

THE CARBONATE-HOSTED Zn-Pb DEPOSITS OF NW SPAIN: STRATABOUND AND DISCORDANT DEPOSITS RELATED TO THE VARISCAN DEFORMATION

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The carbonate Vegadeo Fm (Lower-Middle Cambrian, NW Spain) hosts abundant Zn-Pb mineralization. Minor stratiform ore showings occur in mineralogically and geochemically undisturbed limestones of the Lower Member. They are interpreted as related to diagenetic processes, with sulfur derived from the abiogenic reduction of sulfates interbedded in the carbonates and lead leached from the nearby detrital rocks. The major mineralization, stratabound deposits in the Upper Vegadeo Fm and discordant replacements (Rubiales-type), occurs in relationship with pervasive epigenetic silicification and minor hydrothermal breccias. They are interpreted as of Late Variscan age. Here, the mineralization seems to be formed by reaction of the hosting carbonates with low-saline (<7 wt% NaCl eq.) water-rich fluids that circulated along major lithologic contacts or extensional faults. Isotopic composition of the hydrothermal fluids falls within the field of low-grade metamorphic or basinal waters ($\delta^{18}\text{O} = -1.0$ to $+6.3$ ‰; $\delta\text{D} = -43$ to -31 ‰). The ore-forming process occurred at temperatures between 150 and 250°C and at low fluid pressures (<500 b). Lead isotopes suggest that most of the base metals were derived from the hydrothermal remobilization of the diagenetic ores in a "lead-frozen" system. Some of the sulfur appears to have had the same source, but there was also a significant input from biogenically-reduced sulfur from the endosing shales. These Variscan ores have many of the descriptive features of carbonate-hosted deposits, but the fluid compositions, P-T conditions of formation, and tectonic setting were fundamentally different. They can be interpreted as equivalent to MVT deposits, but formed in the internal zones of orogenic belts.

INTRODUCTION

The carbonate rocks of the Astur Leonese Zone (NW Spain) host abundant Zn-Pb deposits (Fig. 1) with about 3 Mt Zn+Pb of exploited plus known reserves, but copper, silver and mercury have been also recovered. They define an important carbonate-hosted Zn-Pb belt similar to those reported in other areas of the southern Variscan Belt, such as the French Massif Central (e.g., Brevart et al., 1982) and Sardinia (e.g., Boni, 1985). Despite the common occurrence in a restricted setting, the different deposits of the West Astur Leonese Zone show features that suggest that the existing ore showings cannot be assigned to a single hydrothermal event. In fact, as a major difference with other Zn-Pb areas of the Southern Variscan belt, bulk reserves are related to a Late

Variscan hydrothermal activity. In the Massif Central or Sardinia most of the carbonate-hosted mineralizations are interpreted as synsedimentary or diagenetic.

This work presents a synthesis of available geological and geochemical data and a regional model for the genesis of these mineralizations. More specific information about the different ore deposits can be found in Arias et al. (1991) or Tomos et al. (1996).

GEOLOGIC SETTING

The studied mineralizations are located in the carbonate Vegadeo Formation, in West Asturian Leonese Zone of the Variscan Belt (Fig. 1). This Zone represents the transition zone between the foreland area (Cantabrian Zone) and the

