

COMPARING TRACE-ELEMENT SIGNATURES OF SULPHIDES FROM NEOARCHEAN AND PALEOPROTEROZOIC Cu-Au SYSTEMS OF THE CARAJÁS MINERAL PROVINCE (AMAZON CRATON)

Érika Santiago (*esbsantiago@gmail.com*)¹, Roberto Xavier (*xavier@ige.unicamp.br*)¹, Lena Monteiro (*lena.monteiro@usp.br*)², Steffen Hagemman (*steffen.hagemann@uwa.edu.au*)³

¹Universidade Estadual de Campinas; ²Universidade de São Paulo; ³University of Western Australia

INTRODUCTION

Cu-Au systems in the Carajás Mineral Province (CMP), southeastern of the Amazon Craton, are mainly represented by iron oxide Cu-Au (IOCG) and Cu-Au-(Mo-W-Bi-Sn) deposits. The former are hosted by Mesoarchean tonalite and gneiss, as well as meta-volcanic-sedimentary units, mafic and felsic intrusive rocks of Neoarchean age. The latter are spatially and temporally associated with Paleoproterozoic A-type granites and Neoarchean metasedimentary rocks. Recent geochronological data obtained in deposits from the southern sector of the Carajás Province have constrained the timing of IOCG formation into two stages. The first is related to ca. 2.71-2.68 Ga in the Sossego (Sequeirinho orebody), Bacuri and Bacaba deposits (Moreto *et al.* 2013), whereas the second, ca. 1.90-1.87 Ga, is recorded at Sossego (Sossego orebody) and Alvo 118 deposits (Tallarico 2003; Moreto *et al.* 2013). In the northern sector of CMP, an event of ca. 2.57 Ga has been recognized for Salobo and Igarapé Bahia IOCG deposits (Requia *et al.* 2003; Tallarico *et al.* 2005). Cu-Au-(Mo-W-Bi-Sn) deposits (e.g., Breves), of the CMP, on the other hand, are essentially Paleoproterozoic, with age of ca. 1.88 Ga.

The mineralized zones in these systems are characterized by a diversity of ore minerals, which implies that variable fO_2 - fS_2 - T conditions controlled the ore formation. Among the IOCG deposits, Salobo exhibits chalcopyrite-bornite-chalcocite as the main ore association (Lindenmayer 1990), whereas Igarapé Bahia is characterized by chalcopyrite (Dreher *et al.* 2011). At Castanha deposit, pyrrhotite is an important sulphide, together with chalcopyrite and pyrite (Pestilho 2011). Sulphides at the Sossego and Alvo 118 deposits are also represented by variable amounts of chalcopyrite and pyrite (Monteiro *et al.* 2008; Torresi *et al.* 2012). On the other hand, at the Breves deposit, the ore association includes mainly pyrite-chalcopyrite-arsenopyrite (Botelho *et al.* 2005).

In this work, we explore the trace element contents in pyrite, pyrrhotite, chalcopyrite, and chalcocite from Cu-Au systems of the CMP, including Neoarchean (Salobo, Castanha and Igarapé Bahia) and Paleoproterozoic IOCG (Sossego orebody and Alvo 118) deposits and the Paleoproterozoic Breves Cu-Au-(Mo-W-Bi-Sn) deposit. The aims are to: (1) compare trace elements variations in sulphides from these Cu-Au systems; and (2) constrain physicochemical parameters that may unravel the evolution of these systems with implications on their ore genesis.

MATERIALS AND METHODS

Trace elements compositions of chalcopyrite, pyrite, pyrrhotite, and chalcocite were determined in polished sections in a New Wave UP-213 Nd:YAG Q-switched Laser Ablation System coupled with an Agilent 7700s Quadrupole ICP-MS at the ARC Centre of Excellence in Ore Deposits (CODES) of the University of Tasmania, Australia. Beam size was chosen depending on the sulphide grain size and textural homogeneity and varied between 14 and 31 μ m. The analytical mass spectra were reduced and evaluated individually in order to eliminate contamination effects due to the ablation of solid inclusions of other coexisting minerals, such as quartz, carbonates, silicates or phosphates. Each analytical spectrum was reduced manually. Trace elements in chalcopyrite were analyzed for all the investigated Cu-Au deposits. Pyrite analyses were carried out for the Castanha and Breves deposits, whereas pyrrhotite analyses were restricted to Castanha. Chalcocite was analyzed for the Salobo. This study concentrates mainly on the variations of trace elements with concentrations above the minimum detection limit (MDL), which for the investigated Cu-Au systems include Pb, Zn, Bi, Ag, Au, Se, Te, Co, Ni, and As.

