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THE ARCHEAN AND PROTEROZOIC MOLYBDENUM MINERALIZATIONS OF THE BAHIA STATE, BRAZIL: METALLOGENETIC IMPLICATIONS

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RESUMO

As ocorrências molibdeníferas de Campo Formoso-Carnaíba e Itaberaba são relacionadas a granitos peraluminosos transamazônicos e intrusivos em formações Arqueanas e/ou do Proterozóico inferior. Estas ocorrências constituem as maiores concentrações de molibdênio conhecidas no estado da Bahia. O plúton de Campo Formoso representa uma intrusão multifásica, homogênea em composição, com um facies equivalente no maciço de Carnaíba. Intensas alterações deutéricas - hidrotermais associadas a um importante enxame pegmatítico, testemunham as condições de saturação em fluido do magma parental. Ao contrário, o leucogranito de Itaberaba (maciço de Pedra d'Água) apresenta uma composição heterogênea com contatos difusos e muitos enclaves de granulitos; as alterações pós-magmáticas limitam-se a uma silicificação difusa. Estas características mostram que o granito de Pedrá d'Água foi gerado por um magma pobre em água, possuindo uma fraca mobilidade e uma leve diferenciação. Enquanto as ocorrências são relacionadas a granitóides, apresentam diferenças maiores: - a molibdenita de Itaberaba encontra-se tanto em forma de manchas ou disseminações no granito como em veio de sem concentração quartzo ou em zonas de silicificação difusa, significativa; - em Campo Formoso - Carnaíba, a molibdenita localiza-se em veios pegmatíticos intragraníticos, ou em concentrações mais importantes, na zona que bordeja o granito, em veios pegmatoides esmeraldíferos intrudindo serpentinitos. No caso dos pegmatóides esmeraldíferos, é evidente que o fluor, boró e berilio estavam presentes na fase fluida associada. Estes componentes (F,B). produzem magmas residuais ricos em albita normativa mas também uma depolimerização e criação de complexos capazes de carregar elementos litofilos como o molibdênio. Nos granitos pobres em F e B, como no caso de Itaberaba, o volume e a força mecânica da fase vapor foi pequeno, e em consequência as mineralizações são fracas e disseminadas. Por outro lado, as intensas mineralizações de Carnaíba relacionam-se a presença de um líquido residual silicatado, hidratado e alcalino, que gerou um importante volume de fase vapor, onde o F, B, Be e Mo se particionaram, responsavel provavelmente por a importante fraturação do granito e do seu encaixante, a redor dos quais se desenvolveu um consequente sistema mineralizações. hidrotermal responsável pela deposição · das Enriquecimentos molibdeníferos em leucossomas graníticos associados a migmatitos Arqueanos da região de Queimadas permitem discutir a origem do molibdênio.

INTRODUCTION

Precambrian shields of Brazil enclose the most important ore

deposits of this country (Beurlen and Cassedanne, 1981; Damasceno, 1982; Schobbenhaus et al., 1984). Among these mineralizations, molybdenum ore deposits are absent and most of the Brazilian occurrences of molybdenite are linked to granitoid and its associated hydrothermal alterations, calc-silicate bands-skarn type-, and metamorphosed volcano-sedimentary series. All these prospects are related to Precambrian rocks and closely associated with various episodes of granitization developed during the Transamazonic orogeny or the Brazilian cycle (Fig. 1). The single Brazilian production is related to the occurrence of Pindobaçu (Bahia State) which has produced in the period 1970 - 1986, 135 tons of Mo; this district corresponds to the famous emerald prospecting pits of Carnaiba (Moreira and Santana, 1982; Couto and Almeida, 1982, Rudowski et al., 1987 a,b).

The scope of this paper is to present the main occurrences from the Bahia State including Pindobaçu molybdenum-emerald prospecting pits related to the emplacement of a transamazonian granitoid intruding basic and ultrabasic sequences, Itaberaba prospecting field, a typical orthomagmatic mineralization and finally, the molybdenum ore associated to leucosome veins occurring in Queimadas migmatites. The description of these differents types of mineralization will allow us to approach the conditions of concentration and deposition of molybdenite apparently prevailing along processes of differentiation. segregation and crystallisation within magmas and it associated hydrotermal system. Therefore, this should contribute to the understanding of the mechanism of ore formation and to the establishment of hypothesis about its origin.

