SULFUR, CARBON, OXYGEN AND STRONTIUM ISOTOPIC EVIDENCES FOR THE GENESIS OF THE HYDROTHERMAL ZINC NON-SULFIDE AND SULFIDE MINERALIZATIONS IN THE VAZANTE, AMBRÓSIA AND FAGUNDES DEPOSITS, MG, BRAZIL

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INTRODUCTION

The Vazante-Paracatu region (Fig. 1), situated in the northwest part of Minas Gerais State, is host to the most important zinc district known in Brazil. Within this region, which extends up to 250 Km long in N-S direction, various zinc deposits are described, such as, Vazante, Morro Agudo, Ambrósia and Fagundes, and several zinc occurrences. The deposits are hosted by metapelitic-dolomitic sequences of the Vazante Group (Dardenne et al., 1998) and have contrasting geological characteristics.

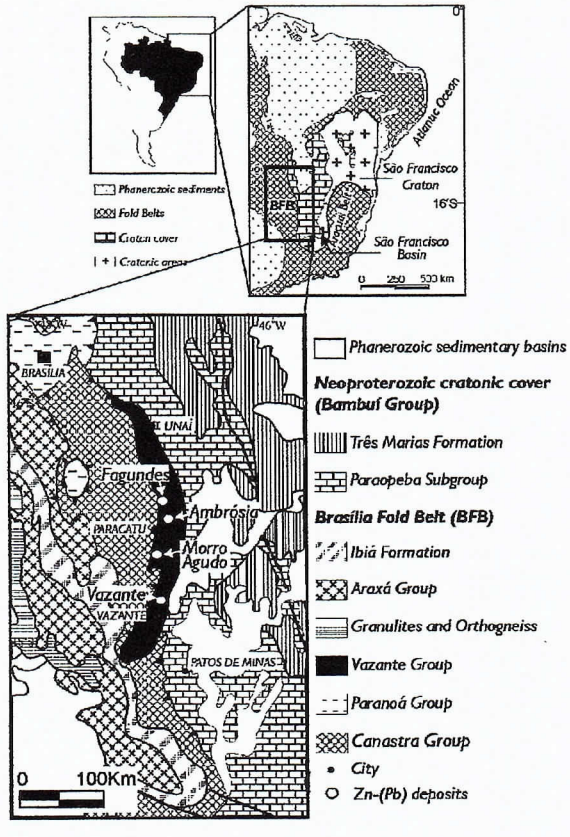

Figure 1. Geological setting of the Vazante-Group (Dardenne & Schobbenhaus, 2001).

The Vazante deposit is known as the major example of a new deposit class, named as carbonate-hosted willemite deposits or non-sulfide zinc deposits (Hitzman, 2001). The Vazante main ore is made of willemite (Zn_2SiO_4), dolomite, quartz, siderite, hematite, barite, franklinite, zincite, magnetite and Zn-chlorite (Monteiro, 1997). Small sulfide bodies composed mainly by Cd-rich sphalerite and galena occur tectonically imbricate with the willemitic ore and with the intensely hydrothermalized host rocks within the Vazante Fault.

The zinc ore from Morro Agudo, Fagundes and Ambrósia, however, are composed mainly of sphalerite, galena, pyrite, marcasite, dolomite and quartz. The mineralization styles in Fagundes deposit are late diagenetic, related with open space filling, and epigenetic, characterized by a late fissural stage. In Ambrósia deposit the predominant mineralization style is epigenetic. Several stages of mobilization of preexisting ore, related to ductile-brittle and brittle deformation, are common in both deposits (Monteiro, 2002).

These distinct mineralization episodes share a common evolutionary history related to diagenesis and deformation of the Vazante Group, during the Neoproterozoic.

The present paper aims to document isotopic variations related to well-constrained paragenetic sequence and to profile the geochemical processes associated with the genesis of non-sulfide and sulfide zinc deposits of the Vazante-Paracatu region.

