

# High and intermediate sulphidation environment in the same hydrothermal deposit: the example of Au-Cu Palai–Islica deposit, Carboneras (Almería)

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**Keywords:** Gold, volcanic hosted deposit, high and intermediate sulphidation

**ABSTRACT:** Two epithermal environments have been identified in the Miocene Palai–Islica Au–Cu deposit: A) Intermediate sulphidation, hosted mainly in quartz veins, comprises pyrite, chalcopyrite, sphalerite and galena as the major sulphides, which are accompanied by a variety of Ag-bearing accessory minerals. Au–Ag alloys are the only gold-bearing phase. The veins are enclosed by sericitic and chloritic alteration. Fluid inclusions in quartz, sphalerite and calcite give  $T_h$  between 118–453 °C, and salinities between 0.2–51.4 wt.% NaCl eq, with high salinities being related to high-grade mineralisation. Stable isotopes indicate magmatic and marine fluids. B) High sulphidation consists of massive host rock silicification with disseminated pyrite and minor chalcocite, covellite, native copper and native gold. The surrounding alteration is advanced argillic/argillic in style. Fluids have  $T_h$  between 224–381 °C have salinities between 0.4 and 41.1 wt.% NaCl eq. The stable isotope data demonstrate the dominance of magmatic fluids, and disproportion processes.

## 1 INTRODUCTION

A large number of polymetallic hydrothermal deposits containing Au–Ag and base metals (Fe–Zn–Cu–Bi–Hg–Pb–As–Sb–Sn–Ba–REE–Te) have been exploited since ancient times in the Cabo de Gata–Cartagena volcanic belt, in South-eastern Spain (e.g., Arribas & Tosdal 1994; Morales et al. 2000 and references therein). These various hydrothermal deposits have different host rocks, alteration assemblages and mineralogical characteristics. One of the best-known gold deposits of this area is the Rodalquilar deposit (Arribas et al. 1995), a good example of a high sulphidation epithermal deposit. The Palai-Islica area is an Au-Cu prospect with significant amounts of economically important metals (Au locally  $\leq 23$  g/ton, Ag  $\leq 110$  g/ton and Cu  $\leq 8\%$  wt). This deposit exhibits distinctive zonation in ore assemblages and associated hydrothermal alteration and, thus, exhibits different styles of mineralisation. The aim of this paper is to clarify these characteristics, establish genetic constraints, and assign the mineralisation to the epithermal classification scheme of Hedenquist et al. (2000).

## 2 GEOLOGICAL CONTEXT

The Cabo de Gata–Cartagena volcanic belt and its continuation under the Mediterranean Sea in the Alboran basin comprises part of the eastern end of the Internal Zone of the Betic cordillera, the westernmost part of the Alpine edifice. This Neogene volcanic belt was formed within a compressive tectonic regime, followed by an extensional event (Dewey 1988; García Dueñas et al. 1992). Several series of volcanic rocks (Fig. 1), enclosed at various levels within the metamorphic basement of the Alpujarride and Nevado–Filábride complex, are developed, these are calc-alkaline, potassic calc-alkaline and shoshonitic, ultrapotassic and basaltic in nature (López-Ruiz & Rodríguez-Badiola 1980).

Numerous hydrothermal deposits are associated with this volcanic belt (Fig. 1). Calc-alkaline volcanic rocks are, volumetrically, the most important and directly enclose gold and base metal deposits (Rodalquilar, Cabo de Gata, Palai-Islica) associated with areas of intense hydrothermal alteration (Fernández-Soler 1996). The Au–Cu mineralisation of Palai–Islica, which is the subject of this paper, is located near the town of Carboneras (Fig. 1). It is hosted within strongly hydrothermally altered calc-alkaline andesites and dacites that display a domal structure (Morales et al. 2000).

