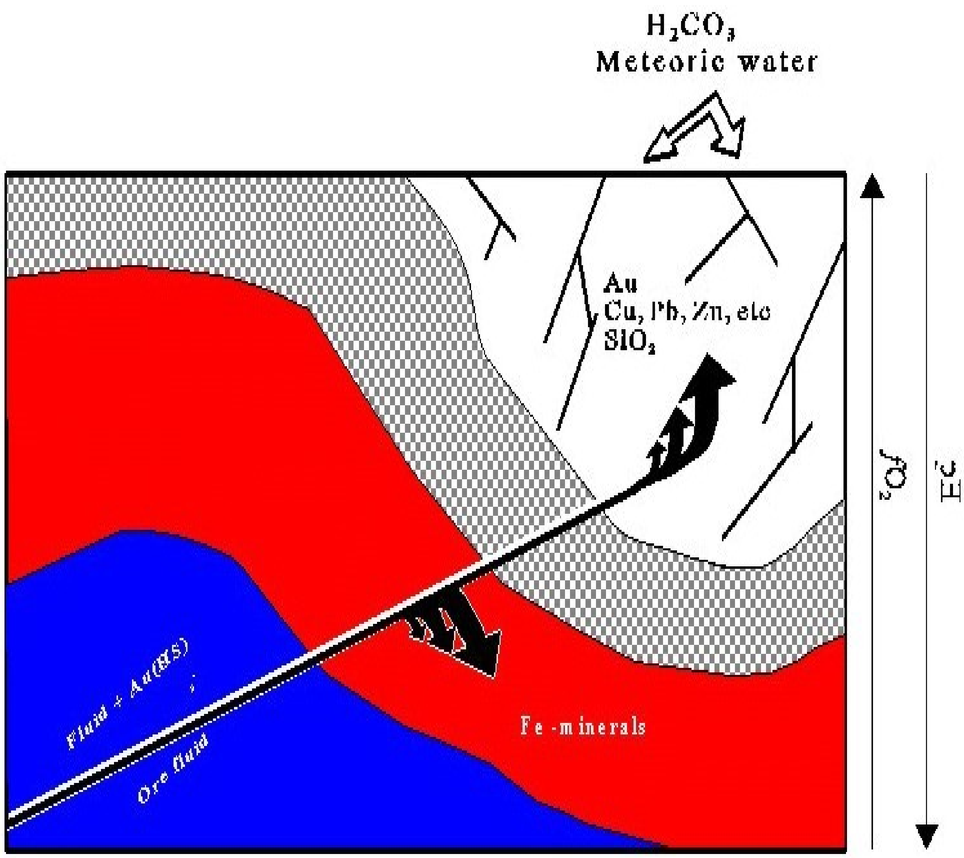
The Role of Manganese as a Controller for Gold Mineralization in the Serpentinites of the San José de las Malezas Gold-Quartz Deposit in Santa Clara,Villa Clara, Cuba.



Ricardo A. Valls Álvarez
Valls Geoconsultant
vallsvg@gmail.com

ABSTRACT

The San José de Las Malezas quartz-gold deposit is located on the North side of the Cuban Ophiolitic Complex, within the Structural-Facial Zone "Zaza", Province of Villa Clara, Cuba. In the area of the deposit there is a well developed listwaenitic zone that begins with (i) massive and relatively little altered serpentinites that pass into (ii) iron-altered serpentinites which are in gradational contact with (iii) completely carbonatized rocks and (iv) a core of silicified rocks and quartz veins. Copper and gold mineralizations are associated with these quartz bodies, but binary correlation analysis of geochemical data suggests that the ores are genetically independent of one another. In concordance with the proposed genetic model supported by thermodynamic calculations and field observations, copper is thought to be introduced by a hydrothermal process, whereas gold was leached from the serpentinites. The evolution of manganese minerals from anaerobic to aerobic species provoked a reducing environment which hampered the precipitation of gold and other ores inside and near the serpentinites. Accordingly, a significant negative correlation between gold and manganese in similar areas of hydrothermally altered serpentinites, may be good indicators of possible gold concentrations.

