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# Mineralogy and mineral chemistry of precious metals of the Cu-Au mineralisation at the Palai-Islica deposit, Almeria, SE Spain.

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ABSTRACT: The Au-Cu mineralisation of Palai-Islica is hosted within strongly hydrothermally altered calcalkaline rocks of the Cabo de Gata-Cartagena volcanic belt. Mineralisation is related to subhorizontal levels (named levels A, B, C and D, from bottom to top). Au and Cu are economically the most important elements, with Ag also being of potential interest. The Au-bearing phases of the Palai-Islica deposits are restricted to Au-Ag alloys (present at levels A, B and C) and native gold (found only at level D). The Ag-bearing minerals in levels A, B and C are fahlore, Au-Ag alloys, Ag-Bi-Pb sulphosalts, Ag sulphides, Ag tellurides, collomorphic pyrite, and galena. Within level D, the only significant values of Ag are found in some collomorphic pyrite. As deduced from textural studies and chemical features of different mineral phases, the noble metals at levels A, B and C evolved from Au-rich to Ag-rich as time progressed. Level D is a gold-rich silver-poor level and is apparently not connected with the genesis of the rest of the deposit.

### **1 INTRODUCTION**

A large number of polymetallic hydrothermal deposits containing, varying proportions of gold, silver and related metals, such as 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 and Tosdal, 1994; Morales et al. 2000 and references therein). These hydrothermal deposits vary greatly in their host rocks, alteration assemblages and mineralogical characteristics. Au-bearing deposits are more common in the southern part of the belt whereas Ag-base metal-bearing deposits are more common towards the northern parts.

In recent times, exploration activity for gold mineralisation has increased in the region. Because of this, we have access to samples from 21 drill cores from areas related to high-grade gold mineralisation and also to barren mineralisation from the Palai-Islica deposit (Carboneras, Almería, SE of Spain). This sampling permits the study of the threedimensional distribution of ore minerals and related alteration processes.

As a consequence of this work, a previous paper (Morales et al. 2000) has demonstrated the presence of economically important quantities of gold (locally up to until 23 g/ton), silver (up to 110 g/ton) and other metals (e.g. copper up to 8% wt) This paper demonstrates that these elements are distributed in

four sub-horizontal horizons: level A (-70 to -60 m.a.s.l.), level B (-25 m.a.s.l.), level C (+37.6 to +56.3 m.a.s.l.), and level D (at +98.2 m.a.s.l), with levels A and C being the most important geochemical anomalies in this deposits.

These levels have distinctive characteristics in respect of the rest of the deposit: (1) anomalous concentrations of metallic elements: Au, Ag, Cu, Zn, Pb, Cd, As, Sb, (2) the presence of fluids with characteristics different to those in the remainder of the deposit (a high variation in salinity over a narrow temperature range), and (3) a wide variety of ore minerals and textures. These levels were studied by Morales et al. (2000) regarding points (1) and (2). In order to complete this study, the aim of this paper is to characterise (using optical microscopy, SEM and EPMA) the mineralogy and mineral chemistry at mineralisated levels of the Palai-Islica deposit, with special emphasis on the different mineralogical and chemical expressions of the precious metals (Au-Ag). This characterisation permits a better understanding of the evolution of noble metals in the hydrothermal system and provides criteria for mineral exploration.

## 2 GEOLOGICAL SETTING

The Cabo de Gata-Cartagena volcanic belt 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 formed within a compressive tectonic regime, followed by an extensional event (Dewey 1988; García Dueñas et al. 1992). Different series of volcanic rocks, enclosed at various levels within of the metamorphic basement of the Alpujárride and Nevado-Filábride complex, are developed: calc-alkaline, potassic calcalkaline and shoshonitic, ultrapotassic, and basaltic series (López-Ruiz & Rodriguez-Badiola 1980). A series of hydrothermal systems developed during the Miocene in association with this volcanic activity and the system of fractures controlling it. Hot fluids are responsible for different mineralisation and alteration areas (Fernández-Soler 1996). One of the most important of these areas is the Au-Cu mineralisation of Palai-Islica, near the town of Carboneras (Almería), which is hosted within strongly hydrothermally altered calc-alkaline andesites and dacites (Morales et al. 1999 and 2000).

