Ore genesis at the Camaquã copper mine, a neoproterozoic sediment-hosted deposit in Southern Brazil

Jorge Henrique Laux a, Zara Gerhardt Lindenmayer b,*, João Batista Guimarães Teixeira c, Artur Bastos Neto d

aPPGeo-UNISINOS/UnB, Universidade de Brasília, Instituto de Geociências, Campus Universitário Darcy Ribeiro, Asa Norte, Brasília, CEP 70910-900, Brazil
bPPGeo-UNISINOS, Centro de Ciências Exatas e Tecnológicas. Av. Unisinos, 950, São Leopoldo, Rio Grande do Sul, CEP 93022-000, Brazil
CIPGG-UFBA, Rua Caetano Moura, 123, Federação, Salvador, Bahia, CEP 40210-340, Brazil

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Abstract

The Camaquã copper mine includes the Uruguai and the São Luiz orebodies, hosted by sandstone and conglomerate of the Neoproterozoic to Early Paleozoic Camaquã basin. Despite a great controversy regarding the evolution of the Camaquã basin, it is generally accepted that the basin was initially marine and progressively changed into a definite continental environment. The ore consists of massive sulfides in veins, pipes and stringers, and disseminated sulfides. The sulfide paragenesis in the primary ore consists of chalcopyrite, bornite, chalcocite, and pyrite. Other sulfides, such as wittichenite, idaite, molybdenite and carrollite are minor phases. Native gold is closely associated with hematite. A number of supergene minerals occur in the weathering zone, including covellite, digenite, antlerite, chrysocolla, brochantite, cuprite, malachite, azurite, tenorite, and native copper. Traces of gold and silver have also been found in the oxidized zone close to surface. Primary ore formation could be the result of multiple mineralization events. In a discrete mineralizing event, quartz was the first mineral to form, followed by pyrite, chalcopyrite and bornite. Carbonate and barite appeared by the end of the process. Sulfur isotope analyses of pyrite, chalcopyrite and bornite show little variation, $\delta^{34}\text{S}_{\text{CDT}}$ clustering around 0%, indicating a magmatic origin for the sulfur. On the other hand, $\delta^{34}\text{S}$ values of +10.30‰ to +14.24‰ for barite indicate probable oxidation due to the mixing of magmatic and meteoric $\text{SO}_4^{2-}$-rich fluids. Analyses of Pb isotopes in chalcopyrite, pyrite and bornite from the Camaquã deposit plot conformably with the reference isochron of 592 Ma built for regional igneous rocks (SHRIMP U/Pb zircon analyses) specifically the Lavras-Caçapava granite. Microthermometric measurements in fluid inclusions of quartz veins indicated temperatures varying from 236 to 60 °C. Fluid inclusion in carbonate displayed trapping temperatures between 150 and 50 °C, whereas the trapping temperatures in barite are below 80 °C. The fluid salinity varies largely from one mineral to another: 2.7 wt.% eq. NaCl to near pure water in quartz; 14 wt.% eq. NaCl in carbonate; 8 to 10 wt.% eq. NaCl in barite. The structural control of mineralization, the occurrence of superimposed mineralizing events, the temperature of deposition of the early-

* Corresponding author.
E-mail address: zara@euler.unisinos.br (Z.G. Lindenmayer).

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formed ore minerals (330 to 190 °C), and the sulfur isotope ratios, indicate that the Camaqua Mine may be considered as a hydrothermal type deposit, resulting of distal magmatic fluids focused into a relatively oxidized clastic succession.
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1. Introduction

The Camaqua mine in Rio Grande do Sul has been the main source of copper in Brazil for approximately 100 years. Economic interest in the region started around 1870, following the discovery of copper oxides by British gold prospectors (Teixeira and Gonzalez, 1988). The orebodies consist of veins, stockworks and disseminations of copper sulfides, hosted by sandstone and conglomerate of the Neoproterozoic to Early Paleozoic Camaqua Basin. Until their closure in 1996, the most important deposits were the Uruguai (open-pit and underground mine) and the São Luiz (underground mine), located in the Caçapava municipality, close to latitude 30°47’S and longitude 52°24’ W. The ore contains Cu- and Cu–Fe-sulfides associated with a gangue consisting of quartz, hematite, chlorite, carbonate and barite. Traces of gold are found in the crystalline structure of sulfides, and native gold occurs in the supergene zone. The Camaqua mines produced 76,000 t of copper up to December 1985. In 1978, the ore reserves of the Camaqua deposits were 30.8 Mt, at an average Cu grade of 1.06% Cu (Teixeira and Gonzalez, 1988).

Genetic models offered for the Camaqua mineralization have always followed the type of ores being worked at the time, adapted to the solution of immediate mining problems. From the start of mining operations, in the thicker veins, a high temperature magmatic–hydrothermal model was adopted without restriction (Teixeira, 1941; Leinz and Almeida, 1941). Coupled with narrowing of the veins at depth, the discovery of stratiform and disseminated sulfides in the sedimentary host rocks allowed the proposition of a sedimentary syngenetic to diagenetic model (Veigel, 1989). Nearing exhaustion of ore reserves, a hydrothermal (epithermal) theory became widely accepted (Lima et al., 1997; Laux and Lindenmayer, 1998, 2000a,b; Remus et al., 1997a, 1999, 2000).

This contribution presents a detailed description of the geology, stratigraphy, mineralogy, and geochemistry of the mineralization at the Camaqua mine, and critically evaluates the various genetic hypotheses proposed.