The mechanical transportation of very small and thin scales of native gold from the serpentinites by the fluids is also suggested as a possible mechanism to explain the presence of this kind of scales inside the iron-altered zone.

INTRODUCTION

The San José de Las Malezas deposit is located within the Structural-Facial Zone (S.F.Z.) "Zaza", in the province of Villa Clara in Central Cuba. This S.F.Z. is composed of (i) a volcano-sedimentary complex of Lower Cretaceous age (turonian) located to the South, (ii) the Ochoa Formation composed of limestones and marls of the Eocene in discordant contact to the North, and (iii) the Zurrapandilla Complex, composed of diabasic porphyries, spilites, gabbro diabase, gabbro diabase porphyries, and other gabbroic rocks that cut both described complexes (Cabrera and Tolkunov, 1979). Within the S.F.Z. "Zaza" and in tectonic contact with the volcano-sedimentary complex are serpentinitic bodies, that form a large massif with an east-west massif. These intrusions form part of the Cuban Hyperbasitic Belt of the Upper Cretaceous, and they are commonly interpreted as the remains of an ancient oceanic crust.

These serpentinites are massive, crushed, light green rocks, with a reticular structure due to the uneven distribution of chrysolite and antigorite, and the presence of metallic minerals, such as magnetite, chromite and spinel. This mineralogical composition, suggests that the original rock was a harzburgite, however the original texture has been completely erased. The serpentinites are frequently cut by diabasic, microdiabasic and porphyritic diabasic dikes from the Zurrapandilla Complex.

A more detailed geological description of the region and the outcrop, including maps and cross-sections, appears elsewhere (Valls Álvarez, 1995a)

In this paper we will study the formation and evolution of manganese minerals within these serpentinites and their relationship with gold mineralization.

THE FORMATION OF THE SAN JOSÉ DE LAS MALEZAS DEPOSIT

Our model begins with the protrusion of an ultramafic body of harzburgite composition through a ridge axis. It has been suggested elsewhere (Valls and Gonzalez, 1987), that this ultramafic magma could have been subjected to a partial melting process, due to which we could have obtained an area of gold enrichment by gravitational separation inside a magma chamber.

After the protrusion, the sea water and the heat from the upwelling zone initiated the serpentinization of the rocks. During this process, Mn^{2+} was liberated because of the decomposition of olivine. Another possible mineral that could liberate Mn^{2+} during the serpentinization of these rocks is pyrophenite ($MnTiO_3$) (W.Trzcienski, Ecole Politecnique, Montreal, personal communication).

Under these anaerobic conditions, only divalent manganese minerals could be formed. Two possible contributing reactions are given bellow, (i) the formation of pyrochroite from tephroite (1), and (ii) the formation of rhodochrosite from tephroite by carbonatic sea water (2).

(1) $Mn_2SiO_4 + 2H_2O \text{ ---> } 2Mn(OH)_2 + SiO_2$

(2) $Mn_2SiO_4 + 2H_2CO_3 \text{ ---> } 2MnCO_3 + SiO_2 + 2H_2O$

Since pyrochroite is a much less common mineral than rhodochrosite (Crerar et al., 1976), we can assume that the formation of rhodochrosite was the most probable reaction. In fact, when we study the mineralogy of this type of deposit World-wide, we usually find references to the presence of rhodochrosite, rhodonite, pyrolusite, and other manganese minerals (Baranova and Ryzhenko, 1981; Farfel, 1984; Baranova and Koltsov, 1987; Camus, 1990; Rodriguez and Warden, 1993, etc.).

The formation of rhodochrosite will take place for as long as olivine is decomposed during the serpentinization of the rocks in the heated zone near the rift. Since we find relics of olivine crystals in these serpentinites, we can assume that serpentinization was stopped before the obduction onto the colliding continental plate during the final stage of the ocean closure.

After the obduction of these rocks onto an aerobic environment, the evolution of the manganese minerals responded to the increasingly oxidizing conditions, as shown in Fig. 1. First we have the oxidation of the rhodochrosite into hausmannite (3), second the oxidation of hausmannite into bixbyite (4), third the hydratation of bixbite into manganite (5), and finally the oxidation of manganite into pyrolusite (6).

