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# Metallogenesis at the Terramonte Pb–Zn–Ag quartz vein, Portugal: Geological, mineralogical and geochemical evidences



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## ABSTRACT

The Pb-Zn-Ag quartz vein from Terramonte cuts the Neoproterozoic-Cambrian schist-greywacke complex. This orebody was partially exploited. The paragenetic sequence consists of four stages containing quartz accompanied mainly by arsenopyrite and pyrite in the first stage, sphalerite in the second stage, galena showing many inclusions of several sulphosalts in the third stage and carbonates in the fourth remobilization stage. Several sulphide and sulphosalt grains are oscillatory zoned. The chemical distinction between lighter and darker zones in backscattered images of arsenopyrite, pyrite, sphalerite and freibergite is due to substitutions in the mineral lattices. But the distinction between these zones in semseyite is due to a higher Pb content and a lower Sb content in the lighter zone than in the darker zone and the metal and metalloid are the main constituents in the solid solution, but are not correlated. The Sb, Ag and Bi substitute for Pb in galena, but did not cause any zoning. Ore deposition was possible due to mixing of a hypersaline fluid with up to 26 wt.% NaCl equivalent (and occasionally with CaCl<sub>2</sub> up to 17 wt.%), which carried the metallic content of the fluid, with an extremely low salinity fluid of presumed meteoric origin that percolated down into the basement. The metals could have been leached from a mixture of mainly metasediments and also previous Sb–Au deposits by fluids that acquire high salinity in one of two probable ways: leaching of salt beds or following seawater evaporation. The entire mineralizing event probably occurred at a relatively low temperature, possibly between 120 and 230 °C. Remobilization of Pb, Zn, Ag, As, Sb and Cu will be due to the tectonic evolution of the opening of the Atlantic Ocean. This vein is probably of Alpine age.

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# 1. Introduction

The Pb–Zn–Ag veins are widespread throughout Europe. Some occupy compressional faults, are spatially related to granitic plutons and may have been formed by hydrothermal activity that accompanied pluton emplacement (e.g., Behr et al., 1987). Others occupy extensional faults, crosscut sedimentary rocks, were formed in Early Triassic to Paleogenic and Neogenic and developed during the breakup of Pangea (e.g., Krahn and Baumann, 1996). Both vein types occur in the Iberian Peninsula and have been studied (e.g., Johnson et al., 1996 and references therein; Subías et al., 2010).

In Pb–Zn–Ag veins from the Iberian Range at NE Spain, fluids intersected different lithologies in the upper crust and the metals deposited correspond to a mixture of components leached from Paleozoic country rocks and previously formed Variscan ore deposits (Subías et al., 2010). The hydrothermal activity was related to the extensional regime. The Terramonte mine was one of the most important European silver mines between 1966 and 1973 (Moura, 2010), as it produced up to 10.3 t in 1967, about 0.13% of the world production in that year. The Terramonte orebody is the only Portuguese Pb–Zn–Ag vein where Ag has been exploited (Moura, 2010). It has been studied by Medeiros (1964), Thadeu (1977), Marsella (1966), Gaspar (1967, 1971), Couto et al. (1990) and Couto (1993). Other similar veins from northern Portugal are Facuca, Olgas, Várzea de Trevões, Ribeiro da Estivada, Ribeiro da Lomba and Ribeiro da Castanheira (Figs. 1, 2). The Braçal Pb–(Zn–Ag) veins do not contain sulphosalts and the gangue consists mainly of dolomite (Marques de Sá and Noronha, 2011).

This paper presents the geology, mineralogy, mineral paragenesis and fluid inclusion studies of the Terramonte Pb–Zn–Ag quartz vein to provide information concerning the origin of this ore deposit and to contribute to the knowledge of Pb–Zn–Ag veins of the Iberian Peninsula.

#### 2. Geological setting and the Terramonte orebody

The Pb–Zn–Ag Terramonte mine is located about 18 km east of Porto in northern Portugal (Fig. 1), close to the south bank of the Douro river.

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**Fig. 1.** Location of the Terramonte area and other similar Pb–Zn–Ag quartz veins from northern Portugal in the Iberian Peninsula tectonic zones: CZ–Cantabrian Zone, WALZ–West Asturian–Leonese Zone, GTMZ–Galicia Trás-os-Montes Zone, CIZ–Central Iberian Zone, OMZ–Ossa Morena Zone, SPZ–South Portuguese Zone defined by Julivert et al. (1974) and Farias et al. (1987). 1–5 Other Pb–Zn–Ag quartz veins.

This area belongs to the Central Iberian Zone, which is one of the main tectonic zones of the Iberian Massif.

The Neoproterozoic–Cambrian schist–greywacke complex (SGC) predominates in the area (Fig. 2a) and occurs at the core of a large Variscan fold, the Valongo anticline, which contacts Variscan granitic rocks to the east (Carvalho et al., 2012) and the Porto–Tomar–Córdoba shear zone to the west. Over the last decade, the U–Pb zircon ages have confirmed the Ediacaran to Cambrian age of the SGC (Rodriguez Alonso et al., 2004; Teixeira et al., 2011; Talavera et al., 2012). The SGC cropping out at the core of the Valongo anticline belongs to the Valongo domain defined by Martinéz-García (2006) and includes a post-Cadomian low grade metasedimentary succession.

In the Terramonte area, the SGC is represented by two lithological associations that belong to a thick flyschoïd sequence (Medeiros, 1964; Marsella, 1966; Thadeu, 1977; Couto and Sodré Borges, 2005) (Fig. 2b). Lithologic association A consists of black schists containing alternating siliceous and pelitic bands. Lithologic association B is composed of alternating metapelites and metagreywackes, containing metaconglomerate and marble lenses. The transition from A to B is gradational with an increase in the metamorphic grade. Lithological association B is folded into the northeast-trending anticline structure.

