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Spangenberg, Jorge Enrique; Fontboté, Lluís; Sharp, Zachary D.; Hunziker, J.

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STABLE ISOTOPE (C, O) CONSTRAINTS ON THE GENESIS OF THE MISSISSIPPI VALLEY TYPE ZINC-LEAD DEPOSIT OF SAN VICENTE, CENTRAL PERU*

J. Spangenberg**, L. Fontboté**, Z. Sharp***, and J. Hunziker***

ABSTRACT

The Mississippi Valley-type (MVT) Zn-Pb district of San Vicente is located in central Peru (300 km east of Lima) within the carbonate rocks of the Triassic-Jurassic Pucará basin. Detailed carbon and oxygen isotope studies of the carbonates and associated organic matter from the main deposit and minor ore-occurrences provide new insights on the mechanism of ore-precipitation in San Vicente. The regional homogeneity of the isotopic composition of the altered host and gangue carbonates, coupled with the strong mineralogical and petrographic similarities of the distinct MVT-occurrences reflects that the mineralizing processes were similar in the whole San Vicente belt, suggesting the existence of a regional mineralizing hydrothermal system with interconnected plumbing.

INTRODUCTION

San Vicente is the largest South American example of a MVT Zn-Pb deposit (14 Mt, 11% Zn, 0.8% Pb). It occurs mainly in oolitic calcarenite in the eastern part of the Pucará basin, a carbonate platform at the western margin of the Brazilian Shield. The marine carbonate sequence of the Pucará Group lies over clastic sediments and volcanoclastic rocks of the Permian-Triassic Mitu Group. San Vicente formed at burial of about 2-3 km at a temperature range of 70 to 160°C by influx of Zn-Pb-bearing brines characterized by radiogenic Sr and Pb¹. A series of normal faults

of general direction NE-SW and NW-SE cut the carbonate units in the proximity to the orebodies. These tectonic lineaments may have played an important role in the genesis of San Vicente ore, as channel pathways of the ore solutions.

Important petrographic and isotopic (C, O, Sr, S, and Pb) information is available on the San Vicente main deposit¹⁻² and the Pucará basin³, the ore-precipitation mechanism remaining unclear. This contribution presents a stable isotope (C, O) study in San Vicente belt in order to get a better understanding on the chemistry of the ore solutions and the mechanisms of ore precipitation.

SAMPLE MATERIAL

Three dolomitic units (San Judas Dolomite, San Vicente Dolomite, Alfonso Dolomite) host the mineralization (sphalerite and subordinate galena) in form of lens-shaped mantos (Fig. 2). The mineralization appears typically as a zebra ore, within alternating bands of dark and white dolomite, or as cement in breccias and fissures. The ore-bearing dolomite units together with the bituminous silty Uncush Limestone (UL), that occurs between the two higher dolomite units and serves as a stratigraphic reference, were studied in detail. A hierarchical multiple sampling plan that consider different variation levels, district, mine scale, manto, outcrop, and handspecimen was used. San Vicente district was studied at orebodies and barren areas in fourteen localities along a 27 km long N-S traverse centered in the main deposit (Fig. 1). The following distinct carbonate generations were selectively analyzed for their stable isotope composition: dark replacement dolomite (DRD, I), white sparry dolomite (WSD, II), late void-filling dolomite (IIId) or calcite (IIc), and carbonates replacing sulfate evaporites (EPd, EPc). Furthermore, three types of organic matter were studied: 1) total organic carbon (TOC) associated to the DRD, 2)

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**Département de Minéralogie, 13, Rue des Maraîchers, CH-1211 Geneva 4, Switzerland

