

## STABLE ISOTOPE CONSTRAINTS ON THE GENESIS OF THE WILLEMITIC ORE, VAZANTE MINE, MG, BRAZIL.

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### INTRODUCTION

The Vazante mine, which is the largest zinc mine in Brazil, is located in the northwest part of the Minas Gerais State. This mine has been worked since 1968. Production has been from both an open pit and an underground mine started in 1969 and 1983, respectively. Up to December 1997, the measured reserves to a depth of 250 m were estimated at 8.9 million tonnes with an average grade of 22-wt. % Zn.

Willemite ore is the main base-metal ore type. It is composed of willemite, quartz, dolomite, ankerite, siderite, hematite, chlorite, barite, franklinite and zincite (Monteiro, 1997). This association seems to be unusual in relation to base-metal deposits and it is clearly different from the other deposits that occur in the same ore-field, such as the Morro Agudo deposit, which is a sulfide dominated zinc-ore and is similar to IRISH-type deposit (Hitzman et al., 1995).

### REGIONAL GEOLOGIC SETTING

The Vazante Mine is located in the eastern part of the Brasília Fold Belt, which is one of the longest continuous units related to the Brasiliano Orogeny (~600 Ma) extending for 800 km over a width of 300 Km along the São Francisco Craton. The Brasília Fold Belt displays sequences of rocks thrust to the east with increasing deformation and metamorphism westward. During the Brasiliano Orogeny, the region was affected by a regional compressive stress regime related to the closure of the basins, which resulted in deformation and metamorphism (lower greenschist facies) of the Vazante Formation, the host of the zinc ore. In addition, the transpressive tectonic regime permitted the development of brittle-ductile shear zones, which is the main structural feature of the area.

### THE VAZANTE MINE GEOLOGY

The bulk of the mineralization is associated with two distinct facies of the Neoproterozoic Vazante

Formation (Dardenne, 1978): the Morro do Pinheiro Member Upper Facies (footwall sequence) and the overlying Pamplona Member Lower Facies (Rigobello *et al.*, 1988).

The Morro do Pinheiro Member includes gray metadolomites, pyrite-bearing carbonaceous black shale and marble with textures indicating low-energy (inter/subtidal flat) environment. The Lower Facies of Pamplona Member is made of slate and sericite phyllite interbedded with light gray to pink metadolomites, which display features typical of an inter/supratidal setting, with local evaporitic condition and periods of subaerial exposure.

Minor magmatism is represented by small bodies of metabasic rocks tectonically imbricated with these sequences and with willemite ore along shear zones (Monteiro, 1997).

### HYDROTHERMAL ALTERATION

Within the Vazante shear zone the hydrothermal alteration is largely fracture controlled, producing a complex zone of net veined breccia.

The shear zone trends N50E, plunges 60NW and displays a dominant sinistral transcurrent displacement (Pinho, 1989). It is characterized by complex zones of irregular anastomosing geometry that result from the intersections between C foliation planes and R, R', P and T Riedel-type shear fractures. Within this zone, the metadolomites are bleached and metasomatically altered along the contact with metabasic rocks and exhibit calcite fillings in fractures parallel to the mylonitic C fabric. The metabasic rock comprises chlorite, talc, dolomite, leucosene, hematite and serpentine, the alteration minerals.

The Morro do Pinheiro dolostone displays color alteration, from dark gray to pink, due to ankerite and siderite formation along of the mylonitic planes. The original textures of Pamplona dolostone (microspar or pseudospar) are replaced by closely packed anhedral



dolomite with undulatory extinction. Silicification occurs in Pamplona dolomites and slates, which are, also, strongly brecciated and cut by hydrothermal veins.

The veins are sub-parallel to the original metadolomite banding or are hosted by the principal displacement shear (C), secondary synthetic (P) and T-type Riedel tension shears. These veins display crustiform texture, resulting of progressive infilling of open fractures by successive layers of texturally and/or mineralogically different precipitates, which include dolomite, ankerite, siderite, hematite and jasper. A foliated texture due to mylonitization also occurs in some veins.

### ZINC MINERALIZATION: WILLEMITIC AND SULFIDE ORE BODIES

The main ore type in the Vazante deposit is the willemite ore, which occurs, associated to small sulfide ore bodies.