The N60°E, 82°NW-trending Pb–Zn–Ag quartz vein from Terramonte cuts the lithologic associations A and B (Fig. 2b), is about 1.5 km long, 5–15 m thick and hosted by a N70°E shear zone. The Pb,

Zn and Ag mineralization occurs in the NW hanging wall of the quartz vein and is 1–2 m thick (Marsella, 1966). Its exploration was carried out underground, in five levels and reached 270 m below the surface (Marsella, 1966). The mineralization was 450 m long at the 100 m level and 550 m long at the 150 m level (Carvalho, 1960). The main gallery of the mine intersected several centimetric N60–70°E, 70–85°S-trending mineralized quartz veins, over about 600 m, before the Terramonte vein. The mine started production in 1885, but stopped soon after due to the low metal prices in the market. Portuguese Government exploration in the period of 1955–60 revealed important reserves and exploitation restarted in 1966 and continued until 1973. In this period, about 300 t of ore averaging 2% Pb, 3% Zn and 110 g/t Ag were extracted per day (Moura, 2010). In the best year (1969), the mine sold 2730 t with 61.5% Pb, 8.9% Zn and 2800 ppm Ag, plus 2615 t with 50.1% Zn, 5.6% Pb and 605 ppm Ag (Moura and Velho, 2011).

#### 3. Sampling and analytical methods

Samples were collected from the Terramonte Pb–Zn–Ag quartz vein, but other samples from this vein kept at the National Laboratory of Energy and Geology (LNEG), S. Mamede de Infesta, Portugal, were available for this study. Our studies included transmitted and reflected-light microscopy, electron microprobe analyses and fluid inclusions.

Ore minerals were analyzed on a Hyperprobe Jeol-8500F electron microprobe, operating at 20 kV accelerating voltage and 20 nA beam current. Standards used are metallic Ni and Co; synthetic cuprite Cu<sub>2</sub>O (Cu); metallic Ag; metallic Au; sphalerite (Zn); pyrite (Fe, S); MnTiO<sub>3</sub> (Mn); CdS (Cd); stibnite, Sb<sub>2</sub>S<sub>3</sub> (Sb); AsGa (As); galena (Pb); Bi<sub>2</sub>Se<sub>3</sub> (Bi). Each element was counted for 20 s and XPP corrections were applied. Backscattered electron images (BSE) were also obtained with the same equipment at LNEG.

Petrography of fluid inclusions has been carried out on 0.3 mm thick doubly-polished wafers. Microthermometric characterization of the fluids was performed using a Chaixmeca heating-freezing stage (Poty et al., 1976) for cryometry, and a Linkam 600 stage (Shepherd, 1981) for the heating studies (Shepherd et al., 1985). The accuracy was  $\pm 0.1$  °C during cryometry and  $\pm 1$  °C during heating. Both stages were periodically calibrated using synthetic fluid inclusions (SynFlinc) with known melting points. A Chaixmeca crushing stage was used to determine if there was any gas within the fluids. Quartz grains (0.2– 0.3 mm) immersed in anhydrous glycerine were crushed between two thick glass plates and observed under the binocular stereomicroscope. Fluid salinities were calculated based on the expression given in Bodnar (1993) for inclusions where the last phase to melt was ice. The expression given in Sterner et al. (1988) was used for inclusions where the last melting was hydrohalite melting. Compositions for fluids with very low first melting (<40 °C), where both hydrohalite and ice melting were recorded, were obtained by plotting microthermometric data in the ternary diagram H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> constructed from data taken from Borisenko (1977) and Oakes et al. (1990). Bulk-fluid compositions and isochors were calculated using Bakker (2003) software.

# 4. Mineralogical and chemical characteristics of ore minerals of the Terramonte Pb–Zn–Ag quartz vein

The mineral characteristics given are based on our studies on several samples collected from the Terramonte Pb–Zn–Ag quartz vein, as well as samples from this vein kept at LNEG and earlier publications (Gaspar, 1967, 1971; Couto et al., 1990). All ore minerals are fine-grained.

Arsenopyrite, pyrite and pyrrhotite are the earliest sulphides to form. Arsenopyrite and pyrite are common and pyrrhotite is very rare. The earlier arsenopyrite is unzoned and included in pyrite. But the later arsenopyrite is occasionally zoned, surrounds and penetrates pyrite (Fig. 3a) and is included in quartz, sphalerite and galena (Fig. 3a). The oscillatory zoned grains show alternating darker and lighter zones



Fig. 2. a) Location of the Terramonte mine on the Valongo anticline, northern Portugal (modified from Couto and Sodré Borges, 2005). Geological map of the Terramonte area (modified from Marsella, 1966).

that have a sharp contact (Fig. 4a). The lighter zone has a higher Sb content and a lower As content than the darker zone (Table 1, Fig. 4b, c, d). Most of the analyzed arsenopyrites are S-rich. The earlier generation is S-deficient and has the highest As + Sb content (Fig. 5a, b). There is a negative correlation between As and Sb in arsenopyrite which is better shown for the zoned arsenopyrite (Fig. 4d). The Ag and Au contents in arsenopyrite are only up to 0.02 and 0.08 wt.%, respectively.

Most euhedral pyrite grains are unzoned and have inclusions of arsenopyrite, rutile, apatite and muscovite. Pyrite is included in quartz (Fig. 3b), sphalerite, chalcopyrite and galena. Rare zoned grains have a larger darker core and a smaller oscillatory zoned rim consisting of two thinner lighter zones containing either As up to 3.21 wt.% or Sb up to 2.90 wt.% and lower S content than the darker core (Table 1, Fig. 5c, d). The contrast between core and rim shows up better if the lighter zones contain some As (Fig. 3b). The larger darker zone between the lighter zones of the rim has a similar chemical composition to that of the core. The composition of the darker core of zoned grains is similar to that of unzoned grains, but the lighter zones of the rim have a distinct composition (Fig. 5e). The Au and Ag contents of pyrite are up to 0.11 and 0.04 wt.%, respectively.