THE CAMPO FORMOSO AND PINDOBAÇU MINING DISTRICTS: THE PROSPECTING PITS OF SOCOTÓ AND CARNAÍBA

The Proterozoic granite massifs of Campo Formoso and Carnaiba intruded at 1.9 G.Y in the volcano-sedimentary terranes of the Serra da Jacobina and the gneissic-migmatitic Archean basement (fig. 2).

The Campo Formoso granitoid complex presents an elliptic form and a concentric structure formed by a peripheric coarse-grained two-mica granite (Y1) and a central fined-grained to porphyritic two-mica granite (Y2). The Carnaíba massif occurs in an antiform structure developed in the intercalated quartzites and ultramafic rocks from the Serra de Jacobina, and it forms a subcircular pluton. Petrographic descriptions of these granites have previously been given by Rudowski et al. (1987 a,b) and show the similarity between the & 2 Campo Formoso facies and the Carnaíba granite.

These two granitic massifs are characterized by the presence of Be, Mo, W mineralizations, ocurring in the emerald prospecting pits of Socoto and Carnaiba. The emerald and green beryl mineralization is contained in fluor-rich phlogopitites resulting from metasomatic transformation developped in ultrabasic rocks from plagioclasic (albite, oligoclase), quartz ÷ plagioclase, tourmaline ± plagioclase. quartz-veins. Locally, intercalated tremolitic and talcose formations are found sometimes with disseminated scheelite mineralization.

In the Socotó prospecting field (Fig. 2a), the occurrences of serpentinites are observed as imbricated structures in the gneissic Archean basement. The ultrabasic horizon, oriented N150-180°, dipping 50 to 80° to the northeast, presents an extension of 2.5 Km and a width of 0.5 Km, In this area, facies equivalent of Campo Formoso granitic complex are not found. The molybdenite mineralization is occasional and it is often encountered in phlogopitites from the deepest levels of the mining district (Momona prospecting pit). Rare crystals of molybdenite

(0.5 cm long), pyrite and chalcopyrite can be also observed in aplopegmatitic veins from the 2 Campo Formoso granite, along with garnet, potash feldspar, muscovite, biotite and quartz.

The Pindobaçu mining district is developed around the Carnaíba granite with its famous emerald prospecting pits. The emerald bearing rocks are similar to those of Socotó but the district appears more complex and interesting.

The mining district is divided into two main subareas (Fig. 2b): the prospecting pits of Carnaíba de Cima (Trecho Velho. Trecho Novo, Trecho da Bica and Trecho da Cabra), situated at 1.000 m above sea level, and those of Carnaíba de Baixo, located at an altitude of 550 to 600 m (developed in roof pendants in the granite: Bode, Gavião, Lagarta prospecting pits, or in country rock terranes around the granite: Marota. Braúlia and Formiga prospecting pits). The emerald mineralization is encountered mainly in plagioclase, quartz-plagioclase or quartz veins crosscutting the ultrabasic formations, oriented N50 to 95° and dipping 40° to 80° to North-Northeast. Two kinds of veins arė distinguished by the prospectors: the fracture veins called "frincha" and contact veins "esteira". The second one corresponds to the mineralization developed at the contact zone between quartzite and the intercalated serpentinites (Trecho novo, Bica and Cabra), and it assumes the main production of the Pindobaçu emerald deposit.

Five different types of molybdenite mineralizations occur in the Pindobaçu district: - disseminations (crystals up to 2 cm) in joins of aplopegmatite related to the Carnaíba granite along with yellow beryl and sulphides (Bode Prospecting pit). - intense mineralizations (crystals up to 1 cm long) in plagioclase-rich dykes (Marota prospecting pit) - molybdenite-bearing quartz veins associated with yellow beryl, fluoroapatite, muscovite (Braúlia). - molybdenite emerale-bearing quartz veins enriched in plagioclase (Trecho Velho). It characterizes the so called "frincha" i. e fracture veins, which can be vertical with an average width of 0.5m.