SULFUR ISOTOPES

In Vazante deposit, sulfides show a narrow range of $\delta^{34}S$ values between +11.8‰ and +14.4‰ (Monteiro, 1997). This is a distinct sulfur isotopic signature in relation to sulfides from the other deposits in the district, such as Ambrósia ($\delta^{34}S$ = –5.4‰ to +22.2‰) and Fagundes ($\delta^{34}S$ = +14.8‰ to +36.3‰), which display a remarkable wide sulfur isotopic variation and a complex isotopic distribution related to the textural and paragenetic evolution of each deposit.

In Fagundes, early colloform sulfides are ^{34}S-enriched (up to +36.3‰), whereas mobilized sulfides and late epigenetic sulfides display lower $\delta^{34}S$ values ($\delta^{34}S$ = +14.8‰).

In Ambrósia, where the epigenetic style of mineralization is predominant, the same tendency of

isotopically lighter values toward the late sulfide phases is observed ($\delta^{34}S$ = +12.2‰ to -5.4‰).

In these deposits, a relationship between $\delta^{34}S$ values and minor elements in sphalerite is also observed. The Fagundes early sphalerite is characterized by the highest $\delta^{34}S$ values, low average iron content (0.42 %) and low Zn/Cd ratio (= 140). The decrease in $\delta^{34}S$ values in late sphalerite is accompanied by slight increase of average iron content (0.56 %) and in Zn/Cd ratio (= 226). Sphalerite associated with epigenetic mineralization of Ambrósia is ^{34}S-depleted, iron-rich (until 1.57%) and has the highest Zn/Cd ratio (=1510).

In the Morro Agudo deposit, Cunha (1999) and Misi et al. (1999) described a wide range of sulfur isotopic values ($\delta^{34}S$ = -8.7‰ to +40.0‰), which are related to the deposit geometry and morphology. The highest values have a spatial relationship with deeper ore levels and with a fault zone considered as a feeder zone for mineralizing fluids.

OXYGEN AND CARBON ISOTOPES

Previous studies on the Vazante hydrothermal carbonates indicate that the gangue carbonates related with sulfide ore bodies and with willemitic ore reflect two different covariant trends. The first is characterized by ^{18}O-enrichment accompanied by ^{13}C-depletion. The trend related with the willemitic ore is characterized by decrease of $\delta^{18}O$ and $\delta^{13}C$ values (Monteiro, 1997; Monteiro et al., 1999).

The carbon and oxygen signature of the gangue carbonate related to Vazante sulfide ore ($\delta^{18}O$ = +21.58‰ to +31.85‰; $\delta^{13}C$ = -5.94‰ to +1.66‰) are quite different of those of Fagundes ($\delta^{18}O$ = +12.4‰ to +19.9‰; $\delta^{13}C$ = -2.3‰ to –0.2‰) and Ambrósia ($\delta^{18}O$ = +15.1‰ to +20.3‰; $\delta^{13}C$ = -2.3‰ to + 0.3‰) sulfide-rich deposits (Fig. 2).

In the $\delta^{18}O$ vs. $\delta^{13}C$ space (Fig. 2), the fields of hydrothermal gangue carbonates from Fagundes and Ambrósia are partially overlain by the carbonate field associated with the Vazante carbonates. However, the Fagundes and Ambrósia carbonates show, in general, lower $\delta^{18}O$ and $\delta^{13}C$ values than those of the gangue carbonates of the willemitic ore ($\delta^{18}O$ = +20.4‰ to +17.43‰; $\delta^{13}C$ = 0.29‰ to +0.86‰).

The individualization of the carbonate generations permit also the characterization of two evolutionary tendencies related to Ambrósia and Fagundes deposits.

The first tendency is referred to carbonates from early hydrothermal alteration, main mineralization and late epigenetic fissural mineralization. This trend is characterized by decrease of $\delta^{18}O$ and $\delta^{13}C$ values accompanying the evolution of each deposit. The lowest $\delta^{13}C$ values are related to late fissural stages.

The second tendency is associated to mobilization of the Fagundes and Ambrósia ore and post-mineralization pervasive alteration of Fagundes. This trend is characterized by decrease of $\delta^{18}O$ values, without significant $\delta^{13}C$ variation.

