METALLOGENETIC POTENCIAL FOR THE OCURRENCE OF EXHALATIVE GOLD AND BASE METALS DEPOSITS IN THE CENTRAL SEGMENT OF THE RIBEIRA FOLD BELT

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INTRODUCTION

The central segment of the Ribeira fold belt (RFB), as named in this paper, comprises the supracrustal units present in the São Paulo State and in the northeastern part of the Paraná State. These supracrustal rocks are limited at north by the Amparo Complex, at south by the Cristalino Complex, and at west by the Paraná Basin (Hasui *et al.*, 1980; Almeida *et al.*, 1981). These rocks were subdivided by Hasui *et al.* (1980) into the Apiaí and the São Roque fold belts, which were intruded by several Neoproterozoic to Phanerozoic granitic plutons and batholiths, and were affected by several NE–SW trending shear zones (Almeida *et al.*, 1981). The main known exhalative gold and base metal mineralizations mineralizations are present in the Serra do Itaberaba Group, located at northeast São Paulo city and in the Vale do Ribeira Metallogenetic Province, in the southern part of the São Paulo State and eastern part of the Paraná State.

SERRA DO ITABERABA GROUP

At northeast of the São Paulo city, the São Roque Fold Belt was divided in the basal Serra do Itaberaba Group that corresponds to a Mesoproterozoic metavolcano-sedimentary sequence and the essentially metasedimentary Neoproterozoic São Roque Group (Hackspacher *et al.*, 1999; Juliani *et al.*, 2000). The Serra do Itaberaba Group, which is comprised of the Morro da Pedra Preta, Nhanguçu and Pirucaia formations, was affected by two medium-graded and one low-grade metamorphic events. The basal Morro da Pedra Preta Formation is composed of metamorphosed normal mid-ocean ridge basalts (N-MORB), metavolcaniclastic rocks, graphite schists, sulfide-rich schists, Algoma-type banded-iron formations (BIFs), tourmalinites, and calc-silicate rocks. In the upper part of the Morro da Pedra Preta Formation, small dome-like brecciated andesitic and rhyodacitic intrusions occur, being spatially and genetically related to Mesoproterozoic paleo-hydrothermal systems, which were responsible for gold mineralizations and possible base metal ores (Juliani *et al.*, 1992; Beljavskis *et al.*, 1999; Pérez-Aguilar, 2001; Garda *et al.*, 2002). The Nanguçu Formation was deposited in a back-arc environment, and is mainly composed of iron-manganiferous schists and andalusite-chlorite schists. The Pirucaia Formation comprises quartzites and quartz-rich schists, which represent a shoreline sedimentary facies of the Nhanguçu Formation.

Gold - In the Morro da Pedra Preta Formation four sulfidation stages were distinguished, corresponding the first to a syngenetic event to which are associated sulfides with negative $\delta^{34}S$ values, and the other three stages to epigenetic mainly quartz-vein related events to which are associated sulfides with positive $\delta^{34}S$ values (Beljavskis *et al.*, 1999; Garda *et al.*, 2002). These authors describe the following mineralizations stages:

Stage I is represented by the mineral assemblage pyrrhotite–pyrite–(chalcopyrite), predominating pyrrhotite. Sulfides are disseminated and concentrated in films or very thin lenses parallel to S_o/S_2 within banded graphitic schists. Bands may be folded (D_1/D_2) and sheared. Gold is present as disseminated submicron-sized grains. Not very significant negative $\delta^{34}S$ values were obtained for stage I pyrrhotite, –8.7 to –5.5‰, which suggest that sulfur supply was obtained from bacterial reduction of seawater sulfate and from volcanogenic hydrothermal fluids exhaled from nearby fumaroles.

Stage II mineralogical assemblage corresponds to Au–Ag–pyrrhotite–pyrite–chalcopyrite–scheelite–Bi tellurides–galena–REE phosphates, predominating pyrite and pyrrhotite. Sulfides occur as stringers in volcaniclastic rocks and in metandesites and metadacite intrusions, or as deformed and metamorphosed quartz veins that crosscut the graphitic schists and metatuffs. Gold is disseminated in the quartz veins and associated with Cu minerals in crystal rims. The $\delta^{34}S$ values obtained for stage II pyrrhotite and pyrite crystals vary from +4.5 to +7.4‰, having sulfides crystallized from a fluid phase enriched in sulfur from several sources, thus obtained from thermochemical reduction of seawater sulfate, leaching of igneous sulfides present in the volcanic pile, and magmatic sulfur related to intermediate andesitic and rhyodacitic intrusions, having pervasive fluids percolated along stress zones.

Stage III is represented by the assemblage pyrite–pyrrhotite–(chalcopyrite)–galena–Bi tellurides–Ag, predominating pyrrhotite and pyrite. Sulfides generally infill microfactures and/or form aggregates. Gold is associated to chalcocite and covellite, which crystallized as alteration products after stage III chalcopyrite. The $\delta^{34}S$ values obtained for chalcopyrites from this stage varies from +2.6 to +3.6‰, which are interpreted as due to a mixture of sulfur from the volcano-sedimentary sequence leached by fluids derived from I-type granites.