In this case, no lithological control as in the "esteira" vein can be allowed. The emerald is of good quality but the molybdenite (crystals up to 2 cm) is more abundant. This type of vein is also called by the prospectors "veio de estanho" i.e "tin vein" (in relation with metallic aspect of molybdenite recording tin). the vein molybdenite-tourmaline-plagioclasic (Marota, Braúlia) 🕔 or molybdenite-plagioclase-pale green beryl vein (Marota, Bode), (Photo 1).

In all cases, molybdenite mineralization can occur in the phlogopitite rock related to its adjacent vein (Photo 2).

The molybdenite mineralization is always associated to а fracture vein type but rarely with the contact vein type. At the scale of the district, a vertical repartition of the mineralization is observed with a notably enrichment of molybdenite and quartz near to the granite (Marota, Braúlia, Bode, Trecho Velho) and a decrease in the quantity and quality of emerald. Marota prospecting pit is an illustrative example: the emerald production is insignificant and the pits are the deepest in the area (80-100m). They show the presence of numerous fine to coarse-grained plagioclasic veins with important molybdenite disseminations. Sometimes, millimetric to centimetric molybdenite veins constitute rich ore zones.

A dressing unit for the recovery of molybdenite was built in Marota by the Electrometal Aços finos Company. A flotation cell with a capacity of 200 Kg/hour assumes a maximum production of 1.5 tons/month of concentrate (Danese, 1987). For instance, there is no molybdenum exploitation and the molybdenite is brought by the prospectors (1U.S\$/Kg of molybdenite, november, 1987); no exploration program for molybdenite is planned but Pindobaçu mining district assumes the total molybdenum brazilian production.

THE ITABERABA PROSPECTING FIELD

The region around Itaberaba city is located on the limit between the Archean granulitic Jequié cratonic nucleous and the Transamazonic Salvador-Juazeiro Mobile belt. The transition between these two geotectonic domains is marked by changes in the lithologies and structural trends, and by the effects in the early Proterozoic, of an intensive granitization to which the molybdenite occurrences are related.

The largest granitic bodies are the Pedra d'Água and Itaberaba massifs, along with other minor intrusions (fig. 3). Host rocks include, to the East, an assemblage of gneisses, leptynites, mafic-ultramafic rocks and granulites strongly affected by anatexis, and, to the South and West, areas of locally migmatized granulites and charnockites. Small lenses of biotite-garnet-cordierite-green spinel-sillimanite gneisses can be found, as well as diatexic bodies. The region suffered at least three deformational events (Fernandes and Sabaté, 1987), the last one (reported as Fn+1) being responsible for the N-S to NNE-SSW folds and associated axial plane gneissic banding.

four molybdenite occurrences have been recognized (Fig. 3). Three of them are linked to minor aplo-pegmatitic bodies intrusive either in granulites or in the Itaberaba massif. The most expressive molybdenite prospect is located in the Pedra d'Água massif.

The Pedra d'Água massif is a small elliptical body of hololeucocratic medium-grained granite. It contains quartz, sodic oligoclase mesoperthitic zoned orthoclase partially replaced by microcline, accessory biotite and garnet, remnants of orthopyroxene, biotite and brown oxides. Accessory minerals include zircon, apatite, allanite, magnetite and pyrite.

This granitic massif is intruded in a partly concordant fashion in granulites and granulitic metatexites, and its magmatic preferred orientation, which is defined by alignments of quartz, feldspars and mafics, has been folded still under magmatic conditions during the Fn+1 deformation. Metric to centimetric schlieren enclaves and nodules of biotite-granulites and garnet-cordierite-sillimanitegreen spinel gneisses are common and locally the proportion of this material is high, so that the granite takes a migmatitic appearance, especially at the southwestern border.

Molybdenite mineralization was first reported by Seixas et al. (1975). It occupies a maximum area of 0.2 Km^2 , to the East of Pedra d'Água farm (fig. 3). Ore enrichment occurs in granite, granulitic and kinzigitic schlieren and nodules, and finally, in quartz veins.