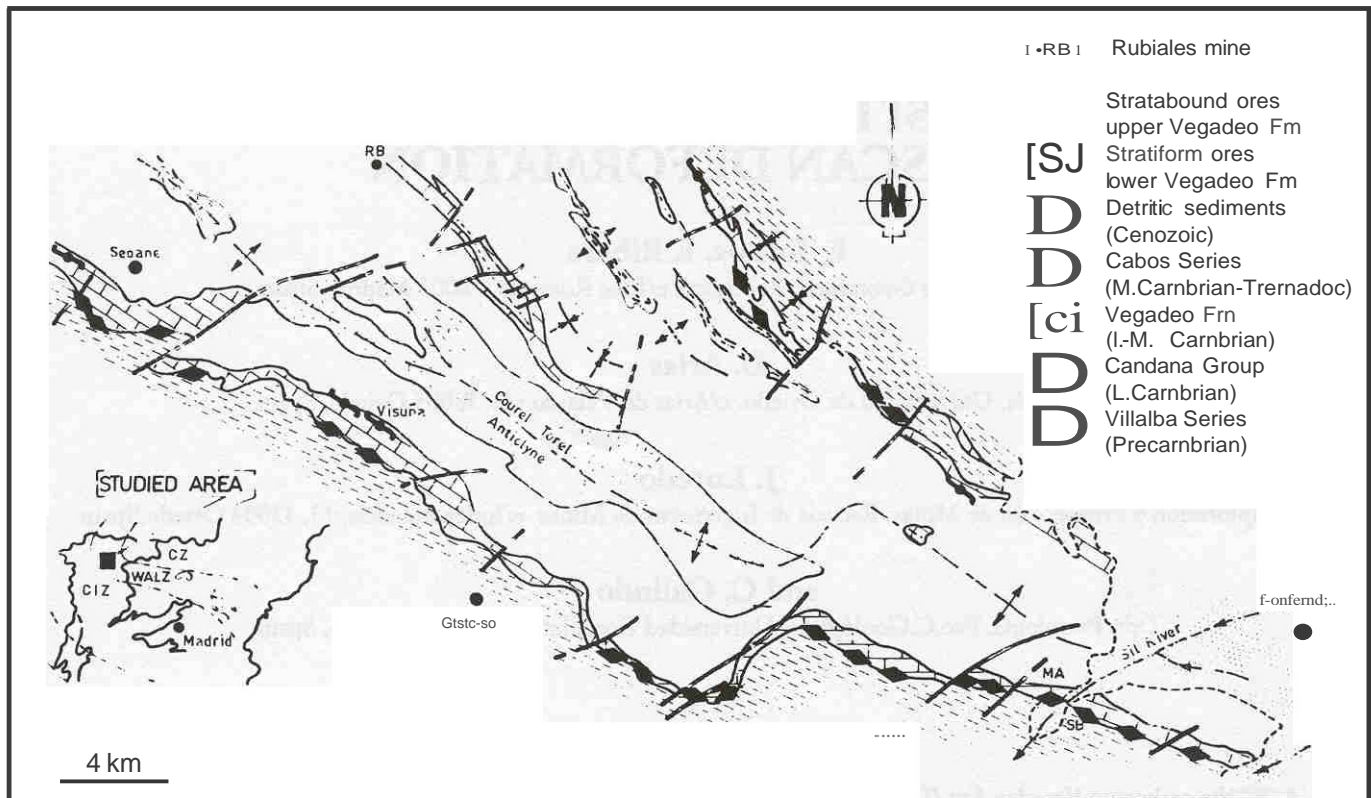


FIGURE 1-Location map of the carbonate-hosted Zn-Pb deposits in NW Spain. SB: Santa Bárbara. MA: Antonina Mine.

more internal zone (the Centro Iberian Zone) to the westward (inset in Fig. 1). It is characterized by the presence of a thick sequence of Upper Proterozoic terrigenous sediments unconformably overlain by shallow-water Lower Cambrian to Lower Devonian successions of up to 11,000 m thick.

The Vegadeo Formation, of Lower-Middle Cambrian age, has been traditionally divided in three members (e.g., Zamarreño, 1983). The Lower Member (V_1) is up to 135 m thick and consists of alternating limestones and shales that were deposited in subtidal conditions. The Intermediate Member (V_i , 90-150 m) consists of tabular and massive limestones and dolostones. In the upper part there are grey tidal and supratidal dolostones and limestones with abundant sedimentary structures such as algal mats, pisolites, oolites, pseudomorphs of evaporitic sulfates, and fenestra and "teepee" structures. The Upper Member (V_1), which is discontinuous (0-50 m), consists of fossiliferous limestones, pyrite-rich black shales, calcite-rich schists, and green phyllites. This Member was deposited in a shallow subtidal or beach zone. However, the variety of sedimentary facies and widespread superimposed epigenetic dolomitization throughout the mineralized area makes the definition of a composite stratigraphic section difficult.

The Vegadeo Formation is intercalated between two detrital groups, the Cándana Group (Lower Cambrian) and the Cabos Series (Middle Cambrian-Tremadoc). The Cándana Group consists of up to 1,600 m of sandstones and shales with minor intercalations of limestones, conglomerates and quartzites. It unconformably overlies Precambrian

schists (Villalba Series). The Vegadeo Formation is sharply overlain by the Cabos Series, a lithologically varied sequence of 1,000-2,000 m of sandstones, shales and quartzites that increases its detrital proportion towards the top (Pérez Estaún et al., 1990).

The structure of the area consists of large recumbent NNW-SSW trending folds of Variscan first phase (D_1) with a related regional slaty cleavage. The second phase (D_2) produced thrust-type structures with the same orientation. It developed schistosity in only the more deformed bands. The third deformation episode (D_3) is represented by vertical folds, nearly coaxial with the previous ones (N-S). Metamorphism associated with D_1 and D_2 is of low-grade (within or below the chlorite zone). Igneous rocks have been reported in the area (Martínez Catalán et al., 1990).

DESCRIPTION OF THE MINERALIZATION

The Rubiales deposit

The Rubiales Mine, which was exploited between 1977 and 1992, had original reserves of 18.6 Mt with an ore grade of 7.3% Zn, 1.3% Pb and 13 g/m³ Ag. The ore deposit consists of a subvertical lens-shaped orebody, N150° in trend, within the Lower Member of the Vegadeo Formation. It is located at the intersection between a D_2 shear zone and D_1 - D_3 extensional faults with the carbonate rocks, defining a large aureole of hydrothermal replacement and mineralization that cuts across stratigraphic contacts (Fig. 2)

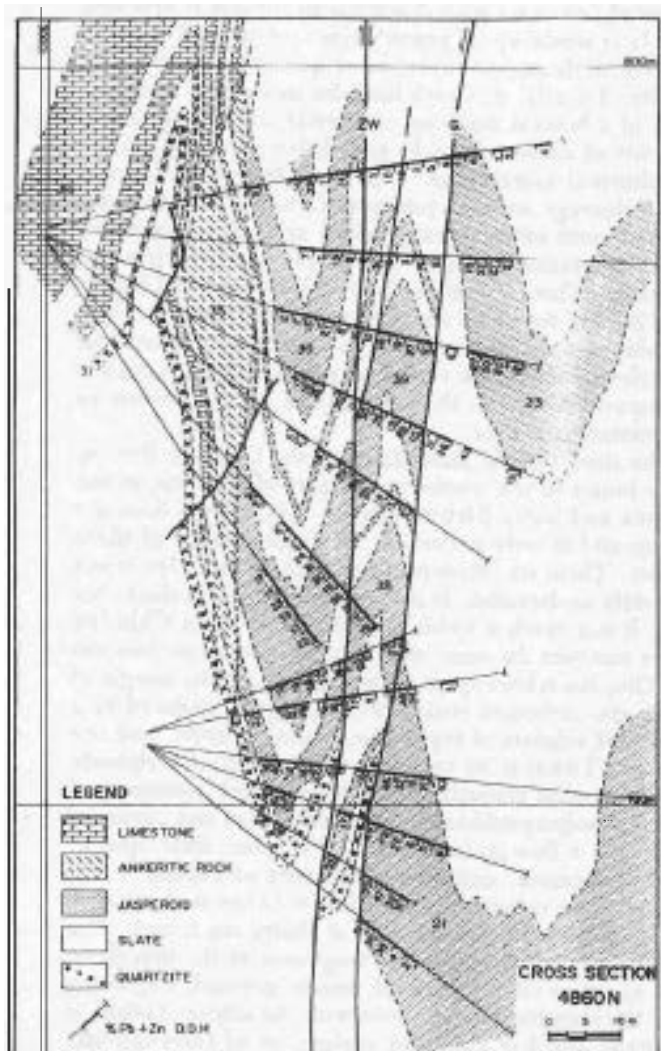


FIGURE 2 -Typical cross section of the Rubiales Mine. The ore deposit is hosted by limestones and shales of the Lower Vegadeo Formation. Close to the major faults, limestones are replaced by early ankerite (ankeritic rock) and later silica-rich mineralized rock (jasperoid).

