MULTIANALYTICAL CONSTRAINTS ON THE HYDROTHERMAL ORIGIN OF NATIVE COPPER MINERALIZATION IN THE PARANÁ VOLCANIC PROVINCE

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ABSTRACT: The hydrothermal native copper of Paraná volcanic province occurs as dendrites in cooling joints, fractures and cavities of the flows. Secondary copper mineral phases occur in hydrothermal breccias at the top of the flows. The holocrystalline and microporphyritic volcanic rocks (n = 16) have average Cu content of 207 ppm and SiO_2 content between 49.5-50.9 wt.% for basalts and 53.0 wt.% for basaltic andesite. Plagioclase, clinopyroxene and opaque mineral phenocrysts (0.6 to 1.5 mm) form intergranular or glomeroporphyritic textures. The identification of copper minerals was supported by X-ray diffraction (cuprite and malachite) and Raman spectrometry (native copper, tenorite, chrysocolla and azurite). Electron microprobe analyses of native copper display nearly pure Cu with less than 0.3 wt % of other elements (e.g. Sn, Ca, Co, Ni, U, S and Al). The LA-ICP-MS analyses were carried out in magnetite, ilmenite, clinopyroxene, plagioclase and smectite. The highest copper content was observed in magnetite (>9000 ppm) followed by Ilmenite (~3500 ppm), clinopyroxene (431 ppm) and plagioclase (92 ppm). The LA-ICP-MS analyses of smectite displayed higher copper contents which increase with the hydrothermal alteration of the volcanic rocks. A novel approach of this study is the use of copper isotope ratios to discuss the origin of the copper. The results display three different populations. The first one shows values between -0.20 ‰ and 0.71 ‰ (n = 41). The second displays values between 1.07 ‰ and 1.89 ‰ (n = 9) with a predominance of lower values (<1.2 ‰). The third population shows negative $\delta^{65}Cu$ values between -0.59 ‰ and -0.91 ‰. These populations are not related with one or another specific hydrothermal event. They represent a regional isotope variation. In some occurrences, different $\delta^{65}Cu$ of native copper crystals (mm and cm-sized) are present in the same sample or one crystal shows distinct Cu isotope composition from core to rim. This indicates multiple copper mineralization processes with leaching and mineral precipitation at different times. The conclusion of this study demonstrates that three (H1, H2 and H3) Cretaceous hydrothermal events altered the volcanic rocks and generated smectite. The mineral alteration resulted in the release of Cu from igneous minerals (primarily magnetite, ilmenite and clinopyroxene). Copper was concentrated on smectite, subsequently was transported by boiling water at temperatures of 100 - 150 °C and deposited along the pathways of hydrothermal fluids (cooling joints and porosity). Similarly, the copper mineralization was precipitated in the cavities of the amygdaloidal crust. The supergene enrichment of the native copper mineralization resulted in oxidized secondary phases (e.g., cuprite) with isotopic ratios higher than native copper. Thus, this study integrates chemical analyses, XRD, Raman, EMP, LA-ICP-MS and Cu isotope analyses to understand the hydrothermal origin of copper mineralization in the Paraná volcanic province.

KEY WORDS: COPPER, PARANÁ VOLCANIC PROVINCE, Cu ISOTOPES, HYDROTHERMAL ALTERATION