- In the granite, quartz-molybdenite enrichment is observed as millimetric to centimetric-sized diffuse disseminations elongated parallel to the magmatic preferred orientation. Non metallic minerals are biotite and garnet.
- Centimetric to metric nodules, schlieren and enclaves of biotite granulites and kinzigites contain also small molybdenite crystals, located mainly in biotite-rich bands, or in marginal quartz-garnet pockets or envelopes.
- Quartz veins vary in thickness from a few millimeters to 8 cm, with a length up to 1.5 m. Most of the veins are concordant to the N30-N50^o trend of the syn-Fn+1 magmatic orientation. Some of them show boudinage or close folds whose axial planes are also concordant. Vein trends vary, from N10-N120^o(Fig.3), thin veins lying at low angle to

the Fn+1 direction show clear evidence of transposition at the crystal scale. In this case, the general trend of the vein is preserved; it gets discontinuous and individual crystals get parallel to the granite flow structure. Mineral paragenesis in the veins include quartz, molybdenite and minor biotite (Photo 3). Although K-feldspar is not present inside the veins, it can occur at their borders as coarse crystals. Dynamite shots which exposed unweathered rock down to 20 cm allowed Barros (1979) to estimate reserves of 0.17% of molybdenite.

Three other molybdenite occurrences can be reported from the Itaberaba region (Fig. 3): at 2.5 km SSE From the Pedra d'Água farm, in the Fazenda Lagedinho and finally on the Piranhas River. Occurrences II and III (Fig. 3) correspond to molybdenite-bearing coarse-grained granite dykes concordant within the metatexitic granulites; occurrence IV (Fig. 4) consists of a centimetric aplopegmatoid body intruding the porphyroid Itaberaba granite.

THE QUEIMADAS MOLYBDENITE-BEARING MIGMATITE

This migmatite belongs to the Archean basement and specially to the Serrinha craton which was rejuvenated during the Transamazonic Cycle (Fig. 1).

The migmatite exhibits a gneissic texture, foliated along a $N-\dot{N}15^{\circ}$ direction and dipping 75-80°W. the mineralogical composition is quartz, feldspar, biotite, opaques. Granitic pink mobilizates are found as concordant vein or as discordant fine-grained mobilizate veins, or filling open sigmoid fractures (Sabaté et al., 1987).

The concordant mobilizates exhibit a coarse pegmatoid texture composed of quartz, plagioclase, K-feldspar, magnetite and sometimes bordered by biotite accumulations. The presence of molybdenite, previously recorded by Sabaté et al. (1987), is not constant for all the veins. The mineralization in one vein consists of regular disseminated flakes of molybdenite (3 to 5 mm) without other sulphides (Photo 4).

We can also note the development of a late fracturing event crosscutting the migmatites and the mobilizates, and characterized by a chalcopyrite quartz infilling. The molybdenite-bearing mobilizate veins are not deformed and they constitute at the moment, a unique molybdenum Archean mineralization in Bahia.

DISCUSSION AND CONCLUSION

The Campo Formoso - Carnaíba and Itaberaba molybdenum occurrences are associated with Proterozoic peraluminous granites intrusive in migmatitic to granulitic Archean formations and they constitute the major concentrations of molybdenum known in Bahia. The Campo formoso pluton is homogeneous in composition and does not present basic enclaves or material of its original source. It represents a multiphase intrusion where the magmatic differentiation induced a regular variation in time of its composition with equivalent facies found in Carnaíba granite. These leucogranites are affected by intense deuteric-hydrothermal alterations and by the emission of a dyke swarm of pegmatites, testifying of the saturated fluid conditions of their parent magma.

On the other hand, the Itaberaba leucogranite presents an heterogeneous composition, diffuse contacts and metric enclaves or septas of the granulitic rocks and also of the restite minerals. No magmatic differentiation is observed and tardi-magmatic phenomena are limited to a diffuse silicification. These features show that this muscovite-free leucogranite was generated by H₂O-poor magma, possessing a weak mobility and unable to differentiate.

