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The Zn-Pb-rich belt of NW Iberia. Syn-tectonic stratabound mineralization?

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Abstract: NW Iberia has regionally extensive zones of carbonate-hosted Zn-Pb mineralization within the early-Middle Cambrian carbonate dominant Vegadeo Formation which hosts three major deposits as well as tens of small mines and prospects. The most common style occurs as stratabound bodies directly related with widespread silicification developed along the upper contact of the Vegadeo Formation with overlying shales. Laterally, silicified zones grade into carbonate-chlorite breccias with fragments of the host-rock supported by calcite, chlorite and sulphides. Replacive and breccia zones of mineralization are interpreted as being related to large syn-D₃ Variscan structures that probably remobilized earlier, disseminated early diagenetic Zn-Pb stratiform sulphides within oolitic lenses at the base of the Vegadeo Formation. Stable and radiogenic isotope geochemistry and K-Ar geochronology confirm that economic mineralization is Variscan in age and was related to regionally extensive flow of fluids equilibrated with the underlying siliciclastic-carbonate sedimentary rocks. The key control for mineralization was the existence of an extensive aquifer within highly permeable limestones below an overlying impermeable shale that allowed extensive lateral fluid flow and the likely mixing of metal-rich fluids with confined water rich in biogenically-reduced sulphur. This mineralization event appears to be unrelated to a regionally extensive, barren dolomitization event. The Zn-Pb deposits of NW Iberia are fundamentally distinct from Irish-type mineralizing systems in that they are not associated with syn-sedimentary faulting, involve significant and extensive silicification, and appear to be clearly epigenetic. Like the Irish-type Zn-Pb deposits they appear to have resulted from fluid mixing between metal-rich and reduced sulphur-rich fluids, though the evidence for fluid mixing is more muted in the Iberian deposits.

Keywords: NW Iberia, Cambrian, Vegadeo Formation, silicification, Variscan orogeny, fluid mixing.

Introduction

Northwestern Spain hosts a large but rather unusual Zn-Pb-rich belt of mineralization that extends for several tens of kilometers from close to the northern coast of Iberia to the Bierzo Basin (Fig. 1). Mineralization was concentrated both near the footwall and the hanging wall of a regionally extensive carbonate unit, known as the Vegadeo Formation (Fm), of early to Middle Cambrian age and includes three large deposits at Rubiales, Antonina and Toral. Estimated resources are probably more than 10Mt of Zn+Pb of mineralized material of which approximately 60% remains unmined to date.

Rubiales has been mined by EXMINESA, a subsidiary company of COMINCO, whilst only the uppermost levels at Antonina were mined between 1965 and 1972 by Rio Kumer SA. Toral is the most recent discovery and presently remains unmined, awaiting final development permits; it is expected to open in the very near future. The belt also hosts tens of small mines worked between the 1910s and 1930s mainly by Real Compañía Asturiana de Minas. Systematic exploration of the area started in the 1950's-1960's by Asturiana de Zinc. Later

some of the most promising areas were explored with geophysics and geochemistry and have been drilled by various companies including Rio Kumer, SMMPE, ENADIMSA, EXMINESA and Outokumpu España. These efforts failed to define an economic orebody.

To our knowledge, no significant exploration at the regional scale has been carried out since 1992. These deposits are in the same sequence that also hosts carbonate-hosted Zn-Pb mineralization in the French Massif Central (Brevart *et al.*, 1982) and Sardinia (Boni *et al.*, 1992).

This review presents a synthesis of the current knowledge of these deposits, principally based upon studies carried out in the late 1990's (Tornos & Arias, 1993; Tornos *et al.*, 1996a, 1996b; Ribera, 1999), upon recent exploration at the Toral mine and from new field and geochemical data. Earlier studies include those of Rabu (1977), Luque & Ruiz (1990), Arias *et al.* (1991) and Hermosa, (1995). However, some of the major scientific questions remain unresolved and there is no definitive genetic model that fully explains the controls on mineralization in this region.

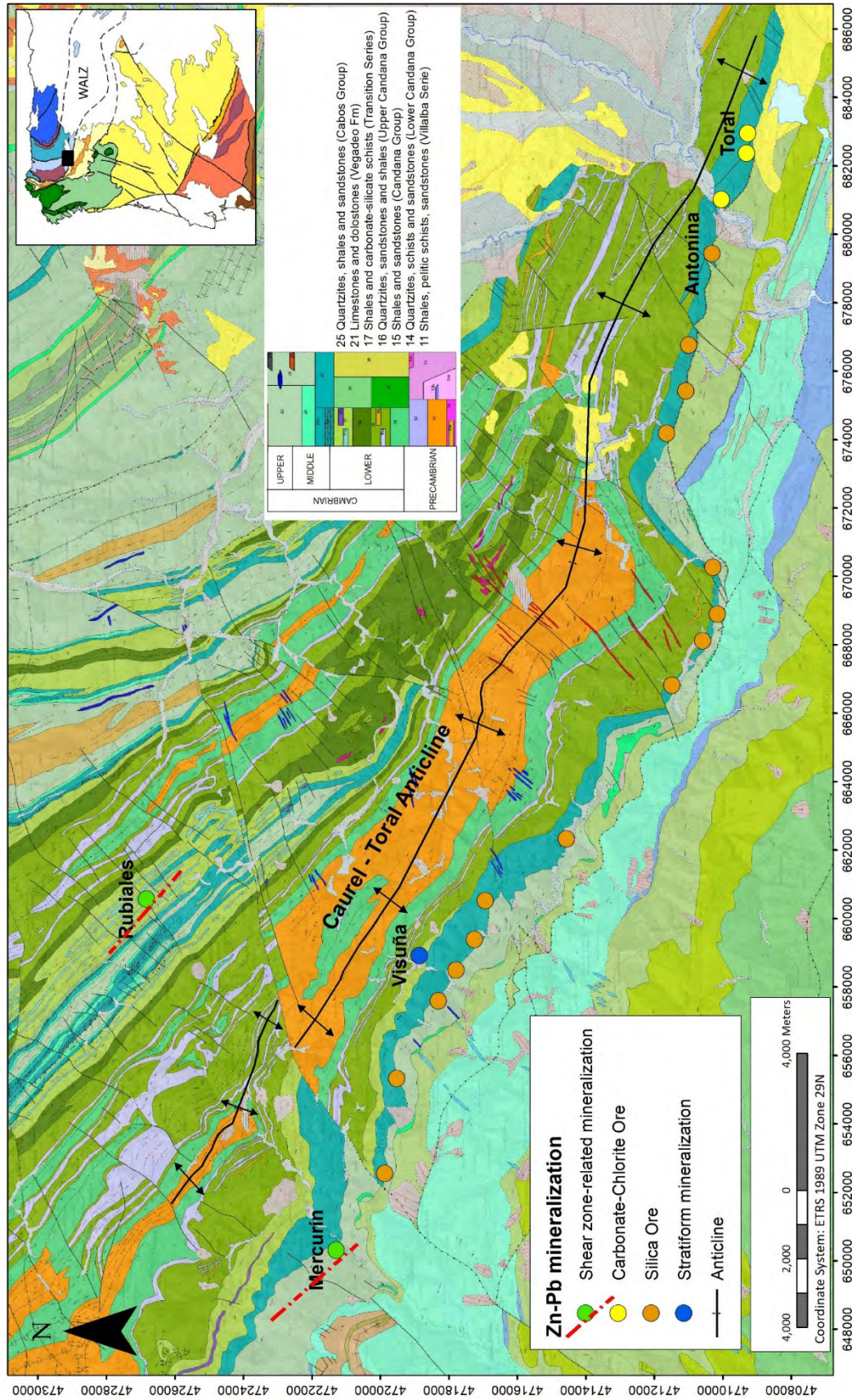


Figure 1: Regional setting of the Zn-Pb deposits of NW Iberia showing the location of deposits and prospects Modified from IGME (2012).

Geologic setting

The Vegadeo Formation is one of the most characteristic units of the West Asturian Leonese Zone ("WALZ"), which is one of several tectonic zones in the Variscan Belt of Iberia (Martinez Catalan, 1990a; Perez Estaun, 1990; Farias *et al.*, 1987; Martinez Catalan *et al.*, 1997). The WALZ represents the transition zone between the most internal zones of the orogen to the west and the foreland area to the east. The WALZ is dominated by a thick (>11,000m) sequence of Palaeozoic shallow marine sediments of early Cambrian to early Devonian age unconformably overlying late Neoproterozoic terrigenous basement rocks (Villalba Series). The structure is of Variscan age and dominated by large NNW-SSE west-verging large recumbent folds (D₁) and thrusts (D₂) coeval with the development of a widespread slaty cleavage that evolves to a schistosity in the most deformed areas; related metamorphism is of low grade, sometimes reaching the chlorite grade. There is a late deformational phase (D₃) which produced vertical folds and large subvertical shear zones (Martinez Catalan, 1990b). Magmatism of Variscan age is sparse and usually in the form of small epizonal granitic intrusions or dykes of microdiorite along major structures.