Sulfide ore-bodies occur either as irregular bodies elongate parallel to C shear planes, with a well-developed mylonitic fabric, or as late-vein filling. They are composed mainly of colorless sphalerite, with galena, hematite, quartz and dolomite inclusions, which are strongly deformed and stretched along the mylonitic foliation. The brittle-ductile shear zone development results in mechanical remobilization, recrystallization and the replacement of the sulfides by the willemite assemblage. The willemite formation in the sulfide bodies occurs, initially, along the mylonitic foliation and results in two distinct associations: willemite, sphalerite, franklinite and zincite (without quartz) and willemite, quartz, dolomite and franklinite (without sphalerite). These assemblages suggest the formation of willemite from the sphalerite and quartz. Structures of brittle character are related to the fracturing of willemite crystals, which are filled in turn by galena and sphalerite, resulting in cataclastic textures.

The main ore type of the Vazante Mine is the willemite ore, which rarely presents sulfide phases. The willemite ore displays pod morphology and is tectonically imbricated with small sulfide ore-bodies, metabasites and brecciated metadolomites. This ore type contains willemite (70-50%); dolomite (40-10%), quartz (15-10%), hematite (10-05%), barite (<5%), franklinite (<5%) and zincite (<5%).

The brittle-ductile deformation of willemite ore results in a granoblastic texture and mineral stretching and is accompanied by the formation of hematite and

Zn-rich chlorite. Cataclastic breccia comprises willemite fragments surrounded by cloudy saddle dolomite and cut by barite, hematite and chlorite.

The petrographic evidence, such as the relationship between willemite formation and the development of microstructures, suggests that the willemite mineralization and deformation are synchronous episodes inter-related to the Vazante Shear Zone. A condition of high  $fO_2$  and low  $fS_2$  appears to be valid for Vazante mineralizations. This could explain the absence of pyrite in the Vazante deposit, which is a common mineral phase in the majority of base metal deposits. In addition, the replacement of sphalerite by willemite could be related to variations of  $fO_2/fS_2$  ratio during fluid evolution.

### STABLE ISOTOPIC CONSTRAINTS

#### GEO THERMOMETRY

The geothermometric calculations were done using the isotopic compositions of cogenetic pairs of sulfide bodies (sphalerite-galena), willemite ore (willemite-quartz and hematite-quartz) and hydrothermal phases of veins (siderite-quartz). The mineral pairs were chosen from petrographic studies, which indicate the relative chronology of mineral formation and equilibrium textures. The temperatures for sulfide related to ductile-brittle structures (330°C) was obtained. The estimated temperatures of the willemite mineralization vary from 206°C to 294°C, and are similar to those estimated for sulfides.

#### OXYGEN AND CARBON ISOTOPIC CHARACTERISTICS

The unaltered metadolomites of the Pamplona and the Morro do Pinheiro Member yield isotopic compositions consistent with Proterozoic marine rocks. In  $\delta^{18}O$  vs.  $\delta^{13}C$  space (Fig. 1), the samples cluster into a uniform group. However, the hydrothermally altered metadolomites and hydrothermal carbonate of vein systems display a covariance of the oxygen and carbon isotopic values, which represent a progressive isotopic shift from the unaltered rocks. This feature could reflect an alteration halo, which might be considered as an prospective guide.

The metadolomites in contact with metabasic rocks yield the highest isotopic shift in relation to unaltered metadolomites. The calcite of this bleached metadolomite has the most distinct  $\delta^{13}C$  value (-10.31‰), suggesting a different source of carbon.