RESULTS

PYRITE AND PYRRHOTITE

At Castanha, As concentrations are below MDL in pyrrhotite, whereas in pyrite mean concentrations are at 37 ppm. Zinc and Pb contents in pyrite and pyrrhotite are low, with average values for pyrite (3.14 ppm and 5.51 ppm) slightly higher than those for pyrrhotite (1.50 ppm and 1.70 ppm). Bi content of Castanha pyrite and pyrrhotite are also low, with averages of 3.51 ppm and 1.40 ppm, respectively. Pyrite and pyrrhotite show negligible Au and very low Ag (up to 6 ppm) and Te (up to 2.4 ppm) values. On the other hand, Se contents of pyrite and pyrrhotite are significant, with averages of 45 ppm and 55 ppm, respectively. Cobalt and Ni contents are the highest among all selected trace elements in Castanha pyrite and pyrrhotite. Average values of Ni and Co for pyrrhotite are 38,690 ppm and 5,113 ppm, respectively, and for pyrite are 1,902 ppm and 3,881 ppm.

Pyrite from the Breves deposit contains average concentrations of As at 2 ppm, Zn and Pb, respectively, at 6.60 ppm and 13.74 ppm, and Bi at 543.60 ppm. Breves pyrite exhibits low Au contents (average 1.60 ppm), whereas Ag may reach up to 15 ppm. Breves pyrite shows high Se (average of 203.50 ppm) and Te (47.85 ppm) contents. Cobalt displays the highest values among the trace elements in Breves pyrite, with average of 14,710 ppm, whereas Ni contents average 218 ppm.

CHALCOPYRITE

Concentrations of Zn, Pb, Bi, and Sn are significantly variable in chalcopyrite from all the investigated Cu-Au deposits. Castanha chalcopyrite shows much higher Zn contents (325.40 ppm) than that of Igarapé Bahia (31.70 ppm) and Salobo (2.24 ppm). Salobo chalcopyrite, on the other hand, presents high Pb contents (18.40 ppm) compared to Castanha (4.30 ppm) and Igarapé Bahia (0.50 ppm). Igarapé Bahia chalcopyrite shows Bi (6.63 ppm) and Sn (6.71 ppm) contents higher than those of Castanha (1.5 ppm and 1.14 ppm) and Salobo (0.95 ppm and 1.02 ppm) chalcopyrite. Alvo 118 chalcopyrite contains much higher average Zn (1,669.30 ppm) and Pb (114.75 ppm) than that of Sossego chalcopyrite (Zn = 1.67 ppm; Pb = 8 ppm). Sossego chalcopyrite has slightly higher Bi (1.67 ppm) and Sn (8 ppm) than values obtained in Alvo 118 chalcopyrite (0.5 ppm and 3.5 ppm).

Average Ag contents of chalcopyrite from the IOCG deposits are low: 8.80 ppm for Igarapé Bahia, 4.73 ppm for Salobo and 0.60 ppm for Castanha. Au values are generally lower (< than 0.86 ppm) than Ag. Higher Ag values have been yielded by Salobo (average of 3.72 ppm) and Alvo 118 (average of 5 ppm) chalcopyrite, whereas averages for the other IOCG chalcopyrite are much lower (Igarapé Bahia = 0.86 ppm; Castanha below MDL; and Sossego = 1.30 ppm). Au contents of Alvo 118 and Sossego are the lowest among the IOCG deposits (< than 0.04 ppm).

Salobo chalcopyrite shows the highest Se and Te concentrations (111.30 ppm and 29 ppm), followed by Igarapé Bahia (70 ppm and 19 ppm), Castanha (49 ppm and 1.30 ppm), Sossego (42 ppm) and Alvo 118 (31 ppm). Sossego chalcopyrite displays the highest Te values (65 ppm) among the IOCG deposits. Co in IOCG chalcopyrite is generally low: Castanha = 1.12 ppm, Igarapé Bahia = 2.00 ppm, Salobo = 5.40 ppm, Sossego = 0.41 ppm, and Alvo 118 = 2.90 ppm. Castanha chalcopyrite shows the highest Ni concentrations (37.12 ppm), together with Sossego chalcopyrite (18.80 ppm), whereas the lowest are shown by Salobo (1.00 ppm), Igarapé Bahia (2.24 ppm) and Alvo 118 (0.06 ppm) chalcopyrite.