2. Geological setting

The Camaqua region is part of a molasse sequence that developed around the Dom Feliciano mobile belt, and partially overlaid the rocks of the Rio de La Plata Craton (Ribeiro and Fantinel, 1978; Fragoso-César, 1980) near the end of the Brasiliano cycle (Almeida et al., 1976). This sedimentary cover, named the Camaqua Group in Rio Grande do Sul, extends south into Uruguay (Barriga Verde Formation), and also northward as far as the Itajaí valley in Santa Catarina (Fig. 1). The basement of the Camaqua basin is composed of Paleoproterozoic rocks belonging to the Dom Feliciano, Tijucas, and the Vila Nova granite–gneiss belts, and also to the Santa Maria Chico granulite complex (Fig. 2). The basin has its maximum length in a NE–SW direction, and is filled by immature siliciclastic sediments interbedded with intermediate to acidic volcanic rocks. Ages of deposition are in the interval between the Neoproterozoic and the Ordovician (Cordani et al., 1974; Sartori and Kawashita, 1985). Early granitoid intrusions and volcanic rocks of shoshonitic affinity are associated with the early stages of molasse sedimentation (640 to 590 Ma; Rb–Sr and U–Pb data; Lima and Nardi, 1998). The later granitoids (e.g., the Lavras and the Caçapava granites) were emplaced in the interval between 590 and 560 Ma (SHRIMP U–Pb data; Remus et al., 1997b).

The Camaqua deposits occur in the central part of a northeast-oriented graben, in the median zone of the Sul-Riograndense Shield (Ribeiro and Fantinel, 1978), inside a local structure called the "Bom Jardim
Window’ (Fig. 3). A simple origin and evolution for the Camaqua basin have been postulated by several investigators (e.g., Loss and Roinsenberg, 1972; Fernandes et al., 1992). The suggested tectonic regimes varied from compressive stress, with production of a marginal basin, to transpressional stress, which allowed the development of a strike-slip basin. A multiple evolution for the Camaqua basin was proposed by Fragoso-César (1980), consisting of a primitive fore-arc basin associated with thrust faults and nappes, which evolved into piggy-back and graben structures under an ultimate tensile stress field.
Fig. 2. Simplified geology of the Sul-Riograndense shield (after Paim and Lopes, 2000).
According to Beckel (1992a), the Camaqua basin was originally a foreland basin that has been disrupted into several piggy-back basins. These evolved afterwards into strike–slip, and finally into graben structures at the end of the Brasiliano cycle.

Despite the great controversy regarding the evolution of the Camaqua basin, the majority of the investigators (e.g., Ribeiro and Fantinel, 1978; Gonzalez and Teixeira, 1980; Fragoso-César, 1980; Paim et al., 1995) concur that the basin was initially marine and progressively changed into a definite continental environment.

2.1. Stratigraphy

The oldest rocks of the region belong to the Bom Jardim Group, divided, from base to top, into two formations, Arroio dos Nobres and Crespos. The Arroio dos Nobres Formation encompasses all the sedimentary rocks of the mine area. The Hilário Member of the Crespos Formation includes amygdaloidal andesite lavas of brown color, associated with regional, northeast-trending faults (Teixeira et al., 1978a,b). The Arroio dos Nobres Formation has been divided into the Mangueirão and the Vargas Members.
the latter being the host for all the disseminated and vein copper mineralization. The Mangueirão Member is more than 2000 m thick, and is composed of interlayered fine-grained sandstone and siltstone, with reddish-brown to greenish-grey colors (Teixeira et al., 1978a,b). The overlying Vargas Member consists of a sequence of immature and arkose sandstone and lithic conglomerate, which has been subdivided into five lithologic units in the mine area (Fig. 3; Bettencourt, 1972; Teixeira et al., 1978a,b; Gonzalez and Teixeira, 1980). The composition and depositional environments of these five units are described below.

2.1.1. The Lower Sandstone
This 350 to 400 m thick unit consists of laminations of alternating pelite–sandstone layers, with minor interbedded conglomeratic lenses. The pelite–sandstone commonly comprises 60-cm-thick tabular layers, showing upward coarsening and grading to the overlying Lower Conglomerate (Gonzalez and Teixeira, 1980). Lenses of fine- to medium-grained sandstone with sigmoidal and climbing ripples occur to the distal portions (Faccini et al., 1987; Veigel, 1989). The conglomerates are grey, greenish-grey, pink, or brownish, and include well-rounded granules and pebbles, with interbedded lenses of cobble material and scarce boulders of granites, quartzites, mylonites, volcanic rocks, schists, quartz and feldspar. The boulders are angular, with low sphericity, attaining up to 60 cm in diameter. The layers show generally upward fining bedding, or can be massive. Clast orientation is commonly parallel to the stratification, which is marked by tabular, medium- to fine-grained, laminated sandy layers (Faccini et al., 1987; Veigel, 1989). The whole sequence exhibit upward coarsening, but the contact with the Middle Sandstone is transitional (Veigel, 1989). According to Faccini et al. (1987), the Lower Conglomerate represents the distal facies of an alluvial fan.

2.1.2. The Lower Conglomerate
This unit is 120 m thick, and comprises a sequence of immature and arkose sandstone and lithic conglomerate, which has been subdivided into five lithologic units in the mine area (Fig. 3; Bettencourt, 1972; Teixeira et al., 1978a,b; Gonzalez and Teixeira, 1980). The composition and depositional environments of these five units are described below.

