<th>Sample</th>
<th>Host mineral</th>
<th>N</th>
<th>Tmice (°C) range</th>
<th>Salinity (wt% NaCl eq.)</th>
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</thead>
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<tr>
<td>S</td>
<td>S-69-183</td>
<td>Ba</td>
<td>19</td>
<td>185/291 (237)</td>
<td>-21/−22</td>
</tr>
<tr>
<td>LS</td>
<td>488–310</td>
<td>Anh</td>
<td>6</td>
<td>196/222 (208)</td>
<td>-22</td>
</tr>
<tr>
<td>LS</td>
<td>488–310</td>
<td>Cc</td>
<td>1</td>
<td>262</td>
<td>-</td>
</tr>
<tr>
<td>IS</td>
<td>S-13a-190</td>
<td>Cc</td>
<td>38</td>
<td>150/216 (170)</td>
<td>-22/−22</td>
</tr>
<tr>
<td>IS</td>
<td>S-39-285</td>
<td>Anh</td>
<td>5</td>
<td>178/226 (197)</td>
<td>-22</td>
</tr>
<tr>
<td>US</td>
<td>S-42-141.3</td>
<td>Sph I</td>
<td>15</td>
<td>215/264 (243)</td>
<td>-21</td>
</tr>
<tr>
<td>US</td>
<td>S-42-140</td>
<td>Sph II</td>
<td>26</td>
<td>217/268 (248)</td>
<td>-21/−22</td>
</tr>
<tr>
<td>US</td>
<td>S-8-28</td>
<td>Sph II</td>
<td>20</td>
<td>189/245 (218)</td>
<td>-21/−22</td>
</tr>
<tr>
<td>US</td>
<td>560-158</td>
<td>Sph II</td>
<td>8</td>
<td>173/277 (227)</td>
<td>-21/−22</td>
</tr>
<tr>
<td>US</td>
<td>560–170.5</td>
<td>Sph II</td>
<td>12</td>
<td>176/259 (230)</td>
<td>-21/−22</td>
</tr>
<tr>
<td>US</td>
<td>517–161</td>
<td>Sph II</td>
<td>1</td>
<td>214</td>
<td>-</td>
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<tr>
<td>US</td>
<td>S-42-140</td>
<td>Qtz</td>
<td>2</td>
<td>207/230</td>
<td>-</td>
</tr>
<tr>
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<td>517–161</td>
<td>Qtz</td>
<td>1</td>
<td>225</td>
<td>-</td>
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<tr>
<td>US</td>
<td>560–170.5</td>
<td>Anh</td>
<td>2</td>
<td>161/169</td>
<td>-22</td>
</tr>
<tr>
<td>FHS</td>
<td>S-76-158</td>
<td>Sph II</td>
<td>4</td>
<td>205/265 (247)</td>
<td>-22</td>
</tr>
<tr>
<td>AEV</td>
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<td>Sph II</td>
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<td>205/265 (247)</td>
<td>-22</td>
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<td>Anh</td>
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<td>164/246 (206)</td>
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<tr>
<td>SS</td>
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<td>Qtz</td>
<td>8</td>
<td>259/299 (279)</td>
<td>-21/−23</td>
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<tr>
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<td>17-1</td>
<td>Qtz</td>
<td>24</td>
<td>263/293 (281)</td>
<td>-21/−22</td>
</tr>
</tbody>
</table>

Average results are given in parentheses

Fig. 9 Frequency histograms of the salinity and homogenisation temperatures of fluid inclusions from the different mineralisation styles of the El Cobre deposit.
Table 1 and Fig. 9 summarise the microthermometric results of the fluid inclusions from the different minerals and units. The homogenisation is always to liquid, homogenisation temperatures ($T_{\text{h}(L-V)}$) range between 150°C and 300°C (Fig. 9). The highest temperatures belong to inclusions hosted within quartz from the siliceous stockwork (258–300°C), whereas calcite and anhydrite from the intermediate stratabound mineralisation exhibit the lowest homogenisation temperatures, between 150°C and 200°C. Early sphalerite (I) shows a narrow range of homogenisation temperatures, 243°C to 264°C ($n=15$), whereas late sphalerite (II) has a wide range, between 150°C and 268°C ($n=82$). Usually, inclusions in minerals from the stockwork and subparallel siliceous veins display higher homogenisation temperatures than those in minerals from the stratabound bodies; this is in agreement with the fact that these units represent the feeder zones of the deposit.