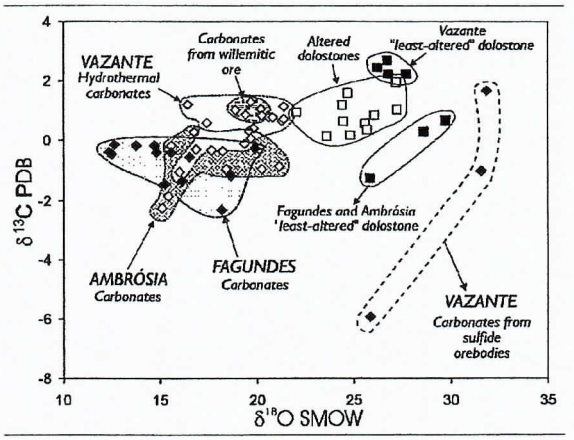

Figure 2. C and O isotopic compositions of host rocks and hydrothermal carbonates.

STRONTIUM ISOTOPES

The least-altered host dolostones exhibit $^{87}Sr/^{86}Sr$ ratios between 0.709764 and 0.71582. These signatures are more radiogenic than that relative to the best preserved dolostone of the Vazante Group ($^{87}Sr/^{86}Sr$ = 0.706144) reported by Azmy et al. (2001). This could reflect ^{87}Sr increase due to the radioactive decay of ^{87}Rb after the deposition. Calculated initial ratios for 750 Ma ($^{87}Sr/^{86}Sr_0$ = 0.705273 to 0.710458) however, are imprecise due to elevated errors in analytic measurement of Rb and Sr concentrations and to the uncertainties concerning the Vazante Group age and the nature of the system (closed or opened) during the post-depositional diagenetic process.

The altered dolostones (Fig. 3) have more radiogenic signatures ($^{87}Sr/^{86}Sr$ = 0.711126 to 0.7500399), and show, in Vazante and Ambrósia, positive correlation between $^{87}Sr/^{86}Sr$ values and Mn/Sr ratios, indicating that the more radiogenic ratios are related with the progressive hydrothermal alteration.

In all deposits, the strontium isotopic compositions in hydrothermal carbonates (siderite and dolomite) and sphalerite show a clear relationship with the paragenetic evolution of each deposit (Fig. 3).

In Vazante deposit, least-mylonitized sphalerite are less radiogenic ($^{87}Sr/^{86}Sr$ = 0.715380) than sphalerite strongly mobilized/mylonitized ($^{87}Sr/^{86}Sr$ = 0.729736). Seemingly siderite, related to the willemitic ore, is more radiogenic than sphalerite ($^{87}Sr/^{86}Sr$ = 0.721904 to 0.722250). In Fagundes, hydrothermal mineral phases are progressively more radiogenic. Dolomite associated with early colloform sphalerite has $^{87}Sr/^{86}Sr$ ratios of 0.713871, whereas late sphalerite shows $^{87}Sr/^{86}Sr$ ratios of 0.722737. Ore minerals from the epigenetic veins from Ambrósia deposit display the highest $^{87}Sr/^{86}Sr$ ratios (0.742125 to 0.53835). These strongly radiogenic signatures, however, define a narrow interval of strontium composition.