The earliest Cambrian sequence includes *ca.* 1,600m of shale and sandstone with a few intercalations of limestone (Candana Group). The overlying Vegadeo Formation, of early to Middle Cambrian age is the unit that hosts the Zn-Pb mineralization. At a regional scale, the Vegadeo Formation has abundant lateral changes in thickness (80-370m) and facies suggesting deposition in an unstable setting during post-Cadomian rifting.

In the western limb of the Caurel-Toral anticline, the Vegadeo Formation is divided into three major units (Zamarreño, 1983). The Lower Member (V₁) is characterized by alternations of shale and limestone and can be between 30 and 150m thick, including local nodular limestones and marly schists alternating with pale green shales. Locally, and especially where it is thickest in the Visuña area (Fig. 1), the carbonate rocks contain large bodies of sparite and dolosparite rich in remnants of oolites that are interbedded with sandstones and calcarenites rich in fragments of oncolites and with biostromes of archaeocyata - the V₁ Member (Zamarreño *et al.*, 1975) (Fig. 2a). These rocks were likely deposited in a sub- to inter-tidal environment dominated by high energy facies.

The Intermediate Member (V₂) is the thickest and most continuous unit of the Vegadeo Formation and is dominated by massive, monotonous, limestones that only locally show large-scale parallel bedding. This homogeneity is probably related to widespread recrystallization since in the best-preserved zones there is evidence of multiple facies changes indicative of inter- to supratidal, probably lagoon-like, conditions with local subaerial emergence (Zamarreño *et al.*, 1975). Features present include stylolites, algal mats and stromatolites, intraclasts, oncoliths, pisolites, and teepee-like structures and desiccation cracks and some intercalations rich in birds-eyes and ghosts of evaporites; diagenetic pyrite is locally present. There is minor detritic input in the form of sparse quartz grains and phengite.

The Upper Member (V₃), with a thickness of up to 20m, is not always present and comprises a wide range of lithologies including marly schist, shale, thin calc-arenite lenses and

discontinuous layers, up to 3m thick, of fine-grained green shales. These shales are considered to be fine-grained felsic tuff (Zamarreño *et al.*, 1975; Rabu, 1977) dominantly comprising phengite with minor pyrite and ilmenite altered to rutile. The lithological association as well as the abundance of fragments of echinoderms and trilobites suggest a shallow marine subtidal environment with local deeper depressions. The age is likely to be Middle Cambrian (Zamarreño *et al.*, 1975).

The Vegadeo Formation is best exposed in the SW limb of the Caurel-Toral anticline (Fig. 1). On the NE limb, the rocks are more recrystallized and homogeneous with a total thickness of up to 300m and individual members cannot be recognized. Near the Rubiales mine, Arias (1987) describes 135m of alternating layers of green shale and quartz-rich sandstone that he called the Transition Series however Zamarreño (1983) included these beds in the Lower Member of the Vegadeo Formation. The Intermediate Member, *ca.* 200m thick, includes dolomitized limestone with minor shale and sandstone; with its footwall having a *ca.* 15m thick marker layer of feldspar-rich sandstone alternating with shale. The Upper Member (<45m) includes dark limestone and shale.

The Vegadeo Formation is strongly dolomitized (Zamarreño, 1983; Ribera, 1999) by an early, pervasive, stratabound grey dolomitization that is difficult to distinguish from the adjacent limestone and is thought to be syn-diagenetic. There is also a much more obvious, pervasive, usually texturally destructive regional dolomitization with replacement of the limestone by highly porous beige dolostone that is barren of sulphides, but has abundant veins and joints infilled by hydrothermal calcite; locally it is associated with large breccia bodies of quartz + dolomite groundmass. This late dolomitization can sometimes replace the whole Vegadeo Formation and is controlled by bedding and late faults suggesting that it is Variscan in age. The common xenotropic textures (Gregg & Sibley, 1984) suggest temperatures above 50°C that are inconsistent with an early diagenetic age.

Overlying the Vegadeo Formation is a thick (1,000-2,000m) siliciclastic unit of Middle Cambrian-early Ordovician (Tremadoc Stage) aged sediments, dominated by pyrite-bearing dark shale with minor sandstone (Los Cabos Group), which was deposited at a passive continental margin. The proportion of sandstone increases towards the top of the unit probably in response to the onset of the Sardic orogeny. In the study area, the contact between the Vegadeo Formation and the Los Cabos Group is probably tectonic, supported by the common presence of cataclasite and fault gouge along the contact. The area is crosscut by abundant N35°E, N85°E, and N125°E trending faults of late Variscan to Alpine age.

The WALZ also contains a large number of different styles of mineralization, including sediment-hosted orogenic gold deposits (Arias, 1993; Villa *et al.*, 1993; Tornos *et al.*, 1997), intrusion-related gold, (Harris, 1980; Gutierrez Claverol *et al.*, 1991) and abundant related gold placer deposits (Saenz & Velez, 1974; Domergue & Herail, 1978; Herail, 1984), including the World Heritage site at Las Medulas (Perez Garcia, 1992), large ironstone bodies of Ordovician age (Lunar, 1977), and tin-tungsten deposits (Leduc, 1978; Arribas, 1983). A detailed description of the metallogeny of the zone can be found in Luque and Ruiz (1990) and ITGE (1994).

The mineralization

There are six types of Zn-Pb mineralization within the Vegadeo Fm:

- Small stratiform bodies in the Lower Member as disseminations and layers of sphalerite and galena (“Stratiform Ore”).
- Small bodies of coarse-grained sphalerite and galena within regional dolostone.
- Large regional, stratabound orebodies confined to the contact between the Vegadeo Formation and the overlying Los Cabos Group, characterized by the direct association of Zn-Pb ore with pervasive silicification (“Silica Ore”).
- Large breccia bodies and hydrothermal karst infillings of calcite, phengite and sulphides in the limestone laterally adjacent to the Silica Ore (“Carbonate-Chlorite Ore”).
- Minor stratabound breccias related to dolomitization in the immediate footwall of the Silica Ore (“Lower Breccia Ore”).
- Discordant replacements of the Lower Member along Variscan shear-zones (“Shear Zone-Related Ore”).

The ore mineral assemblages are very similar, being dominated by Fe-poor and Hg-rich coarse-grained sphalerite and galena. Chalcopyrite, pyrite and As-Co-Ni-bearing sulphides also occur in trace amounts. Most of the contained silver occurs as inclusions of tetrahedrite in the sphalerite and as Pb-Bi-Ag sulphosalts in galena. On a regional scale there seems to be a well-developed Zn/Pb zonation. In the SW zone (Toral), the ratio is 1-2 which increases to 3-5 northwards and to above 10 in the northernmost areas (Rubiales).

Stratiform ore

The oolitic limestone-dolostone bodies within the middle section of the Lower Member of the Vegadeo Formation in the Visuña area (Fig. 1) include abundant mm thick stratiform layers of coarse-grained sphalerite and galena with minor pyrite and chalcopyrite (Fig. 2a & b) forming a mineralized package between 9 and 20m in thickness that can extend laterally over more than 2km. The sphalerite and galena seem to replace earlier pyrite in carbonates; ore grades are low typically only 2-4 wt% Zn+Pb. This mineralization represents a large laterally extensive geochemical anomaly.

This stratiform mineralization was crosscut and remobilized during a later period of pervasive epigenetic dolomitization, with sulphides being concentrated in metre-sized, locally high-grade irregular pods and breccias cutting the bedding. The breccias contain fragments of limestone supported by coarse grained sphalerite and dolomite cement with minor calcite, quartz, galena and some phengite. At Visuña (Fig. 1), the mineralization was worked in the early 20th century from two adits some 200m in length, extracting *ca.* 15,000 tonnes of ore.

The NE limb of the Caurel-Toral Anticline hosts several small poorly known showings with a similar mineral assemblage but containing barite (Luque, 1985).

Silica Ore and related Lower Breccia Ore

The Silica Ore is the most regionally extensive style of mineralization and is located along the contact between the Vegadeo Formation and the Los Cabos Group. The mineralization is related to a central crest of quartz that bounds the hangingwall of the carbonate rocks and can be traced for more than 40km in length along both limbs of the Caurel-Toral anticline (Fig. 1). Zones of almost barren quartz alternate with sparse zones with high Zn+Pb grades (Luque, 1985).

Fine to medium grained, almost massive multi-layered, quartz replaces the limestone and dolostone of the Upper Member and uppermost part of the Intermediate Member of the Vegadeo Formation along tight metasomatic contacts. Replacement is dominantly isovolumetric and the silicification preserves faint remnants of sedimentary structures and fossils and may include some unreplaced carbonates. Shale, originally interbedded with the limestone, is usually preserved. There seems to be several generations of quartz, suggesting multiple events of precipitation and dissolution with evidence of deformation, and recrystallization.