2.1.3. The Middle Sandstone
This unit is 20 to 25 m thick and comprises lenticular clastic beds, starting with basal conglomeratic layers, and interrupted by frequent channel deposits. These are 2 to 4 m wide and 50 cm thick, filled with coarse- to fine-grained, angular to subangular, greenish to brownish sandstone displaying cross-bedding. Sandstone layers with sparse ripple marks occur at the top of the sequence. The transition from this sequence to the Upper Conglomerate is marked by upward coarsening and thickening of the conglomeratic layers, which characterize a progradation cycle (Faccini et al., 1987; Veigel, 1989). The Middle Sandstone is interpreted as a fluvial sediment deposited on a deltaic front (Faccini et al., 1987).

2.1.4. The Upper Conglomerate
This unit is more than 200 m thick and is composed of poorly-sorted, coarse- to medium-grained conglomerate (10 cm to 1 m; Gonzalez and Teixeira, 1980). The clasts are composed of rock fragments (granite, quartzite, rhyolite, mylonite, cataclasite, mica–schist, quartzofeldspathic and sedimentary rocks), besides feldspar and quartz grains. The matrix is arkositic in composition (Teixeira et al., 1978a; Gonzalez and Teixeira, 1980; Teixeira and Gonzalez, 1988; Veigel, 1992). Veigel (1989) described some shallow water features in this sequence, such as mud cracks in thin muddy layers, which are interbedded within the Upper Conglomerate at Uruguai mine. The contact of this sequence with the overlying Upper Sandstone is transitional. The Upper Conglomerate represents the proximal facies of an alluvial fan (Faccini et al., 1987).

2.1.5. The Upper Sandstone
This unit is 2000 m thick and consists of parallel-laminated alternating pelite and sandstone layers with climbing cross-bedding and local conglomerate lenses. The sequence grades vertically into finer sediments, and shows interfingered lenticular, sigmoidal sandstones which are locally associated with
cross-bedded conglomeratic sandstone (Faccini et al., 1987; Veigel, 1989). The facies vertical succession indicates a typical progradational cycle, with coarsening and thickening upwards. There is no copper mineralization associated with the Upper Sandstone, which has been interpreted as a partly subaerial (?) flysch-like delta front (Faccini et al., 1987).

3. Mineralization

The Camaquã copper mine contains the Uruguai and the São Luiz orebodies (Fig. 4). The ore is formed by (1) massive sulfides in veins, pipes and stringers, and (2) disseminated sulfides (Leinz and Almeida, 1941; Bettencourt, 1972; Gonzalez and Teixeira, 1980; Teixeira and Gonzalez, 1988; Veigel, 1989; Veigel and Dardenne, 1990; Lima, 1998; Laux, 1999; Laux and Lindenmayer, 2000a,b; Ronchi et al., 2000).

3.1. Primary ore

The primary sulfide mineralogy includes chalcopyrite, bornite, chalcocite, and pyrite. Other sulfides, e.g., wittichenite, idaite, molybdenite and carrollite, as well as native gold, have been identified in low concentrations. The vein and disseminated ore have a similar mineralogy, although gold occurs exclusively in the veins. Chalcopyrite predominates in veins and in the disseminated sulfide together with chalcocite (Bettencourt, 1972; Gonzalez and Teixeira, 1980; Teixeira and Gonzalez, 1988; Veigel, 1989; Veigel and Dardenne, 1990; Lima, 1998; Laux, 1999; Laux and Lindenmayer, 2000b; Ronchi et al., 2000). Gold and silver are mostly associated with chalcopyrite, bornite, pyrite and hematite (Teixeira, 1978; Ribeiro, 1991; Lima, 1998; Laux, 1999; Laux and Lindenmayer, 2000b).

3.2. Veins

The most important ore is contained in veins, up to 2 m thick, controlled by subvertical, N50°W to N80°W trending faults, which outside the ore zones are infilled by quartz, hematite, barite and clay minerals (Bettencourt, 1972; Teixeira et al., 1978b; Gonzalez and Teixeira, 1980; Teixeira and Gonzalez, 1988; Veigel, 1989; Ribeiro, 1991). The local sedimentary rocks strike N20–30°E and dip 30–40°.
to NW, which establishes the discordant relationship of the vein system with the host lithologies. Brecciation and jointing provided the means for development of vein stockworks in the central part of the orebodies (Bettencourt, 1972; Teixeira et al., 1978a; Teixeira and Gonzalez, 1988; Ribeiro, 1991; Laux, 1999; Laux and Lindenmayer, 2000b; Ronchi et al., 2000). In the ore zone, the vein margins are marked by an intensive hydrothermal alteration represented by silicification, chloritization, kaolinization and sulfidation, the last containing the disseminated ore. The vein mineralogy consists of quartz, pyrite, chalcopyrite, bornite, hematite and gold. Calcite and barite post-date the sulfide minerals and sealed the veins.