Breves chalcopyrite presents high Zn (611.90 ppm), Pb (102.60 ppm), Bi (153.90 ppm) and Sn (161.90) compared to IOCG deposits, except for Zn in Alvo 118 chalcopyrite. Chalcopyrite at Breves shows Ag contents (77 ppm) much higher than those of IOCG chalcopyrite, but much lower Au contents (0.12 ppm). Selenium and Te in Breves chalcopyrite exhibit similar average values of 18 ppm and 20 ppm, respectively. In addition, Breves chalcopyrite shows very low Co contents (0.46 ppm) and Ni values below MDL.

CHALCOCITE

Chalcocite at the Salobo IOCG deposit shows low contents of Zn, Pb and Bi, averaging 30 ppm, 155 ppm and 83 ppm, respectively. Silver exhibits the highest contents of all analyzed trace elements in chalcocite, with average values of 4,143 ppm. Gold contents are also high in chalcocite (7 ppm). Mean concentrations of Te and Se for chalcocite are 972 ppm and 368 ppm. Chalcocite displays contents of Ni below of MDL and Co of 254 ppm.

PRELIMINARY DISCUSSIONS

In general, Se, Te, Ag, and Bi in chalcopyrite and Co and Ni in pyrite and pyrrhotite may be used to distinguish between different IOCG deposits and Breves deposits in the CMP. Se + Te values of chalcopyrite from Neoproterozoic Salobo and Igarapé Bahia deposits are the highest amongst the IOCG deposits, but display similar ranges in chalcopyrite from Castanha and Paleoproterozoic Alvo 118 and Sossego (Sossego orebody) IOCG deposits (Fig. 1A). Bi + Ag values in chalcopyrite from all IOCG deposits vary in the same range. On the other hand, chalcopyrite from Paleoproterozoic Breves deposit presents lower Se+Te and higher Bi+Ag values than chalcopyrite from IOCG deposits (Fig. 1A). Concentrations of Se, Te, Ag, and Bi of chalcocite from Salobo deposit are much higher than chalcopyrite from other IOCG and Breves deposits.

Pyrite and pyrrhotite from Neoproterozoic Castanha IOCG deposit contain high concentrations of Ni and Co, with Co/Ni ratios in pyrite (0.02 to 0.11) similar to those in pyrrhotite (0.02 to 0.14) (Fig. 1B), despite of outliers of 277.71 and 973.76 for pyrite. On the other hand, compared to Castanha pyrite and pyrrhotite, Breves pyrite is more depleted in Ni and presents similar contents of Co. Breves pyrite has Co/Ni ratios, in general, larger than IOCG deposits, in the range of 0.76 to 2.23, and an outlier of 114.50 (Fig. 1B).

EPMA analyses of pyrite from Sossego deposit (Sossego and Sequeirinho orebodies) performed by Monteiro *et al.* (2008) have shown high contents of Co and Ni, and a wide variation of Co/Ni ratios (Fig. 1B). Compared to Sossego and Sequeirinho pyrite, Castanha pyrite and pyrrhotite are much less enriched in Co, but Castanha pyrrhotite shows similar Ni concentrations. Breves pyrite also has lower concentrations of Co and Ni than Sossego and Sequeirinho pyrite. The highest Co/Ni ratios of Castanha and Breves pyrite are close to those of Sequeirinho and Sossego pyrite (Fig. 1B).

Enrichments of Co and Ni documented in other IOCG deposits have commonly been associated with the occurrence of mafic-ultramafic rocks in the deposit areas (Mazdab 2001). It has been argued in these cases Co and Ni contents in pyrite and pyrrhotite are directly related to fluid salinity and host rock composition (Mazdab 2001).

At the Castanha IOCG deposit, large amounts of Co and Ni in pyrite and pyrrhotite are likely due to leaching of these metals by highly saline fluids which interacted with gabbro intrusions that occur in the deposit area (Pestilho 2011). Nevertheless, pyrite is enriched in Co and Ni at Breves deposit despite the association of the Cu-Au mineralization with A-type granite. Low contents of Co and Ni in fluids derived from the immiscibility of felsic magmas are expected as these metals are preferentially compatible with mafic phases at high temperatures. Mazdab (2001) proposed that high concentrations of Co and Ni in hydrothermal pyrite are likely originated from leaching of mafic rocks by highly saline external-derived hydrothermal fluids. An alternative is that Co and Ni were also leached by highly saline hydrothermal fluids from mafic rocks, such as the ca. 2.65 Ga dykes reported to occur in the Breves deposit area (Dias *et al.* 1996).

