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## Interconnected plumbing system at the Mississippi Valley-type zinc-lead district of San Vicente, central Peru: Geochemical (elemental and isotopic) evidences

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**ABSTRACT:** Mississippi Valley-type (MVT) zinc-lead deposits and ore occurrences of the San Vicente belt are hosted in dolostones of the eastern Upper Triassic to Lower Jurassic Pucará basin, central Peru. The elemental (Ca, Mg, Fe, Mn, Sr, Na, Ba, Zn, Corg, S, and rare earth elements) and isotopic (C, O) compositions of the different generations of the host and gangue carbonates from 20 localities were used to constrain the ore fluid pathway and the ore precipitation mechanisms.

### 1 INTRODUCTION

The San Vicente Mississippi Valley-type (MVT) Zn-Pb zinc-lead district is located 300 km east of Lima in central Peru, in the eastern flank of the Andes covered by tropical rain forest (Fig. 1). The accumulated production and reserves exceed 20 million tons ore of 10 % Zn and 0.8 % Pb (Fontboté et al., 1995). The Upper Triassic - Lower Jurassic Pucará basin, host of the San Vicente deposit and other non mined MVT occurrences, is a carbonate platform at the western margin of the Brazilian Shield developed at the beginning of the Andean cycle (Norian to Toarcian) by marine transgression over clastic sediments and volcanoclastic rocks of the Upper Permian to Lower Triassic Mitu Group (Fontboté, 1990; Rosas, 1994). The mineralization (sphalerite and subordinate galena) largely replaces dolomitized subtidal oolitic grainstones interlayered with dolomitized mudstones rich in organic matter and bearing evaporitic sulfate pseudomorphs (sabkha facies), and occurs mainly as lens-shaped bodies (mantos). It appears in part as zebra ore and occasionally as cement in breccias or veinlets (Fontboté and Gorzawski, 1990; Spangenberg et al., 1995). Fontboté and Gorzawski (1990) proposed that San Vicente formed at a burial depth of about 2-3 km and a temperature range of about 70 to 160°C by influx of a metal-bearing saline brine characterized by radiogenic Sr and Pb. Extensive petrographic and isotopic (C, O, Sr, S, and Pb) information is available on the San Vicente main deposit. The results of preliminary fluid inclusion studies indicate that the white sparry dolomite was precipitated from hot (115 to 162°C) and saline (up to 26 wt.% eq. NaCl) fluids (Moritz et al. in press). A series of normal faults and tectonic lineaments of general direction NE-SW, NW-SE, and N-S cut the carbonate units in the proximity of the orebodies. These fault systems and the basement highs may