Although the ore deposits are related to granitoids, there exist major differences: the Pedra d'Água molybdenite is found as specks and disseminations in the granite, as well as in quartz vein or associated to diffuse silicification; this indicates that deposition of molybdenite began during the magmatic until late magmatic stages but without major concentration. In Campo Formoso and Carnaíba, molybdenite is found seldomly in pegmatitic veins of the granites, meanwhile, the economically most important type deposit is related to green-beryl pegmatoid veins, corresponding to desilicated pegmatites (Giuliani and Couto, 1988) intruding serpentinite formations, as well as muscovite (exocontact molybdenite concentrations). guartz veins Carnaiba molybdenite district forms a very uncommon deposit because it is directly associated to emerald mineralization. In the case of the pegmatites involved in emerald formation, it is clear that fluorine, boron plus beryllium were present in the associated fluid. Such components are generally encountered with chemically specialised Sn-W-Mo granites (Tischendorf, 1977). Effects of such components as F and B will produce at the magmatic stage residual magmas rich in normative albite with both a depression of solidus and liquidus temperature (Pichavant and Manning, 1984; Manning and Pichavant, 1987).

In consequence, melt viscosity decreases, diffusion rate increases and a reorganisation of the chemical crystallography of the melt components promotes a depolymerisation and creation of complexes especies in the melt (Manning, 1981); Such F, B`and Be-Cl complexes will be favourable for the transport of lithophile elements as Mo and W which are intimately associated with emerald mineralization.

The importance and the timing of the vapour phase during vapour generation may be essential in the precipitation of massive economic mineralization. Thus, the water content of the magma appears critical for vapour phase formation and exolution. In the F, B, water-poor Itaberaba granite, the volume and the mechanical strenght of the vapour phase is small and in consequence the Mo mineralizations appear as in miaroles, small veinlets and disseminated in the host granite. On the other hand, Carnaíba mineralizations express the presence of a hydrous alkalic silicic melt which generated an important volume of vapour phase where F, B, Be, Mo have been partitioned, responsible probably for the important fracturation in the granite and its surroundings, provoking the development of a huge hydrothermal convective system around the granite (Giuliani and Couto, 1988) and Be, Mo and W mineralization deposition Furthermore, the intense Carnaiba mineralizations and its associated stockwork lead us to consider that the vapour phase has evolved early in the magma history.

The origin of Mo in the magma remains a question of academic interest and a source of controversial debate as in the case of the Colorado Mineral Belt (Wallace et al., 1978; Routhier, 1980; Lehmann, 1987). In addition to the Proterozoic molybdenum occurrences of Bahia, molybdenite also occurs in leucosomes resulting from the injection of granitic material into Archean migmatites as in Queimadas. This type of enrichment let us to consider that Mo can be preconcentrated in the Archean crust and reactived during the formation of granitic melts. These melts according to Collerson and Fryer (1978) would be enriched in volatiles (CO₂, F, Cl and SO₂) and able to form soluble complexes with incompatible elements in the source as heavy REE, U, Th and also Mo. In conclusion, a geochemical heritage in the sense of Archean rocks preenriched in molybdenum is advanced and, appears of first importance in the geration of these Proterozoic leucogranites of Bahia.

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Following this possibility, the granitoids can have a Mo specialization. The acquisition of this metallogenetic potential will depend on several factors as mainly the degree of partial melting of the source rocks i. e degree of stability of the metal-halogen bearing minerals.

Additional and further geochemical data on the metal and halogen content of these leucogranites and associated Archean rocks will allow us to confirm the existence of a regional molybdenum anomaly, but also to follow the different magmatic evolution history and the different degree of partial melting of the source rocks, implicated in the formation of Campo Formoso - Carnaíba and Itaberaba leucogranites.