(3) $3MnCO_3 + ½O_2(g) ---> Mn_3O_4 + 3CO_2(g)$

(4) $Mn_3O_4 + ½O_2(g) ---> 3Mn_2O_3$

(5) $Mn_2O_3 + OH^- + H^+ ---> 2MnOOH$

(6) $2MnOOH + ½O_2(g) ---> 2MnO_2 + H_2O$

Obduction also provoked the crushing of the rocks and the development of several tectonic systems, the main of which had a NE orientation. Along these fractures we observe dikes of diabase from the Zurrapandilla Complex. During the intrusion of these dikes, the area was affected by a low temperature hydrothermal-metasomatic process. This process developed a well formed listwaenitic zone to which the mineralization is related. The provenance of these fluids is yet to be established, but we can propose three possible origins:

a.- Magmatic origin - orthomagmatic fluids related to the Zurrapandilla magmatic complex.

b.- Slab origin - sea water fluids related to the dehydration zone of the subducted slab.

c.- Mixed origin - fluids that are the result of a combination of the first two options.

Studies done by Ploshko (1963), Zuffardi (1977), Pipino (1980), Buisson and Leblanc (1986), and Pallister et al. (1987) on similar listwaenitic zones concluded that these fluids were composed mainly by H_4SiO_4, H_2CO_3, H_2O, H_2S, K, Na, Rb, and probably $CO_2(g)$ and $CH_4(g)$. Mottl (1991) suggests that these type if fluids usually present high values of pH, high carbonate alkalinity, and low chlorinity. In accordance with the mineralogical associations in the area of San José de Las Malezas (Valls, 1995b), I believe that the main metallic component of this fluid should have been copper, with lesser amounts of lead, zinc, silver, and arsenic.

These fluids reactivated the serpentinization of the rocks, so more manganese was released from the remaining olivine crystals. Here, the most probable reaction should have been first- the formation of rhodonite (7), second the oxidation of rhodonite into hausmannite (8), and then the same evolution pattern as shown in equations (4 - 6) to arrive to the formation of pyrolusite.

(7) $Mn_2SiO_4 + H_4SiO_4 ---> 2MnSiO_3 + 2H_2O$

(8) $MnSiO_3 + ½O_2(g) ---> Mn_3O_4 + SiO_2$

All these processes are schematically represented in Fig. 1. The formation of these manganese oxides leads to an increase in fO_2 making difficult the precipitation of gold, copper and other ores in and near the serpentinitic bodies.

