

**THE INFLUENCE OF PRIMARY MINERAL PARAGENESES ON GOLD MOBILITY IN SUPERGENE ENVIRONMENTS; PALAEO-WEATHERING PROFILES IN GOLD OCCURRENCES IN PORTUGAL.**

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**ABSTRACT:** Recent studies on the França gold deposit (Bragança) have shown that gold may be completely removed from surface weathering products. This was explained through solubilization as tiosulphate complexes, stabilized as a consequence of the presence of siderite in the primary paragenesis. On the other hand, many Roman gold exploitations mined weathered ore. This confirms that gold removal was not a general process. We analyse in detail the reactions that can describe the actual processes of gold solubility and precipitation for the weathering conditions in Portugal. The França example shows that the absence of gold at the surface cannot be interpreted as signifying that it is not present in the subsurface; the alteration of arsenopyrite to crystalline scorodite should testify gold immobility. Careful evaluation of primary mineral parageneses can become a powerful tool to hierarchize gold exploration targets.

The present weathering profiles of outcropping gold deposits under arid and tropical climates (such as those in Australia and Brazil), illustrate clearly that gold is mobile in supergene environments. Moreover, gold mobilization from the upper leached horizons and subsequent reprecipitation at or near the water table, is well documented in several deposits (e.g. Mann, 1984; Butt, 1989; Benedetti & Boulègue, 1991; Zeegers & Leduc, 1991). Therefore, the evaluation of the active physico-chemical conditions responsible for gold solubility and reprecipitation in these environments, can be used as a first approach in the characterization of ancient weathering profiles, particularly those where an extensive oxidized zone is present. This may contribute for a correct evaluation of potential ore targets, especially where there is a lack of significant ore grades at surface.

Experimental studies on gold geochemistry (e.g. Webster, 1986; Renders & Seward, 1989; Vlassopoulos & Wood, 1990; Vlassoploulos et al., 1991; Peck et al., 1991; Krupp & Weiser, 1992), have stressed the importance of some ligands, mainly chloride ( $\text{Cl}^-$ ), thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ), hydroxyl ( $\text{OH}^-$ ), and some organic acids (fulvic and humic acids) in Au solubility and transport; their stability is mainly dependent on pH and Eh. On the other hand, given the typical oxidizing conditions in surficial environments, one may conclude that gold chloride complexes are stable for acidic conditions, whereas for near neutral to alkaline conditions the main complex is the thiosulphate. In both cases, hydrolysis of these complexes in aqueous solutions can occur away from their stability field and for extreme alkalinity of the environment. The application of these results on weathering profile studies, should however take into account that the Au mobilization/precipitation in supergene environments cannot

be properly evaluated without the knowledge of the alteration paths experienced by other minerals present in the ore bodies, since they may determine specific pH-Eh conditions.

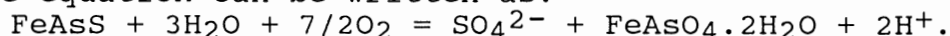
In the majority of gold occurrences in Portugal, gold is intimately associated with arsenopyrite, pyrite and galena. Some of these occurrences exhibit prominent weathering features, closely related to the development of the regional Plio-Quaternary pediplanation. The correlative sedimentary record indicates that climate conditions at the time were suitable for Au mobilization. Gold solubility as well as its reprecipitation can be evaluated on the basis of present day mineral suites (primary and secondary) along the palaeo-weathering profile.