(Arias et al., 1991). There was a first hydrothermal event that consisted of the replacement of limestones by ankerite and of interbedded shales by sericite plus quartz. The mineralizing event included the silicification of ankerite (producing jasperoid) and precipitation of sulfides. Here, pyrite and pyrrhotite occur as early minerals close to the major faults, but sphalerite (Hg, 0.14-0.33%; Fe, 1.3-2.65%) and galena (0.05 % Ag) account for 98% of the ore mineralogy. Chalcopyrite occurs in trace amounts. The jasperoid includes 75% of the lead and 90% of the zinc, but sphalerite and galena also occur as veins along the stratification or cleavage surfaces in the hydrothermalized shales. Late chlorite occurs in the deeper zones of the ore deposit, whereas crosscutting calcite veins are widespread in the deposit. This ore deposit seems to be almost unique, and only minor similar ore showings occur nearby.

Stratiform mineralization in the Lower Vegadeo Formation

The Lower Member of the Vegadeo Formation also hosts a minor stratiform mineralization (Fig. 1) that consists of disseminated sphalerite and subordinate galena in lenses up to several tens m length and up to five m thick interbedded with sparry white recrystallized limestones. In detail, ore minerals occur along discontinuous mm layers that follow the laminations within the host rock. Sphalerite (1.6-2.1 % Fe; 0.01-0.2% Hg) and galena (0.03% Ag) replace earlier coarsely crystalline pyrite, but no products of obvious hydrothermal alteration occur within the limestones. Lateral to the orebodies, limestones exhibit abundant lenses and disseminated pyrite. The orebodies were disrupted and remobilized by dolomitization of Variscan age (Ribera and Tornos, 1993).

This type of mineralization is rare and only occurs in the Visuña and Seoane areas (Fig. 1). However, disseminated sphalerite and galena are widespread in all the Vegadeo Formation.

Stratiform mineralization in the Upper Vegadeo Formation

Most of the Zn-Pb ore showings and deposits of the area occur in the Upper Vegadeo Formation (Middle and Upper Members), along the contact between the massive limestones with shales and minor sandstones of the overlying Cabos Series (Fig. 1). Several tens of ore showings follow this contact, but only two ore deposits have been drilled and evaluated: the Santa Bárbara and Antonina Mines (Fig.3). The

Santa Bárbara Mine is an orebody with 3 Mt of known evaluated: the Santa Bárbara and Antonina Mines (Fig. 3). The reserves with 10.5%Zn, 7.1%Pb and 50 g/mt Ag. The Antonina Mine has about 2 Mt with 5.3%Zn, 5.3%Pb and 48 g/mt Ag.

Three main types of mineralization are distinguished in the Upper Vegadeo Formation: the "Silica Ore," the "Carbonate Ore" and the "Chloritic Breccia" (romos et al., 1996). The first one is volumetrically the most important, whereas the Carbonate Ore and the Chloritic Breccia occur only in some outcrops.

The Silica Ore occurs as stratiform bodies that strictly follow the contact between the Vegadeo Formation and the Cabos Series along more than fifty kilometres in both flanks of the Caurel-Toral anticline and related folds (Fig. 1). The thickness of this rock is variable, from less than 0.5 to up to 15 m. Silica ore is composed mainly of milky to brownish black to banded quartz (>95%) that occurs as, anhedral, medium to fine grained (0.1 to 5 mm) grains that exhibit undulatory extinction. Minor evidence of ductile deformation with local subgrain development occur sparsely. Typical accessory minerals are euhedral calcite and dolomite as replacements of earlier quartz. Also, oriented and fine grained phengite and chlorite occur locally as interstitial crystals or late veinlets. On a mesoscopic scale, common banding and possible fossilized paleochannels can be observed. There is no evidence of large open-space filling. Only some coarse calcite crystals occur within vugs. The replacement morphology, the presence of relics of unreplaced carbonates, and the occurrence of faint sedimentary structures indicate that this rock is a product of the

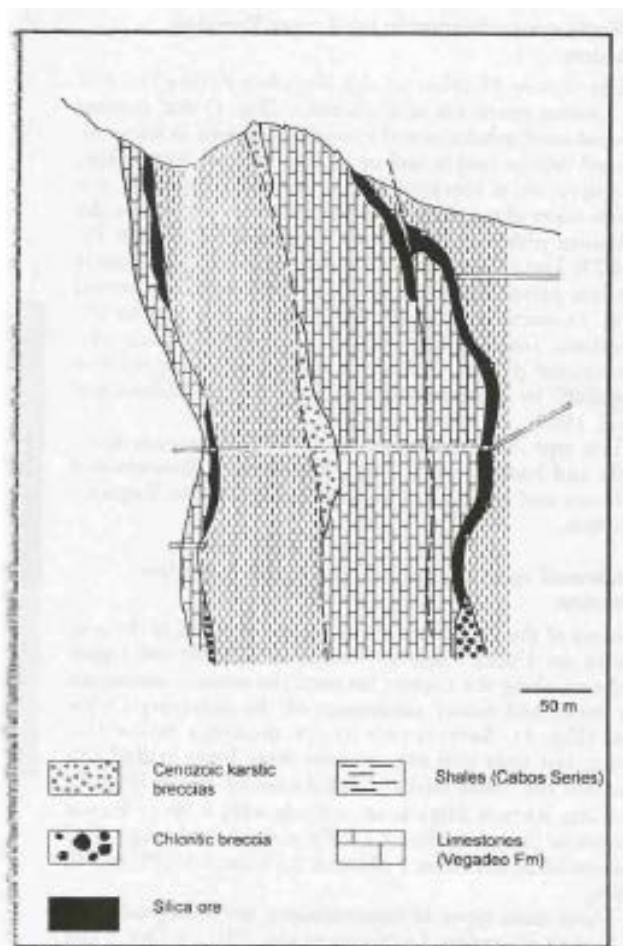


FIGURE 3 - Schematic cross section of the stratabound mineralization in the Upper Vegadeo Formation at the Antonina Mine. The Silica Ore is located in the contact between the Cabos Series and Vegadeo Formation (Vz). The Chloritic Breccia is located in the deeper portions of the mine and its situation in the scheme is only approximate. Slightly modified from SMMPE-ENADIM.SA (1985).