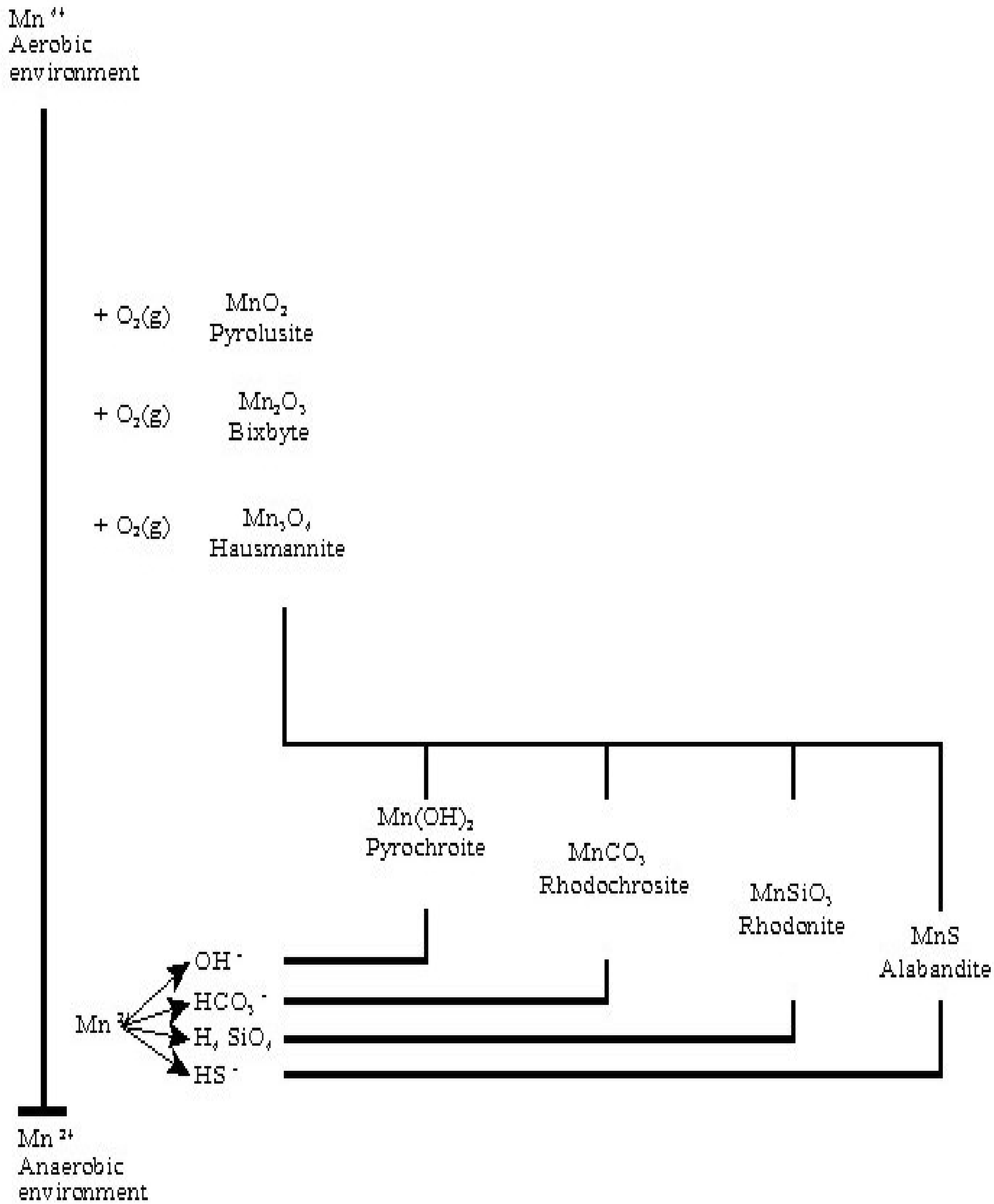


Figure 1. Evolution of Mn2+ in response to increasingly oxidizing conditions, near 283K.

DYNAMIC OF THE HYDROTHERMAL FLUID

Although it has been considered in the past as a typical copper-gold deposit, the correlation study of the existing data from San José de Las Malezas quartz gold vein deposit (Valls Álvarez, 1995b), shows no significant correlation between gold and copper, and a strong positive correlation between gold and lead in the siliceous zone. Therefore we conclude that copper and gold are spatially but not genetically related. In the proposed model, copper was contributed by the hydrothermal system, with Pb, Zn, As, and Ag, while gold was provided by the serpentinites hosting the quartz bodies. A schematic representation of this process is shown in Fig. 2.