# **3 MINERALOGICAL FEATURES**

In the Palai-Islica area, Cu-Au mineralisation generally appears within veins and veinlets of quartz, hosted by the altered volcanic rocks (levels A, B and C) or associated with massive silicification in level D.

The Palai-Islica mineralisation consists principally of pyrite. Chalcopyrite, sphalerite and galena can also be significant, and gold, fahlore, bismuthinite, Ag±Bi±Pb sulphosalts, Ag sulphides, tellurides, pyrrothite, marcasite, bornite, chalcocite, covellite, stannite and Fe, Ti and Sn oxides are always minor phases (Carrillo et al. 1999; Morales et al. 2000). In an economical point of view, Au and Cu are the most important elements, with Ag also being a potentially interesting element.

## 3.1 Gold bearing phases:

Gold-bearing phases at the Palai-Islica deposits are restricted to Au-Ag alloys (present at levels A, B and C) and native gold (found only on level D). Asbearing pyrite is a common phase at the Palai-Islica deposit but is barren of gold at the level of EPMA analyses.

Au-Ag alloys (Fig. 1) appear only in quartz veins with sulphides (on levels A, B and C) and these are of two types:

Type A. Subrounded or subidiomorphic crystals (A1) within the pyrite crystals, mostly in the more external parts of the crystals, or (A2) located at inter-granular positions, in the intersitial space between pyrite aggregates or filling fractures in pyrite. The chemistry of type A alloys have an Ag content varying from 2.34% to 33.96% (note: in the text all contents are expressed as % atm).



Figure 1. BSE image of a zoned crystal of Au-Ag alloy. The width of picture is 350 microns.

Gold crystals of this type are generally homogeneous, with little or no compositional variation. We observed slight compositional differences between subtypes (Fig. 2). Subtype A1 has the lowest Ag values of all the Au-Ag alloys with an Au/Au+Ag ratio of 0.693 to 0.975, although most values range from 0.784 to 0.975. In contrast, subtype A2 crystals are slightly richer in Ag, with the broadest range of Au/Au+Ag values (0.633 - 0.968). In samples, containing both A1 and A2 types of crystals, we also observed a trend towards higher Ag content in the A2 type crystals.

Type B. Gold overgrowing pyrite crystals (B1), which may, in turn, be overgrown by other sulphides such as galena, chalcopyrite and sphalerite (B2). Type B gold crystals normally grow on the flat surfaces of the pyrite faces, or on irregular surfaces. The chemical characteristics of this type also correspond to Au-Ag alloys, with a higher Ag content (13.30% to 39.30%) than the type A alloys. Unlike type A gold, type B crystals commonly exhibit marked chemical zonation (Fig. 1), with up to 18.89% variation of the Ag content in one crystal.



Figure 2. Au/Au-Ag ratio in different types of gold.

The zonation pattern is diverse but there is a consistent trend towards higher Ag contents as growth continues. Moreover, some differences can be detected between subtype B1 and subtype B2 (Fig. 2), as the latter have a narrower compositional range and a higher Ag content (Au/Au+Ag from 0.604 to 0.771) than the former (Au/Au+Ag from 0.606 to 0.866).

Native gold: Gold grains appear only in areas of massive silicification (as found on level D). The gold is found as "free" crystals in the gangue, around the edges of spaces left by dissolution of phenocrystals in the silicified volcanic rocks. Native gold crystals are smaller in size than Au-Ag alloys and are the only gold type showing a colloidal morphology. The chemistry of these crystals (Fig. 2) corresponds to Au with practically no Ag (Au/Au+Ag from 0.997 to 1.000).

# 3.2 Silver bearing phases:

The Ag-bearing minerals in levels A, B, and C are mainly Au-Ag alloys and fahlore, with Ag-Bi-Pb sulphosalts, Ag-sulphides, Ag tellurides and as minor phases. Ag appears also as a minor element in pyrite and galena. Within level D, the only significant values of Ag are found in some collomorphic pyrite.

Au-Ag alloys: see above for description.

Fahlore: agrees with the general formula ( $Cu_{8,10}$ - $(Fe_{0.06-1.66}, Zn_{0.71-1.97})$  $Ag_{0.42-2.20}$ )  $(As_{0.08})$ 10.23,  $_{3.45}$ , Sb<sub>0.57-4.01</sub>) S<sub>13</sub>. Ag values range from 0.12% to 11.00% (average = 4.39%), with higher values of Ag, correlating with the tetrahedrite end-member (Fig. 3). Fahlores evolve in time, from early to late. They can be found included in pyrite, in base metal sulphides, and in open spaces. Fahlore included in pyrite is close to the tennatite end-member and are Ag-poor. At the latest stages, Ag-bearing tetrahedrite is more common and can be zoned or can exhibit complex intergrowth textures with galena and Ag sulphides (Fig. 4).