Stage IV characteristic assemblage is pyrite–(pyrrhotite)–(chalcopyrite), predominating pyrite. Sulfides are present in fluorite- and tourmaline-rich hydrothermal veins found in shear zones, to which is associated a sericitic alteration. These veins are similar to those that crosscut granitic bodies intrusive in the Serra do Itaberaba Group. Pyrite and chalcopyrite may be partially replaced by Zn–Cd sulfides, having molybdenite, native silver, electrum, galena, Bi tellurides, REE phosphates, and scheelite also crystallized during this stage. Sulfides commonly fill microfractures and/or intergranular spaces. In stage IV pyrite are present well-defined rims with no evidence of fracturing, corroborating post-tectonic hydrothermal activity. The $\delta^{34}S$ values from stage IV sulfides that vary from +1.0 to +2.4‰ indicate that the channeling of granite-derived fluids in the shear zones results in a less efficient mixture with sulfur derived from the volcano-sedimentary pile, thus being values closer to those related to igneous sources. In stages III and IV the contribution of meteoric water is not ruled out.

Fluid inclusions in quartz veins gold occurrences indicate that gold deposition was from low-salinity (<5 wt % NaCl equiv.), H_2O-CO_2-rich (15-30 mole % CO_2) ore fluids. No different compositions were found in fluid inclusions associated to syngenetic gold, suggesting that the gold epigenetic mineralization superimposed the syngenetic mineralization.

Base Metals - In the Serra do Itaberaba Group were recognized several pre-metamorphic hydrothermally alteration zones (choritic, argillic and advanced argillic), similar to those present in Kuroko-type base metal mineralizations. The metamorphic products of these zones (cummingtonite-anthophyllite rocks, chlorite-rich rocks, and corundum-rich rocks), stable isotope analysis, and Cu and Zn soil anomalies (Pérez-Aguilar *et al*., this event) suggest potential for the occurrence of base metal in the metavolcano-sedimentary sequence of the Serra do Itaberaba Group. However, low salinity ore fluids associated with gold mineralizations may explain the absence of base metal deposits in or near the gold mineralizing hydrothermal systems (Beljavkis *et al*., 1999).

VALE DO RIBEIRA METALLOGENETIC PROVINCE

A compilation of the geological data from this unit can be found in the work of Silva *et al.* (1982), Daitx (1985; 1996) and Araújo (1999). In this Province the supracrustal rocks form the Apiaí Complex have been separated in several older Mesoproterozoic low- to medium-grade units, including Setuva, Água Clara, Truvo–Cajati, Perau and Abapã units, and several low-grade metamorphosed younger units, including Iporanga, Itaiacoca, Capiru, Votuverava, Antinha and Lageado units. These younger units have been considered as being either from the late Mesoproterozoic or the Neoproterozoic and commonly are referred to as belonging to the Açungui Group (Hasui *et al*., 1984). Different authors characterize these units as sequences, formations, groups, supergroups, or complexes. Most base metal mineralizations from the Ribeira Metallogenetic Province are localized in the supracrustal units of Lageado and Perau, being a small number of them localized in the Água Clara and Itaiacoca units. Mineralizations are essentially hosted in carbonatic or carbonatic/pelitic sequences. The main types of exhalative base metal mineralizations are stratiform and lode types, which are referred to as Perau-type and Panelas-type mineralizations, respectively. Also present are skarn-type base metal mineralizations.

Stratiform Perau-type Pb-Zn-(Cu)-Ba-Ag mineralizations - The Perau unit is subdivided in three sequences, corresponding the basal to a essentially psammitic deposition, which is followed by a carbonate/pelitic sequence, being the upper sequence mainly composed by psammitic/pelitic sediments. The stratiform mineralization is present in the upper portion of the intermediate sequence. The main characteristic of these deposits is the controlled lithoestratigrahic occurrence as SEDEX stratiform or stratabound Pb–Zn sulfide and/or barite mineralizations within the Mesoproterozoic carbonatic/pelitic sequence from the Perau unit. Its genesis was related to a regional dimension geological event. In these mineralizations, a lateral and vertical metallic and/or mineralogical zoning is present, so as alteration halos within wall rocks, as reflected by metal contents, mineral association, or stable isotopic signatures. Mineralizations occurred within feeder zones in unconsolidated sedimentary rocks, as disseminated or massive mineralizations, on ocean floor, or associated to hydrothermal plumes. Mineralizations are present in the interface of the clastic-chemical, and clastic sedimentation, being associated to not common facies within the Perau unit such as conglomerates, extremely K-rich felsic tuffs and tuffites, sericite schist and brecciated felsic volcanic rocks. Mineralizations were affected by the same tectonic events that affected wall rocks. This type of deposits was characterized by Barbour & Oliveira (1979), Silva *et al*. (1982), Macedo (1986) and Daitx (1996), among others, and includes Perau, Canoas, Araçazeiro sulfide deposits and Pretinhas, Água Clara, and Tigre Ba deposits. In the Perau deposit, a chalcopyrite-rich stringer zone is present in the base, which is followed by two massive sulfide bodies (lower and upper), which laterally grade to semi-massive ore. Brecciated structures predominate in the massive ore, being also present banded structures. In the lower massive body sphalerite predominates over galena occurring the inverse in the upper body. Upwards, barite layers are intercalated with layers with disseminated sulfides, metacherts and calc-silicate rocks. In the top of the sequence is present a magnetite rich BIF (Daitx, 1996). In the Canoas deposit, mineralization is represented by disseminated sulfides, which are associated to a barite rich horizon, to calc-silicate and silicate rocks (Daitx, 1996).