High Se concentrations in pyrite possibly indicate relatively high temperature Cu-rich ores (250°–350°C) and metalliferous fluids with $\sum \text{Se}/\sum \text{S}$ ratios consistent with, at least, >10% magmatic input of these elements (Huston *et al.* 1995). In the case of Castanha and Breves deposits, Se values may have not necessarily been originated directly from magmas, but may be the result of leaching of this metal from adjacent mafic rocks by hydrothermal fluids.

Huston *et al.* (1995) have also suggested that chalcopyrite from high-temperature Cu-rich ores is Se-enriched in contrast to low-temperature Cu-rich ores. Maslennikov *et al.* (2009) have also found significant variations in Se contents in chalcopyrite from high and low temperature ore zones in volcanogenic massive sulphide deposit. Thus, Se contents in chalcopyrite likely suggest that ore sulphides from Neoproterozoic IOCG deposits may have precipitated at relatively higher temperatures than Paleoproterozoic IOCG deposits and Breves deposit.

Ag-bearing chalcocite is less documented and there are few published quantitative data (Cook *et al.* 2011). Few published works demonstrate the strong relationship between Ag and chalcocite over other Cu-sulphides. This affinity has been assigned to hot (<350°C), oxidizing and acidic Cu-rich hydrothermal fluids, likely Ag-saturated, which are required to concentrate precious metals in the ore (Shalaby *et al.* 2004; Cook *et al.* 2011). The presence of bornite, magnetite and high Ag/Au ratios of chalcocite supports high T and $f\text{O}_2$ and low pH conditions involved in the formation of Ag-bearing chalcocite at Salobo deposit. High Se and Te contents are also observed in chalcocite, but Se- and Te-minerals have not been recognized at the Salobo deposit. It is suggested that Se and Te may be present as replacements for S in the chalcocite

crystal lattice. The replacement, in the case of Te, likely occurs at high temperatures (Maslennikov *et al.* 2009).

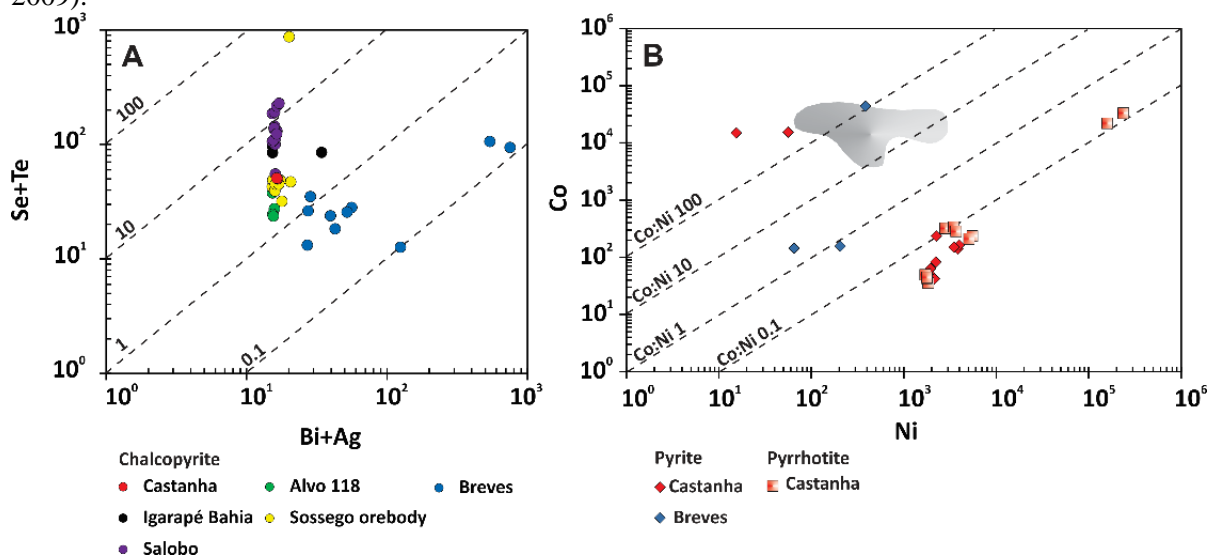


Figure 1 – Correlation diagrams of Co vs. Ni in pyrite (A) and Se+Tevs. Bi+Ag in chalcopyrite (B) from IOCG and Breves deposits. Gray field in (B): pyrite from Sossogodeposit (Sequeirinho and Sossogoorebodies; Monteiro *et al.* 2008).

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