The temperature of first melting ($T_c$), between −22.5°C and −21°C, indicates that the dissolved salts are mainly NaCl (Potter et al. 1978). The temperature of ice melting, ($T_{\text{mice}}$), ranges between −3.7°C and −1.1°C. Clathrates have not been observed in any of the freezing runs. Raman spectrometry confirmed the absence of CO₂ and other volatile components in the fluid inclusions.

Salinities were calculated from the temperature of ice melting using the equation of Bodnar (1993), and they are
Table 2  Sulphur isotope composition ($\delta^{34}S_{CTD}$‰) for sulphides and sulphates from the El Cobre deposit

<table>
<thead>
<tr>
<th>Sample</th>
<th>Style</th>
<th>Host rock</th>
<th>Ccp</th>
<th>Py</th>
<th>Sp</th>
<th>Gn</th>
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expressed as wt% NaCl equivalent. The range of salinity is between 1.9 and 6.0 wt% of NaCl eq. The lowest values of salinity belong to samples of early sphalerite I, highly replaced by chalcopyrite and barite. This sphalerite generation has a salinity range from 1.9 to 2.9 wt% NaCl eq., which is significantly lower than seawater salinity. Fluid inclusions from quartz have similar salinity to seawater, which is significantly lower than seawater salinity. Fluid inclusions from the last minerals to be formed (anhdrite and calcite). Thus, fluid inclusions from El Cobre deposit indicate an increase of salinity with time.

**Sulphur isotope data**

Sulphur isotope results are listed in Table 2 and represented in Fig. 10. Sulphides from the feeder veins have $\delta^{34}S$ values between $-1.4\%o$ and $+6.8\%o$. $\delta^{34}S$ values in sulphides from the stratabound bodies range from $0\%o$ to $+7.3\%o$, except one value of $+10.6\%o$. Chalcopyrite from the feeder veins has $\delta^{34}S$ between $+1.1\%o$ and $+6.8\%o$, whilst for the stratabound bodies, $\delta^{34}S$ is between $+1.9\%o$ and $+3.7\%o$ (except one value of $+5.1\%o$). Sphalerite from the subparallel veins has the lowest $\delta^{34}S$ values, between $-1.4\%o$ and $+3.8\%o$, whereas that located in distal positions (anhdrite–epidote veins) has $\delta^{34}S$ values up to $+6.2\%o$. In the stratabound bodies, $\delta^{34}S$ varies between $+3.3\%o$ and $+7.3\%o$. Pyrite has a similar range of $\delta^{34}S$ in all the mineralisation ($+1.5\%o$ to $+6.5\%o$). The only $\delta^{34}S$ value measured on galena, located in the stratabound mineralisation, is $+2.5\%o$.

The distribution of the isotopic composition of sulphur in the sulphides is not closely related with their distribution in the deposit, but there is a tendency for $\delta^{34}S$ to decrease with stratigraphic height and towards the most distal parts of the deposit. Most sulphides exhibit an intra-grain zonation of the $\delta^{34}S$ values. Sphalerite from the stratiform bodies shows intra-grain variations of about $2\%o$. Usually, the lowest $\delta^{34}S$ values are in the core of grains and the highest in the rims (Fig. 11). Pyrite also shows a concentric zoning in $\delta^{34}S$. Similar fluctuations in the $\delta^{34}S$ values where found in other VHMS deposits (Crowe et al. 1990; Crowe and Valley 1992; Sharp and Gemmell 2000).

