EPITHERMAL Cu-Au MINERALIZATION IN THE PALAI-ISLICA DEPOSIT, ALMERIA, SOUTHEASTERN SPAIN: FLUID-INCLUSION EVIDENCE FOR MIXING OF FLUIDS AS A GUIDE TO GOLD MINERALIZATION

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Abstract

The epithermal gold-copper-bearing deposit of Palai-Islica, near Carboneras, in Almeria, southeastern Spain, is hosted by volcanic rocks of Cabo de Gata - Cartagena volcanic belt (Betic Cordillera). Hydrothermal alteration occurs in the sequence: propylitic, sericitic, argillic (extending over a surface area of some 2.5×1.7 km²), and silicic. Mineralization, consisting of quartz with sulfides (pyrite ± chalcopyrite ± other minor sulfides and native gold), appears in veins, stockworks and layers. Results of a petrographic study of the gold mineralization and a lithogeochemical study reveal a correlation between the position of the horizons bearing gold grains and the location of the geochemical anomalies, in such a way that different mineralized horizons can be defined, the most important being the "upper gold-bearing level" and the "lower gold-bearing level". The precipitation of Au and other metals of economic interest within the mineralized horizons is systematically related to the presence of a fluid with a distinctive salinity, which interacts within a narrow interval of temperature with low-salinity fluids to produce the gold mineralization. In this sense, mineralized horizons systematically contain fluids of highly variable salinity (2-29.3 wt.% NaCl eq.) with a temperature varying some 25 to 50°C (approximately) in the interval of 217 to 315°C. In contrast, above and below the mineralized horizons, low-salinity fluids (6 ± 4 wt.% NaCl eq.) appear across a wide temperature range ($\approx 120-400^{\circ}$ C). The various characteristics of these fluids (due mainly to the isothermal mixing of fluids and a heterogeneous entrapment of the solutions) seem to have been responsible for the transport and precipitation of the metals studied. Gold could have been transported in the form of AuHS° or AuCl₂⁻ complexes and precipitated as a consequence of their destabilization owing to the abrupt change in physical and chemical conditions. Fluid-inclusion studies are shown to serve as a quick, inexpensive and very effective method for the exploration of new mineralized bodies within the gold-bearing deposit of Palai-Islica.

Keywords: epithermal deposit, copper, gold, gold-bearing horizons, fluid inclusions, Palai-Islica, Spain.

Sommaire

Le gisement épithermal (Au-Cu) de Palai-Islica, près de Carboneras, en Almeria, dans le sud-est de l'Espagne, est situé dans les roches volcaniques de la ceinture de Cabo de Gata - Cartagena (Cordillères Bétiques). Une altération hydrothermale s'est développée selon la séquence: propylitique, "séricitique", argillique (sur une superficie d'environ 2.5×1.7 km²), et silicique. La minéralisation, qui se manifeste par la formation de quartz avec sulfures (pyrite ± chalcopyrite ± autres sulfures accessoires et or natif), se présente en veines, en stockwerks et en couches. Les résultats d'une étude pétrographique de la minéralisation aurifère et d'une étude lithogéochimique révèlent une corrélation entre la position des horizons aurifères et celle des anomalies géochimiques, de telle sorte qu'il est possible de distinguer les horizons minéralisés. Les plus importants de ceux-ci seraient les horizons aurifères supérieur et inférieur. La précipitation de l'or et autres métaux d'intérêt économique à ces niveaux est lié de façon systématique à la présence d'une phase fluide de salinité distinctive, qui s'est mélangée sur un intervalle limité de température avec des fluides de faible salinité pour produire la minéralisation. Dans ce sens, les horizons minéralisés contiennent systématiquement des inclusions de fluides de salinité fortement variable (2-29.3% NaCl éq., poids), la température variant sur quelques 25 à 50°C environ dans l'intervalle entre 217 et 315°C. En revanche, en dessus et en dessous des horizons minéralisés, les inclusions indiquent des fluides de faible salinité (6 ± 4% NaCl éq., poids), piégés sur un large intervalle de température (≈120-400°C). Les diverses caractéristiques de ces fluides, dues surtout au mélange isothermique des fluides et à l'occlusion hétérogène des solutions, semblent avoir été responsables du transfert et de la précipitation des métaux. L'or pourrait bien avoir été transporté sous forme des complexes AuHS° ou AuCl₂-, et précipité suite à leur déstabilisation due aux changements abrupts

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des conditions physiques et chimiques. L'étude des inclusions fluides fournit un outil rapide, économique et très efficace dans l'exploration pour découvrir de nouvelles zones minéralisées dans le gisement aurifère de Palai–Islica.

(Traduit par la Rédaction)

Mots-clés: gisement épithermal, cuivre, or, horizons aurifères, inclusions fluides, Palai-Islica, Espagne.

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 southeastern Spain. More than 3,000 mining sites have been identified between Cabo de Gata and Cartagena. Some of the sites date back more than 2,000 years, and some had considerable output in the last century when the region became one of the most important base-metal producers in Europe.