Silicified zones are comprised of almost massive white to brownish quartz with sparse phengite, chlorite and pyrite with abundant cavities and veins infilled with multiple phases of carbonate minerals. Where mineralized, silicified zones contain sphalerite, with accessory galena. Sulphides usually form 1-10cm thick discontinuous bands parallel to the bedding (Fig. 2g & h). These are usually coarse grained (>2 mm) but may include grains of chalcopyrite and small inclusions of arsenopyrite, gersdorffite, and glaucodot. Galena includes minute grains of bismuthinite, native bismuth, tetrahedrite and Pb-Bi-Ag sulphosalts.

Mineralization also occurs as the matrix to irregular breccias or as massive (up to 0.5m thick) veins crosscutting the quartz along the contact with the Los Cabos Group or, locally, as veins in the associated carbonates. Most of these structures are interpreted as fault-related remobilizations.

The Silica Ore sometimes includes a cryptic external aureole of brown dolostone that can be up to tens of meters thick. This dolostone comprises coarse grained dolomite with rhythmic textures with an important porosity marked by the abundance of up to cm-sized cavities infilled with saddle dolomite (Radke & Mathis, 1980). Dolomitization was controlled by the bedding and joints and dolomitized zones have abundant stylolites and disseminations of chlorite, phengite and organic matter, most of which was probably inherited from the original limestone. The dolostone can include minor amounts of disseminated pyrite and sphalerite with zinc concentrations locally up to 0.12% (Ribera, 1999).

Also in the Visuña area, the contact between the limestones and the Silica Ore (Fig. 1) is demarked by a stratabound body of massive breccia up to 3m thick, with cm-sized unoriented heterolithic sub-rounded to angular fragments of unaltered limestone, brown dolostone and different types of shale supported by ferroan and Zn-rich dolomite and calcite with lesser amounts of chlorite, quartz, phengite and fine-grained sphalerite, galena and pyrite (Fig. 2d). The metasomatic contact be

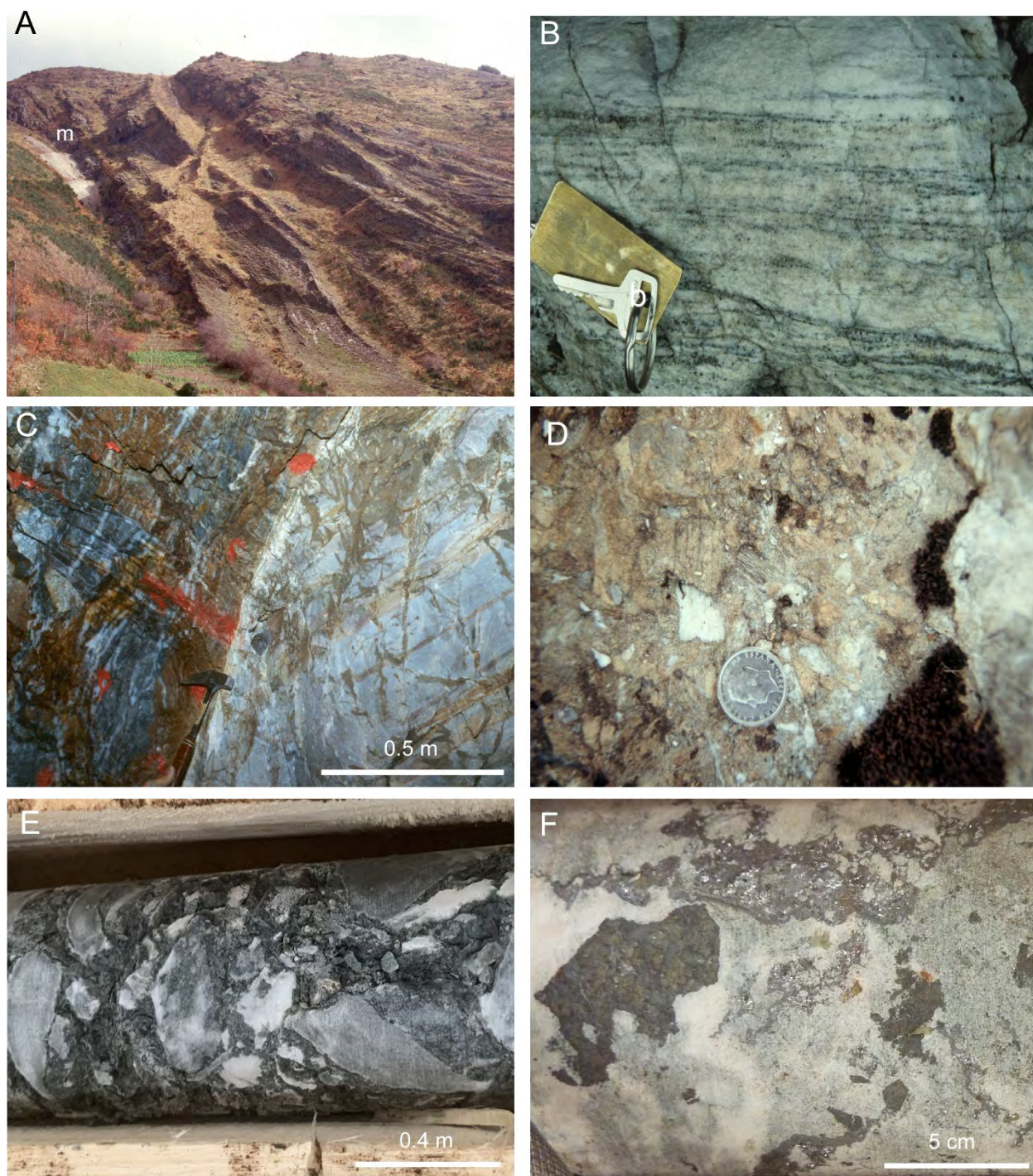


Figure 2: Field aspects of mineralized zones. (A) Thick calcarenite beds in the V₁ member of the Vegadeo Formation; mine workings in the stratiform ore at Visuña ('m'); (B) Stratiform mineralization with mm-sized grains of sphalerite, galena and pyrite in apparently undisturbed limestone, Visuña; (C) Contact between the Silica Ore and the V₂ limestone of the Vegadeo Formation Note that banding in the Silica Ore crosscuts layering, Antonina Mine; (D) Lower Breccia Ore: fragments of shale, limestone and barren and mineralized dolostone supported by dolomite and sulphides, Visuña; (E) Carbonate-Chlorite Ore with fragments of limestone and dolostone supported by chlorite and calcite with minor sulfides, Toral; HQ drillcore; (F) Marginal facies of the Carbonate-Chlorite Ore with sphalerite and galena supported by calcite and minor chlorite, Toral;



Figure 2 (continued): (G) Adit in the silica ore (SO), located between the limestone of the Vegadeo Formation (lm) and shale of Los Cabos Group, Toral; (H) View upwards of subvertical lenses of sphalerite-galena in a banded quartz-rich rock in the adit, Toral; (I) Silica Ore with fragments of quartz supported and replaced by sphalerite, Toral. HQ drillcore; (J) Sphalerite supporting and replacing limestone in the marginal facies of the Carbonate-Chlorite Ore, Toral; HQ drillcore; (K & L) Sphalerite, galena and ankerite replacing and infilling open spaces in variably sheared shale replaced by illite and quartz, Rubiales.