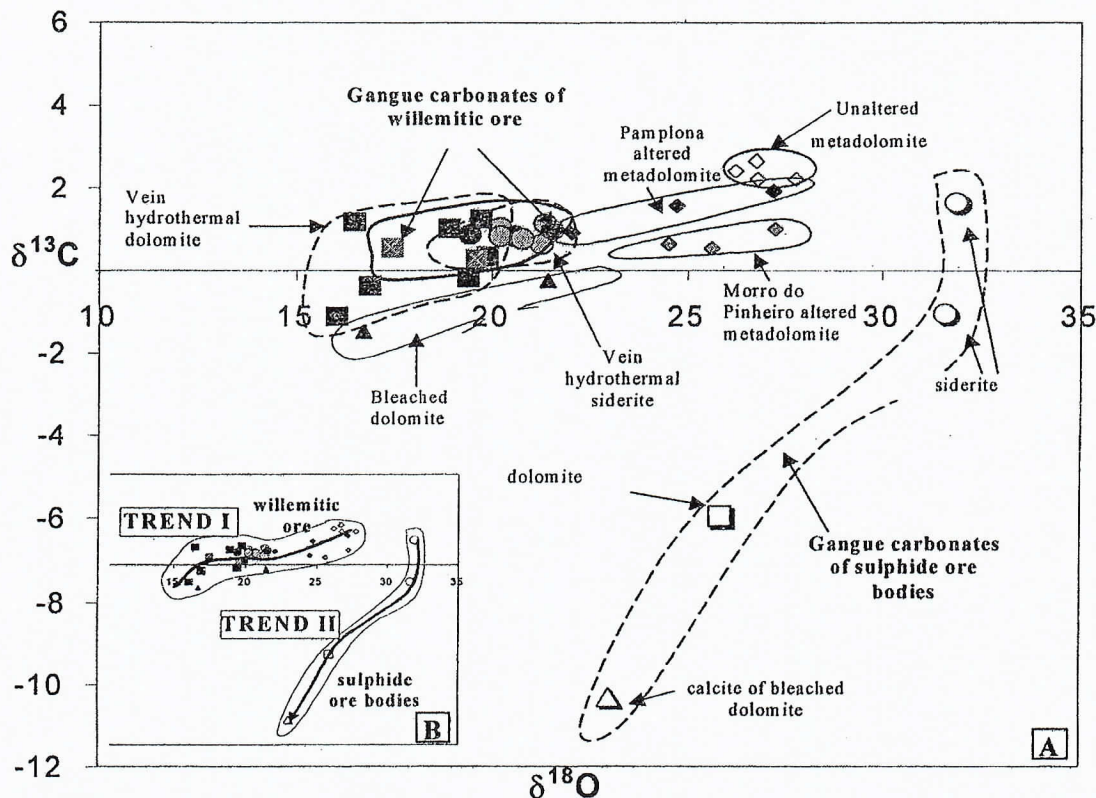


Figure 1. Covariation plot between  $\delta^{18}\text{O}$  vs.  $\delta^{13}\text{C}$  of carbonate generations from host sequence, hydrothermal veins, sulphide ore bodies and willemitic ore.

The gangue carbonates (siderite and dolomite) associated with sulfide bodies have  $\delta^{18}\text{O}$  similar or significantly higher than the  $\delta^{18}\text{O}$  host rocks values. The  $\delta^{13}\text{C}$  are consistently lower than  $\delta^{13}\text{C}$  of unaltered host rocks. These isotopic compositions, in  $\delta^{18}\text{O}$  -  $\delta^{13}\text{C}$  space, define a distinct covariant trend from that determined for isotopic compositions of carbonates from willemitic ore and altered host rocks.

The gangue carbonates of willemitic ore have compositions close to the hydrothermally altered metadolomites and hydrothermal carbonates of veins and breccias and represent the same covariance trend. This suggests a genetic link between the hydraulic brecciation, vein infilling and willemitic mineralization.

#### FLUID EVOLUTION

The oxygen isotopic compositions of the fluids in equilibrium with hydrothermal minerals were estimated by applying the isotopic compositions of minerals, the temperature interval calculated from geothermometric studies and the fractionation factor between mineral- $\text{H}_2\text{O}$ .

The calculated isotopic compositions of fluids in equilibrium with minerals of the vein systems ( $\delta^{18}\text{O} = 11.05\text{‰}$ ), gangue and willemitic ore ( $\delta^{18}\text{O} = 11.81\text{‰}$ ), at  $250^\circ\text{C}$ , are similar. This also suggests that the hydraulic brecciation, vein infilling and willemitic ore could be associated with the same hydrothermal fluid. However, the  $\delta^{18}\text{O}$  of the gangue minerals of the sulfide mineralization, for the same temperature ( $250^\circ\text{C}$ ), indicates that the fluids responsible for those minerals were strongly enriched in  $^{18}\text{O}$ , with an average  $\delta^{18}\text{O}$  composition of  $19.4\text{‰}$ .