These hydrothermal deposits range from epithermal to mesothermal in character, and vary greatly in the nature of their host rocks, types of alteration, mineral associations, textures, paragenetic sequences and proportions of precious metals. The variability makes it difficult to establish general criteria for exploration. Nevertheless, mining activity in the region is presently increasing. An open-pit mine has recently been inaugurated at Herrerías [Ba–Ag–(Fe–Mn)]; a mining project is being considered at Mazarrón [Zn–Cu–(Ag–Au)], and at the Palai–Islica deposit, at Carboneras in the Province of Almería, exploration activity of the Serrata Resources Company has demonstrated the presence of mineralized Au–Cu-bearing horizons, which are the main subject of this paper.

Here, we report on: 1) the hydrothermal alteration in the host rocks, 2) the mineral assemblages of the deposit, especially those involving gold, 3) results of lithogeochemical studies, and 4) the microthermometric analysis of the fluid inclusions and their relationship with the identified gold-bearing horizons. Ours is part of a broader multidisciplinary investigation designed to evaluate the metal potential of the Palai–Islica deposit.

The main object of this study is to characterize gold mineralization (*i.e.*, the type, paragenesis, Au-bearing phases, and their spatial distribution) and mineralizing fluids (nature, spatial distribution, fluid interactions, and reaction mechanisms with the host rock), to arrive at a better understanding of the mechanisms favoring the concentration and precipitation of gold.

GEOLOGICAL SETTING

The Cabo de Gata – Cartagena volcanic belt comprises part of the eastern end of the Internal Zone of the Betic Cordillera. This Neogene volcanic belt formed within the context of a subduction zone, followed by an extensional event (Dewey 1988). Some of the consequences of this extensional regime (García Dueñas *et al.* 1992) were: 1) a thinning of the continental crust, 2) the formation of strike-slip and normal low-angle faults and associated structures (*e.g.*, the N40°–50°E Carboneras and the N10°–20°E Palomares faults), and 3) the development of Neogene volcanic rocks of calc-alkaline, potassic calc-alkaline, shoshonitic, ultrapotassic and basaltic series, enclosed mainly in the various levels of the metamorphic basement of the Alpujarride and Nevado–Filabride complex (López-Ruiz & Rodríguez-Badiola 1980).

A series of hydrothermal systems developed during the Miocene in association with this volcanic activity and the system of faults and fractures controlling it. The hot fluids [up to 400-450°C, according to Morales (1994)] reacted strongly with the host rocks and thus, in some districts, gave rise to the formation of broad and usually zoned areas of mineralization and alteration (Fernández-Soler 1996). The most important of these sites are, from south to north (Fig. 1a): (1, 2 and 3) the Au-Cu-Te and Pb-Zn-(Ag-Cu-Au) mineralization hosted directly within the strongly hydrothermally altered calc-alkaline volcanic rocks of Cabo de Gata, Rodalquilar and Carboneras (Palai-Islica) (e.g., Arribas & Tosdal 1994), (4) the stratiform (SEDEX?) Ba-Ag mineralization overlying the Herrerías volcanism (e.g., Martinez-Frías et al. 1989, Morales et al. 1993, 1995), (5) the Pb-Zn-Ag-Cu-Ba-(Au) veins hosted by the metamorphic basement in proximity with the very weakly hydrothermally altered dacites and latites of Sierra Almagrera (i.e., Morales 1994), (6) the Zn-Pb-Cu-Fe-As-Co-Ni-(Ag-Au) veins located in the metamorphic basement, related with small subvolcanic intrusions at Aguilas (Castroviejo et al. 1991, Morales et al. 1993, 1995, Morales 1994), and (7) the Zn-Cu-(Ag-Au) associated with the Mazarrón stockwork (Corbella 1969).

The Palai–Islica ore deposit corresponds to the mineralization hosted by calc-alkaline volcanic rocks. In this area three main geological units are distinguished (Fig. 1b): (1) *Volcanic rocks of the Cabo de Gata calc-alkaline series* mainly consist of Tortonian amphibole-bearing andesites and dacites, in the form of agglomerates, lavas or pyroclastic deposits. These rocks are commonly brecciated (tectonic and hydrothermal breccias) and show considerable hydrothermal alteration. The Palai–Islica area consists of an oval east–west-striking zone of strongly hydrothermally altered volcanic rocks of 2,500 m long by 1,700 m wide. In this area,



FIG. 1. a. Location of the most important ore deposits at Cabo de Gata – Cartagena volcanic belt (adapted from Lopez Ruiz & Rodriguez-Badiola 1980). (A) Calc-alkaline volcanism, (B) calc-alkaline, potassic and shoshonitic volcanism, (C) ultrapotassic volcanism, (D) basaltic volcanism. (1) Cabo de Gata, (2) Rodalquilar, (3) Carboneras (Palai–Islica), (4) Herrerías, (5) Sierra Almagrera, (6) Aguilas, (7) Mazarrón. b. Schematic geological map showing the location of Islica–Palai deposit (adapted from IGME, 1974). Main geological units: (1) Upper Miocene volcanic rocks of the Cabo de Gata calcalkaline series, (2) Paleozoic–Mesozoic basement rocks belonging to the Alpujarride Complex, (3) Tertiary sedimentary rocks, (4) Quaternary sediments (a) alluvial and (c) colluvial, (5) Faults are outlined in continuous line, and the limit of hydrothermal alteration is outlined in dotted line. (6) Outcropping Palai–Islica deposit.