3.3. Disseminated ore

The disseminated ore is mainly hosted in the upper part of the Lower Conglomerate and within the Middle Sandstone, and weakly within the other formations, except in the Upper Sandstone where it never occurs. This type of mineralization is generally present in conglomerates and sandstones and predominates at the top the Lower Conglomerate, along the contact with the Middle Sandstone (Leinz and Almeida, 1941; Bettencourt, 1972; Teixeira et al., 1978a; Gonzalez and Teixeira, 1980; Bonhome and Ribeiro, 1983; Teixeira and Gonzalez, 1988; Veigel, 1989; Veigel and Dardenne, 1990; Ribeiro, 1991). The disseminated ore is interpreted by many authors as part of the hydrothermal alteration zones that developed around the veins, representing the lateral manifestation of the fault-controlled mineralization, with the sulfides occupying the secondary porosity of the host rocks, closer to the veins. This is supported by the close association of the sulfides with the chloritic or hematitic haloes which surround fault-controlled vein mineralization; sulfide abundance decreasing away from the veins, (Leinz and Almeida, 1941; Bettencourt, 1972; Laux, 1999; Laux and Lindenmayer, 2000b; Ronchi et al., 2000), as well as by the presence of the same paragenetic succession in both disseminated and veined ore. The main ore minerals are idiomorphic pyrite and chalcopyrite, always associated with chlorite and quartz. Pyrite is partly replaced by chalcopyrite, bornite and hematite. All of these minerals are occasionally replaced by digenite and covellite. Wittichenite occurs in association with chalcocite, which replaces chalcopyrite. Hematite is a late phase, occurring as elongated, tabular crystals or in aggregates. Bornite is observed as rims around chalcopyrite, also indicating substitution (Laux, 1999; Laux and Lindenmayer, 2000b; Ronchi et al., 2000). Chalcocite, digenite, covellite, wittichenite and hematite are minor phases.

According to Veigel (1989) and Veigel and Dardenne (1990), the ore assemblage formed according in the following five stages: (1) an eogenetic phase involving mechanical infiltration of clay minerals, alteration of feldspar and Fe–Mg minerals, formation of Fe–Ti oxide pseudomorphs, precipitation of hematite, and secondary growth of quartz; (2) a low temperature mesogenetic phase with secondary growth of quartz and feldspar; (3) higher temperature mesogenetic phase causing albitionization of feldspar, substitution of feldspar by Fe–Ti oxides, quartz and apatite, and precipitation of ankerite; (4) concomitantly and subsequently prograde conversion of clay minerals into illite and/or chlorite, along with neo-formation of chlorite, precipitation of pyrite, and widespread calcite cementation. Both pyrite and calcite replaced silicate minerals, with growth of Cu–Fe sulfides, precipitated in the secondary porosity or replaced the previous phases according to the sequence chalcocite, bornite, chalcopyrite; and (5) a telogenetic phase, after uplift through development of a paleo-oxidation/cementation zone, leading to replacement of earlier-formed sulfides by hematite, bornite, chalcocite and covellite.

3.4. Paragenetic sequence

Formation of primary vein and disseminated ore could be the result of a single or multiple phases of mineralization. Quartz was the first mineral to form in the veins, followed by pyrite, chalcopyrite and bornite; carbonate and barite were deposited towards the end of the process. Pyrite is widely distributed as euhedral or anhedral crystals, normally corroded and/or mechanically deformed. Chalcopyrite is the most abundant sulfide phase, occurring in massive or disseminated crystal aggregates, regularly displaying brittle fractures infilled by gangue minerals, as well as bornite and chalcocite. Bornite appears in two main paragenetic positions: (i) replacing or exsolved in chalcopyrite within myrmekite-like intergrowths, and
(ii) in crystal aggregates that compose the cement for some mineralized breccias. Chalcocite occurs in massive concentrations, or replacing chalcopyrite and bornite in the external zone of the grains. Hematite occurs in tabular or drop-like grains arranged around pyrite–chalcopyrite aggregates surrounded by bornite and chalcocite. This texture suggests that hematite formed from iron released by the substitution of pyrite–chalcopyrite by bornite–chalcocite. Barite composes tabular crystals presenting polysynthetic twinning, or radiaxial fibrous textures. Calcite, together with barite, in fills the later developed fractures, which intersect all sulfides, as well as the earlier-formed gangue minerals (Leinz and Almeida, 1941; Bettencourt, 1972; Laux, 1999; Laux and Lindenmayer, 2000a,b; Ronchi et al., 2000).

The ore in the Uruguai Mine is represented by massive sulfides in veins, constrained by two main fault zones. There are also several vein-type mineralizations, controlled either by recurrent fracturing and/or by compositional changes in the mineralizing fluids. In one sector of the Uruguai mine, three mineral assemblages were identified containing copper sulfides (A1—chalcopyrite–pyrite, A2—chalcopyrite–bornite–hematite, and A3—bornite–chalcopyrite–chalcocite–gold ore), which are associated with two intersecting fault systems (Laux, 1999; Laux and Lindenmayer, 2000b). The older fault (F1) controlled the appearance of the first ore assemblage (A1), and the younger fault (F2) controlled the later assemblage (A2). A distinct third assemblage (A3) was formed when the A2 assemblage locally overprinted the pre-existing A1 assemblage.

3.4.1. Assemblage A1 (quartz–albite–chlorite–pyrite–chalcopyrite ore) associated with F1

The F1 fault strikes N40°W and dips 78° to NE. The rocks in the fault zone have been silicified, and totally or partially replaced by quartz, albite, chlorite, pyrite and chalcopyrite. The A1 assemblage occurs in veins (AV1) or disseminations (AD1). The AV1 zone is about 15 m thick, and consists of this replacement mineral association along with a stockwork of veins and veinlets of quartz, chalcopyrite, pyrite, chlorite, and always associated with a greenish chloritic alteration halo, in which chlorite may make up ~90% of the host rock. The disseminated ore is contained by the chlorite-dominant altered zone and consists of pyrite, chalcopyrite and minor bornite. The AD1 zone extends beyond the AV1 zone and is composed of chlorite, pyrite and chalcopyrite. It is divided into an internal, sulfide-rich, 15 m thick halo and an external, sulfide-poor, 25 m thick halo along the faults.