The $\delta^{34}S$ values of sulphates (gypsum, anhydrite and barite) range from $+16.3\%o$ to $+20.9\%o$, except for two samples of anhydrite from the upper stratabound mineralisation and the subparallel veins with $+7.7\%o$ and $+5.9\%o$, respectively.

**Discussion**

Source of fluids

Most fluid inclusions from the El Cobre deposit exhibit similar or slightly higher salinity than that of seawater. Therefore, it can be assumed that seawater was the main fluid in the formation of the deposit; this is consistent with the paleoenvironmental conditions active during the deposition of the El Cobre Group (Kysar 2001) and its interbedded stratiform mineralisations.

Nevertheless, fluid inclusions from early sphalerite (I) have lower salinity with a mean of 2.3 wt% NaCl eq. Other VHMS deposits have those low values of salinity, mainly in sphalerite (Urabe and Sato 1978; Watanabe 1979, Bryndzia et al. 1983, Lüders et al. 2001; Ulrich et al. 2002). Possible explanations for such values are mixing of hydrothermal and meteoric fluids and a secondary origin of the inclusions (Pisutha-Arnond and Ohmoto 1983; Bryndzia et al. 1983; Ohmoto 1996) or a magmatic fluid input (e.g. de Ronde 1995). Meteoric fluids were unlikely to have been involved, taking into account the paleogeographic environment at the time of formation (Kysar 2001). Although a secondary origin for the inclusions cannot be absolutely ruled out, other possibilities should be taken into account.

A super-critical phase separation or boiling process is often suggested to explain low salinity in massive sulphide deposits. Phase separation can occur in two ways: (1) boiling of the hydrothermal fluids (Bischoff and Pitzer 1985; Rona 1988; Cathles 1993, Scotney et al. 2005) and (2) a separation of phases during the magmatic–hydrothermal transition. A contribution of volatile-rich magmatic fluids was suggested by different authors to explain the salinity of fluids in VHMS deposits (de Ronde 1995; Yang and Scott 1996; Scott et al. 1997; Herzig et al. 1998). Charlou et al. (1996) and Lécuyer et al. (1999) suggest that, after a volcanic eruption, two fluids can be exsolved: one dense, saline- and metal-rich and the other less dense with low salinity and volatile-rich. The model assumes the existence at a depth of magma in which
exsolution produced two fluids: one vapour-rich and of low salinity and the other more saline. The difference in density causes the fluids to rise at different rates. Such unmixing phenomena are used to explain the formation of many deposits (Halter and Webster 2004).

Microthermometric results from fluid inclusions of the El Cobre deposit indicated that fluids involved in the formation of this deposit belong to the H$_2$O–NaCl system. In the El Cobre case, fluid inclusions do not show evidence of boiling. Homogenisation temperatures provide minimum estimated trapping temperatures. To determine the trapping temperatures, the pressure must be evaluated. In case of the absence of boiling, the minimum depth should be about 1 km. Moreover, the average of the present-day ocean depths at which anhydrite-bearing VHMS occur is between 1 and 2.5 km (Fouquet et al. 1993; Scott 1996; Fouquet 1997). Hence, taking into account this range of depths and a lithostatic pressure due to the anhydrite column of 100 m, the range of pressure at the top of the deposit should be between 138 and 270 bar. For such conditions of pressure, the correction of the homogenisation temperature to determine the temperature of entrapment is between 9°C and 15°C (Potter 1977). These data suggest that the deposit was formed within a range of temperatures from 175°C and more than 315°C.