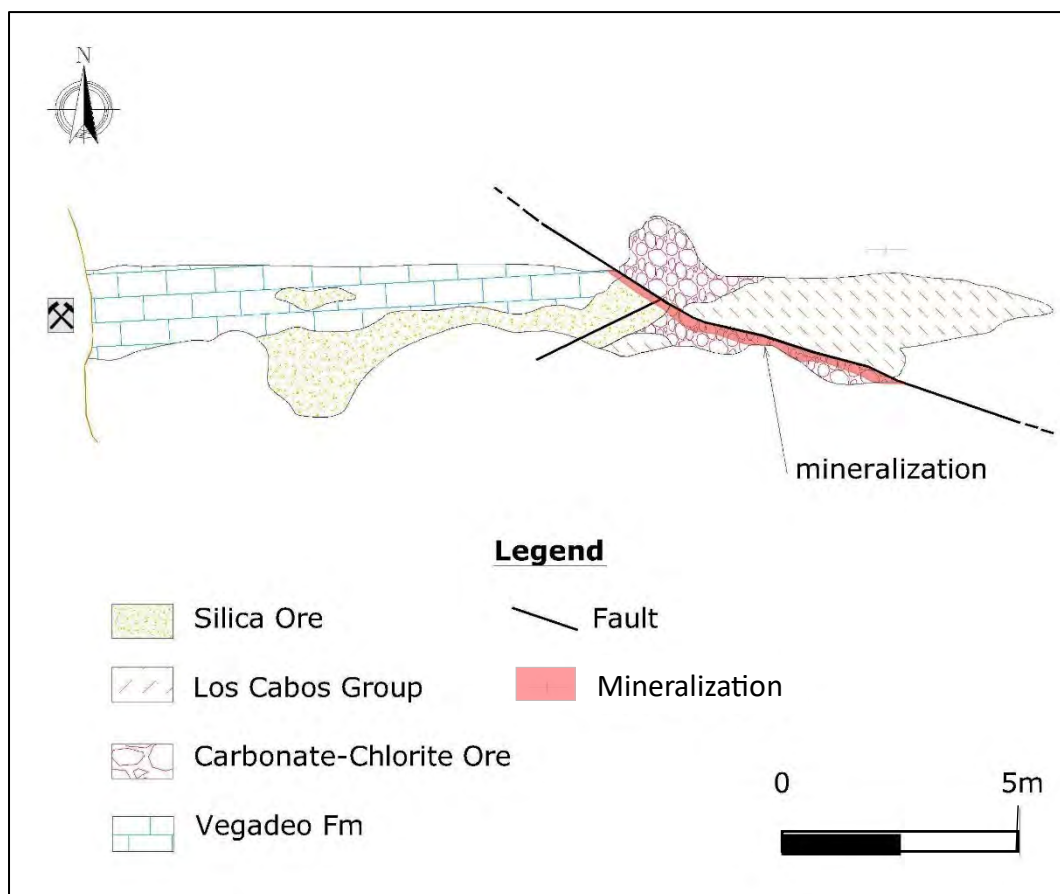


Figure 3: Detailed map of the adit shown in Figure 2g & 2h showing the relationships between the Silica and Carbonate-Chlorite ores.

tween the breccia and limestone contain phengite and fine-grained sulphides. Cleavage in the shale fragments is randomly oriented indicating that the breccia postdates the D₁-D₂ Variscan deformation. This breccia is crosscut by quartz veins related to the Silica Ore, thus also confirming that the Silica Ore is epigenetic and probably related to late Variscan fluid circulation.

Carbonate-Chlorite Ore

In the southernmost part of the Belt and broadly coinciding with the intersection of the Vegadeo Formation with the Sil River (Fig. 1) the stratigraphic position occupied by the Silica Ore transitions to a silica-depleted breccia enriched in chlorite and calcite, the so-called 'Carbonate-Chlorite Ore' (Fig. 2e & f).

In this area, the uppermost Vegadeo Formation, including the Upper Member and the uppermost part of the Intermediate Member, show widespread dissolution and brecciation of the limestone. The thickness of rock affected by these processes is very irregular, usually 4-7m but exceptionally it can be up to 14m thick. However, evidence of dissolution can locally be found in excess of 70m away from the contact with the Los Cabos Group.

The Carbonate-Chlorite Ore generally displays an irregular network of 0.1 to 10cm thick (exceptionally, 60cm) veins of

sulphides and chlorite (Fig. 2i & j) in limestone that grade into crackle breccias and groundmass-supported breccias with carbonate fragments of up to 1m in diameter. A decrease in the fragment/groundmass ratio is accompanied by an increase in the proportion of non-sulphide minerals, including variable proportions of sparry calcite, clays (illite, smectite, kaolinite), and chlorite. The proportions of these phases vary enormously and sometimes the rock consists almost exclusively of large masses of calcite, sphalerite or chlorite. Examination of drill-core shows that most of the sphalerite is located along the edges of these breccia bodies while galena is dominantly concentrated within the breccias with chlorite and calcite. Textures suggest that mineralization took place by gradual dissolution of the most permeable units of the carbonate unit accompanied by the precipitation of calcite, phyllosilicates, and sulphides. The presence of fragments belonging to the Los Cabos Group confirm that mineralization postdated the deposition of these sediments.

The sulphide assemblage also includes minor pyrite. Chalcopyrite, with inclusions of siegenite and gersdorffite is rarely observed and copper grades above 0.1% Cu are rarely noted except in late structures. Galena has the same inclusions as seen the Silica Ore.

Although the contact between the Carbonate-Chlorite Ore and the Silica Ore has been intersected in drillholes and has been observed in mine adits (Fig. 3) it is difficult to determine their

chronological or genetic relationship. The Carbonate-Chlorite Ore does not include fragments of the Silica Ore nor does the Silica Ore appear to replace the Carbonate-Chlorite Ore. When observable, contacts between the two ore types are faulted and often include a small amount of fault gouge. Projection of the contact from drilling suggests a highly irregular boundary between the two ore types (Hermosa, 1995).

Syn-tectonic mineralization

The high-grade Rubiales Mine exploited a large, broadly stratabound, lensoidal orebody with a N150°E trend hosted within alternating shale and limestone of the Lower Member of the Vegadeo Formation. Despite being initially described as a sedimentary-exhalative deposit, Arias *et al.* (1991) have shown that the Zn-Pb-rich mineralization was controlled by a large vertical brittle-ductile deformation zone formed at the intersection of a D₂-related shear zone and D₂-D₃ extensional faults (Fig. 4). Where this structural zone crosscuts the favourable rocks, limestone shows an external aureole of replacive ankerite and a later silicification accompanied by the precipitation of coarse-grained sphalerite and galena. Shale interbedded in the limestone displays pervasive phyllic alteration and a similar mineral assemblage infills stockwork-like veins and open spaces (Fig. 2k & 2l). Arias *et al.* (1991) have shown that at large scale the orebody is controlled by deformation and crosscuts lithological contacts. Pyrite and pyrrhotite are early phases which are close to the faults and focused a late chloritic alteration.

Similar mineralization is seen at Mercurín (Fig. 1) where silicification and related mineralization occurred along steeply dipping syn-D₃ fractures with N140-170° trend in V₃. North of the studied area there are similar altered and mineralized zones located along the contact between quartzite of the Los Cabos Group and overlying shale with the mineralization controlled by D₃ folds with vertical axis and subparallel shear bands.

Supergene mineralization

Outcropping mineralized zones in the region show extensive secondary alteration, especially along faults where supergene effects reached significant depths. Supergene zones were the first to be mined, especially those that contained cinnabar formed during the dissolution of sphalerite. Old miners also worked cerussite, anglesite, and smithsonite. Remaining supergene zones contain a wide variety of secondary minerals that have attracted the interest of mineral collectors (Calvo *et al.*, 2002).

Major ore deposits

Most of the large metal accumulations are hosted in three deposits (Fig. 1) - Rubiales, Toral and Antonina.

Rubiales

Major interest in Rubiales started in 1967 when EXMINESA found a large sub-outcropping deposit when surveying the abandoned small Mina Ricardo. Rubiales has an initial reserve of 18.6Mt @ 17.3% Zn and 1.3% Pb contained within a steeply dipping orebody of ca. 1200m by 600m and up to 30m in thickness (Arias *et al.*, 1991) (Fig. 4). The orebody was exploited

by underground workings between 1977 to 1991 and was almost totally exhausted with only some shallow ore remaining in the uppermost stopes when the mine closed.

Toral (Santa Bárbara)

The Toral deposit is located at the southernmost end of the belt, where Palaeozoic rocks are covered by the Miocene sediments of the Bierzo Basin (Fig. 1). Mineralized zones here are exclusively located at the WNW-ESE trending contact between the Vegadeo Formation and the Los Cabos Group. Toral contains a large but discontinuous sub-vertical stratabound orebody some 3km in length that extends to depths of ca. 900m. The orebody crops out and was investigated in the 1950's with small adits and trenches by Asturiana de Zinc. Close to the Sil River, in the western part of the deposit, the deposit consists of banded Silica Ore up to 3m thick. However, laterally, and downwards it quickly grades into higher grade Carbonate-Chlorite Ore that forms the bulk of the deposit. Broadly, the transition takes place at ca. 300m depth where the silica- and dolomite rich material passes into massive limestone containing mineralized breccia.

The deposit was found when drilling the southward extension of the Antonina Mine on the southern side of the Sil River. First explored by SMMPE (1975-1980) and later during their joint venture with ENADIMSA (1980-1985), some 55 holes with 36 daughter holes were completed for a total of more than 42,000m of core.

Recently Europa Minerals has undertaken exploration and after extensive drilling has delimited a total inferred resource of approximately 20Mt @ 6.8% Zn equivalent (including Pb credits) with an indicated resource of approximately 7.0 Mt @ 8.1% Zn equivalent (4.4% Zn, 2.8% Pb and 23 g/t Ag) at a 5.0% Zn cutoff and a mining width of 3-4m. (www.europametals.com). Tests indicate processing will achieve recoveries above 85wt% Zn, Pb and Ag. Mine development is currently pending environmental permits.