***Institut de Minéralogie, UNIL BFSH-2, CH-1015 Lausanne, Switzerland



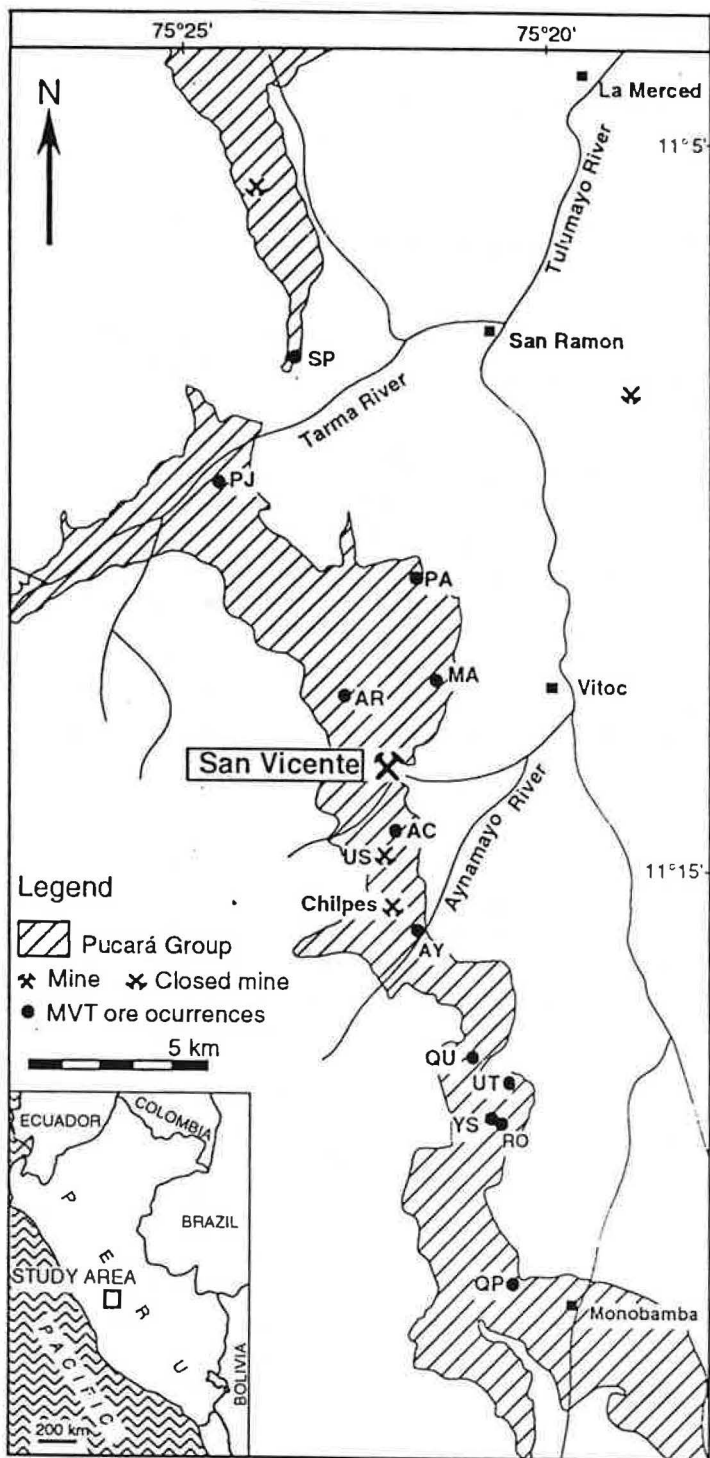


Fig.1. Map of San Vicente MVT belt showing the studied localities. QP=Quebrada Piñon; RO= Rondayacu; YS=Yanachuro Sur; UT=Utcuyacu; QU= Quebrada Utcuyacu; AY=Aynamayo; CH= Chilpes; US=Uncush Sur; AC=Afloramiento Campana; AR=Arcopunco; MA=Machuyacu; PA=Palmapata; PJ=Puntajacu Junior; SP=Sur Pichita.