**Fig. 3.** Backscattered electron images of ore minerals of the Terramonte Pb–Zn–Ag quartz vein. a) Pyrite grain (Py) surrounded and penetrated by the second generation of arsenopyrite (Ars). These minerals are included in galena. b) A zoned pyrite grain included in quartz. c) Sphalerite included in galena and the latter included in quartz. d) Bournonite (Bou) partially surrounded by pyrargyrite (Pyr) and semseyite (Sem); all are included in galena. e) Bournonite partially surrounded by quartz and freibergite (Fr); all included in galena. f) Pyrargyrite included in semseyite and freieslebenite (Frei) and both included in galena. g) Semseyite included in freieslebenite and both included in galena. h) Freieslebenite partially surrounded by diaphorite (Diap) and both partially included in galena. i) Freibergite surrounding galena.

Sphalerite is abundant and subhedral to anhedral. Most sphalerite is earlier than galena and contains arsenopyrite and pyrite inclusions. It occurs as inclusions in quartz and galena (Fig. 3c). The oscillatory zoned grains have alternating darker and lighter zones, showing sharp and irregular contacts (Fig. 6a). The lighter zone has higher Cu and Sb contents and a lower Zn content than the darker zone (Fig. 6a, b, c, Table 1). The positive correlation between Sb and Cu contents in sphalerite from two selected oscillatory zoned grains is shown in Fig. 6d. The negative correlation of (Mn + Sb + Cu + Cd + Fe) versus Zn for these two grains also occurs, but it is only shown for one grain (Fig. 5f). A later unzoned sphalerite contains inclusions of galena and partially surrounds galena and occurs in veinlets cutting it. It has lower Fe and Cd contents and a higher Zn content than the earlier unzoned sphalerite than galena (Table 1, Fig. 5g). The darker and lighter zones have Zn, Fe and Cd contents close to those of unzoned sphalerite later than galena (Table 1), suggesting that they are later than galena. The Mn content is very low or non-existent in sphalerite (Table 1). The most Fe-rich sphalerite contains ~13 Fe wt.%, whereas the most Fe-poor sphalerite has ~3.4 wt.%. Chalcopyrite is rare, anhedral and occurs either associated with sphalerite or as inclusions mainly in galena, but also in quartz, bournonite and freibergite. It has a homogeneous composition (Table 1).

Bournonite, PbCuSbS<sub>3</sub>, is rare, anhedral, included in galena and is partially surrounded by pyrargyrite, semseyite and freibergite (Fig. 3d, e). Pyrargyrite, Ag<sub>3</sub>SbS<sub>3</sub>, is rare, anhedral, partially surrounds bournonite, is included in quartz, semseyite, freieslebenite and galena (Fig. 3d, f) and is partially surrounded by semseyite and diaphorite. It shows a decrease in the Sb content as the Ag content increases (Table 1, Fig. 5h, i). Polybasite, (Ag, Cu)<sub>16</sub>Sb<sub>2</sub>S<sub>11</sub>, is very rare, anhedral and occurs as inclusions in semseyite, but both are included in galena. Semseyite, Pb<sub>9</sub>Sb<sub>8</sub>S<sub>21</sub>, is rare, anhedral, partially surrounds bournonite and pyrargyrite and occurs included in guartz, freieslebenite and galena (Fig. 3d, f, g). It is mainly unzoned, but a few grains are oscillatory zoned, showing alternating darker and lighter zones (Fig. 7a). The lighter zone has a higher Pb content and a lower Sb content than the darker zone (Fig. 7b, c, Table 1). Some unzoned grains have a composition close to that of the darker zone, whereas other unzoned grains have a composition closer to that of the lighter zone (Table 1, Fig. 7b, c). Freieslebenite, PbAgSbS<sub>3</sub>, is rare, anhedral, included in galena, contains inclusions of pyrargyrite and semseyite and is partially surrounded and penetrated by diaphorite (Fig. 3f, g, h). Diaphorite Pb<sub>2</sub>Ag<sub>3</sub>Sb<sub>3</sub>S<sub>8</sub>, is rare, anhedral, included in galena and partially surrounds pyrargyrite and freieslebenite (Fig. 3h). It has higher Sb and Ag contents and a lower Pb content than freieslebenite (Table 1, Fig. 5j, k, l). Boulangerite, Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub>, occurs as many included needles in some reddish quartz that replaces the country schist. Freibergite,  $(AgCu)_{10}(FeZn)_2Sb_4S_{13}$ , is rare, included in quartz and galena, has rare inclusions of sphalerite and partially surrounds bournonite and galena (Fig. 3e, i). In general, it is unzoned, but a few crystals included in quartz are oscillatory zoned, showing sharp contacts between darker zone, grey zone and lighter zone (Fig. 8a). The Ag content increases progressively and Cu content decreases from the dark zone to the grey zone and lighter zone (Fig. 8a, b, c, d). Silver is negatively correlated with Cu (Fig. 8d).



Fig. 4. Arsenopyrite in the Terramonte Pb–Zn–Ag quartz vein. a) Backscattered image of an oscillatory zoned grain; b) Sb and c) As distributions; d) As vs. Sb diagram of unzoned and zoned grains of arsenopyrite, which have similar compositions.

A deficiency in S content occurs in the grey and lighter zones. Unzoned crystals have Cu and Ag contents similar to those of either the grey zone or the lighter zone (Fig. 8d). There is no significant distinction in chemical composition of freibergite included in galena and surrounding galena (Figs. 3e, i; 8d). Freibergite is an argentian tetrahedrite with more than 20 wt.% Ag (Riley, 1974).

Galena is abundant and anhedral. It has a few inclusions of arsenopyrite, pyrite, sphalerite, chalcopyrite and polybasite and several inclusions of bournonite, pyrargyrite, semseyite, freieslebenite, diaphorite (Fig. 3c, d, e, f, g, h) and freibergite. The distinction between inclusions and products of exsolution was based on textural observations and electron microprobe traverses of the host galena. The inclusions occur within the galena grains and do not show any particular orientation. The chemical composition of galena is very helpful to distinguish between inclusions and exsolution products, because galena does not show any significant variations in Pb, Sb, Bi and Ag contents close to the inclusions. Galena has on average 0.42 wt.% Sb, 0.39 wt.% Bi and 0.31 wt.% Ag and contains up to 1.18 wt.% Sb, 0.61 wt.% Bi and 0.94 wt.% Ag (Table 1). The (Sb + Ag + Bi) content is negatively correlated with the Pb content in galena (Fig. 9).