hydrothermal alteration is easily identifiable by the presence of light-colored rocks. Gold-bearing mineralization is invariably related to these zones of hydrothermal alteration. (2) *Tertiary sediments* consist of carbonates, sandstones and marbles. (3) *Paleozoic–Mesozoic basement rocks* (gneisses, schists, mica schists, quartzites and phyllites) belonging to the Alpujarride Complex.

Subhorizontal, *Pliocene–Quaternary* sediments partially cover the volcanic rocks and the metamorphic basement.

Associated with the N40°–50°E Carboneras fault system in the Palai–Islica zone, there are abundant normal faults and secondary strike-slip faults, which facilitated the circulation of gold-bearing hydrothermal fluids.

SAMPLES AND ANALYTICAL TECHNIQUES

In the course of an exploration program for gold in the Palai–Islica area, 21 diamond drill holes were drilled by Serrata Resources, S.A., and 2307 core samples corresponding to 2476 meters from the 21 holes were collected for geochemical analyses and mineralogical studies. These samples were analyzed for thirty-two elements (major elements and selected trace elements). All 21 drill cores were split longitudinally into two halves. One of these halves was completely crushed for analysis. Every core sample consisted of about one meter long of the half drill holes. The analyses were performed at CHEMEX LABS in Vancouver (Canada), using the fire-assay technique for gold.

Samples for the mineralogical study were chosen from various areas related with high-grade gold mineralization, associated zones of hydrothermal alteration, and unmineralized rocks proximal and distal to gold mineralization.

Two hundred and twenty-two polished thin-sections of samples collected from drill-core material were prepared to determine the paragenetic relationships among the ore minerals and to characterize the hydrothermal alteration. The mineralogical characteristics of the ore minerals were documented using reflected- and transmitted-light microscopy, X-ray diffraction and scanning electron microscopy (SEM).

All fluid inclusions studied in the Palai–Islica zone are hosted by quartz in samples from three drill cores (PH–009, PH–011 and PH–008) aligned north–south, cross-cutting the mineralization. Inclusions in quartz were also studied in samples collected from an old mine located in the middle of the study area; it is very likely that the mine samples were originally deeper than the drill-core samples.

Microthermometric determinations were made on doubly polished thin-sections about 100 µm thick using a Linkam[®] THMSG 600 freezing-heating stage, a TMS93 system of temperature control, an LNP2 freezing-control system and an image-analysis system to record phase changes. The stage was previously calibrated by selected Merck® inorganic standards in the range from -95°C to 419°C. The data are reproducible to $\pm 0.5^{\circ}$ C for the freezing runs and $\pm 5^{\circ}$ C for the heating runs. A total of 400 fluid inclusions were analyzed by freezing cycles down to -200°C using the cycling technique described by Goldstein & Reynolds (1994) in order to have a more precise determination of the hydrohalite and ice melting temperatures, and heating up to the corresponding temperature of homogenization to ensure the stability of the cavities and the representativity of the determinations. Values of salinity were obtained using the temperature of dissolution of the last crystal of ice for two-phase fluid inclusions (Potter et al. 1978) and the melting temperature of the last crystal of halite for solid-bearing fluid inclusions (Sterner et al. 1988).

HYDROTHERMAL ALTERATION AND VOLCANIC ROCKS

The Palai–Islica zone displays the effects of a complex geological history involving mineralization and alteration processes that led to the formation of copper– gold deposits. The host rocks of the mineralization (Fig. 2) are amphibole-bearing andesites (and minor dacites), porphyritic in texture. The phenocrysts consist of green hornblende, normally altered to chlorite associated with ore minerals, plagioclase, commonly altered to white mica, and minor amounts of quartz, generally preserved during alteration. The matrix is devitrified glass, occasionally transformed to chlorite, white mica or clay minerals.

Throughout the study area, the host rocks show considerable hydrothermal alteration, caused by their interaction with the mineralizing fluids. Petrographic and X-ray-diffraction studies of the altered rocks reveal the following types of hydrothermal alteration (in ascending order of intensity): propylitic, sericitic, argillic, and silicification. Late carbonation and the presence of gypsum also are observed. A general spatial pattern has been established: the propylitic alteration occupies the outermost part of the deposit, whereas the silicic alteration is found in the inner part of the deposit and is commonly associated with gold.