metasomatic replacement of the carbonate rocks of the Vegadeo Formation. The hydrothermal alteration of the related shales consists of a local but pervasive sericitization and silicification.

Sphalerite (0.7-3.6% Fe, 0.04-0.6% Hg) and minor galena (0.01-0.12% Ag) with some chalcopryrite and pyrite occur as cm to m thick stratabound bodies. Minute grains of tetrahedrite, gersdorffite, arsenopyrite, glaucodot, bismuthinite, bismuth and Pb-Bi-Ag sulphosalts occur sporadically inside the galena. On the ore district scale, there is a zonation in the Zn/Pb ratio which diminishes from NW to SE from 10:1 to 1:1 (SMMPE-ENADIM.SA, 1985).

The contact between the Silica Ore and the carbonate host is in most places sharp. However, in the Visuña area, the contact between the silica-rich rock and the limestones is commonly bounded by 2-3 m of a beige, fine grained and

unoriented dolomite with disseminated sulfides (Carbonate Ore). It is made up of granoblastic calcite and ferroan dolomite with minor amounts of quartz, chlorite, and phenogite. Locally, this rock includes meter-size irregular masses of a breccia made up of angular, centimetre sized, fragments of carbonate rocks and shales cemented by the hydrothermal assemblage. The shale fragments show a distinct cleavage and superimposed crenulation. Accessory sphalerite with minor pyrite, galena and chalcopryrite are found disseminated or as irregular bands inside the carbonates. This Carbonate Ore has been replaced by the Silica Ore and cut by an irregular set of quartz veinlets that prograde from the Silica Ore. These veins do not crosscut the unaltered carbonate rocks, suggesting that this rock is contemporaneous with the silicification and represents an outer metasomatic zone.

The third style of mineralization, the Chloritic Breccia, is only found in the southernmost part of the area, in the Antonina and Santa Bárbara Mines. This breccia does not outcrop and it only occurs in the deeper zones of these deposits. Thus, its relationship with the Silica Ore is not completely understood. It is between 2 and 8 m thick, but locally it can reach a width of up to 30 m. This Chloritic Breccia occupies the same stratigraphic position as does the Silica Ore, but relationships are ambiguous. In the margin of the breccia, carbonate rocks are progressively replaced by a network of veinlets of crystalline calcite, chlorite, and ore minerals. Towards its core, the proportion of carbonate rocks diminishes gradually, resulting in a rock consisting of masses of polycrystalline, white calcite up to one meter of

diameter in a fine-grained matrix of chlorite, illite, quartz, calcite, dolomite, and minor amounts of kaolinite and smectite. The contact with the Cabos Series is sharp, and only some brecciated fragments of shales are found. The sulfides are interstitial between fragments of the breccia or occur as up to centimeter-size, coarse-grained, fragments inside the chlorite or intergrown with the calcite. Galena is dominant and has common inclusions of tetrahedrite. Sphalerite is also abundant and chalcopryrite, with inclusions of siegenite and gersdorffite, is locally important.

AGE OF MINERALIZATION

Stratiform ores in the Lower Vegadeo Formation are interpreted as pre-Variscan, inasmuch as a dolomitization of that age disrupted and remobilized the mineralization. Lead isotopic compositions of galenas (see below) provide model ages of 481-510 Ma with the curve of Sinclair et al. (1993). This model curve has been constructed for the French Massif Central that is located in the same tectonostratigraphic setting, therefore these model ages are interpreted as accurate enough.

The hydrothermal alteration and related mineralization of the Rubiales deposit are associated with subvertical faults of Variscan O_{2,3} phase, of Lower Carboniferous age (Arias et al., 1991). Sericite from a hydrothermally altered shale has been dated as 307±7 Ma (K-Ar), an age consistent with the regional geology.

The Carbonate Ore includes rotated shale fragments with two distinct cleavages that have been interpreted as the regional S₁ slaty cleavage superimposed by the S₂ crenulation

cleavage (Tornos et al., 1996). The silica ore is interpreted to be synchronous with the Carbonate Ore and is affected by late brittle faults. Two sericitic of the Silica Ore have been dated as 320 ± 6 and 323 ± 7 Ma. These results are in agreement with previous ones and support the concept that a late hydrothermal rocks in the region are broadly contemporaneous. However, these stratabound ores seem to predate the discordant ones and are probably related to the climax of the Variscan deformation. ^{206}Pb model ages of Rubiales (486 ± 5 Ma) and the Upper Vegadeo Formation (527 ± 7 Ma) are similar to the ones of the stratiform ores, but are meaningless as discussed in the lead isotope interpretation.

FLUID COMPOSITION

Fluid inclusions of likely primary origin were not found in the stratiform ores of the Lower Vegadeo Formation and are scarce in the stratabound mineralizations of the Upper Vegadeo Formation. They appear as two-phase aqueous inclusions up to $15 \mu\text{m}$ in length. Secondary fluid inclusions in quartz of the Silica Ore homogenize to liquid between 155 and 274°C , whereas primary ones in the calcite of the Chloritic Breccia homogenize at 163 to 224°C . Bulk salinities are 0 - 1.2 wt% NaCl eq. Bulk gas analysis by mass spectrometry following the methodology of Shepherd et al. (1991) confirm that these fluid inclusions are water-rich ($X_{\text{H}_2\text{O}} > 0.99$), with very minor amounts of CO_2 and only traces of CO , C_2 , and Ni .