Source of S

Sulphur in VHMS deposits usually comes from: (1) the inorganic reduction of seawater sulphate; (2) a magmatic source (Ohmoto 1996) that can result from a direct contribution from a vapour-rich magmatic fluid (Ohmoto 1986; Stanton 1990; Gemmell and Large 1992; Sillitoe et al. 1996, Herzig et al. 1998, Galley et al. 2000; Solomon et al. 2004) or (3) leaching of the volcanic host rocks (Solomon et al. 1988). Although the two magmatic sources produces a similar sulphur isotope composition, the direct magmatic contribution is more effective in the supply of metals, particularly Cu, Au, Bi and Te (Large 1992), and can be necessary to justify giant volcanogenic deposits (Ulrich et al. 2002).

Although sulphur from the bacteriogenic reduction of seawater sulphate has been considered important in some VHMS deposits (Sangster 1976; Çağatay and Eastoe 1995), the narrow range of δ$^{34}$S values observed in many VHMS deposits and the high temperature of formation are indicative of an inorganic reduction process of seawater sulphate (Sasaki and Kajiwara 1971). The inorganic reduction of seawater sulphate takes place easily in presence of ferrous iron when temperatures are above 250°C (Shanks et al. 1981; Shanks and Seyfried 1987). This process has been attributed to the presence of ferrous iron as reduction agent (Ohmoto et al. 1976; Ripley and Ohmoto 1977; Mottl et al. 1979; Shanks et al. 1981; Kerridge et al. 1983; Reed 1983). This origin has been considered for recent analogues to VHMS deposits (Arnold and Sheppard 1981; Styr et al. 1981).

The relatively narrow range and positive δ$^{34}$S values of sulphides from the El Cobre deposit (−1.4‰ to +7.3‰) rules out a bacteriogenic source for the sulphur. This range is in agreement with sulphide derived from inorganic reduction of seawater sulphate, a process favoured by the high temperatures of the formation of the deposit and by the Fe-rich host rocks (Shanks et al. 1981; Shanks and Seyfried 1987). A similar origin has been considered for recent analogues to VHMS deposits (Arnold and Sheppard 1981; Styr et al. 1981). The small variations in the sulphur isotopic composition of sulphides, sulphates (+16.3‰ to +20.9‰) and the intra-grain variations of the δ$^{34}$S values (up to 2‰) can be explained by the fractionation of sulphur isotopes during the thermochemical reduction of sulphate when seawater circulates deeply in a convective system.

However, a minor magmatic contribution of sulphide cannot be ruled out in interpreting these results. An important input of magmatic sulphur would produce negative δ$^{34}$S values as in the Hine Hina Mount (Herzig et al. 1998), yet these are not observed in the El Cobre case. Most sulphates from El Cobre have δ$^{34}$S values (+16.3‰ to +20.9‰) similar to or slightly higher than Paleocene–Eocene seawater sulphate (+16‰ to +18‰; Claypool et al. 1980). These values indicate that sulphates were mostly formed from seawater sulphate and the higher δ$^{34}$S values could be due to minor contribution of hydrothermal sulphate, as occurs in other volcanic-hosted massive deposits (Ohmoto 1996; Solomon et al. 2004; Scotney et al. 2005). Two sulphate samples with very low δ$^{34}$S (+5.9‰ and +7.7‰) were likely formed from the oxidation of hydrothermal sulphide (Shanks and Seyfried 1987; Çağatay and Eastoe 1995; Lüders et al. 2001).

Genetic model

The El Cobre fault and its associated vein mineralisation, and the stratabound and stratiform ore mineralisations are clearly spatially related. Most of the mineralisation takes place in the footwall of the fault, which is in accordance with the synchronous character of both. Three stages are considered in the development of the El Cobre deposit (Fig. 12).