Figure 3. Sb vs. Ag variations in fahlore.



Figure 4. BSE image of an intergrowth texture. Fahlore (light grey), galena (white) and Ag sulphides (fine white points). The width of the picture is 80 microns.

Ag-Bi-(Pb) sulphosalts: Ag-Bi-Pb sulphosalts appear as individual crystals or are intergrown with bismuthinite and galena. Two types (Fig. 5) are found: (a) included in pyrite, with Ag values between 1.91% and 19.39%, showing two compositional trends: varying Pb-Bi with constant values Ag or varying Ag-Bi with constant Pb values; (b) mainly overgrowing chalcopyrite crystals with Ag values ranging from 9.44% to 22.63% (mainly ranging from matildite<sub>70-88</sub> to galena<sub>12-30</sub>). Minor Ag-Bi sulphosalts (matildite) have also been found.

Ag sulphides and Ag tellurides: Small quantities of these minerals can be found associated with fahlore and galena (Fig. 4).

Ag as minor element in pyrite: Pyrite is by far the most abundant sulphide in this deposit and displays a wide range of textures and chemical varieties (Carrillo et al. 2000). Of these varieties, collomorphic pyrite contains the higher values of Ag. Collomorphic pyrite is paragenetically late in the sequence, always overgrowing on other sulphides. Collomorphic pyrite is made up of alternating Agrich (up to 0.1%) and Ag-poor bands.

Ag as minor element in galena: Galena appears as disseminated crystals in the gangue, as veinlets or within the pyrite. Galena is sometimes intergrown with other phases (fahlore, Ag sulphides or Pb-Bi sulphosalts). Ag can be found in galena in one of two ways: (a) as a minor element in galena, with values up to 2.47%. Ag values show a positive correlation with respect to Bi; (b) as small inclusions of Ag-bearing phases (fahlore and other sulphosalts) within galena. In the latter case, inclusions of Agbearing minerals follow crystallographic orientations in galena, suggesting a genesis related to exsolution.



Figure 5. Chemical composition of Ag-Bi-Pb sulphosalts (A) within pyrite and (B) overgrowing chalcopyrite.

# 4 DISCUSSION AND CONCLUSIONS

Au-Ag alloys (located in levels A, B, and C) and native gold (found only in the uppermost level D) are the only Au-bearing phases. Alternatively, Agbearing minerals in levels A, B and C show more diversity: Au-Ag alloys, fahlore, Ag-Bi-Pb sulphosalts, Ag sulphides, Ag tellurides collomorphic pyrite, and galena. With the exception of some collomorphic pyrite, no noteworthy phases containing Ag are found in level D.

In levels A, B and C, detailed petrographic studies demonstrate a distinctive sequence of sulphide precipitation: (1) a pyrite stage, with minor amounts of base metal sulphides and gold-rich Au-Ag alloys, and (2) a base metal stage with silver-rich Au-Ag allovs and significant amounts of Ag-bearing minerals. In this sequence, the behaviour of Au and Ag is as follows: Au only appears at the end of stage 1 towards the beginning of stage 2. Au is hosted in Au-Ag alloys with the Au content decreasing through the A1-, A2-, B-type alloys. Ag is primarily related to sulphides and sulphosalts (fahlore, Ag-Bi-Pb sulfosalts, type B of Au-Ag alloys, Ag sulphides, galena, and Ag tellurides) of stage 2. There is a general trend of enrichement in Ag with time, as observed in the Ag-bearing minerals (mainly at Au-Ag alloys, fahlore, and Ag-Bi-Pb sulphosalts).

The mineralogy of the uppermost level (level D) is different from the others levels: massive silicification with native gold and occasional Ag-bearing collomorphic pyrite. This mineralisation is apparently not connected with the genesis of the rest of the deposit.

In summary, the noble metals evolve from Aurich to Ag-rich at levels A, B and C through time. Level D is apparently not connected with the genesis of the rest of the deposit.

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