In the Rubiales Mine, fluid inclusions in the quartz provide similar results. They are also biphasic (LV), up to $20 \mu\text{m}$ in length and exhibit small vapor bubbles ($< 20\%$ vol.). First melting temperatures are between -28 and -23°C , indicating that CaCl₂ can be an important component of the system. Ice melting temperatures are between -3.9 and -2.2°C , suggesting low salinities, between 3 and 7 wt% NaCl eq. They homogenize to liquid between 200 and 240°C , with a mode at $215 \pm 5^\circ\text{C}$.

PRESSURE-TEMPERATURE CONDITIONS OF FORMATION

In addition to the minimum trapping temperatures obtained from microthermometry, stable isotopes can provide an independent geothermometer. In the Rubiales deposit, the remarkable $\delta^{18}\text{O}$ homogeneity of the ore deposit suggests that isotopic equilibrium was achieved (Tornos and Arias, 1993). Individual galena-sphalerite geothermometry, using fractionation coefficients from Ohmoto and Rye (1979) give temperatures between 157 and $218 \pm 25^\circ\text{C}$. These temperatures are within the temperature calculated using the

deposit ($206 \pm 51^\circ\text{C}$) and the pyrite-pyrrotite pair ($229 \pm 40^\circ\text{C}$). A comparison of isotopic with microthermometric results suggests that the maximum fluid pressures was low. The absence of fluid inclusions homogenizing to vapor and hydraulic breccias indicate that extensive boiling did not occur. The minimum fluid pressure required to prevent boiling of these fluids is very low, about 15 bars at 200°C . Comparison of the calculated isochores with maximum uncertainty in the sphalerite-galena geothermometry lead to a

maximum fluid pressure of about 400 bars. Since both the estimated pressures are probably in excess, a value of 125 bars has been assumed as representative. This value implies about 440 m depth in a lithostatic dominated system ($\rho = 2.9 \text{ gr/cm}^3$) and 1600 m depth in an open system dominated by hydrostatic pressures. The first result is low for a hydrothermal system developed between the D2 and O3 Variscan phases, even if high erosion rates existed. A depth close to 1.5 km is more consistent with the tectonometamorphic evolution of the area.

The temperature of formation of the stratabound ores in the Upper Vegadeo Formation can be established only by fluid inclusion data, which provide minimum temperatures of 155 to 274°C . These temperatures must be close to the formation ones, inasmuch as the isochores of the fluid inclusions are very steep. Isotopic temperatures calculated from the galena-sphalerite pair are unrealistic (see below) and suggest that isotopic equilibrium was not attained.

ISOTOPIC GEOCHEMISTRY

Carbon-oxygen isotopes

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signature of the calcite enclosing the stratiform ores in the Lower Vegadeo Formation is very similar to that of the nearby unmineralized carbonates (Fig. 4), demonstrating that fluids related with the ore-forming event were in isotopic equilibrium with the host rock. Carbonates of the stratabound ores in the Upper Vegadeo Formation and the Rubiales deposit are significantly different and depleted in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ relative to regional values, suggesting that they developed in relationship with the influx of an external fluid in isotopic disequilibrium with the enclosing carbonates. Ankerites of the Rubiales deposit (Table 1) and calcites of the Chloritic Breccia have the lighter isotopic signatures, probably implying that they grew at the

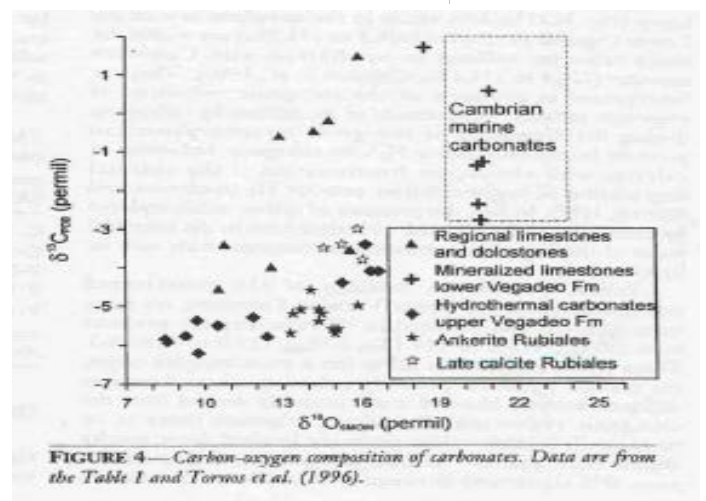


FIGURE 4—Carbon-oxygen composition of carbonates. Data are from the Table 1 and Tornos et al. (1996).

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highest fluid/rock ratios. Thus, for a mean temperature of 200°C, the heaviest isotopic composition of the hydrothermal fluid must be between -1 and 3.4‰ ($\delta^{18}\text{O}_{\text{SMOW}}$) and -5.8 to -4.2‰ ($\delta^{13}\text{C}_{\text{PDB}}$). Heavier isotopic compositions of the late calcite in Rubiales or the vuggy calcite in the Silica Ore are consistent with their formation at lower fluid/rock ratios or with a later crystallization at lower temperatures (=130-150°C).