Silicification has taken place to varying degrees and is locally associated with zones of intense chloritization. The mildest alteration involves a partial replacement of the original volcanic components by silica. In more advanced cases, alteration has resulted in the formation of veins and masses of quartz (quartz–sulfide veins, silica–pyrite stockwork, vuggy silica or silica caps). The economically interesting mineralization is commonly associated with the most intense silicification. In the case of the mineralized zones, the silica is massive and appears either in the form of xenomorphic granular aggregates or with growth textures typical of open spaces (crustifications, comb structures, epitactic



FIG. 2. Photomicrographs of different examples of hydrothermally altered volcanic rocks (cross-polarized light). (a) Porphyritic texture of volcanic rock showing phenocrysts of plagioclase altered to white mica and clay minerals. The matrix is transformed to quartz and clay minerals. (b) Hornblende phenocryst transformed to chlorite (in the cleavage planes and rims of hornblende) and to quartz. The matrix is mainly quartz. (c) Incipient transformation of plagioclase to white mica in a matrix totally altered to quartz, chlorite and clay minerals. (d) Zone of intense silicification surrounded by fine intergrowth of clay minerals, pyrite and quartz. Scale bars are 100, 160, 210 and 100 μm respectively.

growths of euhedral crystals, *etc.*). Quartz crystals rarely can be found as rhombohedral pseudomorphs of carbonate crystals.

MINERALIZATION

Ore mineralogy

In the Palai–Islica area, mineralization generally appears in association with veins and veinlets of quartz enclosed within the altered volcanic rocks and, to a much lesser extent, as disseminations. In places, these veins form stockworks and silica caps with sulfides.

The Palai–Islica mineralization is of the Fe–Cu–Au type and consists principally of fine-grained, xenomorphic iron and copper sulfides and quartz. The ore minerals may include pyrite \pm chalcopyrite as major phases, and minor amounts of sphalerite, galena, pyrrhotite, bornite, grains of the tetrahedrite–tennantite series, bismuthinite, Bi \pm Pb \pm Ag sulfosalts, marcasite, rutile and covellite. Also noteworthy are native gold (Fig. 3) and tellurides.

On the basis of the most important sulfide phases found in the Palai-Islica zone, four types of assemblages can be distinguished. Type I is characterized by pyrite as the major sulfide phase, with very small amounts of accessory minerals. Type II is typified by having pyrite and chalcopyrite as the major sulfides; the accessory minerals (bornite, galena, pyrrhotite, Bi-minerals, tellurides, tetrahedrite) with which gold is associated are more abundant and different from those in Type I. Type III consists of pyrite with sphalerite and galena as major phases; chalcopyrite, tetrahedrite and, occasionally, gold are present as minor phases. Type IV is characterized by pyrite as the major phase, and with covellite and gold as minor phases; vuggy silica is associated. On the whole, the Type-I assemblage is the most abundant, Types II and III are less frequent, and Type IV appears only occasionally.



FIG. 3. Photomicrographs (reflected light) of occurrences of grains of free gold: (a) Large, rounded grain included in pyrite. (b) Pyrite and gold hosted by galena, Type-III paragenesis. (c) Gold grain growing on pyrite. (d) General overview of a typical assemblage of gold with pyrite, galena, sphalerite, tetrahedrite and quartz. (e) Xenomorphic, elongate crystal included in pyrite. (f) Two roundish grains of gold growing on pyrite in the contact with sphalerite. (Au: gold, py: pyrite, gn: galena, sph: sphalerite, thd: tetrahedrite). Scale bars are 12, 20, 12, 50, 12, and 20 μm, respectively.

Gold mineralization

All the gold grains identified by the petrographic study are related only with the silicification of the host volcanic rocks. The gold-bearing samples are closely related spatially to the quartz-mineralized veins crosscutting the altered volcanic rocks.

A detailed study of 113 gold grains has been carried out to characterize their most significant features (Fig. 3, Table 1). The grains are irregular or subrounded in shape, ranging in size from 2 to 89 μ m. They are generally found with the Type-II assemblage (69.0% of cases), although grains also occasionally occur with the assemblages of types I, III and IV (8.9, 17.7 and 4.4% of the cases, respectively). The grains are consistently closely associated to pyrite, in which they are included, although they can in some cases be found at the boundaries of pyrite and quartz. Furthermore, gold grains are much less commonly located within quartz interstices

TABLE 1. CHARACTERISTICS OF GOLD-BEARING SAMPLES: SIZE OF GOLD GRAINS, PARAGENESIS TYPE, AND DEPTH OF SAMPLES IN THE DRILL CORES, PALAI-ISLICA DEPOSIT, SOUTHEASTERN SPAIN

Samples	Number of gold crystals	Size of gold crystals*	Type of mineralization	Depth (masl)
S-211-1	5	10-15	IV	98.2
S-155-1	11	3-89	Ш	56.3
S-156-2	7	2-29	111	55.3
S-019-1	2	9-12	Π	46.7
S-139-1	65	2-37	11	43.1
S-022-1	2	5-7	II	41.5
S-022-2	1	14	п	41.5
S-125-1	1	65	П	39.7
S-167-1	1	10	Π	39.2
S-199-2	10	7-59	I	37.6
S-170-1	2	15-16	III	-25.9
S-154-1	6	4-28	п	-69.0
Total	113	289		

* minimum and maximum sizes in each case.

of the Type-IV assemblage or included within galena or sphalerite in the Type-III assemblages.