The mineral paragenetic sequence is given in Fig. 10. Four stages are distinguished. Quartz occurs in all stages. It is mainly accompanied by arsenopyrite and pyrite in the first stage, sphalerite in the second stage, galena containing several inclusions of Cu–Sb–Pb, Sb–Ag, Sb–Pb, Ag–Sb–Pb and Cu–Ag–Sb sulphosalts in the third stage and frequent carbonates in the fourth remobilization stage. This mineral paragenesis differs from that of Gaspar (1967), because his stage 1 consists only of quartz, his stage 2 corresponds to the stages 2 and 3 presented here, as his stage 3 contains some recurrences of ore minerals which are shown here in stage 3. He also found a later pyrite on top of carbonates, which we did not observe. Polybasite, semseyite, freieslebenite and diaphorite are also now given in Fig. 10. The mineral paragenetic

sequence (Fig. 10) is similar to that of the Pb–Zn–Ag deposit of Ribeiro da Castanheira (Couto et al., 1990), which occurs close to the Terramonte deposit. However, some differences occur in the sequence of sulphosalts and galena within stage 3.

Locally some hydrothermal alteration of pyrrhotite into marcasite, arsenopyrite into scorodite and galena into anglesite occur. The hydrothermal minerals surround the respective sulphide.

## 5. Fluid inclusion studies

The study was done on guartz crystals enclosed in ore minerals in order to better interpret the textural relations between sulphides and quartz. Macroscopically there are two types of quartz: one milky and another hyaline (Fig. 11). Occasionally this last quartz has a reddish appearance due to micrometric needle-like inclusions of boulangerite. Under the microscope it is possible to distinguish four quartz types (Fig. 12). One (Q1) with a dark nucleus due to many fluid inclusions, another (Q2) hyaline alternating with Q1 and with few inclusions; domains of hyaline microgranular quartz (Q3) and a last quartz (Q4), also clear in appearance, with big (up to several millimetres) grains and few fluid inclusions. The first two types dominate in all the samples and clearly predate the main galena deposition. In general, intracrystalline deformation is weak or absent in quartz types, although in some places it has evident undulose extinction and subgrains. Q1 and Q2 correspond to quartz from stage 2, Q3 represents the initial quartz in stage 3 and Q4 corresponds to quartz of stage 4.

#### 5.1. Fluid inclusion petrography and fluid types

Fluid inclusions were studied in Q1 and Q2 because in the other types of quartz are rare or absent. One of the important aspects of fluid inclusion petrography is the *degree of fill* (Flw) which could be

Table 1

Selected electron-microprobe chemical analyses in wt.% of sulphides and sulphosalts of the lead-zinc-silver quartz vein from Terramonte, northern Portugal.

	Ni	Со	Cu	Ag	Au	Zn	Fe	Mn	Cd	Sb	As	Pb	Bi	S	Total
Zoned arsenopyrite															
Darker zone	0.23	0.23	0.03	0.01	0.02	_	33.30	0.02	_	1.87	42.92	_	_	21.28	99.91
Lighter zone	0.12	0.95	0.06	0.02	0.05	_	32.46	0.02	-	6.83	38.23	_	-	21.22	99.96
Unzoned arsenopyrite															
Included in pyrite	0.68	0.95	-	-	-	-	31.08	-	-	1.66	46.73	_	-	18.60	99.70
Included in sphalerite	0.02	0.11	0.03	-	-	0.03	33.63	0.04	-	5.74	37.65	-	-	22.30	99.55
Surrounding pyrite	-	-	-	-	0.06	-	33.71	0.02	0.01	2.73	41.85	-	-	21.56	99.94
Zoned pyrite															
Darker core	-	0.07	0.04	-	-	0.01	45.66	-	-	-	-	0.12	-	54.10	100.00
Lighter rim	-	0.08	0.02	0.02	0.01	-	44.91	-	-	0.04	2.77	0.11	-	51.79	99.75
Darker core	-	0.05	0.01	0.01	0.02	0.02	45.63	-	-	0.10	0.01	0.15	-	53.98	99.98
Lighter rim	0.09	0.07	0.02	0.04	0.02	0.01	44.84	0.01	-	2.36	-	0.07	-	52.51	100.04
Unzoned pyrite															
Included in sphalerite	-	-	0.05	0.01	-	-	45.64	-	-	-	-	0.10	-	53.76	99.56
Zoned sphalerite															
Darker zone	-	-	0.01	-	0.02	61.13	5.51	0.01	0.16	-	-	0.05	-	33.03	99.92
Lighter zone	-	-	0.13	-	0.02	60.93	5.21	-	0.26	0.15	-	0.07	-	33.23	100.00
Unzoned sphalerite															
Earlier than galena	-	-	0.06	0.04	0.11	52.12	11.58	-	0.67	0.24	-	0.06	-	34.93	99.81
Later than galena	-	-	-	-	-	60.92	5.14	-	0.27	0.01	-	0.07	-	33.56	99.97
Chalcopyrite	-	-	34.17	0.01	0.01	-	30.09	-	-	0.11	-	0.11	-	35.37	99.87
Bournonite	-	-	12.45	0.01	-	0.05	0.02	-	0.03	25.50	-	41.77	0.12	19.85	99.80
Pyragyrite (the poorest in Ag)	-	-	-	52.69	0.04	0.07	-	-	-	27.07	-	1.82	-	17.99	99.68
Pyragyrite (the richest in Ag)	-	-	-	61.71	-	0.05	-	-	-	21.80	-	0.09	-	16.34	99.99
Polybasite	-	-	4.01	68.70	0.01	0.10	-	-	-	11.38	-	0.75	-	15.09	100.04
Zoned semseyite															
Darker zone	-	-	-	-	-	-	-	-	-	29.16	-	51.34	0.25	19.25	100.00
Lighter zone	-	-	-	-	-	-	-	-	-	27.25	-	53.23	0.28	18.89	99.65
Unzoned semseyite															
Similar to the darker zone	-	-	-	-	-	-	-	-	-	28.54	-	51.92	0.27	19.37	100.10
Similar to the lighter zone	-	-	-	-	-	-	-	-	-	27.77	-	52.53	0.29	18.96	99.55
Freieslebenite	-	-	-	19.94	-	-	-	-	-	23.26	-	38.31	0.15	17.92	99.58
Diaphorite	-	-	-	24.03	-	-	-	-	-	27.69	-	29.19	0.05	18.70	99.66
Boulangerite	-	-	-	-	-	-	-	-	-	25.65	-	55.51	-	18.51	99.67
Zoned freibergite															
Darker zone (Dz)	-	-	21.35	23.30	-	1.19	4.94	-	-	27.17	-	-	-	22.21	100.16
Grey zone (Gz)	-	-	19.03	27.21	-	1.09	4.76	-	-	26.47	-	-	-	21.42	99.98
Lighter zone (Lz)	-	-	15.92	30.99	-	1.19	4.56	-	-	26.87	-	-	-	20.74	100.27
Galena <sup>a</sup>	-	-	-	0.94	-	-	-	-	-	1.18	-	83.97	0.55	13.38	100.02