Sulphides oxidize rapidly when exposed to the atmosphere in the presence of meteoric water. In general, one could envisage the weathering of pyrite as a complex sequence of reactions, producing acid solutions and iron hydroxides. Nevertheless, the first steps of this chemical path, can be represented by the following equation:



Under similar conditions, the alteration of arsenopyrite should produce scorodite, according to the following equilibrium (Dove & Rimstidt, 1985):

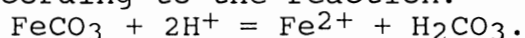
$\text{FeAsS} + 14 \text{Fe}^{3+} + 10\text{H}_2\text{O} = 14\text{Fe}^{2+} + \text{SO}_4^{2-} + \text{FeAsO}_4 \cdot 2\text{H}_2\text{O} + 16 \text{H}^+$ ,  
in which the excess ferric iron is reduced due to the breakdown and subsequent oxidation of the arsenopyrite. However, according to available geological data, scorodite may occur in environments characterized by low-iron content. Thus, we suggest for scorodite a similar genetic process involving oxygen as the oxidizing agent; this is in better agreement with the observations in some occurrences, as is the case of Chiqueiro (ENE of Arouca) where some of the mineralized quartz veins contain arsenopyrite as the only sulphide. The equation can be written as:



In this context, it is important to point out that the stability of scorodite depends strongly on its cristallinity and on pH. As a matter of fact, the available experimental data shows that this mineral is stable for pH conditions ranging from 3 to 5 (Krause & Ettel, 1988), and dissolves incongruently outside these values, causing ferric hydroxide to precipitate (Robins, 1987); crystalline scorodite (like the characteristic specimens of Chaminés - ESE of Évora - and Chiqueiro gold occurrences) is much less soluble than the amorphous ferric arsenate. The importance of these observations on gold solubility is worth noting: the acidic conditions inferred from the presence of scorodite will favour Au solubility, if the activity of  $\text{Cl}^-$  is high. This requires development of the weathering profile under arid climates. Therefore, the chemical paths due to weathering should preferably produce chloride gold complexes instead of thiosulphate gold complexes. The efficiency of this process requires, however, strong aridity (like present conditions in Western Australia). This is not compatible with the palaeoclimate evolution in Portugal during the Pliocene-Quaternary, put in evidence by sedimentary and micropaleontological (palinological and microfauna) records. Therefore, gold should remain in the higher weathering

horizons, as a residual mineral, together with iron hydroxides (Machesky et al., 1991). This is probably why most of the weathering zones of primary deposits in the NW of Iberian Peninsula were exploited by the Romans.

In more humid climates, like those compatible with sedimentary and paleontological record of Pliocene-Quaternary age, thiosulphate gold complexes may be stabilized during the weathering process, if the destruction of other primary minerals (as carbonates) inhibits the acidity increase due to the gradual alteration of sulphides. Thus, gold mobilization should occur in the course of the first steps of sulphide weathering, as long as carbonates are present; the absence of scorodite could be used as a macroscopic criterion to infer on such chemical processes. The França gold deposit (N of Bragança), constitute an example where a weathering profile of this type has developed (Mateus & Barriga, 1993). In this deposit, mineralized quartz breccias related to the Vilariça strike-slip fault contain gold (as electrum) associated to arsenopyrite, pyrite and siderite. During the weathering of these highly permeable fault rocks, the breakdown of siderite act as an alkalinity buffer for the system, described according to the reaction:

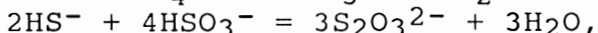
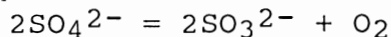


Under these conditions, the chemical path of pyrite oxidation is essentially the same as the already mentioned, and the alteration of arsenopyrite may lead to scorodite formation as a metastable and intermediate product which dissolves, causing iron hydroxide and a soluble arsenate anion ( $\text{H}_2\text{AsO}_4^-$ ). This mechanism can be illustrated by the general equation:

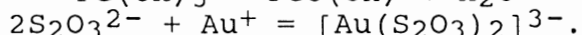
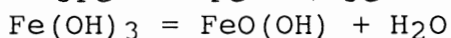
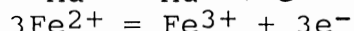
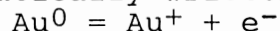


These results are coherent with the mineral parageneses exhibited by the weathered quartz breccias in the França Mine, where goethite is the main hydroxide in the upper weathering horizons, and as one moves downwards, relics of primary minerals (mostly arsenopyrite and pyrite) are found. In this deposit, geochemical distribution of As (as well as of S and Sb) along the weathering profile (strongly depleted in these elements) is also consistent with the proposed chemical mechanisms (Mateus & Barriga, 1991, 1993).