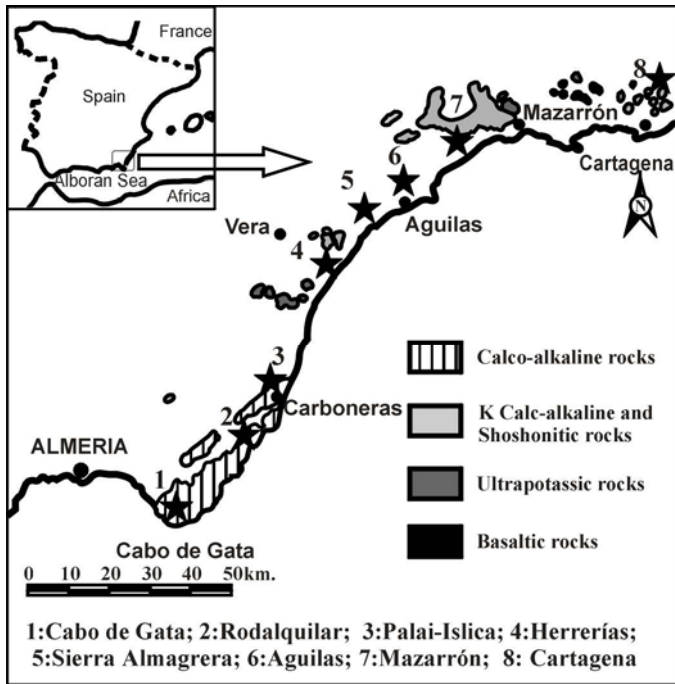


Figure 1: Location of hydrothermal deposits associated with the Cabo de Gata-Cartagena volcanic belt.

### 3 RESULTS

From a study of drill holes (21 in total, from +100 m asl to -107 m asl) and outcrop, two types of mineralisation with economic potential have been characterized: (i) veins and veinlets of quartz with sulphides and (ii) massive silicification. The former are located at elevations between +70 and -90 m asl while the latter, consisting of volcanic rock completely transformed into quartz, is found at the surface of the deposit between +70 and +100 m asl. These two types of mineralisation and related hydrothermal alteration exhibit distinctive mineralogical and geochemical characteristics. In addition, there is a third type of mineralisation, which has no potentially economic value. This consists of disseminated sulphides in hydrothermally altered volcanic rock.

#### 3.1 Veins and veinlets of quartz with sulphides.

This is the principal style of mineralisation in the Palai-Islica deposit. Macroscopically, the veins can be classified into two types: (i) Type A, which is the most common set and consists of veins rich in sulphides that are often coarse grained and locally form massive aggregates and (ii) Type B that are quartz-rich, with rarer finer grained sulphides.

The veins have an ore mineralogy comprising pyrite with lesser chalcopryrite, sphalerite and galena. There is also a range of accessory minerals (Carrillo et al., 2002a) that has more variety in Type A veins than in Type B. Gold is present in the form of Au-Ag alloys with Au/(Au+Ag) between 0.577 and 0.975 (Carrillo et al. 2002b).

The principal gangue minerals are quartz, white mica, and chlorite with minor quantities of barite, gypsum, dolomite and siderite (Carrillo et al.

2002a). EPMA analyses of the white mica (Table 1), reveal that it is potassic, with a small phengitic component, and a relatively low interlaminal charge — characteristics typical of hydromuscovite. The chlorite has a chamositic composition with relatively high Al and low Si contents (Table 1).

(A)	Si	<sup>IV</sup> Al	<sup>VI</sup> Al	Fe	Mg	<sup>VI</sup> Σ	K	Na	Σinter.
Mica	3,32	0,68	1,90	0,04	0,09	2,03	0,73	0,02	0,75
Chlorite	2,79	1,21	1,37	2,91	1,58	5,95	0,00	0,00	0,00
(B)	Si	<sup>IV</sup> Al	<sup>VI</sup> Al	Fe	Mg	<sup>VI</sup> Σ	K	Na	Σinter.
Mica	3,39	0,61	1,83	0,03	0,18	2,05	0,60	0,04	0,68
Chlorite	3,02	0,98	1,24	1,10	3,53	5,89	0,01	0,01	0,02
(C)	Si	<sup>IV</sup> Al	<sup>VI</sup> Al	Fe	Mg	<sup>VI</sup> Σ	K	Na	Σinter.
Interstratified	4,21	0,35	1,91	0,01	0,03	1,97	0,45	0,03	0,50
(D)	Si	<sup>IV</sup> Al	<sup>VI</sup> Al	Fe	Mg	<sup>VI</sup> Σ	K	Na	Σinter.
Interstratified	3,89	0,11	1,80	0,01	0,06	1,88	0,51	0,03	0,55

Table 1: Representative chemical analyses of phyllosilicates by EPMA. (A) veins; (B) alteration associated with veins; (C) massive silicification; (D) alteration associated with massive silicification

Two main stages of mineralisation are distinguished. First, there is a pyrite stage, where pyrite is the main sulphide, and this is followed by a base metal stage with the formation of chalcopryrite, sphalerite and galena. Gold, in the form of Au-Ag alloys, is mainly associated with the pyrite stage, whereas silver, in a variety of mineralogies (e.g. fahlore, Ag-Bi-Pb sulphosalts, acanthite, pyrargyrite, polybasite & Ag tellurides) was predominantly precipitated during the base metal stage.

It is notable that the Au-Ag alloys and Ag-bearing phases are mainly concentrated in two sub-horizontal levels: at around +45masl and -75 m asl (Morales et al., 2000, Carrillo et al., 2001). Litho-geochemical analysis of around 2300 samples shows that in these zones, there are geochemical anomalies of Au and Ag plus a number of other metals such as Cu, Zn, Pb Cd, As and Sb (Morales et al. 2000). In addition, within the veins Au/Ag is <1.