The gold mineralization found here has a peculiar spatial distribution. Most of the samples in which grains of free gold have been identified lie in subhorizontal layers, regardless of the type of host rock. The main layer lies between 37.6 and 56.3 (average value of 44.6) meters above sea level (masl), which is constant throughout the study zone. Roughly speaking, this layer extends at least 1035 m in northwest–southeast direction and 300 m in northeast–southwest direction, resulting in a mineralized level of a minimum extent of 155,250 m² and some 20 m thick. As the average collar elevation of the drillholes is 85 masl, the main mineralized level (X = 44.6) is estimated to be some 40 m under the topographic surface.

In addition to the samples comprising the main subhorizontal gold-bearing layer, we have also found grains of free gold in other three levels, one above (at +98.2 masl) and two beneath the main layer (at -25.9 and at -69.0 masl). As explained below, it is logical to assume that at least the -69.0 masl position (and perhaps the -25.9 masl one as well) is a sheet-like gold-mineralized subhorizontal layer.

LITHOGEOCHEMISTRY

A geochemical study of the rocks in this area has revealed the presence of two zones of gold anomalies in two levels, one from +40 to +50 masl (hereafter termed the "upper geochemical anomaly", UGA) and another from -60 to -70 masl (hereafter called the "lower geochemical anomaly", LGA). In association with these gold anomalies, there is also an anomalous enrichment in other metallic elements of economic interest (Cu, Ag, Pb, Zn, Cd, As, Sb, Bi, Co, Ni, Hg). Anomalies of some metallic elements are displayed in Figure 4.

FLUID INCLUSIONS

Petrographic characterization of fluid inclusions

All fluid inclusions have characteristics of primary inclusions; they have a random distribution or are isolated in the quartz crystals. The petrographic and microthermometric characterization of the fluid inclusions has led us to separate them into three types and two subtypes.

On the basis of number of phases present at room temperature, three types of fluid inclusions have been distinguished (Fig. 5). *Type 1* (L + V + S): relatively scarce three-phase fluid inclusions, with a bubble of gas, a liquid and a solid at room temperature (Fig. 5a). The size is less than 30 µm and the volume percent of the gas phase varies from 30 to 50%. *Type 2* (L + V): two-phase fluid inclusions, by far the most abundant. At room temperature, they consist of gas and liquid (Fig. 5b). The size is less than 30 µm, and they contain

a variable percentage of the gas phase (between 20 and 50%). *Type 3* (*V*): a few, very small single-phase (gas at room temperature) fluid inclusions, randomly scattered throughout the quartz crystals (Fig. 5c). The size is less than 10 μ m.

Although no petrographic differences have been observed among type-2 fluid inclusions, using microthermometric data as described below, we have divided them into two subtypes: *subtype 2.1* (variable salinity and fairly constant temperature of total homogenization), and *subtype 2.2* (low salinity and variable temperature of total homogenization).

Microthermometric determinations

The values obtained from the microthermometric study are summarized in Table 2. The main characteristics of each type of fluid inclusion are summarized below.

Type 1. These are three-phase hypersaline inclusions (comprising a gas bubble, a liquid phase and a solid, seemingly halite). During the course of the freezing process, these inclusions underwent no phase changes in the gas, suggesting that the amount of volatile present in the vapor phase is negligible. The temperature of first melting is approximately -21° C, and therefore this type of inclusions can be related to the system H₂O–NaCl (Crawford 1981). The determination of the melting

TABLE 2. MICROTHERMOMETRIC DATA ABOUT FLUID INCLUSIONS, PALAI-ISLICA DEPOSIT, SOUTHEASTERN SPAIN

	Type 1	Type 2	Т	ype 3
Phases	V + L + S	V+L		v
System	H ₂ O – NaCl	H ₂ O - NaCl - CaCl ₂		n.d.
VPGP	3050	20-50		100
Tfm	-21	-60 to -50		n.d.
Tm hydrohalite	n.d.	-54 to -30		n.d.
Tm ice	-5.0 to -0.9	-30,1 to -0.2		n.d.
TDB	289 to 338	n.d.		n.d.
TDS	304 to 361	n.d.		n.d.
TTH	304 to 361	120 to 401*		n.d.
Salinity	38.5 to 43.4	0.4 to 29.3**		n.d.
	Type 2	Subtype 2.1	Subtype 2.2	
TTH*	120 to 4	01 217 to 315	120 to 401	
	(144 to 3	51) (239 to 303)	(140 to 383)	
Salinity**	0.4 to 29	.3 2 to 29.3	0.4 to 11	

V: Vapor phase, L: liquid phase, S: solid phase. VPGP: volume percent of the gas phase. Tfm: temperature of first melting. Tm hydrohalite: temperature of final melting of hydrohalite. Tm ice: temperature of final melting of ice. TDB: temperature of disappearance of the gas bubble. TDS: temperature of disappearance of halite. TTH: temperature of total homogenization. Salinity was calculated using the melting temperature of the last crystal of halite in the case of fluid inclusions of type 1 (Sterner et al. 1988), and the temperature of dissolution of the last crystal of ice in the case of fluid inclusions of type 2 (Potter et al. 1978). All values of temperature are quoted in °C. n.d.: not determined. Shown in parentheses is the interval for 95% of the values.