Antonina

The Antonina mine is the extension of the Toral deposit on the north bank of the Sil River; thus, is part of the same deposit but separated due to administrative boundaries. Mining at Antonina initially focused on the exploitation of secondary Hg, Ag and Zn ores by Rio Kumer from 1935. From 1965 to 1972 they extracted ca. 185,000 tonnes with ca. 6.3% Pb, 3.2% Zn and 59 g/t Ag (ITGE, 1994).

Between 1972 and 1978, SMMPE completed an extensive drilling campaign (41 drillholes for more than 15,000m) and the construction of two major adits, delineating a potential orebody of the silica-rich ore type. They excavated a large access ramp but the mine never went into production. However, in the deepest parts of the mine workings they found the first evidence of the breccia ore that now makes up the bulk of the Toral orebody.

Drilling by SMMPE defined an orebody with 4.74Mt @ 4.39% Pb, 5.4% Zn at a minimum thickness of 2m. The mineralization at Antonina is open at depth. EXMINESA has reevaluated the deposit including completing underground drilling and concluded that the deposit was significantly smaller, ca. 2Mt with

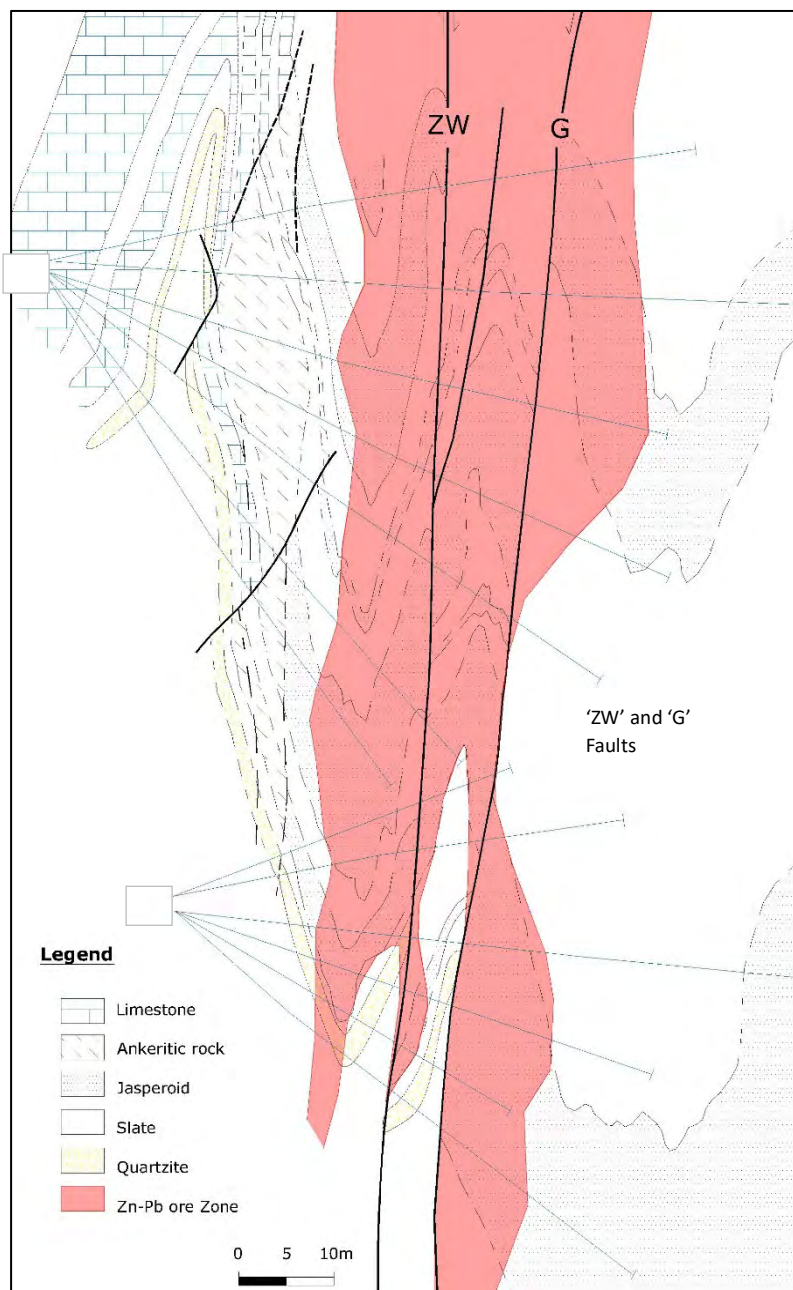


Figure 4: Schematic cross section (4860 N) of the Rubiales mine. Modified from Tornos *et al.* (1996)

5.28% Pb, 5.25% Zn and 47.7 g/t Ag over a thickness of 3.17m (Hermosa, 1995).

Geochemistry of the Zn-Pb ores

Sulphur isotopic values of the sulphide minerals in the footwall mineralized zones are strikingly high (+28.2 to +35.0‰) and even higher than average Cambrian seawater sulphate values (\approx +27 to +30‰; Fauré, 1986) which are some of the highest in the geological record. This leaves little doubt that the reduced sulphur necessary for sulphide precipitation came from the reduction of local, probably confined, seawater sulphate with little, if any, isotope fractionation by either thermogenic sulphate reduction (TSR) or biogenic reduction (BSR). The available

geological evidence for mineralization suggests temperatures well below those for TSR. Our best interpretation is that the low $\delta_{SO_4-H_2S}$ was related to biogenic reduction of sulphate during early diagenesis in an almost closed system with an excess of organic matter and little availability of sulphate (see discussion in Tornos *et al.*, 2017).

The Vegadeo Formation has abundant ghosts of evaporites interbedded with former algal mats, suggesting that coupled carbon oxidation-sulphate reduction may have been the source for reduced sulphur. Sulphides related to late remobilization have equivalent values (+28.7 to +32.8‰) indicating conservation of sulphur during this mineralizing process.

Sample	Location	Description	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm\text{StdErr}^*10^{-6}$
SR-16	Visuña *	Limestone Vegadeo Fm (V1)	0.710570	106
SR-17	Visuña *	Limestone Vegadeo Fm (V1)	0.708710	188
SB-12	Toral surface	Limestone Vegadeo Fm (V2)	0.713207	2
SB-05	Toral	Pyrite-rich shale Cabos Group, hangingwall Silica Ore	0.718832	2
SR-14	Visuña *	Barren dolostone Vegadeo Fm (V2)	0.710281	14
SR-21	Visuña *	Barren dolostone Vegadeo Fm (V2)	0.710675	37
SR-11	Visuña *	Dolostone. Lower Breccia Ore	0.713532	14
SB-09	Toral. DDH TO 26-D1	Silica ore with sphalerite and dolomite	0.713984	2
SB-10	Toral. DDH TO 25-D2	Silica ore with sphalerite, galena and dolomite	0.714082	2
SB-11	Toral. DDH TO 23-D3	Silica ore with sphalerite and dolomite	0.712299	2
SB-04	Toral. Main adit	Silica ore with sphalerite and dolomite	0.711082	2
SR-01	Toral *	Calcite. Carbonate-Chlorite Ore	0.713681	16
SR-02	Toral *	Calcite. Carbonate-Chlorite Ore	0.712940	35
SB-06	Toral. Lower adit	Calcite. Carbonate-Chlorite Ore	0.713250	2
SB-07	Toral. DDH TO 23-D1	Calcite. Carbonate-Chlorite Ore rich in sphalerite	0.714858	2
SB-08	Toral. DDH TO 25-1	Calcite. Carbonate-Chlorite Ore rich in sphalerite	0.714501	2
SB-13	Toral surface	Calcite. Carbonate-Chlorite Ore	0.709488	2
SB-03	Toral	Semi-massive sphalerite	0.714890	3
SR-24	Antonina *	Calcite. Carbonate-Chlorite Ore	0.714220	73

* Data from (Ribera 1999)

Table 1: Strontium isotope compositions of carbonates from the different types of ores.

However, sulphides from the mineralized zones in the hangingwall of the Vegadeo Formation have strikingly lower $\delta^{34}\text{S}$ values (+18.2 to +25.3‰) indicating there was significant input of reduced from a more $\delta^{34}\text{S}$ depleted source for this mineralization event. Pyrite collected from the footwall of the Los Cabos Group has similar values between +23.3 and +25.1‰ that are equivalent to those of sulphides in presumed volcanic rocks (see below) in the Upper Member in the Vegadeo Formation (23.6‰). These values are significantly higher than the $\delta^{34}\text{S}$ values of sulphides in orogenic gold veins in the Los Cabos Group, that range between +9.8 and +15.9‰ (Tornos *et al.*, 1997) and are thought to be of local derivation. At the Rubiales mine, $\delta^{34}\text{S}$ values are strikingly homogeneous at the deposit scale with $\delta^{34}\text{S}_{\text{sphalerite}}$ of $+25.6\pm 0.5\text{‰}$ and $\delta^{34}\text{S}_{\text{galena}}$ of $22.5\pm 0.4\text{‰}$; pyrite, pyrrhotite and chalcopyrite have slightly lower values (+20.4 to +23.8‰). These values match the highest values in the uppermost Vegadeo Formation and suggest a similar origin, but significant homogenization of sulphur isotope values occurred during fluid flow along the shear zone.