TABLE 1-Isotopic composition of carbonates from Rubiales

SAMPLE	MINERAL	$\delta^{18}\text{O}_{\text{SMOW}} \text{‰}$	$\delta^{13}\text{C}_{\text{PDB}} \text{‰}$
VC-1	Regional limestone V1	20.0	-0.4
K-174	Ankerite, ankerite rock	13.3	-5.7
K-176		14.1	-4.6
K-179		14.4	-5.4
K-180		15.1	-5.6
K-181		14.9	-5.6
K-181b		15.0	-5.7
K-182		14.5	-5.2
K-185		13.7	-5.1
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K-186		13.4	-5.2
K-187		14.4	-5.1
K-188		15.9	-5.0
K-159	Late calcite in veins	16.1	-3.8
K-178		15.3	-3.4
K-183		14.6	-3.5
K-188		15.9	-3.0

Analysis BRGM. Analytical precision $\pm 0.1\text{‰}$

Sulfur isotopes

The $\delta^{34}\text{S}$ of sulfides from all the deposits is relatively heavy (Fig. 5). The $\delta^{34}\text{S}$ values in the stratiform ores of the Lower Vegadeo Formation (+28.2 to +35.0‰) are within the mean value for sulfates in equilibrium with Cambrian seawater (+26.4 to +34.4‰, Claypool et al., 1980). They are interpreted as products of the abiogenic reduction of evaporitic sulfates. Replacement of the sulfates by carbonates during the diagenesis or low-grade metamorphism can produce isotopically heavy H_2S by abiogenic reduction of sulfates with almost no fractionation if the thermal degradation of organic matter provides H_2 (Anderson and Garven, 1987). In fact, the presence of sulfate molds replaced by carbonates and associated with algal mats in the intertidal facies of the Vegadeo Formation is consistent with such an hypothesis.

Sulfur isotopes in sulfides of the stratabound mineralizations in the Upper Vegadeo Formation are more heterogeneous and depleted in HS regarding the previous ones ($\delta^{34}\text{S}_{\text{Galena}}$ +18.2 to +24.1‰, $\delta^{34}\text{S}_{\text{Sph}}$ +19.0 to +28.6‰). These results suggest that sulfur has a more complex origin, the isotopic signatures probably reflecting mixing from two different sources. Most of it was probably derived from the abiogenic reduction of sulfates, whereas there is an isotopically lighter sulfur probably leached from nearby shales. Here, pyrites with likely biogenically-reduced sulfur have $\delta^{34}\text{S}$ signatures between +3.2 and +41.3‰, but its

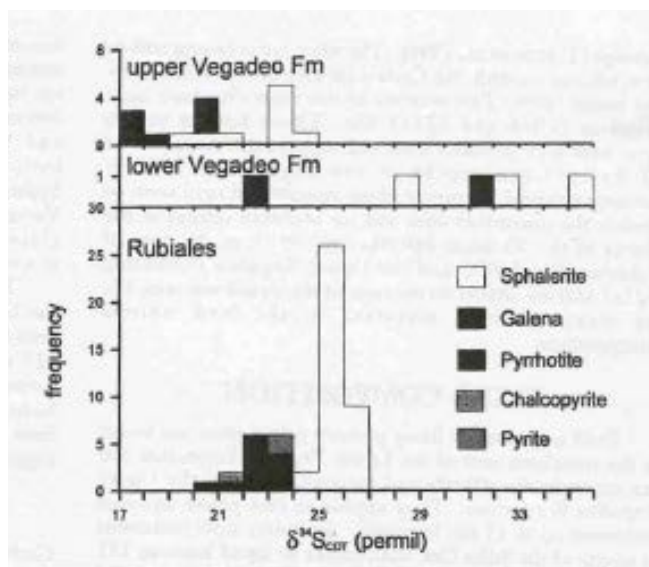


FIGURE 5-Sulfur isotopic composition of the different ores. Data from the Table 2, Tornosanti Arias (1993) and Tornos et al. (1996).

hydrothermal homogenization leads to signatures close to +10-15‰ (Tornos et al., 1993).

The $\delta^{34}\text{S}$ signatures in Rubiales are similar to the previous ones, but strikingly homogeneous and with no vertical or lateral variation. The $\delta^{34}\text{S}$ signatures of sphalerites are $+25.6 \pm 0.5\text{‰}$ (n=35) and the galena has a $\delta^{34}\text{S}$ signature of $+22.5 \pm 0.4\text{‰}$ (n=8) (Tornos and Arias, 1993). More recent analyses of chalcopyrite, pyrrhotite, and pyrite have also consistent signatures (Table 2). These values are interpreted in a similar way as those of the Upper Vegadeo Formation, but show that here isotopic homogenization was completely attained. However, the isotopic composition of the iron sulfides show that they were precipitated from fluids enriched in S^{32} (+17 to +20.5‰) than the sphalerite and galena of the main mineralizing stage ($+24.3 \pm 1.5\text{‰}$).

TABLE 2-Isotopic composition of sulfides (excluding galena and sphalerite from Rubiales)

SAMPLE	MINERAL	$\delta^{34}\text{S}_{\text{Sulf}} \text{‰}$
C-171	Chalcopyrite	+23.5
C-310	Chalcopyrite	+23.8
P-20	Pyrrhotite	+21.2
P-157	Pyrrhotite	+20.4
P-157	Pyrite	+21.6

Analysis BRGM. Analytical precision $\pm 0.2\text{‰}$

Oxygen-deuterium isotopes in silicates

Hydrothermal quartz in Rubiales has homogeneous O^{18}O signatures between +15.2 and +16.6‰ (Table 3). These compositions are only slightly lower than the $\delta^{18}\text{O}$ values of

the quartz in the Silica Ore (+17.0 to +18.3‰) (Ribera and Tornos, 1994). $\delta^{18}\text{O}$ - δD compositions of two sericites and one chlorite from Rubiales are shown in the Table 3.