3.4.2. Assemblage A2 (hematite–quartz–bornite–chalcopyrite ore) associated with F2

The F2 fault strikes N50°W and dips 78° towards NE. The A2 assemblage may be veined (AV2) or brecciated (AB2). The brecciated AB2 assemblage marks the fault zone, with a maximum thickness of 10 m. The AB2 is composed of angular fragments, up to 10 cm in size, of bornite, chalcopyrite, pyrite, and unaltered or chloritized host rock. The fragments are cemented by hematite, quartz, bornite and chalcopyrite. Surrounding the fault zone there is a veined AV2 zone that can be some 10 m thick. The AV2 is made of a network of veins and veinlets of quartz and hematite. Reddish colors, given by the presence of hematite, are typically associated with this late assemblage formed by quartz, chalcopyrite, bornite and hematite with minor digenite, pyrite, molybdenite and kaolinite. Bornite is the most common Cu–Fe sulfide in the brecciated ore. Hematite is very important in the brecciated ore, suggesting increased oxidation of the mineralizing fluids.

3.4.3. Assemblage A3 (bornite–chalcopyrite–gold–pyrite ore)

The A3 assemblage is characterized by the highest Cu contents, because it is located in the intersection of both fault systems. The assemblage is composed of bornite and chalcopyrite with minor gold and pyrite. The substitution of pyrite by chalcopyrite and the latter by bornite indicates progressive enrichment in Cu and decreasing of the sulfur content in the ore minerals. Gold is observed as drop-like inclusions in pyrite, bornite, hematite and chalcopyrite. The paragenetic sequence of this sector of the Uruguai mine is shown in Fig. 5.

3.5. Age of mineralization

The age of mineralization is still uncertain. K–Ar isotopic analyses on whole rock yielded ages between 457 and 474±11 Ma for clay minerals (illites) from
the São Luiz and Uruguai veins, interpreted as the minimum age of vein formation (Bonhome and Ribeiro, 1983). On the other hand, Biondi (personal communication) reported K–Ar isotopic ages of $515\pm12$ Ma for chlorite from alteration haloes next to the veins; $538\pm7$ Ma for sericite from alteration haloes far from the veins, and $350\pm8$ Ma for clay minerals from the veins. Recent Pb–Pb isotopic systematics applied to the Camaquã sulfides, coupled with U–Pb geochronological data for the main granitoid intrusions (see below), have constrained the age of mineralization, both disseminated and veined, to the period of 590 to 560 Ma ago (Remus et al., 1997a,b, 1999). These recent data suggest that the Camaquã Mine sulfides are related to a distal hydrothermal–magmatic system associated with granitoid emplacement. It also suggests that the Cu-sulfides are genetically related to a magmatic–hydrothermal system coeval to the granitoids.

3.6. Supergene ore

A variety of supergene minerals, including covellite, digenite, antlerite, chrysocolla, brochantite, cuprite, malachite, azurite, tenorite, and native copper, are mentioned from the weathering zone. Traces of gold and silver have also been found in the oxidized zone, near the surface. For detailed descriptions the reader is referred to publications by Leinz and Almeida (1941), Bettencourt (1972), Teixeira (1978), Gonzalez and Teixeira (1980), Teixeira and Gonzalez (1988), Veigel (1989), Veigel and Dardenne (1990), and Ribeiro (1991).

4. Geochemistry

Relatively little high quality geochemical data are available on the Camaquã basin, including the Camaquã mine. These data were discussed in the papers of Laux et al. (1998), Laux (1999), Laux and Lindenmayer (2000b) and Ronchi et al. (2000). A short overview of the data is given below.

4.1. Lithogeochemistry

The lithogeochemical studies aimed at two main objectives: (1) determination of the source of the conglomerates and sandstones of the Vargas formation, and especially those that host the mineralization; and (2) investigation of the trace metal association in the ore, as well as their relationships with the mineralizing fluids.

Rare-earth elements (REE) were used as indicators for the provenance of the clastic sequence by Laux et al. (1998) and Laux (1999). The authors analyzed
several least altered samples of medium-grained sandstones from the Uruguai mine. The REE patterns found are very similar to the Post-Archean Average Australian Shales—PAAS (Fig. 6), European Shales—ES, and North American Shales Composite—NASC (Taylor and McLennan, 1985). This uniform pattern can be interpreted as the result of an efficient mixture of various source rocks, or as recycled material during the sedimentary process (e.g., Nance and Taylor, 1976; Taylor and McLennan, 1985; McLennan et al., 1984, 1990). The total REE content (∑REE) of the analyzed sandstone is lower than that of PAAS, and this is probably because of the greater dilution by SiO₂, as a result of coarser grain size. The negative Eu anomaly is also larger for the sandstone. The association of the Eu depletion with higher Zr contents along with lower concentrations of Cr, Nb, Y, and V, indicate the contribution of a possible granitic source for the sediments of the Uruguai mine. The U concentration is relatively high (28 ppm) for sedimentary rocks. Uranium also displays a good positive correlation coefficient with Ag (ρ=0.82), Ni (ρ=0.78) and Cu (ρ=0.77), indicating a strong linkage with the mineralizing fluids. A strong correlation (ρ=0.83) between Cu and Ag is observed; gold correlates well with both metals.

The REE pattern for sedimentary rocks of the Uruguai mine closely matches the average REE pattern of the Acampamento Velho volcanic rocks (Fig. 7b). The latter is distinct from that of volcanic rocks from Rodeio Velho and Hilário members (Fig. 7c,d). The Camaquã Mine and Acampamento Velho volcanic rocks show parallel fractionation patterns, as well as similar negative Eu anomalies, although the sandstones are less enriched in REE, probably because of quartz dilution (Fig. 7b). This led Laux et al. (1998) to interpret these volcanic rocks as the main source of the host rocks of the Uruguai mine. This is also confirmed by the more recent reviews of stratigraphy in the area, which demonstrated that the Acampamento Velho volcanic rocks are older than the Uruguai mine sandstones (Paim and Lopes, 2000), as had been considered previously.