These calculated isotopic compositions of the hydrothermal fluids should reflect final compositions, due to interaction processes, such as, fluid-rock exchange, fluid mixing and secondary fluid percolation, which result, generally, in values of  $\delta^{18}\text{O}$  more enriched in  $^{18}\text{O}$  than original fluids. The covariance trends of  $^{18}\text{O}$  and  $\delta^{13}\text{C}$  of carbonates may inform about the processes related to fluid evolution, which can be investigated through quantitative models. Thus, the models of fluid/rock interaction and fluid mixing (Zheng and Hoefs, 1993) were used for



the hydrothermal dolomite related to sulfide and willemite mineralization.

#### SULFIDE ORE LINKED TO FLUID-ROCK INTERACTION

The fluid-rock interaction model (Zheng and Hoefs, 1993) is probably the most appropriate method to constrain the isotopic signature of gangue carbonates associated with sulfide mineralization. The isotopic compositions of the hydrothermal carbonate are calculated from the known isotopic compositions of unaltered and altered host rocks and the estimated temperature (300°C). A progressive decrease of temperature associated with variations in the material-balance R/W ratio, in the range of 0.1 to 1, was also considered.

The above model was applied for a large interval of hydrothermal fluid composition ( $\delta^{13}\text{C}_{\text{fluid}}^{\text{i}}$  and  $\delta^{18}\text{O}_{\text{fluid}}^{\text{i}}$ ), which represents all known fluid reservoirs. In this way, the original isotopic composition of hydrothermal fluid of  $\delta^{18}\text{O} = +10\text{‰}$  and  $\delta^{13}\text{C} = -7\text{‰}$  fits better to the model and could match the gangue carbonate isotopic compositions. However, this composition would be compatible with different reservoirs. The isotopic composition of magmatic fluids vary between  $\delta^{18}\text{O} = +5.5$  to  $+10\text{‰}$  (Taylor, 1987) and the exsolved  $\text{CO}_2$  present in this fluid type has  $\delta^{13}\text{C}$  composition between  $-3.5$  to  $-7\text{‰}$  (Zheng and Hoefs, 1993).  $^{13}\text{C}$  depleted calcite occurs only in metadolomites in contact with metabasites, which could indicate an igneous source of carbon. However, the  $^{12}\text{C}$  contribution of the small metabasic bodies to the hydrothermal system and their implications in the formation of sulfide bodies cannot be estimated.

A metamorphic origin mainly due to liberation of volatile constituents of the host sequence could have mixed characteristics, with both sedimentary and igneous similarities. This origin could be responsible for a local contribution of depleted carbon from metabasites. The main sulfide and carbonate precipitation mechanism are probably related to temperature decrease and the positive correlation of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  could be associated with  $\text{CO}_2$  degassing, produced by temperature changes during fluid-rock interaction.

#### WILLEMITE ORE FROM A MIXTURE OF DIFFERENT FLUIDS

The observed characteristics of gangue carbonates related to willemite ore could reflect fluid

mixture within the shear zone. Using the Zheng and Hoefs (1993) model, the hydrothermal carbonates isotopic composition, formed by interaction of two distinct fluids (A and B), can be calculated.

A mixture of a fluid A, having composition of  $\delta^{18}\text{O} = 0\text{‰}$  and  $\delta^{13}\text{C} = -7\text{‰}$  and a temperature of 50°C, with a hot hydrothermal fluid B with  $\delta^{18}\text{O} = +10\text{‰}$  and  $\delta^{13}\text{C} = +2\text{‰}$  and a temperature of 300°C, was considered. The distribution of Vazante hydrothermal carbonates in the  $\delta^{18}\text{O} - \delta^{13}\text{C}$  space coincide with the compositions obtained for a temperature interval of 100 to 300°C, with proportion of fluid A of 0.8 to 0.2.

The isotopic composition of fluid A could be related to meteoric fluids, which according to Taylor (1987) has  $\delta^{18}\text{O}$  near of 0‰ and can display negative values of  $\delta^{13}\text{C}$  (to  $-7\text{‰}$ ) associated with dissolved atmospheric  $\text{CO}_2$ . The isotopic composition of fluid B would be similar, mainly in  $\delta^{18}\text{O}$  value, to fluids involved with the carbonate gangue of sulfide bodies.

Thus, the willemite ore formation might be explained by the interplay of various factors, such as, specific physico-chemical conditions and a coeval local-stress regime, responsible for the Vazante Shear Zone. These conditions would permit the interaction and mixing of metalliferous metamorphic and  $\text{SiO}_2$ -bearing meteoric fluids.

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