Carbonates associated with sulphides in the deposits show two distinct groups of $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ isotopic compositions. Carbonates associated with mineralized zones in the Lower Member have values close to the average of limestone suggesting that the Zn-Pb mineralization event resulted from fluids buffered by unaltered limestone and at low temperatures, *i.e.*, are of local derivation.

However, carbonate minerals in mineralized zones in the hanging wall, including the Ore Breccia and Carbonate-Chlorite Ore, display less enriched $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ values suggesting

circulation of hot fluids and/or in isotopic disequilibrium with the host limestone. This isotopic depletion is more pronounced in carbonate minerals adjacent to the hanging wall of the Vegadeo Formation and the compositions plot in a different field than the widespread barren dolomitization suggesting that the ore-related carbonates and regional dolomitization formed by the circulation of isotopically different fluids (Tornos *et al.*, 1996b). The Carbonate-Chlorite and Silica ores have similar isotopic values suggesting that fluids had a similar source and temperature. Variations between individual analyses may be due to variations in the fluid/rock ratios. Isotope values at Rubiales are also similar (Tornos *et al.*, 1996a).

Quartz should be potentially more resistant to alteration than the associated carbonates and better reflect the $\delta^{18}\text{O}$ values of the fluids. Quartz $\delta^{18}\text{O}$ values in the Silica Ore are very homogeneous at between +17.0 and +18.3‰, something that at an average temperature of 200°C (see below) would suggest a $\delta^{18}\text{O}_{\text{fluid}}$ composition of +4.8 and +6.1‰. Interestingly, quartz intergrown with sulphides in mineralized zones along late structural zones in the Lower Member has isotopically heavier values (7.6-8.5‰). Lower $\delta^{18}\text{O}$ values were obtained from the quartz at Rubiales (+15.2 to 16.2‰) which are compatible with slightly hotter fluids than in the Silica Ore. $\delta^{18}\text{O}$ - δD signatures of phyllosilicates, phengite and chlorite, are also consistent with a $\delta^{18}\text{O}_{\text{fluid}}$ near 5-7‰ and $\text{D}\delta_{\text{fluid}}$ values in the -53 to -48‰ range.

The quartz isotopic data indicates fluids responsible for alteration and mineralization do not plot along the meteoric water line or in the field of igneous waters but are more consistent

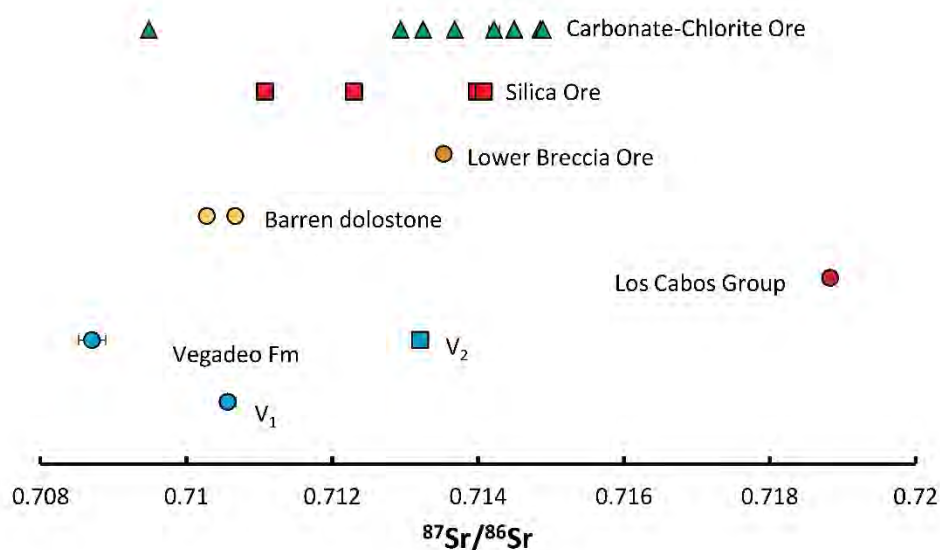


Figure 5: Sr isotope geochemistry of unaltered host and mineralized rocks.

with values for diagenetic/low grade metamorphic waters.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonates in the Vegadeo Formation (0.70871-0.71057) are within the range for Cambrian seawater (>0.709 ; Veizer *et al.*, 1999) and similar to those of the regional dolomites (0.71028-0.71068) suggesting that most of the Sr in the regional and barren dolomitization is inherited from the host limestone (Table 1 and Fig. 5), one sample (SB-12) has significantly higher values (0.71321) suggesting significant interchange with ^{87}Sr -rich fluids. However, carbonate minerals in altered zones in the hanging wall are significantly more radiogenic (>0.71489), indicating input from a much more radiogenic fluid with the Sr probably inherited from the erosion/hydrothermal leaching of basement rocks rather than a significant juvenile or igneous contribution. Intermediate values were observed in samples from the Silica and Carbonate-Chlorite ore, though these ore types do not display significant differences in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

A similar trend of Sr inherited from the host carbonates mixing with a more radiogenic Sr inherited from (older) siliciclastic rocks has been observed in many carbonate-hosted deposits such as the Viburnum Trend (Lange *et al.*, 1983), the San Vicente deposit in Peru (Fontboté & Gorzawski, 1990), MVT deposits in Belgium (DemaiFFE & Dejonghe, 1990) and in the carbonate-hosted deposits of Sardinia (Boni *et al.*, 1992).

Minerals in the Silica Ore assemblage contain abundant secondary fluid inclusions, most of which are minute ($<2\ \mu\text{m}$), along cleavage planes or fractures, very few primary fluid inclusions of a size that would allow measurement to be made. The few permissive fluid inclusions in the Silica Ore homogenize to liquid between 155 and 295°C and have low ice melting temperatures close to those of pure water (-0.4 and -0.2°C) suggesting very low salinities. Those in the Carbonate Ore have slightly lower homogenization temperatures (163 to 224°C) and equivalent salinities (T_{mice} , -0.9 to 0°C). Fluid inclusions in quartz and calcite of the Remobilized Stratiform Ore in the Lower Member homogenize to liquid between 127 and 207°C

and have ice melting temperatures of -1.3 to 0°C . Homogenization temperatures are consistent with the $^{34}\text{S}_{\text{sph-gn}}$ values that are around $154\pm 20^\circ\text{C}$ in the stratiform sulphides and $212\pm 50^\circ\text{C}$ in sulphides in zones of structural remobilization. Sphalerite and galena in the Silica and the Carbonate-Chlorite Ore give unrealistic $\delta^{34}\text{S}_{\text{sph-gn}}$ values suggesting major isotopic disequilibrium. The opposite holds true at Rubiales, where there is a remarkable isotopic homogeneity at the deposit scale and $^{34}\text{S}_{\text{sph-gn}}$ values suggest temperatures of $206\pm 50^\circ\text{C}$ (Tornos & Arias, 1993) equivalent to fluid inclusion homogenization temperatures (200-240°C). Fluid inclusion salinities in quartz from Rubiales are only slightly higher than in the stratabound deposits (3-7 wt% NaCl eq.).

Bulk analyses of gas released during decrepitation of the total population of fluid inclusions in the Silica and Carbonate-Chlorite ores suggest that fluids were dominated by H_2O with variable contents of CO_2 . Analyses of samples from structurally remobilized ores suggest that CO_2 became a major component, as high as 7%. N_2 , H_2 , CO and CH_4 contents in all analyses were always below 1 wt%. Bulk fluid inclusion decrepitation suggest that the predominant solutes were Na-K chlorides with the proportion of $\text{Na}/\text{Na}+\text{K}$ equal to 0.8-0.9 (Ribera, 1999).

White mica in phyllic alteration assemblages from Rubiales yielded a K-Ar age of $307\pm 7\text{Ma}$ consistent with a syn-D₃ Variscan age for the deposit. Two similar samples from the Silica Ore yielded older ages of 323 ± 7 and $320\pm 6\text{Ma}$ (Tornos *et al.*, 1996a).

Lead isotope geochemistry suggests that lead and similarly Zn and Ag were derived from a U-Th-bearing sequence, that could well be the siliciclastic rocks below or above the Vegadeo Formation. $^{206}/^{204}\text{Pb}$, $^{207}/^{204}\text{Pb}$ and $^{208}/^{204}\text{Pb}$ values of the different styles of mineralization are similar suggesting equivalent sources. Overall, they define a mixing isochron between an upper continental crust and a more juvenile orogenic (?) source. Values are similar to those in the Montagne Noire in the Massif

Central of France (Brevart *et al.*, 1982) but less crustal than the highly radiogenic lead at Sardinia (Boni & Koeppl, 1985; Caron *et al.*, 1993). Interestingly, model ages following the growth curve of Sinclair *et al.* (1993) are Early Palaeozoic, strongly suggesting that Pb separated from the U-Th reservoir and remained sequestered in sulphides till being remobilized and redeposited in the late Variscan ores in shear zones and the hanging wall of the Vegadeo Formation.