FIG. 4. Variations in the concentration of different metals as a function of depth. Note the presence of a general anomaly for all elements around the +40 to +50 masl interval ("upper geochemical anomaly", UGA) and the -60 to -70 masl interval ("lower geochemical anomaly", LGA). Each diagram contains results of 2307 analyses.

temperature of the last ice crystal was difficult to establish with precision, owing to the small amount of the liquid phase in this type of inclusion. Consequently, the microthermometric determinations made during the freezing cycles are not very precise, but the values obtained are estimated to fall within the interval of -5.0to -0.9° C. During the heating process, the gas bubble disappears between 289° and 338°C. Halite invariably melts, with one exception, at a higher temperature, 304° to 361°C. If we take the disappearance of the last phase as the overall temperature of homogenization of this type of inclusion, this temperature lies between 304° and 361°C. The salinity calculated (Sterner *et al.* 1988) for these fluid inclusions varies from 38.5 to 43.4 wt.% eq. NaCl. This type of fluid inclusion has only been identified in samples from the old mine, but not in core samples.

Type 2. This type contains two-phase inclusions (gas bubble plus a liquid phase). These inclusions show no change in the gas phase, indicating that there are practi-



FIG. 5. Types of fluid inclusion from Palai deposit: (a) Solid-bearing fluid inclusion containing a vapor bubble (V), a brine liquid (L) and a daughter mineral (halite) (S). (b) Two-phase aqueous fluid inclusion consisting of a vapor bubble (V) and a liquid phase (L). (c) Vapor-rich fluid inclusion (V). This type consists predominantly of vapor.

cally no volatiles in the vapor phase. In general, inclusions have the following characteristics: a temperature of first melting between -60° and -50° C, a temperature of final melting of hydrohalite between -54° and -30° C, a temperature of final melting of ice between -30.1° and -0.2°C [salinity calculated after Potter et al. (1978) gives a range between 0.4 and 29.3 wt.% eq. NaCl], and a temperature of total homogenization $(L + V \rightarrow L)$ between 120° and 401°C, with 95% of the values between 144° and 351°C. We are dealing therefore with a polysaline fluid composed of H₂O-NaCl-CaCl₂ (Crawford 1981). On the basis of the comparison of the temperature of total homogenization versus salinity parameters (Fig. 6), we can divide inclusions of Type 2 into two groups: The fluid inclusions of Subtype 2.1 are very variable in salinity (between 2.0 and 29.3 wt.% eq. NaCl) and homogenize between 217° and 315°C, with 95% of the values between 239° and 303°C. The fluid inclusions of subtype 2.2 are of low salinity (between 0.4 and 11 wt.% eq. NaCl) and have a variable temperature of homogenization, from 120° to 401°C, with 95% of the values between 140° and 383°C.

Type 3. Owing to the relatively small size (less than 10 μ m), we have not as yet been able to arrive at any microthermometric characterization.

Fluid types

A diagram of the temperature of total homogenization *versus* salinity of all the fluid inclusions studied (Fig. 6) reveals the existence of three fluids: (1) fluid A (corresponding to fluid inclusions of Type 1), a hightemperature fluid (temperature of total homogenization: $330^{\circ} \pm 20^{\circ}$ C), with a salinity of 41 ± 3 wt.% eq. NaCl), (2) fluid B (corresponding to fluid inclusions of subtype 2.1), ranging in temperature (around 240° to 300°C) and extremely variable in salinity (from 2 to 29 wt.% eq. NaCl), and (3) fluid C (corresponding to fluid inclusions of subtype 2.2), a variable-temperature fluid (temperature



FIG. 6. Temperature of homogenization versus salinity diagram from Type-1 (L + V + S, circles) and Type-2 (L + V, squares) fluid inclusions from Palai deposit. Oval fields separate fluid A, fluid B and fluid C. See text for explanation.

of total homogenization between 120° to 400° C), with a relatively constant low salinity of 6 ± 4 wt.% eq. NaCl.

DISCUSSION

Location of the gold-bearing horizons

Our petrographic study of the gold mineralization and our lithogeochemical study reveal a correlation between the position of the horizons bearing gold grains and the location of the geochemical anomalies, such that mineralized horizons can be defined according to the following criteria: 1) The "upper gold-bearing level" is defined on the basis of location of the level bearing most of the samples containing visible gold (between +37.6 and +56.3 masl) and on the position of the upper geochemical anomaly (between +40 and +50 masl). 2) The position of the "lower gold-bearing level" is based on the level with samples bearing visible gold found at -69.0 masl, which in turn coincides with the lower geochemical anomaly (between -60 and -70 masl). 3) In addition to these two gold-bearing levels, there are two other horizons based on samples of visible gold that do not correspond to significant geochemical anomalies. They are located around +98.2 and between -25 and -30 masl.