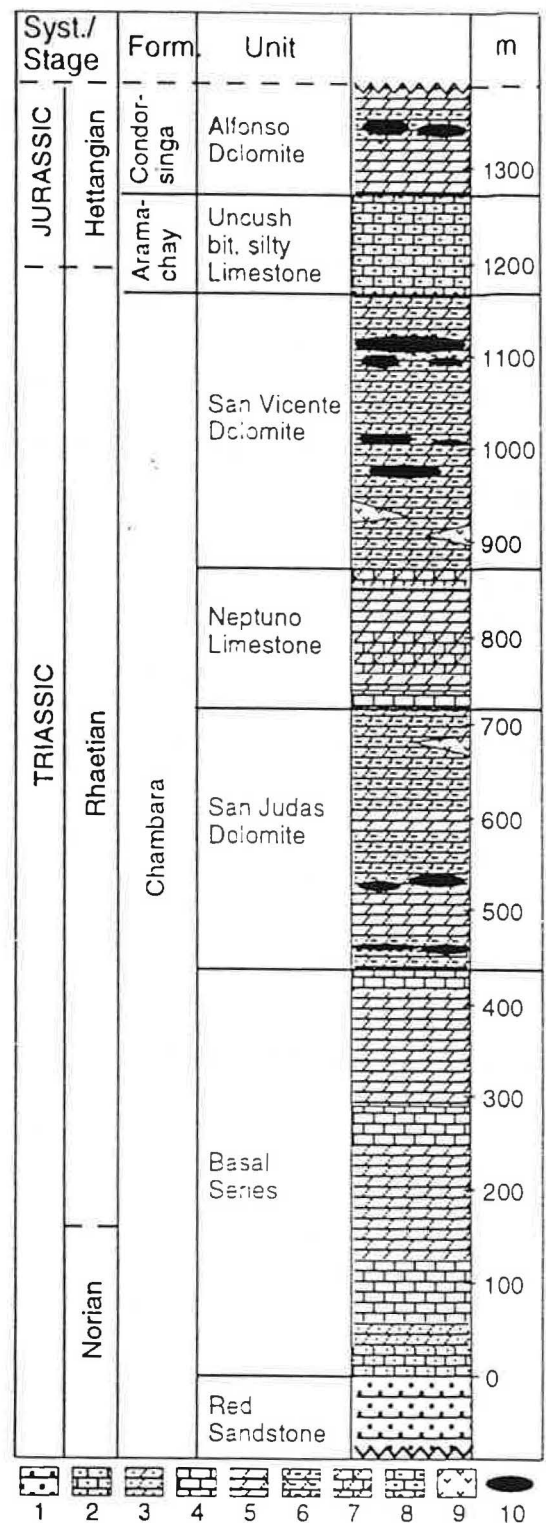


Fig. 2. Stratigraphic column of the Pucará Group in San Vicente mining area (after Rosas⁴). 1=red sandstone; 2= marly limestone; 3=marly dolomite; 4=limestone; 5=dolomite; 6=dolomite with WSD; 7=partly dedolomitized dolomite; 8=bituminous silty limestone; 9=volcanic rocks; 10=ore

late hydrothermal bitumen, and 3) TOC in the UL.

RESULTS

SAN VICENTE DISTRICT

The C and O isotope ranges for the ore-stage dolomites (DRD and WSD) in the studied localities of San Vicente belt are listed in Table 1.

Table 1. C and O isotope ranges of ore-stage dolomites in San Vicente belt. Abbreviations as in Fig. 1.

Local Unit (n)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (PDB ‰)
Dark replacement dolomite (DRD)		
AY SJD (2)	1.6 to 1.7	-8.1 to -8.0
SVD (1)	1.4	-7.6
CH SJD (1)	1.7	-7.8
SVD (2)	1.0 to 1.6	-9.8 to -7.4
AC AD (1)	1.5	-7.6
SV SJD (3)	1.1 to 1.7	-8.2 to -7.4
SVD (23)	0.5 to 2.5	-9.6 to -6.4
AD (4)	1.2 to 1.7	-8.5 to -7.2
AR SVD (2)	1.4	-9.0 to -7.4
PA SVD (1)	0.9	-10.0
White sparry dolomite (WSD)		
QP SJD (7)	1.0 to 1.4	-10.6 to -9.7
RO SJD (3)	0.8 to 0.9	-10.6 to -9.9
YS SJD (2)	1.2 to 1.7	-10.2 to -9.7
UT SVD (2)	1.1	-9.9 to -9.8
QU SVD (2)	0.5 to 1.1	-10.4 to -10.1
AY SJD (2)	1.1 to 1.3	-8.9 to -10.0
SVD (2)	0.8 to 1.1	-11.2 to -10.7
CH SJD (2)	1.4 to 1.7	-8.4 to -8.0
SVD (4)	0.7 to 1.0	-10.0 to -9.5
US AD (1)	1.3	-9.9
AC AD (2)	0.9 to 1.4	-8.2 to -8.7
SV SJD (28)	0.6 to 1.6	-10.5 to -8.0
SVD (90)	-0.1 to 1.6	-11.8 to -7.3
AD (19)	0.8 to 1.7	-10.0 to -8.1
AR SVD (4)	0.7 to 1.2	-10.7 to -8.3
MA SVD (4)	0.7 to 0.9	-10.7 to -9.8
PA SVD (2)	0.9 to 0.9	-10.2 to -10.0
PJ SVD (3)	0.2 to 0.5	-11.4 to -10.0
PS SVD (1)	0.5	-10.8