4.2. Mineral chemistry

Laux and Lindenmayer (1998), Lima (1998), Laux (1999) and Ronchi et al. (2000) analyzed chlorite minerals close to the fault zone in the Camaquã mine, and identified chamosite as the major phase, with secondary clinochlore, in concordance with the classification of Bailey (1980). Formation temperatures of chamosite were between 330 and 190 °C (Lima, 1998; Laux and Lindenmayer, 1998; Ronchi et al., 2000), indicating a hydrothermal, rather than a ‘red-bed’ origin. In the cationic plots of Laird (1988), the analytical data fall in the field of chlorites derived from metamorphosed pelitic rocks (Fig. 8). This probably indicates a low water–rock ratio during chloritization, characterizing a rock-dominated alteration regime. It is worth noting that some optically identified chlorites showed high alkali contents (>0.5 wt.%), especially high K. This could reflect an episode of chlorite formation by alteration of previous high-K mineral phases, or, alternatively, be evidence for partial chlorite–phengite transition. Either hypothesis points to an increase in K-activity during the mineralizing event (Laux, 1999; Laux and Lindenmayer, 1998).

Although pyrite and chalcopyrite appear homogeneous, the first always contains traces of Co, As, Hg and Au, while the latter holds frequently minor amounts of Hg and Au. Bornite always contains Co, Ag and Au, whereas digenite has significant Ag; both explain the highly positive Cu–Ag correlation among the Cu-sulfides. Results of sulfide microprobe analyses indicated that bornite and hematite hold the highest concentrations of Au, which can attain 0.25 ppm.

![REE patterns of the Uruguai Cu mine compared with those of the Santa Maria Pb–Zn mine (SM). After Laux et al. (1998). PAAS, ES and NASC (Taylor and McLennan, 1985). Normalizing factors are those of Nakamura (1974).](image-url)
wt.% Au in the case of hematite. The atomic proportion of gold shows positive correlation with the Cu/S ratio of the sulfides. Native gold is found in association with bornite–hematite or chalcopyrite–pyrite assemblages. Inclusions of gold in bornite display higher Fe and Ag concentrations, whereas
gold in other associations show higher Cu and S values. The weight Au/Ag ratio is always larger than 4, which excludes electrum from the ore association (Laux and Lindenmayer, 2000b; Laux, 1999).

5. Isotope data

5.1. Sulfur isotope data

Sulfur isotope analyses in sulfides and sulfates from Camaquã Mine show a bimodal distribution, $\delta^{34}$S_CDT values for sulfides around $0\%e$ and sulfates around $+13\%e$ (Fig. 9). Vein-type pyrite, chalcopyrite and bornite (Bettencourt, 1976; Beckel, 1992b; Beckel et al., 1991; Remus et al., 1997a, 1999) showed little variation ($\delta^{34}$S to $+5\%e$). Such narrow ranges are usually considered to indicate a magmatic sulfur source, although data on sulfides from the intrusive and/or volcanic country rocks would be necessary for comparison. Nevertheless, this narrow range of $\delta^{34}$S values argues against the proposed red-bed model for Camaquã Mines (see below), since according to Ohmoto and Goldhaber (1997), the $\delta^{34}$S values for Cu-sulfides associated with red-bed should show a wide range, from $0\%e$ to $-20\%e$.

The $\delta^{34}$S_CDT values of 10.30$\%e$ to 14.24$\%e$ for barite indicate that sulfide and sulfate deposited in apparent non-equilibrium fractionation. Possible processes causing apparent disequilibrium relationships are rapid cooling and/or an increase in the concentration of $SO_4^{2-}$. The latter may be due to oxidation, hydrolysis of SO$_2$, and mixing of a sulfate-rich fluid (Ohmoto and Goldhaber, 1997).

Precipitation of hematite, along with the substitution of pyrite by chalcopyrite, suggest that an increase in $SO_4^{2-}$ caused by oxidation played an important influence on barite precipitation and on sulfur fractionation. The absence of major shifts on sulfide $\delta^{34}$S to more negative values suggests that mixing with sulfate-rich solutions might have caused the referred oxidation (Ohmoto and Goldhaber, 1997). In addition to that, the very low salinities found in late calcite fluid inclusions (Ronchi et al., 2000) also suggest fluid mixing.

5.2. Lead isotope data

Remus et al. (1997a) analyzed Pb isotopes in chalcopyrite, pyrite and bornite from the Camaquã Cu Mine, Santa Maria (Cu–Zn) deposit and sandstones from the Arroio dos Nobres Formation (Fig. 10). The results plot conformably with the reference isochron of 592 Ma built for regional igneous rocks (SHRIMP U–Pb zircon data; Remus et al., 1997b) specifically the Lavras granite and the andesite of the Hilário Member. Based on Pb/Pb isotopic constraints, Remus et al. (1997b) concluded that the initial Pb at 590 Ma is very primitive in comparison with the typical lithosphere growth curve of Stacey and Kramers (1975). The sub-parallel array of these data suggests that Pb in sedimentary rocks and sulfides had a similar
source, and that the mineralization may relate to shoshonitic plutonism at ~592 Ma, or alternatively to the 560 Ma Lavras-Caçapava granite (Remus et al., 1999).