<sup>a</sup> The richest grain in Sb and Ag of galena with the composition  $Sb_{1.15}Ag_{1.03}Bi_{0.31}Pb_{48,04}S_{49,47}$ . Freibergite compositions:  $Dz (Ag_{3.93}Cu_{6.12})_{\sum 10.05} (Fe_{1.61}Zn_{0.33})_{\sum 1.94} Sb_{4.07}S_{12.62}$ ;  $Gz(Ag_{4.63}Cu_{5.50})_{\sum 10.13} (Fe_{1.56}Zn_{0.31})_{\sum 1.87} Sb_{3.99}S_{12.27}$  and  $Lz(Ag_{5.40}Cu_{4.71})_{\sum 10.11} (Fe_{1.54}Zn_{0.34})_{\sum 1.88} Sb_{4.15}S_{12.17}$  assuming (Ag + Cu + Fe + Zn) = 12. The minimum detection limit for all elements is 100 ppm. – Less than the minimum detection limit.

defined as the ratio between the liquid phase and the total volume of the inclusion. All the fluid inclusions are biphasic at room temperature with average Flw around 0.90 (estimates based on available charts). All the fluids are aqueous, a fact that was confirmed with the absence of gas bubbles during crushing stage experiments. The majority of the fluid inclusions are found in clusters and more rarely in trails (Fig. 13). Fluids were not observed along intercrystalline boundaries. Occasionally fluid inclusions could be observed in growth zones in the transitions from Q1 and Q2, but it is very difficult to distinguish them because of the overlap of various levels of fluid inclusion and clusters. None of the inclusions in which microthermometry was done from visible clathrates. Very low salinity fluids were observed in intracrystalline trails inside Q2, which suggest that this quartz entrapped fluids of different provenance. Based on microthermometric observations, four main types of fluids could be considered: (1) very low salinity to non-salt inclusions; (2) fluid inclusions with salinity between 5-18 wt.% eq. NaCl; (3) high-salinity fluids ( $\geq$ 20 wt.% eq. NaCl) with first melting between  $-30^{\circ}/-40^{\circ}$ C and melting of hydrohalite (NaCl·2H<sub>2</sub>O) around 0.0 °C and (4) high-salinity with first melting below -40 °C and with hydrohalite melting prior to ice melting. When the hydrohalite appears it forms a mass of tiny greenish crystals. When heated from a temperature slightly below their melting temperature they do not coalesce into a single crystal like ice does, and they do not adhere to the bubble. The H<sub>2</sub>O-CaCl<sub>2</sub>-NaCl fluids correspond to a few inclusions that were found in only two samples. Characteristically, they can be recognized by a brown tint gained after freezing. Many fluid inclusions freeze to metastable assemblages (Goldstein and Reynolds, 1994) and when heated they begin to melt at temperatures as low as -35 °C, for the H<sub>2</sub>O–NaCl system (Davis et al., 1990). The fluids in the central portions of Quartz (Q1) are aqueous, practically without salts (the temperature of the last melting of ice around 0.0 °C) and have Th in the range 140°/230 °C. Inclusions in the hyaline quartz (Q2) surrounding Q1 are very saline with NaCl and occasionally also H<sub>2</sub>O–NaCl– CaCl<sub>2</sub> fluids (Fig. 14). Most of the moderately saline inclusions (and even low-salinity inclusions) are randomly distributed in the same quartz where high salinity fluids are found. However, these fluids are also found in trails crossing Q2 (Fig. 13).

#### 5.2. Microthermometry

Early in the research it was noted that many of the fluids have high salinity. This is first evident when we get a freezing temperature below -50 °C and is confirmed by low first melting (<-30 °C). In such cases, we suspect that the fluid should have bivalent cations. It is thus advisable to use the sequential freezing technique of Haynes (1985) record which makes it possible to record the always difficult to observe, melting of hydrohalite. Precautions were taken to heat these fluid inclusions earlier than the other types because at around 200 °C they all suffered severe leakage, which makes them useless for heating experiments. The less saline inclusions, which correspond to 39% of all measurements, have the last ice melting temperatures between 0.0 °C and -1.8 °C, which correspond to salinity between 0 and 3.1 wt.% NaCl equiv. The medium salinity fluids have the last ice melting in the