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<u>Figure 1</u>: The Brazilian shield with the localization of the main occurrences of molybdenum. 1: Pré-Brasiliano cratons; 2: Brasiliano cycle-fald belts; 3: Phanerozoic covers; 4: molybdenum occurrences with : 1 - Lavras do Sul, Saibro (RS); 2 -São Gabriel, Mina da Palma, Passo do Iro (RS); 3 - Lavras do Sul (RS); 4 - Ilhota, Morro do Báu (SC); 5 - Poços de Caldas (MG); 6 - Pindobaçu, Carnaíba (BA); 7 - Itaberaba, Pedra d'Água (BA); 8 - Queimadas (BA); 9 - Frei Martinho, Jeriçó Sousa (RN); 10 - Pedra lavrada (RN); 11 - Currais Novos (RN); 12 - Boa Vista, Serra Guariba (RR); 13 - Boa Vista, Serra do Mel (RR); 14 - Boa Vista, Serra do Banco, Fazenda Moreninha (RR); 15 - Serra dos Carajas, Salobo (PA). <u>STATES</u>: RS - Rio Grande do Sul; SC - Santa Catarina; MG - Minas Gerais; 8A - Bahia; RN - Rio Grande do Norte; RR - Roraima territory; PA - Parà; 5: the different Prè-Brasiliane cratons with : A - Amazohic; B - São Luis; C - São Francisco; D - Luis Alvés; E - Rio de la Plata. Data synthetized from Damasceno (1982); Sá (1983); Schobbenhaus et al. (1984); Sabaté et al. (1987).





Figure 2 : Geologic sketch maps of the Campo Formoso (2a) and Pindobaçu (2b) mining districts. 1- carbonated Proterozoic cover; 2- Jaguarari granite; 3-Carnaiba leucogranite; 4two-mica coarse-grained Campo Formoso Figure 2 :Geologic sketch maps of the Campo Formoso (2a) and Pindobacu (2b) mining districts. 1- carbonated Proterozoic cover; 2- Jaguarari granitoid; 3 - Carnaíba leucogranite; 4- two-mica porphyroid to fine-grained Campo Formoso leucogranite; 5- twomica coarse-grained Campo Formoso leucogranite; 6chlorite schist phyllites; 7- volcanosedimentary formations of the Serra de Jacobina; 8- serpentinites 9- Archean gneisses; 10silicified zones; 11thrust fault; 12- faults; 13- roads; 14- prospecting pits : 1 : Bode, 2 : Lagerta, 3 : Gavião, 4 : Formiga, 5 : Braulia, 6 : Marota, 7 : Trecho Velho, 8 : Trecho novo, 9 : Bica, 10 : Cabra, 11 : Socotó; 15- Be : green beryl- emerald, Cr : Chromite, Mo : molybdenite.



<u>Figure 3</u>: Geological sketch map of Itaberaba region with the Pedra d'Água leucograni te and its main molybdenum occurrences. l-granulites, charnockites and metatexitic granulites; 2-kinzigites; 3-migmatites, leptinites and biotite-granulites; 4- diatexi tes; 5- fine-grained facies of Itaberaba granitic massif; <u>Molybdenite occurrences</u> : 8: Fazenda Pedra d'Água; 9: Fazenda Pedra d'Água Sul; 10: Fazenda Lagedinho; 11: Rio Piranhas; 12: aplitic body; 13: pegmatitic body; 14: aplopegmatitic body; 15: mineralized area of Fazenda Pedra d'Água; 16-aplopegmatitic dykes; 17-structure planes; 18lineation; 19-attitude; 20-road.

In the left hand of the drawing, distribution of the quartz vein trends from the Pédra d'Água leucogranite.



<u>Photo 1:</u> Typical paragenesis of a molybdenite pegmatoid vein. Mo : molybdenite; Fd : albite-oligoclase feldspar; Be : pale green beryl (Be). Marota prospecting pits - <u>Car</u> naíba de Baixo mining district -



<u>Photo 2</u> : Crystals of molybdenite (Mo) associated to a phlogopitite zone (Bi) adjacent to a plagioclase vein. Marota prospecting pits - <u>Carnaíba de Baixo mining distr-</u> <u>ict -</u>

Photo 3 : Aspect of a molybdenite-bearing veinlet of Pedra d'Água leucogranite. The molybdenite (Mo)crystallized on the border of the veinlet composed of quartz (Qz) and biotite (Bi). Fazenda Pedra d'Água mineralized area.



<u>Photo 4</u>: Molybdenite-bearing laucosome (Le) crosscuting the Queimadas migmatite (Mi) The crystal of molybdenite (Mo) is straightly associated to the quartzo-feldspatic matrix. <u>Queimadas region</u>