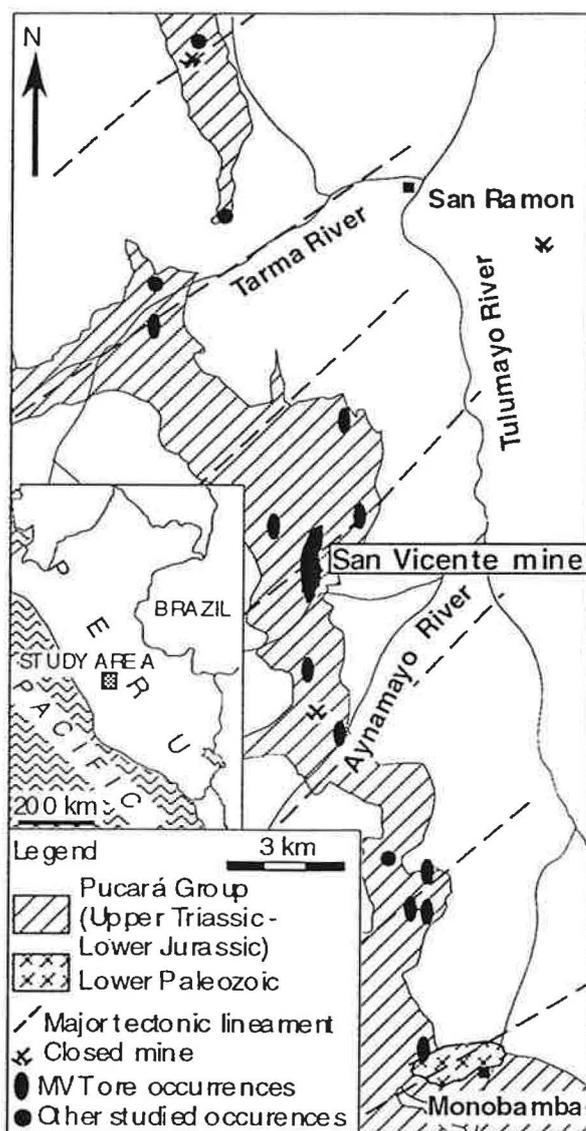


Fig. 1. Location of the San Vicente belt showing the studied localities (barren and mineralized areas).

play an important role in the genesis of San Vicente ore as channel pathways of the mineralizing solutions (Fig. 1).

In the San Vicente mining area the carbonate sequence of the Pucará Group has a thickness of about 1300 m and range in age from Norian to Hettangian. Three dolomitic units (San Judas Dolomite, San Vicente Dolomite, Alfonso Dolomite) host the orebodies. Most of the economic mineralization is contained within the San Vicente Dolomite. White sparry dolomite (WSD) is the main hydrothermal carbonate.

This contribution summarizes new geochemical data (Spangenberg, 1995) of the gangue carbonates of the San Vicente district, which constraint the flow paths of the ore fluid, the pH and Eh changes during ore formation, and the mechanism of ore formation.

## 2 METHODS

The ore-bearing dolomitic units and the Uncush bituminous silty Limestone (UL), that overlies the major ore-bearing dolomitic unit (San Vicente Dolomite), were sampled at district and mine scale in mineralized and barren areas along a 32 km N-S traverse centered in the main deposit (Fig. 1). The San Vicente mining area was submitted to an extensive multiple sampling, which include samples at different mantos from the three ore-bearing dolomitic units and textural carbonate generations sampled at outcrop and handspecimen scale. The following carbonate generations were selectively studied: dark replacement dolomite (DRD, I), white sparry dolomite (WSD, II), late filling dolomite (LFD, III) or calcite (LFC, III), and calcite replacing evaporitic sulfate (EPc). On the basis of fabric and grain size criteria we have distinguished three subgenerations of DRD, which present different degree of hydrothermal alteration. They are: "Ivf" very fine-grained, "If" fine-grained, and "Im" medium-grained.

The different carbonate generations were analyzed for Ca, Mg, Mn, Fe, Sr, Na, Zn and Ba by ICP-AES and microprobe profiles, for the rare earth elements (REE) by ICP-MS, and for the C and O isotopes.

## 3 RESULTS

### 3.1 Carbon and oxygen isotopes

Mixing between an incoming hot, saline, slightly acidic ( $\text{H}_2\text{CO}_3$ -dominant) fluid and the native intraformational alkaline ( $\text{HCO}_3^-$ -dominant) reducing waters explains the overall isotopic variation ( $-11.5$  to  $2.5\text{‰}$   $\delta^{13}\text{C}$  and  $-12.5$  to  $-6.4\text{‰}$  PDB  $\delta^{18}\text{O}$ ) in the different generations of hydrothermal carbonates. The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of the altered host DRD and ore-stage WSD ( $0.2$  to  $1.7\text{‰}$   $\delta^{13}\text{C}$ ,  $-11.4$  to  $7.3\text{‰}$   $\delta^{18}\text{O}$ ), and the carbon isotope composition