6. Fluid inclusion studies

No systematic studies of fluid inclusions have been carried out on the ore from the Camaquã mine. In the veined ore, quartz predates or is coeval to the sulfides; calcite and barite postdate the mineralization. Hence, the temperatures obtained in carbonate and barite most likely represent closure of the mineralizing hydrothermal system.

Microthermometric measurements in fluid inclusions of quartz veins from diverse generations indicated homogenization temperatures varying from 236 to 60 °C, although primary inclusions are very difficult to identify (Lima, 1998; Ronchi et al., 2000). Fluid inclusion in carbonate displayed homogenization temperatures between 150 and 50 °C, whereas the homogenization temperatures in barite are below 80 °C (Bettencourt, 1976; Ronchi et al., 2000). According to Ronchi et al. (2000), primary fluid inclusions in quartz and calcite in sulfide veins are aqueous and contain only a single component, indicating homogenization temperatures as low as 50 to 60 °C. The fluid salinity varies largely from one mineral to another in the mineralized veins: 2.7 wt.% eq. NaCl to near pure water in quartz; 14 wt.% eq. NaCl in carbonate (Beckel et al., 1991); 8 to 10 wt.% eq. NaCl in barite (Bettencourt, 1976). The implications of these data are still poorly understood. Further studies on fluid inclusions coupled with stable isotope analyses are necessary for a better understanding of the fluid evolution in the hydrothermal system.

7. Metallogenic hypotheses

7.1. The magmatic–hydrothermal model

Carvalho (1932) was the first to describe the Cu mineralization, followed by Teixeira (1941) and Leinz and Almeida (1941). These authors ascribed the genesis of the Camaquã sulfides to a high temperature magmatic–hydrothermal process. The interpretation was purely based on field relationships, involving fracturing, veining, and development of hydrothermal alteration aureoles containing sulfide dissemination. The hypothesis considers sulfides to have precipitated from hot fluids derived from cooling magmatic rocks (Leinz and Almeida, 1941). Accordingly, the granitoid plutons, or even the volcanic rocks of the Hilário Member might have been the sources for the mineralizing fluids. With some variations, this model experienced its maximum popularity in the late 1970s, also supported by the observations of Bettencourt (1972, 1976).
Some aspects of the magmatic–hydrothermal hypothesis have been considered by Beckel (1992b), who proposed a porphyry-Cu model for the Camaqua deposits. According to this author, the earlier mineralizing fluids were rich in K, Na, Ca, Fe, Mg, SiO₂ and H₂S. A vertical zoning was created, with Cu-sulfides at the base and Pb–Zn sulfides at upper levels. The hydrothermal system for the Camaqua orebodies could have had a diameter in excess of 6 km. Nevertheless, the typical alteration patterns described for porphyry-Cu systems (e.g., Lowell and Guilbert, 1970) are absent in the Camaqua mine. Additionally, fluid inclusion data and chlorite geothermometry indicated temperatures of 330 to 190 °C for the earlier stages, and 150 to 70 °C for the later stages of vein formation. These low temperatures, allied to the low salinity of the fluid inclusions in quartz veins, give little support to the porphyry-like high-temperature magmatic–hydrothermal hypothesis proposed by Beckel (1992b).

7.2. The sedimentary model

Initially syngenetic, the sedimentary hypothesis evolved toward a diagenetic model after the discovery, in 1978, of the Santa Maria Pb–Zn–Cu mineralization, a stratiform, sandstone-hosted deposit ~3 km SW of the Camaqua mine (Teixeira et al., 1978a). Using the sedimentary model as a prospecting guide, several smaller occurrences of Cu mineralization were discovered. Among these were (a) the Cerro dos Martins occurrence, with chalcocite and malachite hosted by grey siltstone; (b) disseminations of chalcopyrite and pyrite hosted by the Mangueirão Member, underneath the Camaqua orebodies; (c) carbonate-rich veinlets containing chalcopyrite and pyrite, along with mineralized pebbles in sedimentary beds within the Camaqua mine and all around the basin; and (d) chalcopyrite and pyrite disseminated in other areas of the Camaqua basin, such as the Cerro das Ovelhas, Cerro da Angelica, and Salsinho occurrences (Santos and Chaban, 1978).

As described above, Veigel (1989) and Veigel and Dardenne (1990) envisaged a complex diagenetic evolution for the Camaqua sediments and proposed a ‘red-bed copper model’ for the Camaqua mineralization. The Camaqua basin is made of high energy, delta-fan, dominated sediments. These are characteristics contradictory to a syngenetic/diagenetic model, which requires a low energy, marine sequence for deposition (Ohmoto et al., 1990). The absence of a distal evaporite facies (sabkha) is a further argument, as is the fact that both the S and Pb isotope data strongly suggest a magmatic source for both. Moreover, the ‘red-bed copper model’ is weakened by the lack of framboidal pyrite and gypsum, which characterize reduced and saline environments and may develop stratiform deposits (e.g., Haynes, 1986; Brown, 1993). Last but not least, there is an inverted sulfide zoning in the Camaqua Mine: pyrite–chalcopyrite is mostly in conglomerates, whereas bornite–chalcocite is disseminated in sandstones and siltstones.