In terms of alteration, the andesites and dacites, which host the veins, are totally transformed to quartz, white mica plus chlorite, and, to a lesser extent, pyrite, dolomite, albite and epidote (Carrillo et al. 2002a). White mica from alteration zones has a similar composition to white mica in the veins, but with a slightly lower interlayer charge (Table 1), whereas chlorite compositions in the alteration are different to their vein-hosted counterparts (clinoclore type with greater Al and lower Si content, Table 1). Overall, the alteration can be described as sericitic and chloritic in the most proximal zones, and propylitic in the more distal areas. In the deepest hydrothermal alteration zones, Carrillo et al. (2002a) describe a different mineral association to the rest of the deposit. Here, the presence of disseminated bornite, chalcopryrite, pyrite, marcasite and cathodoluminescent sphalerite (Fe-poor) suggests a change in

conditions within the deposit. This mineralogy is compatible with a porphyry, but its shallower location rules out this possibility. However, it may indicate such porphyry mineralisation is present at greater depths.

In all types of vein quartz, bi-phase (L+V) fluid inclusions are the most common amongst several inclusion types. In Type B veins, quartz hosts abundant monophasic (V) and two-phase (L+V) inclusions with variable vapour fills. Three-phase or multi-phase inclusions also occur in dense bands (L+V+S; S = halite or more rarely haematite/sulphide — Fig. 2) and are a minor inclusion type. In addition, some secondary multi-phase inclusions were also located in relict volcanic quartz phenocrysts. The microthermometric data obtained for these inclusions (Morales et al. 2000 and this paper) show a wide range of  $T_h$  (120–435 °C) and salinity (0.4–51.4 wt % NaCl eq). Throughout the deposit as a whole, fluid inclusions in Type A veins, document fluids with salinities up to 10 wt.% NaCl eq. and show the full  $T_h$  range. However, at the level of the geochemical anomalies the fluid inclusion data show some distinct characteristics. In these gold-rich zones, fluids exhibit a significant salinity variation (3–20 wt % NaCl eq.) within a more restricted temperature range (250–300 °C). Concerning the Type B veins, these generally show high  $T_h$  (240–435°C) in comparison to Type A and their salinity varies between 1.7 and 51.4 wt % NaCl eq. Also in the Type B veins, the association of a variety of inclusion types — V, L+V+S with variable salinity coupled with L+V inclusions exhibiting bubble and dew point homogenisation — could be indicative of a boiling process.

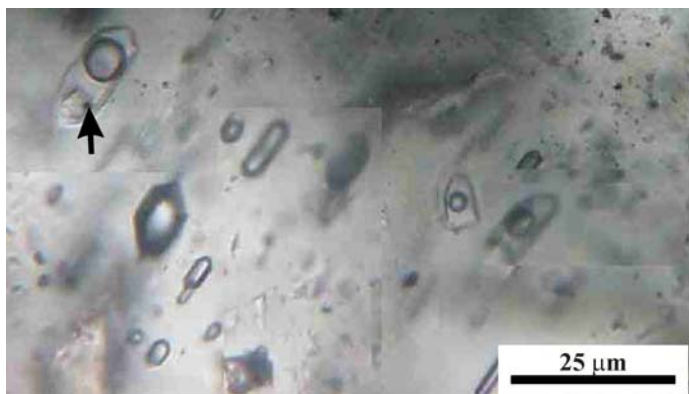


Figure 2: Coexisting multi-phase (L+V+S), two-phase (L+V) and one-phase (V) fluid inclusions (same motive with different focus). The arrow marks a sulphide crystal in a multi-phase FI.

In addition to vein quartz, fluid inclusions hosted in late stage sphalerite and dolomite were also studied. In both minerals the main inclusion type is a biphasic aqueous brine with significantly lower homogenisation temperatures than the quartz-hosted inclusions (sphalerite: 120–251 °C; dolomite: 118°–199°C). In addition, salinity showed a lower and more restricted range (sphalerite: 2.1–7.9 wt % NaCl

eq; dolomite: 1.6–7.2 wt % NaCl eq). This suggests that the gold deposition took place at higher temperatures and from higher salinity fluids (reflected by quartz-hosted fluid inclusions) than the deposition of Ag-bearing phases (reflected by sphalerite-hosted fluid inclusions).