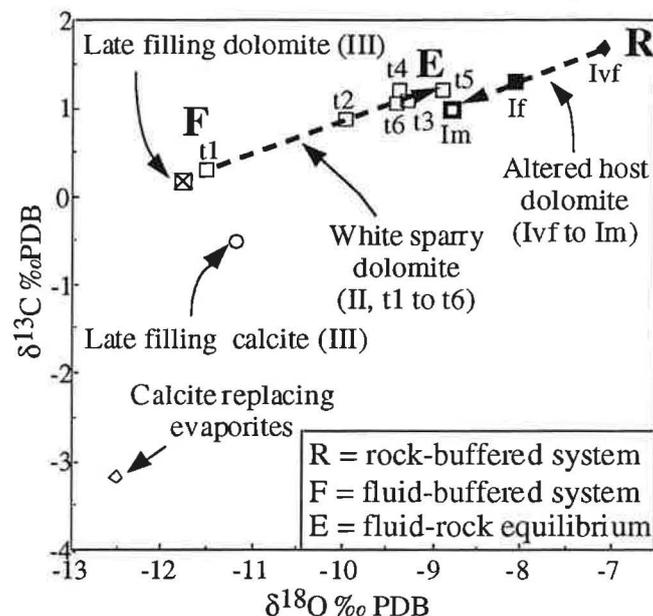


Fig. 2. Median isotopic composition of the different generations and subgenerations of host and gangue carbonates from the San Vicente deposit in the  $\delta^{13}\text{C}$  versus  $\delta^{18}\text{O}$  space.

of the associated organic matter ( $-23.3$  to  $-27.5\text{‰}$   $\delta^{13}\text{C}$ ), show similar patterns throughout the studied area, suggesting the existence of a common regional mineralizing hydrothermal system with interconnected plumbing. The isotopic covariations of the ore-stage dolomites (Fig. 2) is explain by interaction of the mineralizing fluid (F) and the host dolomite ( $R = \text{Ivf}$ ). The trend R-E of DRD towards lighter isotopic composition reflects the progressive alteration of the host dolomite by the hydrothermal ore fluid. The coupled compositional evolution of the ore fluid is recorded by the C and O isotopic enrichment of the WSD textural subtypes (trend F-E in fig. 2), where t1 to t6 are different WSD fabrics: t1=spot, t2=fine veinlets, t3=ordered bands, t4=bands in zebra rock, t5=broad crosscutting veins, and t6=breccia cement. The isotopic composition of both the fluid and the host dolomites were progressively modified until they attain isotopic equilibrium in the fluid-rock system (point E in Fig. 2).

### 3.2 Rare-earth and trace elements

The concentration in Mn, Sr, Na and Ba of the host dolomite (Ivf) increases during advancing alteration: from values of  $730\mu\text{g/g}$ ,  $60\mu\text{g/g}$ ,  $325\mu\text{g/g}$  and  $2\mu\text{g/g}$  in the DRD (Ivf) to values of  $1700\mu\text{g/g}$ ,  $100\mu\text{g/g}$ ,  $400\mu\text{g/g}$ , and  $4.5\mu\text{g/g}$  in the LFD (Fig. 3). The concentration of Fe in the hydrothermal dolomites (DRD, WSD, LFD) are very low, except extremely high Fe ( $>2500\mu\text{g/g}$ ) and Zn values  $>200\mu\text{g/g}$ ) due to sphalerite leaching during the acid-digestion. The measured decrease in Fe and increase in Mn and Sr in the hydrothermal dolomites indicates that the incoming ore fluid was