**Fig. 5.** Compositions of some ore minerals in the Terramonte Pb–Zn–Ag quartz vein. a) S-(Fe + Ni + Co)-(As + Sb) diagram showing the positions of diagrams (b) and (e); b) arsenopyrite included in pyrite is the richest in As + Sb content; c) As vs. S diagram for zoned pyrite, showing that As substitutes for S and the lighter zone is richer in As and poorer in S than the darker zone; d) Sb vs. S diagram for another zoned pyrite grain, showing that Sb substitutes for S and the lighter zone has a higher Sb and a lower S content than the darker zone; e) the darker zone of zoned pyrite grains has a similar composition to the unzoned grains, whereas the lighter zone is the richest in As + Sb; f) (Mn + Sb + Cu + Cd + Fe) vs. Zn in sphalerite, suggesting that these elements substitute for Zn; g) Fe vs. Zn diagram showing that sphalerite later than galena is poorer in Fe and richer in Zn than sphalerite earlier than galena; h) S–Ag–Sb diagram shows the locations of (i, with increase in Ag content, Sb content decreases in pyrargyrite; j) Sb–Ag–Pb diagram shows the locations of (k and 1), diaphorite is richer in Sb and Ag and poorer in Pb than freieslebenite.

range -1.9 °C/-18.0 °C (26% of inclusions) which corresponds to salinity between 3.2 and 21 wt.% NaCl equiv. The high salinity NaCl-rich fluids, corresponding to 21% of the inclusions, have a peak for the last ice melting between - 19.4 °C and - 21.3 °C (22.0-23.2 wt.% NaCl equiv.). The fluids with the highest salinity (14% of the inclusions) correspond to fluid inclusions with hydrohalite melting between 0.0  $^\circ$ C and +4.8  $^\circ$ C (salinity around 26.4 wt.% NaCl equiv.) plus a small group of H<sub>2</sub>O-CaCl<sub>2</sub>-NaCl fluids showing melting of hydrohalite between -28.7 and -23.2, and the last ice melting in the range -19.7 °C/-16.2 °C (Figs. 13 at top, 14); these fluids have salinity in the range 5-12 wt.% NaCl plus 9-17 wt.% CaCl<sub>2</sub>. Hydrohalite melts above +0.1 °C (3 inclusions) denote metastability. The homogenization temperatures have a predominant maximum of around 120 °C for the high-salinity fluids (Fig. 15) and two other maxima of around 150 °C and 190 °C for the medium and low salinity fluids. The H<sub>2</sub>O-CaCl<sub>2</sub>-NaCl fluids have the lowest homogenization temperatures, between 86 and 92 °C.

#### 6. Discussion

#### 6.1. Mineralogical data

The inverse correlation between As and Sb in arsenopyrite (Fig. 4d) suggests that Sb substitutes for As as found by Cathelineau et al. (1988), Couto et al. (1990) and Neiva et al. (2008). Both As and Sb likely replace S in pyrite as the inverse correlations of As vs. S and Sb vs. S occur (Fig. 5c, d), as proposed by Fleet et al. (1989), Deditius et al. (2011) and Agangi et al. (2013). A very good positive correlation between Cu and Sb is observed in sphalerite (Fig. 6d). Copper occurs as Cu<sup>+</sup> in natural sphalerite (Cook et al., 2012; Murakami and Ishihara, 2013). The coupled substitution Cu<sup>+</sup> + Sb<sup>3+</sup>  $\leftrightarrow$  2Zn<sup>2+</sup> is suggested and allows Cu and Sb to enter in the sphalerite structure from Terramonte. The elements Fe<sup>2+</sup>, Mn<sup>2+</sup> and Cd<sup>2+</sup> also enter the structure of this sphalerite. Therefore, a good negative correlation occurs between (Mn + Sb + Cu + Cd + Fe)



Fig. 6. Sphalerite in the Terramonte Pb–Zn–Ag quartz vein. a) Oscillatory zoned grain; b) Cu and c) Sb distributions; d) Sb vs. Cu diagram of two zoned grains, which show a lighter zone richer in Sb and Cu than the darker zone.

and Zn of a selected zoned sphalerite crystal (Fig. 5f). In general, copper is transported as Cu<sup>+</sup> in chloride and hydrosulphide complexes of hydrothermal-ore fluids (e.g., Etschmann et al., 2011). In natural hydrothermal solutions, antimony occurs as Sb<sup>3+</sup> and is mainly transported as Sb(OH)<sub>3(aq)</sub> (Zotov et al., 2003 and references therein). Therefore, Cu<sup>+</sup> and Sb<sup>3+</sup> in sphalerite match their speciation in hydrothermal orefluids. Silver substitutes for Cu in freibergite (Fig. 8d). The inverse correlation between (Sb + Ag + Bi) content and Pb content in galena from

Terramonte (Fig. 9) is supported by the almost negative correlation between the a cell edge versus Sb + Ag + Bi for galena containing less than about 15 wt.% Ag and Bi (Sb) (Foord et al., 1988). At geologically significant temperatures, Ag is quite insoluble in PbS if Sb (or Bi) are absent (Amcoff, 1976). The coupled substitution of Ag<sup>+</sup> + Sb<sup>3+</sup> for 2Pb<sup>2+</sup> in galena is indicated by some authors (e.g., Amcoff, 1976; Lueth et al., 2000). The coupled substitution of Bi<sup>3+</sup> + Ag<sup>+</sup> for 2Pb<sup>2+</sup> is more stable than the former substitution (Amcoff, 1976). Electron transfer between Ag and Sb,



Fig. 7. Semseyite in the Terramonte Pb–Zn–Ag quartz vein. a) Oscillatory zoned grain; b) and c) Compositions of unzoned and zoned grains plotted on the S–Pb–Sb diagram, showing that in zoned grains, the lighter zone has a higher Pb content and a lower Sb content than the darker zone; some unzoned grains have a similar composition to the lighter zone and others are similar to the darker zone.



Fig. 8. Freibegite in the Terramonte Pb–Zn–Ag quartz vein. a) Oscillatory zoned grain; b) Ag and c) Cu distributions; d) Cu vs. Ag diagram, showing that the Cu content decreases and the Ag content increases from the darker zone to the lighter zone; unzoned grains included in galena and others surrounding it have not a distinct composition, which is similar to the lighter and grey zones of the zoned grains.

Bi in galena is shown to affect cation ordering in these systems (Renock and Becker, 2011).