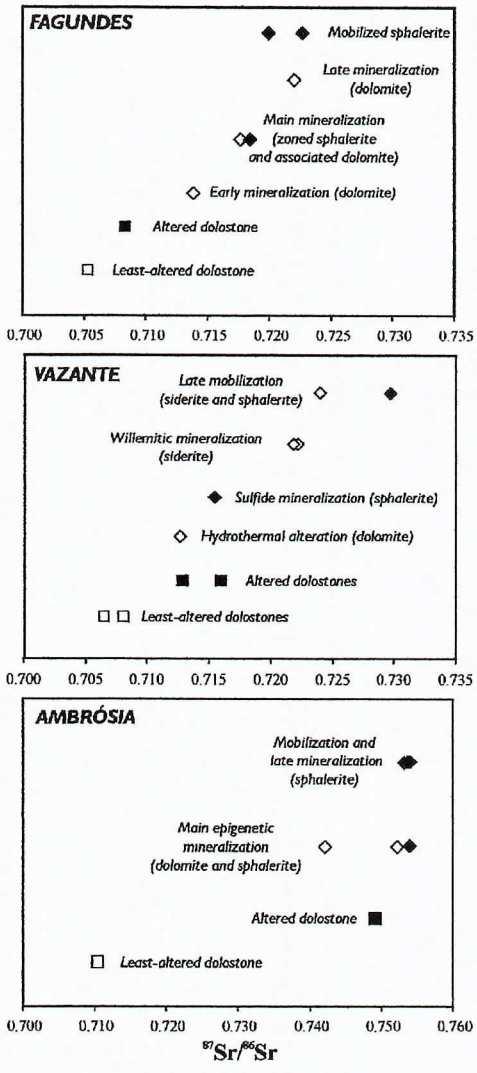

Figure 3. Sr isotopic compositions for host rocks and hydrothermal minerals.

FLUID INCLUSIONS

Fluid inclusion studies on sphalerite, quartz and dolomite from Vazante, Fagundes and Ambrósia deposits permitted the characterization of three aqueous fluid types:

(1) H_2O-NaCl-$CaCl_2$, high-temperature (> 250°C) and moderate salinity (~ 15 wt. % NaCl equiv.) fluid. This fluid type predominates in sphalerite from the early mineralization stages of the Fagundes deposit, but is also identified in quartz and sphalerite from Vazante and Ambrósia.

(2) H_2O-NaCl-$CaCl_2$-$FeCl_2$, moderate-temperature (140 - 190°C) and high salinity (> 23 wt. % NaCl equiv.) fluid, which fluid is associated mainly with the late mineralization stage of Fagundes and Ambrósia.

(3) H_2O-NaCl-$CaCl_2$, moderate to low temperature (~ 150 - 90°C) and low salinity (< 5 wt. % NaCl equiv.) fluid. This fluid type is present in mineral phases from all deposits, mainly in mineral phases formed after the main mineralization stage.

Variations of salinity and eutectic temperatures in primary fluid inclusions in the same mineral, mainly in zoned sphalerite, besides the relationship between homogenization temperature and salinity indicate progressive mixing between fluids (1) and (2), mainly in Fagundes and Ambrósia deposits. Primary fluid inclusions in late mobilized phases and secondary fluid inclusions in early minerals with moderate to low temperature and low salinity also suggest late mixing with meteoric waters (3).

DISCUSSION

SULFUR SOURCE

The Vazante sulfides display $\delta^{34}S$ values that are similar to those reported by Azmy et al. (2001) for trace sulfate trapped in carbonate from the host dolostones ($\delta^{34}S_{sulfate}$ = +8.5‰ to +16.9‰), which represent the best record of the sulfur isotopic composition of the sulfate seawater contemporary with the carbonate deposition. This could suggest that the sulfur source related to Vazante sulfide ore bodies is associated to thermochemical sulfate reduction, without significant fractionation. The main sulfur source could be related to the reduced sulfur content transported by the metalliferous oxidized fluids. The lowest Zn/Cd ratios (= 64 to 98) in Vazante sphalerite, however, could indicate that this metalliferous fluid had low reduced sulfur content (ΣS_{red}), which according to Schwartz (2000) may shift the total Cd distribution coefficient [K_t(ZnS, Cd)] to higher values, and hence favor the formation of Cd-rich sphalerite. Thus, the metalliferous fluid could represent a minimum reduced sulfur reservoir. This could be a important factor for the establishment of high fO_2/fS_2 conditions, which are necessary for the willemite stability (Monteiro, 1987).

The relationship between sulfur isotopic variations and the paragenetic sequences in Fagundes and Ambrósia deposits is systematic. The relation between $\delta^{34}S$ values and minor element contents in sphalerite, besides the evidences supported by fluid inclusions, suggest that mixing processes involving two distinct sulfur sources may be important for the genesis of the sulfide-rich deposits of the district.