The C and O isotopic composition of the ore-stage DRD ($\delta^{13}\text{C}$ = 0.9 to 1.7‰; $\delta^{18}\text{O}$ =-10.0 to -7.4) and the WSD ($\delta^{13}\text{C}$ = 0.2 to 1.6‰; $\delta^{18}\text{O}$ =-11.4 to -7.4) varies within a rather close range for the different lithologic units and sampling sites, and are similar to the isotopic ratios measured at the San Vicente deposit (SV in Table 1, DRD: $\delta^{13}\text{C}$ = 0.5 to 2.5‰ and $\delta^{18}\text{O}$ =-9.6 to -6.4; WSD: $\delta^{13}\text{C}$ =

-0.1 to 1.7‰; $\delta^{18}\text{O}$ =-11.8 to -7.3). The three main generations of carbonates (I, II, III) are well differentiated in the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ space (Fig. 3). The hydrothermal WSD is substantially depleted in O^{18} (up to 3‰) and C^{13} (up to 2‰), and is isotopically similar to the altered DRD. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of five samples of late-stage filling calcite (III) scatter from -3.7 to -0.1‰ and -11.4 to -15.0‰ respectively (Fig. 3). For each locality the isotopic shift from the host DRD to the WSD is of the same order, ranging from 0.5 to 1‰ $\delta^{13}\text{C}$ and up to 4‰ $\delta^{18}\text{O}$ and does not show any significant zonation at the stratigraphic and the district scale (Table 1). The regional homogeneity of the isotopic composition of the altered host and gangue dolomites suggest that the physicochemical conditions and the fluid-rock interaction mechanism were uniform and almost constant during ore and gangue precipitation. From these data, coupled with lithostratigraphic and petrographic considerations, we can infer that the mineralizing processes were similar in the whole San Vicente MVT-district.

SAN VICENTE MAIN DEPOSIT

The host and gangue carbonates from San Vicente main deposit display a general tendency towards lower isotopic composition in the sequence dark replacement dolomite → white sparry dolomite → late filling dolomite (LFC, IIId) → late filling calcite (LFC, IIId) → carbonates replacing evaporites (EP; Table 2). The carbonates exhibit a marked inverted J trend in the $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ space (Fig. 3) that is generally interpreted as indicating the precipitation of carbonates by mixing of isotopically distinct fluids. Note that the values of the samples from the main deposit coincide with the compositional range of the samples from the whole district. At the isotopically heavy end point (A) the isotopic composition of the unaltered very-fine host dolomite ($\delta^{13}\text{C}$ = 1.3 to 2.5‰; $\delta^{18}\text{O}$ =-7.8 to -6.4‰) overlap partially with the composition of the Uncush limestones. These samples, with the highest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, are assumed to represent the original host dolomite. Two light extremes (B and C) can be distinguished. The end composition B is represented by calcite replacing evaporite pseudomorphs that are depleted in both ^{13}C and ^{18}O . The endpoint C is characterized by two strong ^{13}C depleted calcite cements ($\delta^{13}\text{C}$ = -9.3

and -11.5‰) and slightly depleted in ^{18}O ($\delta^{18}\text{O} = -12.1$ and -12.5 ‰). This indicates that extremely C-light CO_2 , probably formed by oxidation of organic matter, was involved in the precipitation of the late carbonate cements. The role of fresh meteoric water in affecting the $\delta^{18}\text{O}$ values of the late open-space filling carbonates can not be ruled out, then these carbonates occur typically in sites of high permeability.