TABLE 3-Isotopic composition of quartz and phyllosilicates from Rubiales

SAMPLE	MINERAL	$\delta^{18}\text{O}_{\text{SMOW}} \text{‰}$	$\delta\text{D}_{\text{SMOW}} \text{‰}$
M-153	Quartz silica rock	15.2	
M-155		16.2	
M-157		15.6	
M-161		16.2	
M-162b		16.6	
M-163		16.2	
M-164		16.2	
M-165		16.2	
M-200		15.8	
P-178	Sericite, altered shale	13.5	-52
P-300		13.8	-53
M-150	Chlorite, altered shale	1.8	-48

Analysis BRGM. Analytical precision, $\delta^{18}\text{O}$: ±0.1‰, δD : ±3‰

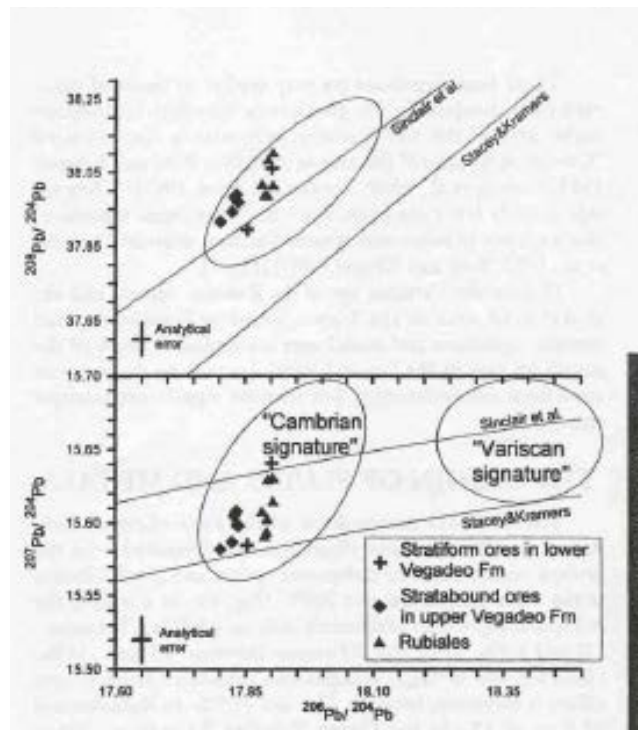


Figure 7

$^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios (Stacey and Kramers curve) of 9.78-9.96 and 38.8-40.2, respectively. The data define a linear array that is only slightly wider than the analytical error, which can be interpreted as reflecting a mixing isochron resulting from mixing of lead from different reservoirs with similar signatures but with different μ values. Similar trends have been observed in many ore deposits (e.g., Dixon et al., 1990; Caron et al., 1993). The more radiogenic lead, that plot close to the Sinclair et al. (1993) curve,

maturity of Archean rocks by metamorphic, magmatic or sedimentary processes can lead to these high μ and ρ values, which are typical of the southern Variscides (e.g., Sinclair et al., 1993; Nagler et al., 1993). The low radiogenic extreme of the mixing isochron is close to the average crustal curve of Stacey and Kramers (1975). A likely candidate are the detrital rocks that were derived from the erosion of igneous rocks with a higher juvenile contribution. It could be a Cadomian sequence similar to the one exposed in the Ossa Morena Zone (SW Spain) that has a significant juvenile component. In fact, Nagler et al. (1993) have reported from central and southern Spain Lower Ordovician detrital rocks with mean μ values of 9.73. Independent of the ultimate origin of the lead, preliminary lead isotope data of the Cándana and Cabos Series are consistent with a separation of lead from nearby detrital rocks during the Early Paleozoic.

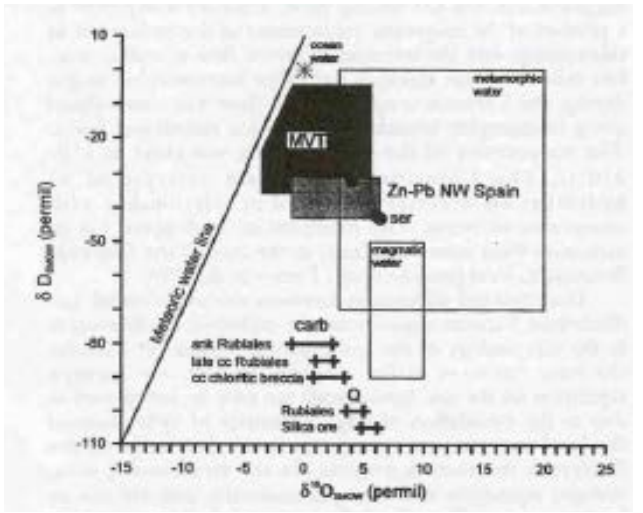


FIGURE 6- $\delta^{18}\text{O}$ vs δD diagram showing the estimated composition of hydrothermal fluids related to the Variscan mineralizations. A mineral-fluid has been calculated at 200°C, except the late ankite of Rubiales, calculated at 140°C. The $\delta^{18}\text{O}$ - δD field of fluids related to Mississippi Valley Type deposits (MVI) is from White (1974). Fractionation factors for mineral-fluid are from Turpin et al. (1990) (sericite, chlorite), Fisher and Land (1986) (ankerite) and Matsuhisa et al. (1979) (quartz). Data from the Table 3 and Ribera and Tornos (1993). carb: carbonates, ank: ankerite, cc: ankite, Q: quartz.

Lead isotopes in galena

Lead isotopes of galenas are very similar to one another (Fig. 7). They plot between the Stacey and Kramers (1975) and the Sinclair et al. (1993) curves and have original

These lead signatures are very similar to those of other carbonate-hosted Zn-Pb districts in Cambro-Ordovician carbonates of the SW Variscan belt, within the so-called "Cambrian signature" (Brevart et al., 1982; Boni and Koppel, 1985; Ludwig et al., 1989; Tornos and Arias, 1993). They are significantly less radiogenic than the "Hercynian signature" that includes granites and several Variscan deposit (Brevart et al., 1982; Ború and Koppel, 1985) (Fig. 7).

Despite the Variscan age of the Rubiales deposit and the stratabound ores in the Upper Vegadeo Formation, lead isotopic signatures and model ages are similar to those of the stratiform ores in the Lower Variscan ores from the previous stratiform mineralization, but without significant isotopic changes.