7.3. The epithermal model

During the last six years a hydrothermal/epithermal hypothesis has prevailed. This model was supported by the clear structural control of the copper mineralization in discordant veins and stockworks, allied to the moderate range of temperatures, and to the low salinity of the (Au-bearing) mineralizing fluids (Lima et al., 1997; Laux et al., 1998; Laux and Lindenmayer, 2000b; Remus et al., 1999, 2000). The term epithermal is applied to hydrothermal ore deposits formed 1 to 2 km beneath the Earth’s surface, in the temperature range of <150 to near 300 °C. Epithermal systems are characterized by low salinity fluids (<5 wt.% eq. NaCl) and generally incorporate a substantial contribution of meteoric water. Fluid circulation is induced by the heat originated from a cooling intrusive body, or from a hot volcanic source, as in many modern geothermal systems (Roedder, 1984; Bodnar et al., 1985). Epithermal deposits are classified into: (1) high-sulfur, or acid-sulfate type, characterized by advanced argillic (kaolinite) to argillic (illite) alteration with abundant hypogene alunite, minor to absent chlorite or adularia, and a vein mineralogy of enargite plus pyrite; and (2) low-sulfur, or adularia-sericite type, characterized by vein adularia and sericite, with presence of chlorite and illite (Hayba et al., 1985; Berger and Henley, 1988; Bates and Jackson, 1985). The acid-sulfate type develops in connection with geothermal systems related to volcanic complexes, from acidic solutions containing residual volatile magmatic components. These are generally calc-alkaline magmatic arcs, with predominance of ande-
sites–dacites formed in back-arc zones. These deposits show a typical alteration zoning that consists, from center to the border of advanced argillic (generally silicified) sericitic, and finally propylitic alteration (e.g., Oyarzún, 1991). The adularia–sericite type develops in association to geothermal systems, where meteoric water mixes with deeper hot (250 to 350 °C) reduced, almost neutral (pH 5.5 to 6.5) groundwater, which contains high Cl and CO2 and is depleted in sulfur. Such deposits are formed in connection with extensional faults, and with magmatic activity varying from andesite–rhyolite to trachyandesite–alkalic rhyolite. Metal contents are variable but typically characterized by low Cu concentrations and low Au/Ag ratios; ore elements also include As, Sb, Hg, Pb and Zn (Berger and Henley, 1988). The alteration pattern consists of a sericitic zone enclosing a silicified section close to the vein. The sericitic zone grades outwards into a propylitic zone (Oyarzún, 1991).

Some major features of epithermal-type deposits, including complex mineral parageneses (including sulfates, selenides, tellurides, sulfosalts, etc.), typical alteration patterns and the appropriate tectonic environment, are conspicuously absent from the Camaquã orebodies. The structural control of the mineralization, the occurrence of superimposed mineralizing events, the temperature of deposition of the early ore minerals (330 to 190 °C), the sulfur isotope ratios (near 0‰ for the sulfides), and the moderate to low salinity fluid inclusions more likely indicate a hydrothermal–epithermal origin or, alternatively, a distal magmatic–hydrothermal deposit.

8. Discussion and conclusions

Mineral deposit modeling, whether empirical (descriptive) or genetically-linked (theoretical), consists of ordering a systematic set of data, thus delineating the basic features of certain classes of mineral deposits (e.g., Cox et al., 1986). Theoretical models are needed in mineral exploration, because they warrant the prediction of meaningful geological features, hence contributing to the improvement of exploration strategy. Frequently however, the geological data are far from adequate for the development of a single consistent model. In other situations, a studied deposit does not fit any current model, because of its special or unique characteristics. This seems to be the case for the Camaquã deposits. As discussed above, three major genetic models have been applied, each acceptable during a given mining period and/or for a particular sector of the mine. These hypotheses are evaluated in comparison with the idealized model of Sillitoe (1995) for mineral deposits and hydrothermal alteration related to the emplacement of an intrusive body.

Available data clearly indicate that the Cu–(Au)–(Ag) Camaquã primary ore is fault controlled. Hydrothermal alteration haloes are narrow (ca. 50 m around the veins) indicating a relatively low water–rock ratio. Disseminated sulfide mineralization infills the secondary porosity of the sedimentary rocks, and is best developed along some lithologic contacts. The paragenetic succession was formed during two main mineralizing events: the first relatively reducing, deposited pyrite, chalcopyrite, quartz, albite, chlorite accompanied by traces of carrollite and molybdenite; the second more oxidizing, deposited chalcopyrite, bornite, digenite, hematite, gold, silver, quartz, kaolinite, phengite (±wittichenite). Calcite and barite veins appeared by the end of the mineralizing process, contributing to fracture sealing. Low to moderately saline and hot mineralizing fluids carrying Fe, Cu and S were responsible for the first stage of sulfide deposition. During the second stage, the increase in oxygen activity probably caused by SO42−/CO3 mixing, as suggested by the sulfur isotope and fluid inclusion data, was allied to decreasing temperatures that resulted in SO42− becoming the dominant sulfur species (e.g., Rimstidt, 1997). Eventual decrease of the lithostatic stress, associated with fracturing during the regional uplift and denudation may have caused barite and calcite deposition in veins.

The Pb isotopic signature in sulfides indicates very primitive Pb, suggesting a crustal, possibly granitic, source (Remus et al., 1999). Metal remobilization and deposition were probably related to magmatic–hydrothermal events that occurred by the end of the Brasiliano cycle, possibly associated with the Lavras–Caçapava granitoid emplacement. This interpretation is based on sandstone provenance discussed by Laux et al. (1998) and on stratigraphical reviews (Paim and Lopes, 2000), which demonstrated that the sedimentary host rocks of the Camaquã Mine did not exist by the time of the Hilário magmatism.
In respect of its overall characteristics, the Camaquã Mine may be considered as a hydrothermal type deposit, which resulted from the infiltration of distal magmatic fluids into a relatively oxidized elastic succession.

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