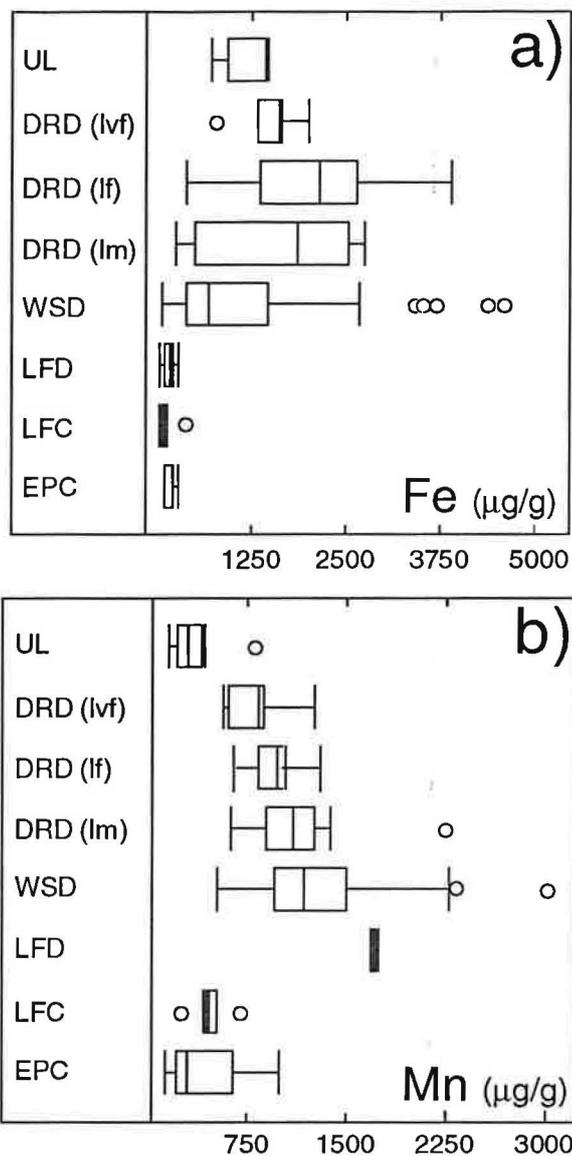


Fig. 3. Ranges and medians of (a) iron and (b) manganese in the hydrothermal carbonates of San Vicente district. WSD=white sparry dolomite (II); LFD=late filling dolomite (III<sub>d</sub>); LFC=late filling calcite (III<sub>Ac</sub>, III<sub>Bc</sub>); EPC=calcite replacing evaporitic sulfate.

rich in Mn and Sr and poor in Fe. The scarcity of pyrite in the San Vicente deposit provides evidence for a Fe-poor ore fluid.

The REE spectra normalized to the average host dolostone (I<sub>vf</sub>) show significant trends (Fig. 4): 1) all the hydrothermal carbonates are markedly depleted in LREE compared to HREE; 2) the ore-stage dolomite (WSD, LFD) show pronounced negative Ce anomalies, suggesting that the incoming ore fluid was depleted in LREE, and particularly in Ce; 3) late filling calcite intergrown with late sphalerite cementing dissolution breccias (III<sub>Ac</sub>) is depleted in LREE but has a significant Eu anomaly ( $Eu/Eu^* = 2.63$ ); 4) the LFC from a large vein in the hydraulic breccia (III<sub>Bc</sub>) shows a pronounced enrichment in MREE and HREE.

The elemental (REE, Fe, Mn, Sr) patterns of the ore-stage dolomites (altered DRD, WSD, LFD) are mostly similar in samples at district and deposit

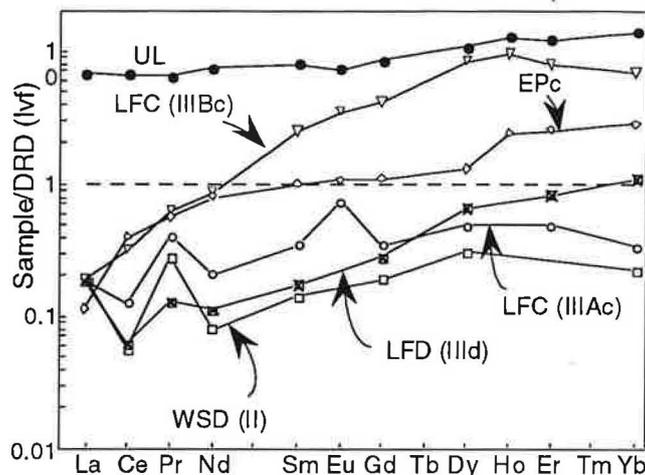


Fig. 4. Median REE patterns of the Uncush limestone, and the hydrothermal carbonates normalized to contents in the very fine-grained DRD (host dolomite). Abbreviations as in figure 3.

scale. This supports the stable isotope evidence of a common hydrothermal system controlling the chemistry of the carbonates of the San Vicente district.

The negative Ce anomaly and the low Fe/Mn ratio in the ore-stage dolomite suggest that the incoming ore fluid was slightly oxidizing. This is consistent with its early (pre-ore) migration along an oxidizing main aquifer, such as the red sandstones and other clastic units at the base of the basin, in which Ce was depleted compared to the neighboring La and Pr, and Fe retained as (hydr)oxides.