THE ORIGIN OF FLUIDS AND METALS

The $\delta^{18}\text{O}$ -80 composition of the hydrothermal fluid during the Variscan mineralization can be estimated from the isotopic composition of carbonates, quartz and phyllosilicates at the mean temperature of 200°C (Fig. 6). As a whole, the isotopic composition of minerals indicate a $\delta^{18}\text{O}$ fluid between -1.0 and 6.3‰ while the $\delta^{18}\text{O}$ ranges between -43 and -31‰. However, the $\delta^{18}\text{O}$ fluid composition calculated from quartz values is narrower, between +3.6 and +5.0‰ in Rubiales and +4.8 to +6.3‰ in the Upper Vegadeo Formation. Since quartz is a phase that only changes its isotopic composition by complete recrystallization, a range of $\delta^{18}\text{O}$ fluid between +3.6 and +6.3‰ is interpreted as the more likely during the ore forming process. $\delta^{18}\text{O}$ fluid values estimated from the other minerals can be more imprecise due to large uncertainties in the mineral-fluid fractionation factors or to easy reequilibration of carbonates and phyllosilicates with later fluids.

In any case, the estimated isotopic composition of these fluids related with the Variscan mineralization defines a field that plot away from the meteoric water line or the magmatic field. They are within the isotopic composition of highly evolved connate waters, meteoric fluids with long residence times in detrital rocks, or waters derived from the dehydration of phyllosilicates during the low grade metamorphism (e.g. Sheppard, 1986), but their exact origin cannot be determined. However, the calculated field is close to the average composition of Mississippi Valley Type deposits of North America (White, 1974).

Carbon isotopes denote that the inflowing fluid had an homogeneous $\delta^{13}\text{C}$ signature between -5.8 and -4.3‰. These values are intermediate between typical values for carbon in carbonate rocks and that derived from organic matter. Thus, the more likely principal source was organic matter associated with the nearby shales, but a contribution from the enclosing carbonates must be viewed as likely.

As discussed above, $\delta^{34}\text{S}$ data suggest that sulfur in the stratiform ores was derived from the enclosing rocks by abiogenic reduction of sulfates, whereas in the Variscan ores there was also a significant contribution from detrital rocks. Lead isotopes also indicate that lead, and by similarity zinc, were leached from the enclosing rocks.

GENETIC MODEL AND CONCLUDING REMARKS

In Cambrian carbonate rocks of NW Spain there are three types of ore deposits: stratiform mineralization in the Lower Vegadeo Formation, stratabound deposits in the Upper Vegadeo Formation and discordant mineralization (Rubiales-type). The first ones are only local, whereas the stratabound and discordant deposits host the bulk reserves.

Stratiform mineralization is interpreted as diagenetic and formed during the Cambro-Ordovician times by the circulation of fluids isotopically equilibrated with host carbonates. Lead was derived from nearby detrital rocks, whereas sulfur is product of the abiogenic reduction of evaporitic sulfates interbedded with the carbonates. These deposits are equivalent to the MVT deposits of the southern Variscan Belt (e.g., Boni, 1985).

Despite their different tectonostratigraphic setting, stratabound mineralization in the Upper Vegadeo Formation and the discordant replacements in the Rubiales Mine share several features such as the mineralogy (paragenesis, presence of Hg-rich and Fe-poor sphalerite), the hydrothermal alteration (pervasive silicification and the presence of chlorite), the isotopic signatures and the age. These features suggest a common link among them. They are interpreted as a product of the epigenetic replacement of the carbonates in relationship with the tectonically driven flow of mildly acid, low saline aqueous fluids of basinal or metamorphic origin during the Variscan orogeny. Fluid flow was channelized along stratigraphic boundaries and major extensional faults. The temperature of the ore formation was close to 150-250°C. The Chloritic Breccias are interpreted as hydrothermal breccias developed in relationship with overpressured zones. Ore precipitation took place due to carbonate-fluid interaction and, in the case of the Chloritic Breccias, to local pressure drop (Tornos et al., 1996).

Geochemical differences between the stratabound and discordant Variscan deposits can be explained by differences in the morphology of the hydrothermal system. In Rubiales the very constant sulfur, oxygen, and carbon isotope signatures on the ore deposit scale can only be interpreted as due to the circulation of large quantities of hydrothermal fluids of constant isotopic composition that buffered the fluid/rock interaction process. In the stratabound ores, isotopic signatures and microthermometric data are not so homogeneous. Slow fluid flow along lithologic contacts would produce lower fluid/rock ratios with a greater control of the hydrothermal process by the host rock. This should lead to a more local derivation of the elements and no isotopic homogenization.

The interpretation of these Variscan deposits is not straightforward. They have some of the descriptive characteristics of the carbonate-hosted Zn-Pb deposits (MVT s.l.), such as paragenesis, with sphalerite and galena with minor amounts of iron and copper sulfides, the presence of stratabound replacements, and the absence of cogenetic igneous rocks. Also the isotopic composition of the fluid is broadly similar. The range of temperatures is close to the upper limit of Mississippi Valley-Type deposits (50-200°C) (Sverjensky, 1987; Sangster, 1990). However, the main difference is the geological setting. Whereas most MVT

deposits occur in the foreland thrust belt (e.g., Plumlee et al., 1994), these deposits are situated in the internal domain of an orogenic belt, postdating Variscan metamorphism. Other major differences are the absence of related hydrocarbons, the low salinity of the hydrothermal fluids, and the hydrothermal alteration, with pervasive silicification and appreciable amounts of sericite and chlorite.

The spatial relationships and the isotopic signatures of the diagenetic and Variscan mineralizations of the area also indicate a link among them. The Variscan mineralizations are interpreted as having been derived from the stratiform, diagenetic precursors. Lead and most of the sulfur have been derived by hydrothermal remobilization from these earlier mineralizations. This remobilization occurred in a isotopically-frozen system where the amount of lead supplied by the sedimentary rocks seems to have been negligible.

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