Table 2. Carbon and oxygen isotope composition of carbonates and associated organic matter in San Vicente deposit. TOC=total organic carbon.

Host mineral (n)	$\delta^{13}\text{C}$ ranges	$\delta^{18}\text{O}$ ranges
	(‰ PDB)	(‰ PDB)
Dark replacement dol. (29)	0.5 to 2.5	-9.6 to -6.3
White sparry dolomite (115)	-0.1 to 1.7	-11.8 to -7.3
Late filling dolomite (10)	-0.3 to 1.1	-12.5 to -9.8
Late filling calcite (25)	-11.5 to 0.7	-15.1 to -9.1
Dol. replacing evaporite (7)	-0.4 to 1.0	-12.1 to -9.8
Cal. replacing evaporite (11)	-4.5 to 0.8	-16.1 to -9.5
Uncush limestone (6)	0.2 to 2.3	-8.4 to 6.3
TOC in dark repl. dol. (3)	-27 to -26.4	
Hydrothermal bitumen (7)	-27.7 to -23	
TOC in Uncush limestone (2)	-28.2 to -27.2	

Furthermore, the isotopic composition of the ore-stage dolomites in the three ore-bearing dolomitic units are independent of the stratigraphic position, and do not show any zonation at orebody or mine scale.

It is noteworthy that the Uncush limestones from barren areas are substantially depleted in ^{13}C (~ 3 ‰) relative to the samples from San Vicente deposit (Fig. 3). This indicates that this limestone interacted with a fluid with dominant C-light HCO_3^- , likely liberated during the oxidation of the native organic matter (NOM). At San Vicente the pore fluid of these limestones was diluted by the incoming C-heavier ore solutions.

The $\delta^{13}\text{C}$ values of the hydrothermal bitumen (ranging between -27.7 to -23.0‰, and median = -24.0‰) are significantly heavier than the organic matter associated to the host dolomite ($\delta^{13}\text{C} = -27.0$ to -26.4 ‰). This isotopic shift is attributed to preferential loss of isotopically light low-molecular hydrocarbons (e.g. CH_4 , C_2H_6) during break-down of the NOM. The liberated light hydrocarbons can reduce thermochemically sulfate or thiosulfate to form native sulfur,

hydrogen sulfide and bicarbonate with very light carbon. Consequently, the fluid can precipitate calcite cements extremely depleted in ^{13}C . In San Vicente the association of sulfates pseudomorphs, sulfides, elemental sulfur, extremely ^{13}C -depleted carbonates, altered NOM in the host dolomite, and isotopically heavier late solid bitumen points to thermochemical sulfate reduction. This could be the source of hydrogen sulfide in the ore fluid.

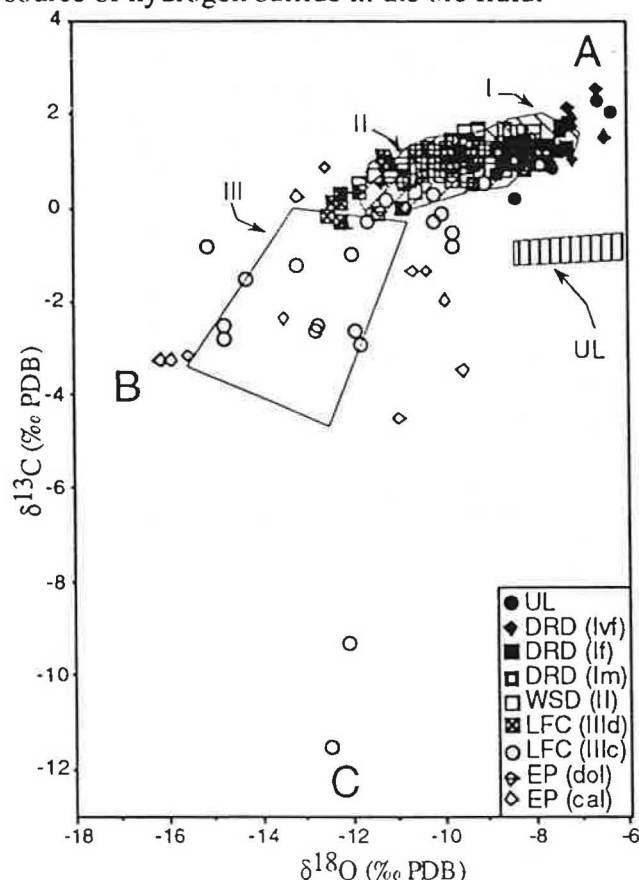


Fig. 3. Distribution of carbonates from San Vicente deposit in $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ space. Outlined fields represent the carbonates from rest of San Vicente belt.