The relationship of temperature of total homogenization versus salinity and gold mineralization

Diagrams showing the temperature of total homogenization *versus* salinity of the fluid inclusions reveal significant differences in the behavior of the fluid inclusions as a function of their position with regard to each gold-bearing level defined above.

Upper gold-bearing level. In drill-core PH–009 (triangles in Figs. 7a, b, c), the fluid inclusions taken above the gold-bearing level are distributed parallel to



FIG. 7. Diagrams showing temperature of homogenization *versus* salinity and differences in the behavior of fluid inclusions as a function of their position with regard to each gold-bearing level. Data related to "upper gold-bearing level" were collected from three different drill-holes (triangles: PH–009; crosses: PH–011; squares: PH–008). For gold-bearing level at –25 to –30 masl (crosses) and for "lower gold-bearing level" (diamonds), data were collected from only one drill-hole (PH–011).

the temperature axis. Thus they lie in a wide band (mostly between 300° and 150°C) and a relatively narrow salinity belt (mainly between 4 and 8 wt. % eq. NaCl). A similar distribution can be seen for fluid inclusions beneath the mineralized level. However, the fluid inclusions taken from samples within the mineralized horizon show a different pattern of fluid behavior, the data points being distributed parallel to the salinity axis. The salinity is therefore quite scattered (from 2 to 22 wt.% eq. NaCl) within a narrower interval of temperature (temperature of total homogenization $\approx 250^{\circ}$ – 350° C).

Drill-core PH–011 (crosses in Figs. 7a, b, c) shows the same general tendency. The distribution of data points is parallel to the temperature axis both above the mineralized level (temperature of total homogenization $\approx 150^{\circ}-300^{\circ}$ C and salinity between 4 and 10 wt.% eq. NaCl) and below it (temperature of total homogenization $\approx 200^{\circ}-350^{\circ}$ C and salinity from 4 to 10 wt.% eq. NaCl). In the mineralized horizon, however, there is once again a strong contrast in salinity (from 2 to 21 wt.% eq. NaCl) around 250°C.

Owing to the poor transparency of the samples from drill-core PH-008 (squares in Fig. 7c), fluid-inclusion data are only available from samples taken below the mineralized level. In spite of this problem, we believe that the fluid inclusions are distributed parallel to the temperature axis (temperature of total homogenization $\approx 150^{\circ}$ -300°C and salinity between 5 and 10 wt.% eq. NaCl).

Lower gold-bearing level. Samples from this level display a marked vertical tendency in the distribution of fluid inclusions (diamonds in Fig. 7e), such that the salinity varies extremely widely (from 4 to 28 wt.% eq. NaCl), but temperature of total homogenization lies in a narrow interval around 300°C. This tendency is similar to that observed above in the main mineralized horizon.

Other gold-bearing locations. To determine whether the characteristic behavior of fluid inclusions is constant between the upper and lower gold-bearing levels, samples were taken from other gold-bearing locations (-25 to -30 masl and +98 masl). In samples from the position -25 to -30 masl (crosses in Fig. 7d), the vertical tendency marking the abrupt drop in salinity (from 2 to 30 wt.% eq. NaCl) occurs within a slightly wider interval of temperature of total homogenization (225°– 300°C). This tendency is similar to that observed within the mineralized levels. At the position near +98 masl, fluid-inclusion data are lacking owing to the lack of transparency of the gangue.

Genetic considerations

As revealed above, the behavior of fluid inclusions in the mineralized horizons is very different with respect to the rest of the deposit. Mineralized horizons invariably contain a fluid of highly variable salinity (2–29.3



FIG. 8. Pattern of fluid evolution in the Palai deposit as inferred from fluid-inclusion data.

wt.% NaCl eq.) with a temperature varying by some 25° to 50°C (approximately) in the interval of 217° to 315°C. In contrast, above and below the mineralized horizons, the fluid has a low salinity (6 ± 4 wt.% NaCl eq.) across a broad range of temperature ($\approx 120^{\circ} - 400^{\circ}$ C).

As for the genetic processes (Fig. 8), we contend that isothermal mixing of fluids is the main process responsible of ore formation. We suggest the mixing of a hot, saline fluid, represented by fluid A (magmatic?) which, during its ascent, mixed with a cooler fluid of much lower salinity (groundwater?), represented by fluid C. If this is the case, then fluid B would represent the evolution between the two former extreme conditions, indicating an isothermal mixing of the high-salinity fluid A with the low-salinity fluid C. We have not found clear evidence to support boiling as a generalized genetic mechanism. In any case, the variable volume percent of the gas phase in some of the fluid inclusions and the presence of single-phase fluid inclusion suggest a heterogeneous entrapment of the solutions, possibly due to boiling in specific areas. In addition, the existence of three-phase fluid inclusions (with high temperatures of total homogenization), presumably located at deeper parts of the system, is in agreement with the hypothesis of local boiling. These genetic processes are in agreement with processes documented by Arribas (1995) for this type of gold deposit.