The distinctions between lighter and darker zones in grains of some sulphides and the sulphosalt freibergite from Terramonte are due to substitutions in the mineral lattices. Arsenopyrite has a higher Sb content and a lower As content in the lighter zone than in the darker zone (Fig. 4). Pyrite has a higher As or Sb content and a lower S content



**Fig. 9.** (Sb + Ag + Bi) versus Pb diagram of galena in the Terramonte Pb–Zn–Ag quartz vein, suggesting that these elements substitute for Pb in galena.

in the lighter zone of the rim than in the darker core (Fig. 5c, d). The lighter zone of sphalerite is richer in Cu and Sb and poorer in Zn than the darker zone (Fig. 6, Table 1). Ag content increases and Cu content decreases from the darker zone to the grey zone and from that to the lighter zone of freibergite (Fig. 8). However, the distinction between the lighter and darker zones of the sulphosalt semseyite is due to the fact that the lighter zone is richer in Pb and poorer in Sb than the darker zone and these metal and metalloid are the main constituents (Table 1, Fig. 7) in the solid solution, but are not correlated. The substitutions of



Fig. 10. Mineral paragenetic sequence at the Terramonte Pb–Zn–Ag quartz vein.



Fig. 11. Pb-Zn-Ag ore from Terramonte hand specimen. The coin has a diameter of 2.2 cm.

Sb, Ag and Bi for Pb in galena (Fig. 9) did not cause any significant zoning, which may be attributed to their low content.

The preserved zoned crystals suggest that significant sulphide recrystallization or fluid-assisted removal or addition of elements along the vein did not take place (Craig et al., 1993), which is supported by the small occurrence of hydrothermal alteration. The oscillatory zoned crystals of arsenopyrite, pyrite, sphalerite, semseyite and freibergite show sharp contacts and locally irregular contacts between darker and lighter zones (Figs. 4a, 3b, 6a, 7a, 8a). This zonation type can be attributed to factors such as changes in fluid chemistry or temperature or pressure, due to variable mixing ratios over time, and element diffusion rates, but also to the hypothesis of faster crystal growth rates than diffusion of selective cations through fluid. The zone thicknesses in sphalerite (Fig. 6a) may be related to the amount of fluid injected into the fracture (Beaudoin, 2000).

The earlier rare and unzoned arsenopyrite has a different composition from the later unzoned and zoned arsenopyrite (Fig. 5b), suggesting that the fluid changed the composition from the starting Fe-As stage (Fig. 10) of the mineralizing sequence. The lighter zones occur in the rim of a few zoned grains of pyrite and are richer in either As or Sb, but poorer in S than the darker core and darker zone of the rim (Figs. 3b, 5c, d, Table 1). Consequently the lighter zones formed later than most pyrite. The unzoned sphalerite, earlier than galena, has between 16 and 21 mol% FeS, whereas the unzoned sphalerite, later than galena, contains 7-12 mol% FeS. However, the zoned sphalerite crystals, later than galena, have 7-23 mol% FeS. This variation in FeS content may reflect variation in the activity of FeS in the fluid and in physical-chemical conditions during precipitation. The highest value of 0.94 wt.% Ag in galena is lower than that of the argentiferous galena from Santa Eulalia, Mexico (Lueth et al., 2000). Textural evidence and electron microprobe traverses of galena indicate that galena has inclusions of sulphosalts. Galena and its inclusions of pyrargyrite, polybasite, freieslebenite, diaphorite and freibergite (Figs. 3d, f, g, h, 8, Table 1) concentrate Ag, whereas Sb is retained in these minerals and also in bournonite and semseyite inclusions in galena (Fig. 3d, e, f, g, Table 1). Galena is the main concentrator of Pb, but bournonite, semseyite, freieslebenite and diaphorite inclusions also retain Pb (Table 1).

### 6.2. Mineralizing environment and mineral deposition

The Pb–Zn–Ag quartz vein from Terramonte is located in the Dúrico-Beirã region, at southeast of Sb–Au quartz veins from this region which were studied by Couto et al. (1990) and Neiva et al. (2008) (Fig. 2a). The Sb content in the Terramonte arsenopyrite reaches a higher value than in arsenopyrite from Sb–Au quartz veins from this region. The Sb–(As, Fe) mineralogical association is also characteristic of the Sb–Pb San José mine at Lanzuela, Spain (López-Ciriano et al., 1993). Bournonite, pyrargyrite, polybasite, semseyite, freieslebenite, diaphorite and freibergite contain significant Sb content (Table 1) and occur as inclusions in the Terramonte galena. The high Sb content of several minerals from the Terramonte Pb-Zn-Ag quartz vein can be attributed to the fluid percolation through Sb rich mineralizations, which are important in the area. This mechanism was also suggested by Marcoux and Moëlo (1991) for other ore deposits in the Variscan orogeny of western Europe. The paragenetic sequence for the Terramonte Pb-Zn-Ag quartz vein (Fig. 10) and that for the Ribeiro da Igreja Sb-Au deposit from the Dúrico-Beirã region (Couto et al., 1990) have some common characteristics: a first Fe-As stage, a second Zn stage, a third Pb-Sb stage and a fourth remobilization stage. However, the first stage is smaller at the Terramonte Pb-Zn-Ag quartz vein, whereas at the Ribeiro da Igreja Sb-Au deposit carbonates occur in the third stage and there is a fourth Sb-stage, indicating that their late hydrothermal fluids are richer in Sb than those from Terramonte. The Pb isotopic compositions of stibnite from the Sb-Au deposits suggest a homogeneous crustal source of lead from the metasedimentary sequences (Neiva et al., 2008).