Ore precipitation decreases fluid pH and destabilizes REE-complexes ( $CO_2$  partial pressure and pH control the stability of the hard REE-carbonate complexes). Thus more evolved fluid enriched in uncomplexed heavy REE precipitates late filling calcites. This enrichment in REE and the positive Eu anomaly may be due to changes of pH and Eh during the mineralizing events in San Vicente. We conclude that the incoming mineralizing fluid (REE-poor) was not in chemical equilibrium with the carbonates of the Pucará Group.

The results of the Rock-Eval pyrolysis (written communication of J.R. Disnar, University of Orléans, 1994) indicate the occurrence of two types of organic matter in the gangue carbonates of San Vicente: a hyper-mature kerogen ( $T_{max}$  about  $500^\circ C$ ), which likely is thermally altered native organic matter, and an allochthonous thermally labile soluble bitumen ( $T_{max}$  about  $230^\circ C$ ). The presence of native sulfur associated with extremely carbon-light calcites replacing evaporitic sulfates (up to  $-11.5\text{‰}$   $\delta^{13}C$ ), altered native organic matter, and heavier hydrothermal bitumen (from  $-27.0$  to  $-23.0\text{‰}$   $\delta^{13}C$ ) point to thermochemical reduction of sulfate and / or thiosulfate. The Rock-Eval results combined with carbon isotope data suggest that the native organic matter was the main source of

reductants in the mineralizing fluid. Alteration of the organic matter disseminated in the host dolomite by the incoming ore fluid liberated hydrocarbons which locally produced reducing conditions that led to sulfate reduction (and reduction of  $\text{Eu}^{+3}$  to  $\text{Eu}^{+2}$ ). After further thermal cracking, water-washing, and polymerization of the released hydrocarbons, solid aggregates of hydrothermal bitumen precipitated.

#### 4. CONCLUSIONS

1. The incoming mineralizing fluid was slightly acidic and oxidizing, probably due to migration along the underlying Red Sandstones and other detrital rocks at the base of the Pucará basin.

2. The regionally uniform isotopic and elemental patterns, coupled with the mineralogical and petrographic similarities among the different MVT occurrences, reflect that similar mineralizing processes occurs in the entire San Vicente belt. This implies the existence of an interconnected mineralizing hydrothermal system.

3. The limited isotopic and elemental equilibration between the incoming fluid and the Pucará rocks indicates that access of the corrosive ore fluid to the mineralized zones was likely by permeable channel-ways (faults, basement highs).

4. Two mechanisms were responsible for precipitation of the ore-stage carbonates and associated sphalerite: a) Temperature-dependent interaction of the mineralizing fluids and the carbonate host rocks explain the alteration and replacement of the dark dolomite (I) and precipitation of early sphalerite (I) and (II). Subsequently, a second generation of hydrothermal white sparry dolomite (II) and sphalerite (II) formed overgrowths on the altered dolomite (I) by filling secondary porosity under fluid-buffered conditions. This main mineralizing stage was the result of prolonged fluid-rock interaction coupled with minor  $\text{CO}_2$  degassing. b) Pressure fall leading to outgassing of  $\text{CO}_2$  and consequent increase in the pH of the ore fluid caused precipitation of late sparry carbonates (dolomite and calcite III) and, likely, sphalerite (III).

5. The Fe-Mn covariations combined with the Eu anomalies of the hydrothermal carbonates are consistent with a change from a reducing ore-forming stage to oxidizing conditions following ore deposition. The REE enrichment, the Mn depletion, and the positive Eu anomalies of the late-stage vug-filling carbonates indicate that the post-ore "residual" acidic fluids were again oxidizing due to continuous influx of fresh basinal waters.

6. Late REE-rich dolomite III (or calcite) and associated sphalerite (III) formed from the slightly acidic ore fluid during  $\text{CO}_2$  degassing, caused in turn by an enhanced hydrothermal porosity. The widespread hydraulic brecciation, upward "escape" veins, and other structures indicate that the fluid was overpressured. An abrupt pressure drop could favor  $\text{CO}_2$  degassing and therefore may play a

major role in the ore precipitation during the late hydrothermal events in San Vicente.

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