Carbonates associated to mineralizations in Perau and Canoas deposits show relative lower $\delta^{13}C$ (–5 to –1‰) and $\delta^{18}O$ (+13 to +20‰) values if compared with $\delta^{13}C$ and $\delta^{18}O$ values obtained for regional carbonates that vary from –2 to 0‰ and from +18 to +24‰, respectively (Daitx, 1996). The oxygen and carbon isotope values from regional carbonates are similar to those of Mesoproterozoic marine carbonates (Ripperdan, 2001), whereas values obtained for carbonates associated to mineralizations are interpreted as being the result of the mixing of deep hydrothermal fluids (which may have had a possible magmatic component or have been enriched in oxidized organic carbon) with seawater, or the interaction of this deep hydrothermal fluids with previously deposited carbonates. Remobilized carbonates from the Canoas deposit show still relative lower $\delta^{13}C$ (–5.1 to -4.2‰) but similar $\delta^{18}O$ (+14.2 to +15.4‰) values, which are interpreted as due to selective low water/rock ratios carbon isotope remobilization during metamorphism (Daitx, 1996). The $\delta^{34}S$ values obtained for sulfides (+1.2 to +8.2‰) and for barites (+20.6 to +24.3‰) form the Canoas deposit (Bettencourt *et al*., 1992; Daitx, 1996) are interpreted as due to the presence, in the first case, of a hydrothermal fluid with a major magmatic component, and in the second case, due to the presence of a fluid phased mainly composed by seawater. In these deposits, fluid temperatures were estimated by Daitx (1996) to have been around 300 ^oC (Canoas deposit) to 350 ^oC (Perau deposit)

Lode Panelas-type PB-Zn-Ag mineralizations - Panelas-type mineralizations are stratabound mineralizations hosted in carbonate rocks from the Açungui Group. Sulfide bodies are present either as concordant lenses or as discordant lenses and veins, which occur near or in the interface of carbonate rocks and metasediments (phylites or sericite schist), being generally associated to bracciated rocks. Wall rocks from sulfide mineralizations are relative enriched in base metals, if compared with regional carbonate rocks (Barbour, *et al*., 1988; 1990). The genesis of these deposits is controversy. Several authors relate mineralizations to granite intrusive bodies (Knecht, 1939; Barbosa & Guimarães, 1946; among others). This had been refuted by other authors (ex. Bettencourt *et al*., 1976), who consider that the ages obtained for galenas are older (~1100 Ma) than those obtained for granite intrusive bodies (~510 Ma) (Damasceno, 1967). Others consider that first occurred a syngenetic base metal enrichment of sediments, which was afterwards reworked by several mechanisms such as metamorphism, granite intrusions, tectonics and hydrothermal activity (Damasceno, 1967; Silva *et al*., 1982; Barbour *et al*., 1990; among others). Barbour *et al*. (1990) consider deposits as being syn-depositional SEDEX type deposits. Examples of Panelas-type mineralizations are Barrinha, Laranjal, Cecrisa, Costão, Rocha, Paqueiro, Pessegueiro, Bueno, Córrego do Eduardo, Diogo Lopes, Furnas, and Lajeado (Barbour *et al*., 1988).

CONCLUDING REMARKS

The Proterozoic was an important metallogenetic time for the genesis of hydrothermal gold and base metals mineralizations in the central segment of the Ribeira fold belt. A multistage hydrothermal history, which implies in a long-lived hydrothermal system, has been characterized in the Serra do Itaberaba Group, associated to gold and probable base metal mineralizations. During systematic geological mapping the diagnostic features that lead to discover this paleohydrothermal system were the metamorphic products of chloritic, argillic and advanced argillic alteration zones. Actually in the Vale do Ribeira base metal mines are exhausted, but hydrothermal processes took place over a long period of the geological time, related to regional dimension geological events, which resulted in different types of ore occurrences (stratiform, stratabound, lode, and skarn). This probably was also consequence of the presence of long-lived hydrothermal systems. In the Vale do Ribeira, base metal mineralizations are also associated to diagnostic features such as lithoestratigrahic controls, presence of typical metamorphic products of hydrothermally altered rocks, brecciated volcanic rocks, extremely K-enriched rocks, and conglomerates. This implies that during systematic geological mapping that will be carry out in the area, special attention shall be given to the presence of outcrops with the diagnostic features above related in order to discover possible blind base metal and gold deposits in this segment of the Ribeira fold belt. Also stable isotope studies, which characterize mineralizing fluids and help constrain genetic models, can be useful for mineral exploration, especially for non exposed bodies.

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