ISOTOPIC VARIATION AT TEXTURAL SCALE

The isotopic composition of the ore-stage dolomites were studied at the textural scale. On the basis of fabric and grain size criteria we have distinguished three subgenerations of DRD which correspond to different degrees of metasomatic alteration of the host carbonates by the hydrothermal mineralizing fluid. They are: Ivf) very fine-grained; If) fine-grained; and Im) a completely recrystallized medium-grained phase.

Figure 4 shows the median isotopic covariations of the carbonate phases in San Vicente deposit.

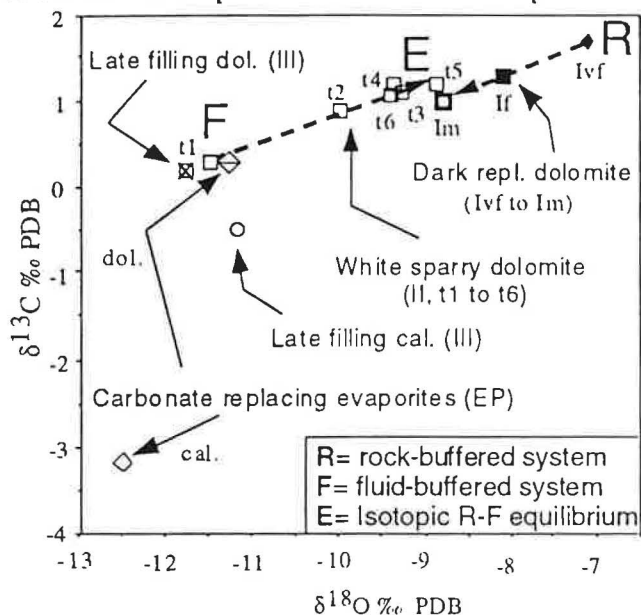


Fig. 4 Median isotopic composition of carbonates in San Vicente.

The very fine DRD (Ivf) represents the heaviest endmember in a rock-buffered system (point R in fig. 4); the opposite situation of a fluid-buffered system is represented by the early spot-like WSD (point F in fig. 4). 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. 4), where t1 to t6 are different WSD fabrics: t1=spot, t2=fine veinlets, t3=ordered bands, t4=bands in cebrera rock, t5=broad crosscutting veins, and t6=breccia cement. This diagram shows that 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. 4).

MODELLING

The $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ covariations of the carbonates of San Vicente main deposit were quantitatively modelled using the equations of Zheng and Hoefs⁴. A mixing model between the native formation fluid (e.g. pore fluid of Ivf at

60°C) and the incoming mineralizing fluid (saline, acidic, 150°C) describes the isotopic composition of the syn- and post-ore carbonates. This fluid can be considered as a thermally and compositionally evolved meteoric groundwater, whose chemistry was controlled during the transport by prolonged and multiple water-rock interaction and mixing with distinct basinal fluids. Models of fluid-rock interaction and secondary alteration explain the isotopic evolution of the ore-stage dolomites.

CONCLUSIONS

The following conclusions are relevant for exploration of MVT deposits in the Pucará basin.

1. A regional uniform hydrothermal system with interconnected plumbing affects the whole San Vicente belt.
2. Ore and gangue precipitate from fluids of specific isotopic composition by regionally unvarying and stratigraphic independent geochemical (mixing) processes.
3. Multiple fluid mixing and water rock interaction have an important role in compositional evolution of the ore fluids.
4. The main mechanism involved in ore precipitation is fluid-rock interaction.
5. The native organic matter in the host dolomite was certainly the main reductant in the processes of ore formation in San Vicente.
6. Probably the chief flow type of the ore fluid was pervasive; consequently the ore distribution is controlled by the porosity (primary or secondary).

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