Genetic interpretation

Zn-Pb mineralization in the West Asturian Leonese Zone, especially the Silica and Carbonate-Chlorite ores, seems to have few equivalents elsewhere. Their geological features are dissimilar to classical Mississippi Valley Type (Leach & Sangster, 1993), Irish-type (Andrew, 1991; Hitzman *et al.*, 1995; Wilkinson, 2003) or shale-hosted (Leach *et al.*, 2005) deposits. However, syn-shear related Zn-Pb mineralization somewhat similar to Rubiales has been described in a few places such as Zawar, India (Talluri *et al.*, 2000). Rocks broadly similar to the Carbonate-Chlorite Ore are described in many MVT systems and silicification is a rather common process in carbonate-hosted deposits such as in the Irish-type (Hitzman *et al.*, 1995), shale-hosted mineralization (Slack *et al.*, 2004) and MVT deposits (Ohle, 1996). However, to our knowledge silicification is not so pervasive or regionally extensive in these deposit types. Perhaps, the only equivalent is the Zn-Pb mineralization related to stratabound silicification and denominated of the siliceous crust type (SCT) in the Eastern Alps and several smaller places worldwide (Brigo *et al.*, 2001). These systems have a similar geological setting with the mineralization being at the contact of a Carboniferous carbonate platform with siliclastic sediments as well as a similar geochemical signature but are enriched in barite and fluorite. Also, regional stratabound to fault-controlled silicification is a common process of shallow marine to subaerial carbonates and have been well studied in oil and gas reservoirs (La Bruna *et al.*, 2021).

The stratiform mineralization in the Lower Member of the Vegadeo Formation has all the features of being syn-sedimentary or early diagenetic, an interpretation based dominantly on the lack of hydrothermal alteration related to the mineralization and the lack of isotopic evidence for hydrothermal overprinting. Similar mineralization has been found in the French Massif Central (Brevart *et al.*, 1982) and in the Gonessa Formation in Sardinia (Boni, 1985; Boni, 1982).

The combined Sr and C-O isotopic composition suggests that the ore forming fluids were in equilibrium with Cambrian seawater while the strikingly high $\delta^{34}\text{S}$ values suggest microbial isotopic fractionation of early Cambrian sulphate. Reduced sulphur would react with limited amounts of available iron to form pyrite that is later replaced by Zn-Pb-bearing sulphur-poor fluids equilibrated with the adjacent siliclastic rocks but at extremely high rock/fluid ratios.

In contrast, the shear-related mineralization that occurs at Rubiales is clearly epigenetic and formed discordant replacements related to syn-orogenic fluid flow during the brittle-ductile deformation (D_3) that followed the major compression and metamorphism of Variscan age. Lower pH, silica, sulphur, metal-rich and isotopically homogeneous fluids in chemical

disequilibrium with the carbonates precipitated large amounts of Zn and Pb by fluid-rock reaction, coeval pH increase and destabilization of transporting chloride complexes. The absence of significant amounts of Cu is consistent with rather low temperatures of formation (200-240°C). The low abundance of pyrite suggest that the system was relatively poor in reduced sulphur and the lack of barite/anhydrite indicate that $\text{H}_2\text{S}_{\text{aq}}$ was the dominant aqueous sulphur species in a reduced environment. The isotope geochemistry suggests that the metals are derived from the same source as the stratiform mineralization while sulphur had a mixed derivation from both the carbonate reservoir and siliclastic sediments. However, the early Palaeozoic model ages are inconsistent with formation ages indicating that metals were leached from an already U-Th-poor reservoir, potentially from earlier precipitated sulphides of Cambrian age, and perhaps similar to those in the stratiform ore.

More complex, however, is the origin of the mineralization located within the uppermost Vegadeo Formation. The few studies carried out on this type of mineralization have proposed three different alternatives, formation of the ores in a shallow marine to subaerial environment, a volcano-sedimentary origin, or formation due to the circulation of external fluids along lithological contacts during Variscan times.

The sedimentary models proposed by Rabu (1977) and Hermosa (1995) are somewhat similar to those of Brigo *et al.* (2001) and imply that mineralization was related to a paleosurface and predates the deposition of the Los Cabos Group. Rabu (1977) proposed that mineralization formed in palaeosoils in a vadose setting. For Hermosa (1995), the Carbonate-Chlorite and the Silica Ore represent two different palaeoenvironments. He postulated that silicification would have slightly postdated the deposition of the Upper Member in a shallow marine to subaerial setting during the transgression preceding the deposition of the Los Cabos Group. Hermosa (1995) also suggested that sulphides had already been precipitated when silicification took place. He suggested that the Carbonate-Chlorite Ore formed coevally in a karst formed on the Middle Member during subaerial exposition. This model implies the existence during late to early Cambrian times of an emergent domain south of the River Sil river and a shallow marine one to the north of the river. Brigo *et al.* (2001) proposed different models for the formation of SCT ores in the eastern Alps ranging from the illitization of clays during diagenesis to the convection of hydrothermal fluids.

An alternative origin for the West Asturian Leonese Zone ores was proposed by Luque (1985) who related the mineralization to exhalative processes similar to those forming volcanogenic massive sulphides. The main argument cited for this origin was the presence of the putative layers of volcanic ash interbedded with the Silica Ore. However, our interpretation is that these "ash layers" represent hydrothermally altered shale within the Los Cabos Group. Volcanic rocks are not described elsewhere in the base of Los Cabos Group. In addition, the Luque (1985) hypothesis fails to explain the geochemical evidence including the temperatures of formation, isotopic data and ages.

Both Luque & Ruiz (1990) and Tornos and others (1996a and b) hypothesize that the stratabound mineralization at Rubiales

was related to the Variscan orogeny. The main arguments supporting this model include:

- The presence of fragments of shale in the Carbonate-Chlorite Ore shows that brecciation and mineralization postdated the deposition of the Los Cabos Group.
- The presence of fragments of shale with two cleavages in polymictic breccia bodies in the Silica Ore indicating that the brecciation postdated Variscan deformation.
- Fluid inclusion and sulphur isotopic temperatures are incompatible with surficial processes.
- The K-Ar ages of hydrothermally altered rocks at Rubiales and the Silica Ore, yield late Variscan ages.

Thus, our best interpretation is that the stratabound mineralization in the hanging wall of the Vegadeo Formation formed during the late stages of Variscan deformation. The Silica Ore was formed by the circulation for tens of km and reaction of mildly acidic, silica-saturated fluids along the relatively highly permeable uppermost Vegadeo Formation. The low solubility of silica in hydrothermal fluids at such relatively low temperatures (*ca.* 190 µg/g at 200°C; Tornos *et al.*, 1996b) suggest that large amounts of water flowed along the contact.

As numerical models (Plumlee *et al.*, 1994) suggest that pH increase due to carbonate-fluid interaction is not able to trigger the massive precipitation of sphalerite and galena, the most plausible explanation for sulphide precipitation is fluid mixing. Our model suggests that the uppermost Vegadeo Formation was a zone of fluid mixing with gradual replacement of fluids in equilibrium with the carbonates that accumulated below the impervious shale by laterally flowing hot silica- and metal-rich, but reduced sulphur-depleted fluids which were equilibrated with shale. In fact, except for the possible cinerites, shales of Los Cabos Group show no hydrothermal alteration suggesting that fluids were in chemical equilibrium with siliciclastic rocks. Fluid mixing should promote alkalization, cooling and coeval quartz and sulphide saturation. The key process is the precipitation of sulphides due to mixing of reduced sulphur from two different reservoirs, the biogenic reduction of seawater sulphate accumulated in the reservoir and the input of sulphur inherited from siliciclastic rocks. In this scheme, the Lower Breccia Ore represents an external metasomatic front.

An important feature of this model is that the external fluids must be able to transport sufficient metals and small amounts of sulphur in order to make the process feasible. The model of Tornos & Heinrich (2008) shows that fluids equilibrated with mildly reduced siliciclastic sediments (redox conditions close to NNO buffer) can transport large amounts of base-metals but only small amounts of H₂S_{aq}. This allows relatively low temperature (<300°C) metal-bearing fluids, equilibrated with sedimentary sequences, to travel far through crustal discontinuities and only form mineralization when mixing with a reduced sulphur-rich reservoir.

The exact nature of the contact between the Vegadeo Formation and Los Cabos Group throughout the mineralized area is poorly known. However, at least locally the contact is tectonic, with the development of a deformation fabric. The Silica Ore shows widespread ductile to brittle deformation and quartz

includes ribbon textures, sub-grain development and widespread grain recovery. The sulphides are always coarse grained and also show granoblastic textures. All these features suggest that most of the banding in the Silica Ore is not sedimentary but tectonic.