An extensive study of stable isotopes was also undertaken and the results are summarised in Table 2. These results suggest that the sulphur in the great majority of sulphides is hydrothermal, and has a magmatic/volcanic origin (Carrillo et al. 2002a). Isotopic data for the quartz show that mineralising fluids are a mixture of magmatic and surface-derived waters. Moreover, the latter were probably marine in origin, and most prevalent in the final stages of the hydrothermal system as shown by the isotopic data for dolomite and barite.

### 3.2 Massive silicification.

The massive silicification consists of complete replacement of the volcanic rock by quartz with the mineralisation occurring as disseminated sulphides (mainly pyrite with minor chalcocite and covellite) with native gold and copper (Carrillo et al. 2002a). Compared to the veins, the ore minerals are less abundant and have a simpler mineralogy — pyrite is the only significant sulphide phase. In addition, silver is less abundant — there are fewer Ag-bearing minerals, native gold only has silver contents up to 1.92 wt %, (Carrillo et al. 2002b), and Au/Ag of the ore is >1 (Morales et al. 2000). Apart from the typical coarse-grained quartz, the gangue minerals comprise microcrystalline quartz (recrystallised chalcedony?), K-rich illite–smectite (Table 1) and later veins with barite, gypsum, jarosite (As- and non As-bearing), natrojarosite and natroalunite.

The massive silicification has halos of advanced argillic and intermediate argillic alterations characterized by kaolinite, illite, interstratified illite-smectite (Table 1) and quartz.

	Veins (‰)	Massive silicification (‰)
Sulphides	$\delta^{34}\text{S}$ : -8.3–12. (mode: 8‰)	$\delta^{34}\text{S}$ : 2.8–5.7
Barite	$\delta^{34}\text{S}$ : 19.3–22.1	$\delta^{34}\text{S}$ : 23.4–24.2
Quartz	$\delta^{18}\text{O}$ : 10.1–14.1	$\delta^{18}\text{O}$ : 12.2–17.8
Dolomite	$\delta^{18}\text{O}$ : 20.1–25.4 // $\delta^{13}\text{C}$ -5.3 – -2.8	

Table 2: Summary of stable isotopic analyses.

Despite its great abundance, quartz hosts very few fluid inclusions (mainly in coarse-grained quartz crystals or in relict volcanic phenocrysts). These are mainly two-phase or occasionally multi-phase with halite and possible sylvite. The argillising fluids are characterised by secondary fluid inclusions hosted in relict volcanic phenocrysts. These are two-phase with  $T_h$  ranging 224–381 °C, and salinities mainly between 0.4 and 11.2 wt % NaCl eq, although this can locally reach 41.1 wt % NaCl eq.

There are no marked differences in the microthermometric values between massive silicification and the argillic alteration, with the exception of the high salinity of inclusions encountered in the massive silicification.

Table 2 summarises the results of the stable isotopic study. Here, the sulphides in the massive silicification have slightly lighter S than the majority of the sulphides of the veins, while the opposite occurs with the barite. These isotopic values are compatible with pyrite–barite isotopic equilibrium at a temperature around 300°C, and with an origin for both phases from disproportionation of magmatic SO<sub>2</sub> (Carrillo et al. 2002a). The calculated fluid δ<sup>18</sup>O suggest dominance of magmatic waters during massive silicification, consistent with the geological setting.

#### 4 CONCLUSIONS

Mineralogical and geochemical studies have revealed two distinct assemblages in the Palai-Islica deposit.

Veins and veinlets of quartz with sulphide and significant Au, Cu and Ag have characteristics that indicate intermediate sulphidation epithermal mineralisation with a transition at depth to porphyry-type deposit. Au–Ag alloy formation occurs at temperatures mainly between 250–300°C, whereas the formation of the different Ag-bearing sulphides and sulphosalts plus the base metal bearing-sulphides usually takes place at temperatures lower than 200°C. Boiling processes are implicated in the formation of type B veins. However the principal process that produces the formation of distinct horizons of gold, silver, copper and other metal enrichment is fluid mixing, with the introduction of high salinity, possibly magmatic, fluids into the system. The isotopic data show that fluids of marine and magmatic origin have taken part in the mineralisation. The massive silicification, which is volumetrically less important, is Au-rich, Ag- and Cu-poor and shows characteristics of a high temperature (>200°C) epithermal deposit. However, in this case it has high sulphidation affiliations. Here, low pH mineralising fluids, principally of magmatic origin, resulted in the wholesale transformation of the volcanic rock into quartz, with the argillitisation occurring whilst the fluids were neutralising.

#### ACKNOWLEDGEMENTS

The authors thank SERRATA RESOURCES S.A. for providing samples during this investigation. The research has been supported by the project BTE 2001-3308 of DGI of Ministerio de Ciencia y Tec-

nología of Spain and the RNM 0131 Research Group of Junta de Andalucía. AJB is funded by NERC support of the Isotope Community Support Facility at SUERC.

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