In the pH-Eh conditions constrained by carbonate and sulphide breakdown near surface, the sulphate ion is readily reduced to  $\text{SO}_3^{2-}$ , favouring the reaction

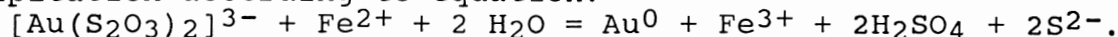


which leads to thiosulphate formation. Reduction of sulphate is accompanied by oxidation of  $\text{Au}^0$ , as well as by free ferrous iron released in the meantime through the alteration of pyrite. This chemical path can be schematically written as:

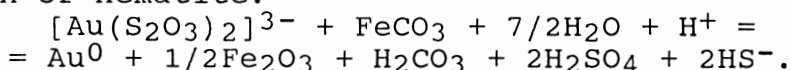


As a consequence of a prevailing vertical fluid flow along the weathering profile, the thiosulphate gold complex becomes unstable near the water table, where the presence of  $\text{Fe}^{2+}$  leads to gold re-

precipitation according to equation:



During the development of the weathering profile in the mineralized breccias of the França Mine, the migration and subsequent unstability of thiosulphate gold complexes should have happened quite quickly, due to the high permeability of the fault zone. Again, the presence of siderite is an important factor, since its alteration in acidic environment leads to the free ferrous iron release required for the  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  destruction, enabling also the deposition of hematite:



Hematite is, in fact, a common oxide in the enrichment horizon of the weathering profile of the Vilariça fault zone, and its preferential deposition along the cleavage directions of the carbonate testifies that chemical relationship.

Another argument that can be used in order to infer the relative importance of chloride and thiosulphate complexes in gold mobilization during the weathering profile development, concerns the electrum particles chemistry. According to the results of different studies (e.g. Mann, 1984; Butt, 1989), if gold/silver transport occurs through the action of chloride complexes, the reprecipitated electrum particles are of high purity (> 99.5 wt% Au) and fineness, as a consequence of the higher stability of chloride silver complexes. If thiosulphate complexes are the prevailing agent of gold/silver solubilization, one might theoretically expect a higher silver content in reprecipitated electrum particles (Krupp & Weiser, 1992). It is important to point out, however, that successive climatic fluctuations from (semi)-arid to humid conditions, like those that characterize Late Pliocene-Early Quaternary transition in Portugal, may cause Ag redistribution in the electrum grains. This process, well documented in Brazil (Grimm & Friedrich, 1991), led to the development of transitional zones in the enrichment horizon of the weathering profile, where electrum grains with relatively high Ag contents are present beneath zones with high gold electrum.

In the França deposit, electrum grains in mineralized quartz breccia matrices exhibit an average silver content of 83 wt.% (4 analyses in a single sample). Chemical data on electrum particles in the weathered quartz breccias (enrichment horizon of the profile) show typically deficient totals, probably due to the highly porous texture exhibited by these grains; the quality of these analyses and the possibility of the presence of other metals in these grains, were tested through successive microprobe standardization and qualitative analyses. Geochemical data of these mineralized rocks show an Ag: Au ratio similar to the one found in electrum particles, suggesting a gold enrichment at a specific level of the weathering profile (Mateus & Barriga, 1993). On the other hand, the results of supergene mass balance estimates for the França deposit, illustrate a different behaviour of gold and silver during the development of the weathering fault zone profile (Mateus & Barriga, 1993): the higher flows of Ag suggests that this metal was easily mobilized from the fault zone, which could be interpreted as an indirect evidence for a

greater stability of silver complexes in the weathering environment.

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