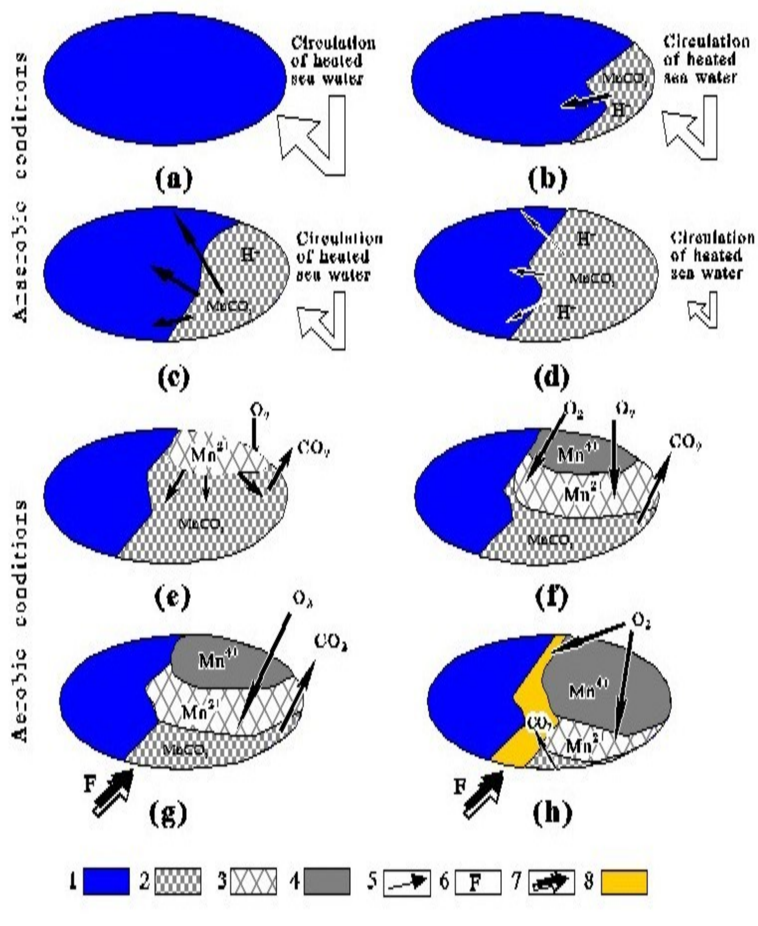


Figure 2. Schematic representation of the alteration of an ultramafic massif and the evolution of the manganese minerals from an anaerobic to an aerobic alteration after the obduction onto the surface of the massif. See text for detailed explanations. 1.- Ultramafic massif, 2.- Formation of rhodochrosite, 3.- Formation of hausmannite, 4.- Formation of manganite, byxbyite and pyrolusite, 5.- Vector of alteration, 6.- Ore fluid, 7.- Vector of mineralization, 8.- Listwaenitic zone.

Since we already deal with the effect of reactivation of the serpentinization of the host rocks, we will focus on the mechanism of transportation and deposition of the ores.

The listwaenitic alteration consists of four zones, (i) less altered serpentinites, (ii) an iron-altered zone, (iii) a carbonatic altered zone, and (iv) a siliceous zone (Sawkins, 1990, Valls Álvarez, 1995b, et al.). These lenses grade laterally into the less altered serpentinites through a talc-carbonated zone.

According to the geochemical results of a meter by meter channel sampling through the four zones (Valls Álvarez, 1995b), gold, copper, silver, zinc, arsenic and lead were found to concentrate mainly in the siliceous zone. Gold also was found concentrated inside the iron-altered zone, while the carbonate-rich zone is almost barren of ores.

It is commonly assumed that gold is transported in the (+1) oxidation state (McKibben et al., 1990). Since gold is a soft electron acceptor, it should form especially stable complex with soft ligands as HS^-.

A probable reaction is its transportation as a thio-complex (9).

(9) $Au + 2H_2S + ¼O_2(g) ---> Au(HS)^-_2 + ½H_2O + H^+$

I also believe that very small and thin scales of native gold could have been mechanically removed by the fluids from the serpentinites. The flat form of these grains allows them to be transported very easily, as seen from our experience during panning to obtain heavy concentrates from these and similar zones. This mechanism of transportation is doubtless less efficient than the one represented earlier (9), but it helps to explain the existence of this kind of native gold scales in the iron-altered zone (Fig. 3).