The origin of the Carbonate-Chlorite Ore and its relationships with the Silica Ore remains elusive. Broadly similar breccia bodies are described in MVT deposits elsewhere (Ohle, 1981; Sangster, 1983) though bodies here appear to contain enhanced chlorite relative to most MVTs. The lack of quartz-rich fragments indicates that this ore type does not correspond to a tectonic or hydrothermal brecciation of a previous Silica Ore while the local presence of fragments of shale indicates that dissolution and breccia formation postdated diagenesis.

Breccias in these mineralized systems could be formed by overpressure of hydrothermal fluids beneath the impervious shale of Los Cabos Group, in a mechanism similar to that of geopressed zones (Fowler & Anderson, 1991) something that would promote the precipitation of calcite and Zn-Pb sulphides (Holland, 1979; Hemley *et al.*, 1986). However, the Carbonate-Chlorite Ore could also represent a first metasomatic front predating silicification in the confined aquifer when in a pH-fluctuating environment at low fluid/rock ratios, fluids are able to alternatively dissolve carbonates or precipitate sulphides + calcite.

In summary, our model suggests that the different types of carbonate-hosted Zn-Pb mineralization in the Vegadeo Formation formed by equivalent processes but represent different ore traps and complex processes of hydrothermal remobilization. Probably, the process involved the circulation of vast amounts of hydrothermal fluids mobilized during uplift and at the ductile-brittle transition during the waning stages of the Variscan Orogeny.

Geochemical data are consistent along the belt and suggest that most of the mineralization formed from the circulation of very low salinity fluids (0-7 wt% NaCl eq.) of low-grade metamorphic origin at temperatures between 150 and 300°C and fluid pressures slightly above the boiling curve (*ca.* 0.5 kb). These temperatures are consistent with the lack of calc-silicates but are somewhat above those expected in MVT and sedimentary-exhalative deposits. What is intriguing are the extremely low salinities that make it difficult for the Zn, Pb and Ag to be transported as chloride complexes suggesting that these fluids are not those that originally transported the base-metals.

Mineralization is interpreted as being due to the interaction of mildly acid, silica-saturated and metal-rich but H₂S-depleted fluids equilibrated with siliciclastic rocks during flow through confined aquifers. Perhaps the key ore-forming mechanism is the mixing of this fluid with a stagnant one enriched in biogenically-reduced sulphur equilibrated with the host carbonate rock (Fig. 6). Rubiales formed at much higher fluid-rock ratios and by larger fluid flow while the stratabound mineralization probably took place more slowly and involved lower fluid-rock ratios. Both these factors were probably critical in influencing the size and tenor of orebodies. Hypothetically, equivalents of the shear-zone controlled mineralization could represent feeder zones to the stratabound ore.

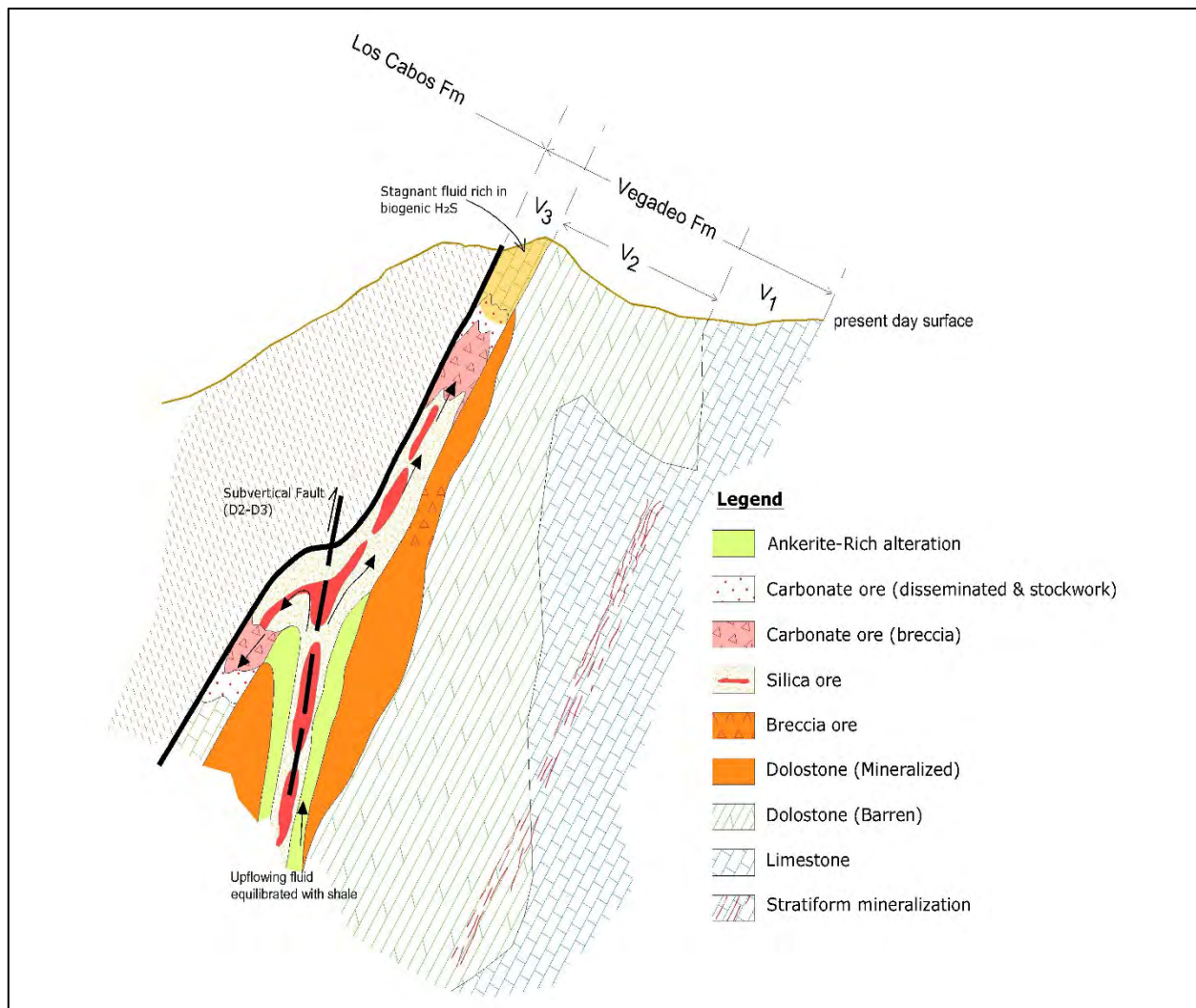


Figure 6: Schematic cartoon cross section showing the contact between the Vegadeo Formation and the overlying Los Cabos Formation and development of multiple altered and mineralized zones. The contact is shown here as being tectonic. The figure indicates the location of early syn-diagenetic mineralization in the Vegadeo Formation as well as the zone of somewhat later (?) diagenetic dolomitization at the top of the Vegadeo Formation. Movement of later hydrothermal fluids, probably during Variscan deformation that resulted in the tectonic formation contact, occurred along structures as well as along the structural formational contact. Fluid movement resulted in zoned arrangement of alteration zones (outer to inner: ankerite, carbonate, silica).

Geochemically, the processes proposed for the WALZ deposits are broadly similar to those operative in MVT and other carbonate-hosted deposits such as the Irish type. The circulation of deeper and hotter low grade metamorphic fluids along major discontinuities is what make these deposits different to conventional MVT deposits formed by the circulation of basinal brines in foreland basins (Garven, 1984; Leach & Rowan, 1986; Fontbote & Gorzawski, 1990; Plumlee *et al.*, 1994). The model here can probably be extended to other silica-rich replacements (Brigo *et al.*, 2001).

Conclusions

The internal zone of the Variscan belt in Iberia host large stratabound to discordant Zn-Pb mineralized zones that share many

features with the MVT type of mineralization. The deposits occur primarily along a single 10km horizon between Cambrian carbonates and overlying shale or along major structures. Stable and radiogenic isotopes suggest that mineralization occurred during late Variscan times when low grade metamorphic fluids circulating along major crustal discontinuities or stratabound aquifers intersected carbonate rocks that acted as reservoirs for stagnant water enriched in reduced sulphur. The ultimate origin of the metals is poorly known but may be stratiform early diagenetic sulphides disseminated in the carbonate rocks (V₁ of the Vegadeo Formation).

These deposits have few exact equivalents worldwide despite the fact that the ore traps and geochemical processes that formed them were equivalent to those of conventional

carbonate-hosted Zn-Pb deposits. The geochemistry, morphology and size of the orebodies were probably controlled by a geodynamic scenario somewhat different to that of other carbonate-hosted deposits.

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