The different characteristics of fluids studied at Palai–Islica seem to have been responsible for the transport and precipitation of the metals studied. As far as gold is concerned, for example, it could have been transported in the form of complexes (AuHS° or AuCl₂⁻, according to Arribas 1995) and precipitated as a consequence of the destabilization of these complexes by the abrupt change in physical and chemical conditions of the fluid. Observations relevant to abrupt changes in temperature and salinity, and mixing of fluids, and other possible phenomena (*e.g.*, boiling, phase separation) could be responsible of this change in conditions, which induced gold precipitation. All these factors are in agreement with causes indicated by Benning & Seward (1996) and Hedenquist *et al.* (1994) as responsible for destabilization of AuHS° and AuCl₂⁻, respectively.

Economic potential of the deposit

The metallogenic study has centered until now on the Palai zone. Preliminary studies in the Islica area (a sector with strong hydrothermal alteration 500 m east of the Palai deposit) provide evidence of the existence of similarities between the two zones, such as a similar sulfide paragenesis, the presence of free gold, lithogeochemical samples with anomalies of up to 20 ppm Au, and analogous characteristics of fluid inclusions.

In the Palai zone, the gold mineralization studied to date is mainly concentrated in the "upper gold-bearing level". This level has been well described (mineralogy, mineralized fluids, metallogenic processes, *etc.*), as it was cross-cut by most of the drillholes. The "lower goldbearing level" is also interesting, as it has characteristics very similar to those of the other level, such as an analogous association of minerals, the presence of free gold, a well-defined geochemical anomaly, and the characteristic fluid with a sharply contrasting salinity. Nevertheless, as this lower level has only been intersected by a few of the deeper holes drilled in the southeastern zone of the deposit, we have been unable to verify its lateral extent throughout the deposit. Its potential is therefore still unknown.

Horizons showing evidence of significant boiling [which could indicate the existence of a greater goldbearing bonanza: Buchanan (1981)] have not yet been identified at this deposit. Note, however, the presence of three-phase inclusions, and their high temperature of total homogenization in certain samples taken from deepest positions corresponding to the old mine (to date no such types have been found in the core samples), and the heterogeneous trapping of fluids. Both features suggest that deeper drill holes would quite likely find samples with a high temperature of total homogenization of triphase fluid inclusions, and therefore possible gold-bearing levels.

CONCLUDING REMARKS

The petrographic study of the Palai–Islica epithermal gold mineralization and results of the lithogeochemical study reveal a correlation between the position of the horizons bearing gold grains and the location of the geochemical anomalies, such that different mineralized levels can be defined: the "upper gold-bearing level" (between +37.6 and +56.3 masl) and the "lower gold-bearing level" (between -60 and -70 masl).

We have demonstrated the interest in the application of fluid inclusions as a quick, inexpensive and very effective method for the exploration of new mineralized bodies within the gold-bearing deposit at Palai-Islica. We have shown that the precipitation of Au and other metals of economic interest within the mineralized levels is systematically related to the presence of a fluid with a high salinity, which interacts over a narrow interval of temperature of total homogenization with a low-salinity fluid to produce the gold mineralization. Mineralized horizons systematically contain a fluid of highly variable salinity (2-29.3 wt.% NaCl eq.) with a temperature varying some 25° to 50°C (approximately) in the interval of 217° to 315°C. In contrast, above and below the mineralized levels, low-salinity fluids $(6 \pm 4 \text{ wt.\% NaCl eq.})$ trapped across a wide range of temperature ($\approx 120^{\circ}-400^{\circ}$ C) seem to be the rule.

The distinct characteristics of these fluids seem to have been responsible for the transport and precipitation of the metals studied. As far as gold is concerned, for example, it could have been transported in the form of AuHS° or AuCl₂⁻ complexes and precipitated as a consequence of the destabilization of these complexes owing to the abrupt change in physical and chemical conditions.

As deduced from the presence of triphase inclusions marked by a high temperature of total homogenization in deep areas and from the heterogeneous trapping of fluids, signs of significant boiling could exist at greater depths. If confirmed, such boiling could indicate the existence of a greater gold-bearing bonanza in this deposit.

ACKNOWLEDGEMENTS

The authors thank Serrata Resources S.A. for the help they have provided during this investigation. This research has also been supported by the project No. PB–97–1211 and the RNM–0131 Research Group of the Junta de Andalucía. The manuscript was significantly improved by helpful suggestions and critiques as a result of reviews by Drs. J.R. Craig and M.M. González. Editor Robert F. Martin provided his usual thorough editorial handling and is sincerely thanked for his constructive comments, improvements and encouragement.

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- Received August 17, 1999, revised manuscript accepted April 13, 2000.