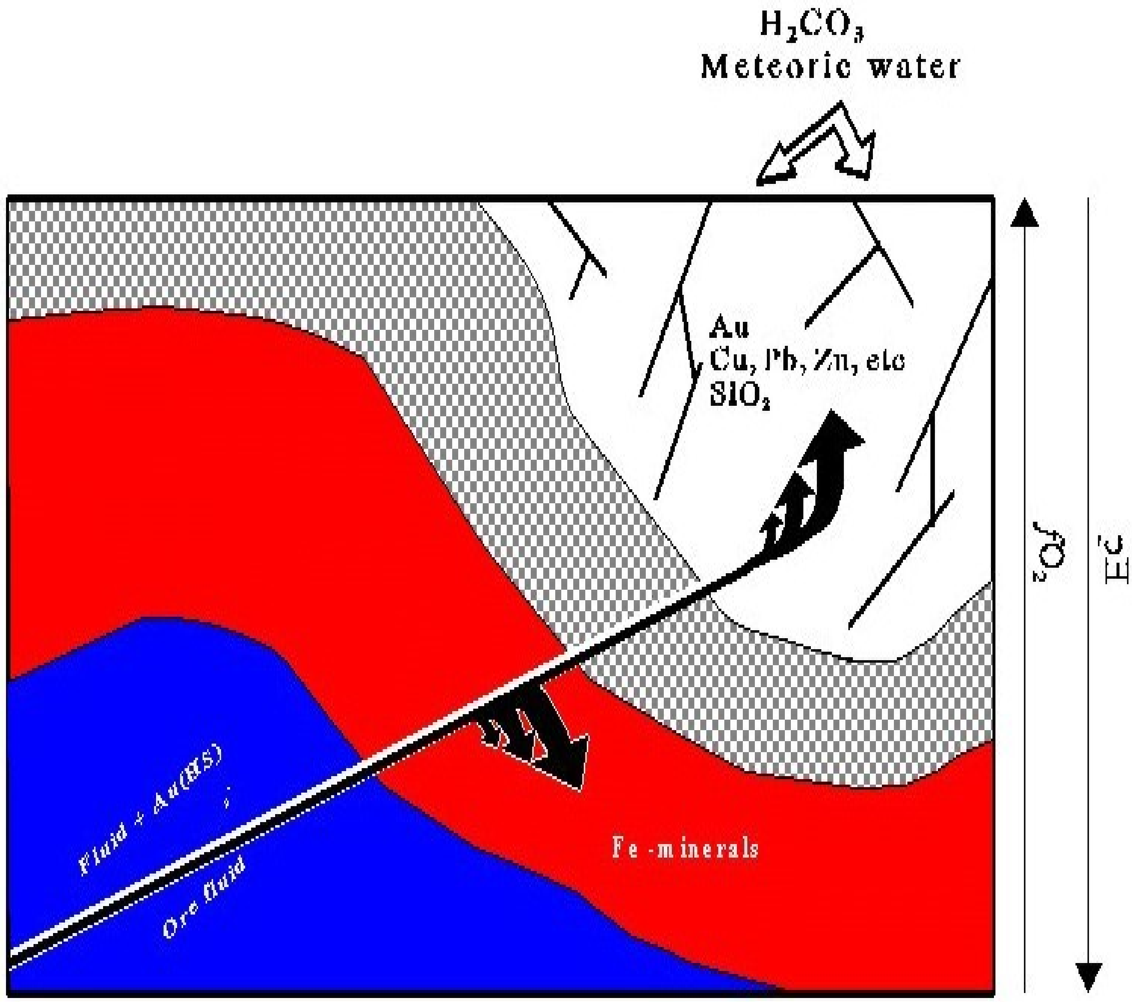


Figure 3. Dynamic of the ore fluid. This model proposes two mechanism for gold transportation: (i) mechanically -as thin scales of native gold-, and (ii) as a thio-complex. Mechanical transportation explains the presence of scales of native gold in the iron altered zone. Main gold and copper concentration are in the siliceous zone, where the ore fluid got mixed with meteoric waters in a more acidic environment, with low values of fO_2 due to the formation of massicot or galena (see text for further details) 1.- Less altered serpentinites or unaltered ultramafic rocks, 2.- Iron-zone, 3.- Carbonatic-zone, 4.- Siliceous zone.

As the hydrothermal fluid moves toward the surface, several important factors will control its stability. Inside and near the serpentinites, the evolution of the manganese minerals to their trivalent states, will consume oxygen provoking a reducing environment that difficult the precipitation of gold and other ores. More near to the surface, we have first the lost of temperature due to the mixing with meteoric waters, and second, the presence of a more oxidizing environment favoured by the existence of faults and fractures of the rocks.