The predominance of highest $\delta^{34}S$ values in the early sulfides, such as in Fagundes, and their relation with feeder zones in Morro Agudo (Misi et al., 1999), could suggest that the ^{34}S-enriched sulfur species were transported by the early high-temperature (>250 °C), moderate salinity (~ 15 wt. % NaCl), metalliferous mineralizing fluid.

Light sulfur was predominant during the epigenetic stages of mineralization, but possibly was also important for the late-diagenetic mineralization stages, judging from the Fagundes zoned sulfides, which exhibit lower $\delta^{34}S$ values than early phases. This isotopically light sulfur could be derived from bacteriogenic sulfate reduction in cold or distal parts of the system.

The predominance of lowest $\delta^{34}S$ values in epigenetic stages of mineralization may result from expulsion of moderate temperature, highly saline basinal fluids from the Vazante basin, related with Brasiliano compressive events. Alternatively, reduced shales that cover the host dolostones in Fagundes, Ambrósia and Morro Agudo deposits, might be mobilized by descending fluids, representing a potential sulfur source.

FLUID EVOLUTION

The $\delta^{18}O$ and $\delta^{13}C$ covariant trends related to sulfide and willemitic ore from the Vazante deposit were interpreted, based on the models of Zheng & Hoefs (1993), as related to fluid-rock interaction and fluid mixing, respectively (Monteiro, 1997, 1999). In the first case, the involved fluid is ^{18}O-enriched and has isotopic characteristics compatible with metamorphic or diagenetically ^{18}O-enriched fluids. In the second case, the covariant trend may be due to mixing between this metalliferous fluid with meteoric water.

The carbon and oxygen isotopic variations in hydrothermal carbonates from Fagundes and Ambrósia are partially overlaid by the field of Vazante carbonates and could also suggest the predominance of mixing processes.

The two identified trends related to Fagundes and Ambrósia may represent evolutionary tendencies related to mixing between the three fluid types identified by the fluid inclusion studies.

The relationship between isotopic variations and paragenetic evolution indicate that the fluids related to Ambrósia epigenetic mineralization are ^{13}C-depleted, suggesting interaction with organic matter. This carbon signature overlap the highest salinity and $^{87}Sr/^{86}Sr$ values for the late mineralization stage, suggesting predominance of radiogenic fluids, derived probably from reduced shale units, in the last stages. This basinal fluid was responsible for transport of isotopically light sulfur and subordinately of metals into the system.

The ^{18}O-impoverishment tendency observed mainly in mobilized and in post-mineralization carbonates could be related to the predominance of ^{18}O depleted, low salinity, meteoric waters during the final evolution of the hydrothermal system.

CONCLUSION

Fluid inclusion and isotopic studies indicate a common long-term evolutionary history of the hydrothermal systems, related to late-diagenesis and epigenetic events, for the genesis of both non-sulfide and sulfide zinc deposits of the Vazante-Paracatu district. The clear relationship between fluid composition, as traced by fluid inclusion and O, C and Sr isotopes, and paragenetic evolution of each deposit strongly suggest that progressive mixing processes were important for the genesis of these deposits.

In sulfide zinc deposits the influence of high salinity, strongly radiogenic basinal fluids is of great importance for ore genesis, mainly by its possible role in reduced sulfur supply.

The low-sulfidizing capacity of the Vazante willemitic system might be related to the scarcity of sulfur supply from upper shale units. The genesis of the sulfide ore from the Vazante deposit involves the interaction of oxidized ascending metalliferous fluids, of limited content of reduced sulfur, and the host dolostones.

The willemitic mineralization is coeval with the Vazante Fault development, which favors the overall mixture of metal-bearing and meteoric fluids channeled to the fault zone. This mixture process between low reduced sulfur-bearing fluids (ΣS_{red}) and oxidizing meteoric fluids favors the Vazante willemitic mineralization.

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