First stage of sulphate mineralisation

Similar to some modern VHMS (Laznicka 1988; Graham et al. 1988; Scott 1996; Lydon 1996; Herzig and Hannington 1995, Roberts et al. 2003; Bach et al. 2003), the El Cobre deposit contains a thick lens of anhydrite in its uppermost section, interbedded between two barite levels. The whole
is overlain by Mn oxide and chert stratiform deposits. A closely similar mineral association has been reported for VHMS deposits in Canada (Ridler 1971) and for several present-day VHMS deposits (Scott 1983, 1987, 1996). In this way, in the present-day Pacmanus hydrothermal system, exhalites formed from a hydrothermal plume of particles composed of anhydrite, barite, amorphous silica, metal sulphides, oxides and hydroxides (Scott et al. 1997). In addition, anhydrite and barite are important in the Kuroko deposits of Japan where the thickness of the bodies can achieve more than 100 m (Ogawa et al. 2007).

Textural and field evidence indicates that mineralisation begins with the precipitation of barite followed by kaolinite alteration and the deposition of anhydrite. Stratiform basal mineralisations of barite and anhydrite are very thick and massive with no petrographic evidence of formation from metasomatic replacement of other preexisting rocks. Moreover, sedimentary and diagenetic textures, nodules or lamination in anhydrite or barite deposits, exclude any replacement processes. The evaporitic origin of anhydrite is discarded for several reasons: (1) the sedimentary basin was deep submarine (Kysar 2001); (2) there are no remains of other evaporitic lithofacies and (3) no similar deposits occur in the rest of the Paleogene arc in Cuba. They are, therefore, chemical precipitates formed on the seafloor or in its vicinity; these sulphates formed through exhalative processes.

The occurrence of kaolinitic alteration in this stage indicates the acidic character of the solutions. Kaolinite occurs in various volcanogenic sulphide deposits where it is
associated with barite (Marumo 1989; Marumo and Hattori 1999; Petersen et al. 2002; Scotney et al. 2005). This acidity could be due to the contribution of a SO₂-rich magmatic fluid, which under cooling is decomposed into H₂SO₄ and H₂S (Herzig et al. 1998). This origin was proposed for kaolinite from high sulphidation epithermal deposits (White and Hedenquist 1995) and could be applied to VHMS deposits (Barrett et al. 2005). Thus, an early exsolved magmatic fluid could be mixed at depth with modified seawater, rise up along the El Cobre fault and other fractures and react with host rocks to form kaolinite.

Under the sulphate beds, a sulphate vein stockwork occurs. These veins can be interpreted as the root zone of an hydrothermal-exhalative sulphate deposit, as implied by: (1) both mineralisation styles coincide spatially; (2) absence of hydrothermal alteration to the top of the anhydrite unit similar to those found at the base of these bodies; (3) Cu±Zn±Pb veins cut the base of anhydrite units but not its top and (4) vertical zoning of the vein mineralisation with transition from a siliceous stockwork zone to an anhydrite stockwork and, finally, stratiform sulphate mineralisation. Such zonal disposition can also be found in Kuroko-type deposits in Japan (Matsukama and Horikoshi 1970; Ohmoto and Skinner 1983), in VHMS deposits in Australia (Large 1992) and Canada (Roscoe 1965; Sangster 1976).

At this stage, the precipitation of sulphides was very low with some sphalerite and pyrite in the anhydrite stockwork. The precipitation of these sulphides might represent the mixing of cool seawater with the magmatic ascending fluid.

Second stage of mineralisation

Most of the sulphide mineralisation precipitated at this stage. This mineralisation fills all the channels and preexisting porosity and replaces previous mineralisation. The ore textures and the mineral composition of the alteration zones depend on the depth of formation.

The deep subparallel veins represent the feeder channels, which thin and converge at depth. These were formed at high temperature, around 300°C. In this study, there was relatively high tellurium abundance, and Au–Bi–Hg–tellurides were formed. The main source of fluid was modified seawater, which was the main source of sulphur, whilst the metals, as Cu, Bi, Au and Te, were probably mainly provided by a magmatic fluid, as occurs in other VHMS deposits (Large 1992), or leached from the host volcanic rocks (Huston et al. 2001).