A phase relations in the system S - H - O as a function of fO_2 and pH, at 413 □K will show that both, the decreases of the pH and the increment of the $fO_{2,}$ will provoke the precipitation of gold. The precipitation of Au because of a decrement of pH is shown in equation 10 (Spycher and Reed, 1989; McKibben et al., 1990). Equation 11 shows the precipitation of gold due to an increment of the fO_2 (Chris Gammons, personal communication).

(10) $8Au(HS)_2^- + 6H^+(aq) + 4H_2O(aq)$ ---> $8Au(s) + SO^{2-}{}_4(aq) + 15H_2S(aq)$

(11) $4Au(HS)_2^- + 15O_2(g) + 2H_2O(aq)$ ---> $4Au(s) + 8SO^{2-}{}_4(aq) + 12H^+$

Very often we find strong correlations between gold and lead and we find native gold in galena and lead oxides like massicot (PbO) and crocoite ($PbCrO_4$). This leads us to assume that another possible mechanism of gold precipitation is the formation of galena or massicot as it is represented in equations 12 and 13.

(12) $4Au(HS)_2^- + 4PbCl_2 + 7O_2(g) + 2H_2O(aq)$ --->

$4Au(s) + 4PbS + 8Cl^- + 4SO^{2-}{}_4(aq) + 12H^+$

(13) $4Au(HS)_2^- + 4PbCl_2 + 15O_2(g) + 6H_2O(aq)$ --->

$4Au(s) + 4PbO + 8Cl^- + 8SO^{2-}{}_4(aq) + 20H^+$

These reactions could explain the strong positive correlations between gold and lead in the siliceous zone (Valls, 1995b).

CONCLUSIONS AND RECOMMENDATIONS

Based on the information available up to this moment, a model has been presented to explain the geochemical characteristics of the ore distribution in the San José de Las Malezas gold-quartz vein deposit, in Santa Clara, Cuba.

This model describes the serpentinization of an ultramafic protrusion, which is later obducted onto the surface to form part of an ophiolitic complex. Special attention has been given to the formation and evolution of different manganese minerals during the serpentinization of the host rocks. The model helps to explain the negative correlation between gold and manganese over the serpentinites.

It has been suggested elsewhere the possibility of a partial melting process of this ultramafic body before its protrusion. This process could have provoked the formation of a gold enriched zone due to the gravitational separation of this mineral. Although the partial melting of these rocks is possible, this idea needs to be tested in the future. The existence of a gold enriched zone in the serpentinites will not only help to explain the remobilization of gold in the hydrothermal-metasomatic fluid, but also it could become a prospecting objective in the area.

After the obduction, the area was affected by hydrothermal-metasomatic fluids along the developed tectonic system. The origin of these fluids is yet to be determined, but due to the presence of H_2CO_3, H_4SiO_4, and H_2S, it is possible to suggest a magmatic or magmatic-slab origin in preference to a pure slab source.

These fluids reactivated the serpentinization of the host rocks, and provoked the formation of a listwaenitic zone toward the less altered serpentinites. The model assumes that gold was leached from the serpentinites by the fluids and considers two mechanisms for its transportation. The first one is the mechanical transportation of thin scales of native gold by the fluid. This may explain the existence of a gold enrichment zone in the iron-altered serpentinites. The second mechanism is the transportation of gold as thio-complexes and its precipitation in the siliceous zone due to a decrease in pH and/or an increment of the fO_2 provoked by the formation of galena, massicot or other lead minerals (chrochoite?), and the loss of temperature due to the mixing of the fluids with meteoric waters.

The same conditions of pH, fO_2, and loss of temperature in the siliceous zone, provoked the precipitation of copper, lead, zinc, arsenic and silver from the fluid, and the formation of copper and lead-zinc minerals in the contact of the quartz bodies with the crushed host rocks.

Although this model can presently explain all the known characteristics of the distribution of gold and other ores in this deposit, I am not presenting it as uncontroversial model, but as a working hypothesis to formulate what needs to be tested in future studies.

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