The vertical zoning of the alteration with chlorite at its deeper sections, sericite and kaolinite at higher levels and talc at the top is characteristic of many massive sulphide deposits (Riverin and Hodgson 1980; Lydon and Galley 1986; Lydon 1996). This zoning can be considered a consequence of the thermal gradient established by the inflow of seawater from the surface.

Replacement zones or stratabound mineralisation are widely developed at this stage at the vicinity of the emission channels. Much of the previous mineralisation is replaced. The association quartz–illite–chlorite–apatite–sulphides of the anhydrite stockwork replaces that of calcite–anhydrite–kaolinite. Moreover, this association also replaces the stratiform barite and anhydrite mineralisations. The base of the anhydrite body is nearly completely replaced by aggregates of pyrite, chalcopyrite, sphalerite and bornite. The replacement of the anhydrite grains progress irregularly and usually it takes place in the intra-granular spaces of the anhydrite nodules.

In the stratabound mineralisation, carbonates are firstly replaced by an association of calcite+anhydrite and after, and especially near the El Cobre fault, by another of higher temperature, chalcopyrite+pyrite+sphalerite and silification and pyritisation of the host rocks. Later, fracturing occurs in the upper stratabound mineralisation; the fractures are filled by siliceous mineralisation.

The El Cobre deposit zoning is characterised by a decrease in the chalcopyrite/sphalerite ratio towards the uppermost section and flanks of the deposit, as it draws further from its feeding zone. A similar zonation has been described by Lydon (1996) for VHMS and can be interpreted as a consequence of a thermal gradient during sulphide deposition. Chalcopyrite disease (Barton 1978) in sphalerite is abundant and occurs because of the replacement of sphalerite, formed at lower temperature, by chalcopyrite, formed at higher temperature.

Finally, anhydrite–epidote veins occur distally to the El Cobre fault and have been formed by the mixing of seawater and saline magmatic fluid; the temperatures were lower due to the distance from the higher temperature source.

Third stage of mineralisation

Finally, the development of barite at the top of the deposit and manganese mineralisation occurs. The occurrence of chalcopyrite and other sulphides with barite indicates that this mineralisation formed at relatively high temperature.

Conclusions

Based on the island arc geodynamic context in which it was formed, its localisation within a basaltic and andesitic submarine volcanic complex, its mineralogy, structure, texture and mineralogical zonation and sulphur isotopic composition the El Cobre can be considered to be a Cu–Zn–Pb sulphide volcanic-hosted deposit.

The ore mineralisation is the result of deposition from hydrothermal fluids circulating through the seafloor. These fluids produced three types of mineralisation: (1) vein mineralisation, formed by precipitation in feeder channels.
with Cu at deeper levels and Zn at higher levels; (2) stratiform mineralisation with Zn–Cu–Pb–(Au), formed by partial replacement of some favourable levels (limestones at deeper levels and gypsum beds at the top of the sequence) and (3) stratiform anhydrite body at higher levels and stratiform mineralisation formed by exhalative processes at the Middle Eocene seafloor with anhydrite and barite at the base, barite towards the top and manganese bodies in distal position. As the deposit evolved, a telescoping effect was produced with low-temperature anhydrite stratiform deposits eventually being replaced and cut by new high-temperature vein generations.

The salinity of the fluid inclusions in the El Cobre deposit suggests that two fluids were involved in its formation: modified convective seawater and, to a lesser extent, a low salinity fluid, probably of magmatic origin. The sulphur isotopic composition of sulphides indicates that their source sulphur was mainly thermochemical reduction of seawater and, in minor amount, magmatic sulphur. Although no stratiform sulphide mineralisation has been found, the existence of abundant replacement of anhydrite mineralisation by sulphide mineralisation suggests the possibility that these sulphides could have been formed in the previously eroded part of the deposit. Nevertheless, the occurrence of massive sulphide lenses at the anhydrite levels yet to be explored in the deposit must not be discarded, particularly, in the Melgarejo sector.

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