Arsenopyrite was the earliest sulphide to crystallize and belongs to the first Fe–As stage of deposition (Fig. 10). Its composition is independent of fS<sub>2</sub> and is only dependent on temperature in the pyrite stability field (Sharp et al., 1985). The analyzed arsenopyrite grains have Sb  $\geq$  1.03 wt.%. Therefore, the arsenopyrite geothermometry cannot be applied to them (Sundblab et al., 1984). An increase of one pH unit can cause the deposition of up to 99% of metal from a sulphidesaturated solution (Barnes, 1979). Arsenopyrite and pyrite are the first ore minerals to precipitate in the first stage of the Terramonte orebody (Fig. 10). They may have precipitated from the interaction of the hydrothermal fluid with the Fe-bearing wall rocks and they depleted the fluid in H<sub>2</sub>S (e.g., Williams-Jones and Heinrich, 2005).

Sphalerite belongs to the second stage of deposition (Fig. 10). It shows diffusion-induced segregations of chalcopyrite and consequently cannot be used for geobarometry (Bente and Doering, 1993). The maximum variation of 7 to 23 mol% FeS values in the sphalerite of the studied samples from the Terramonte quartz vein may reflect changes in several fluid parameters (T, P, fO<sub>2</sub>, fS<sub>2</sub>). Argentiferous galena is the most abundant ore mineral, reflecting its greater stability. It belongs to the third stage of deposition (Fig. 10). Chloride and bisulphide complexes are important for the transportation of zinc (e.g., Barnes, 1979; Hedenquist and Lowenstern, 1994; Seward and Barnes, 1997) and lead (Giordano and Barnes, 1979; Seward, 1984; Wood and Samson, 1998). Zn-sulphide systems are rather complicated (Wood and Samson, 1998). We suggest that in the Terramonte orebody any of the complexes  $ZnCl^{-}$  to  $ZnCl_{4}^{2-}$  could have transported this metal, due to the strong salinity of the fluid. Probably Pb could also have been transported as a chloride complex. Silver is transported as AgHS(aq) in acid conditions,  $Ag(HS)_2^-$  under neutral pH conditions and  $Ag_2S(HS)_2^{2-}$  in alkaline solutions (Stefansson and Seward, 2003). Wood and Samson (1998) pointed out that chloride complexes are more efficient than bisulphide complexes transporting silver in a wide variety hydrothermal environments. However, at Terramonte we cannot eliminate the possibility that silver was transported as  $Ag(HS)_2^-$  or  $Ag_2S(HS)_2^2$  complexes or even as  $Ag_2S$  colloids. Antimony would have been transported as  $Sb(OH)_{3(aq)}$  in the hydrothermal fluid, especially at temperatures >200 to 250 °C (Zotov et al., 2003).

Carbonates are paragenetically late in the mineralizing sequence and belong to the fourth stage of precipitation (Fig. 10), which can be explained by an increase in pH with time, as the loss of  $H^+$  to wall–rock alteration causes an increase in carbonate and they precipitate (Holland and Malinin, 1979).

High saline aqueous hydrothermal fluids can form in four possible ways: 1. magmatic (as a consequence of boiling); 2. by retrograde metamorphism and metasomatism (following fluid rock reactions and the formation of hydrous minerals, like muscovite); 3. by dissolving halide minerals; and 4. by seawater evaporation.



**Fig. 12.** Quartz textures under the microscope (a, b) and binocular stereomicroscope (c, d): a) Q1 and Q2 quartz (see text explanations) with galena; b) Zoned quartz, Q2 with clear (free of fluids) and Q1 dark zones (with many inclusions); c) Q3 microcrystalline quartz, and it relation to ore minerals (mainly galena); d) Macrogranular quartz (Q4) and ore minerals (black) and associated microgranular Q3.

Orogenic (hyper)saline aqueous fluids have been studied by several researchers (e.g., Crawford et al., 1979a,b; Pêcher, 1979; Banks et al., 1991; Bennett and Barker, 1992; O'Hara and Haak, 1992; Barker, 1995; Murphy and Roberts, 1997). Several authors have studied fluids from Pb-Zn-Ag vein deposits. Akande et al. (1989) studied Pb-Zn-F-Ba Cretaceous veins in Nigeria and concluded that they formed from compaction-driven hot (90-200 °C) mineralized brine (14-24 wt.% eq. NaCl) that possibly evolved from evaporative sulphate-rich sequences. Heijlen et al. (2001) found high salinity fluids (2.9-5.0% Na and 2.6-4.6% Ca) in MVT deposits and calcitic veins from a Paleozoic deposit in Belgium and interpreted the fluids as bittern brine that migrated down into the subsurface (due to density) and was later expelled along extensional faults forming the deposits. Gleeson and Turner (2007) studied the Pb-Zn deposits found in paleokarsts in the Pine Point region (Canada) and concluded that they formed from a mixture of CaCl<sub>2</sub>-NaCl-rich fluids, one derived from evaporated seawater and another from dissolved halide minerals.

In the Iberian Peninsula, Pb–Zn vein related orebodies were also studied. Tornos et al. (1991) stated that the genesis of the Ba–F–(Pb– Zn) lodes of the Spanish Central System is related to fluid mixing of a hot (>300 °C) Na–K deep fluid that carried the lead and zinc in the form of chloride metal complexes, with a phreatic-like cool (<100 °C), oxidised and four times more saline fluid. According to this study, deposition took place from 270 °C to 120 °C at a relatively low depth, presumably during the Permo-Triassic extension. Concha et al. (1992) studied the Hiendelaencina (central Spain) Pb–Ag veins and concluded that the ores originated from a complex interaction of hot and saline magmatic fluids with meteoric low salinity (up to 24 wt.% eq. NaCl) cooler fluids (as low as 80 °C). Johnson et al. (1996) studied the Cierco Pb–Zn–Ag veins formed during the Mesozoic extension in the Spanish Pyrenees and found fluids with salinity between 3 and 29 wt.% NaCl



**Fig. 13.** Fluid inclusions. a) to e) sequence of cryometry and heating in an H<sub>2</sub>O–CaCl<sub>2</sub>–NaCl fluid inclusion from a crystal shown on Fig. 12c. The last hydrohalite melting and the last ice melting were -28.7 °C and -19.7 °C, respectively. Above H<sub>2</sub>O fluids from the central part of the same crystal (left), and an intracrystalline trail in a nearby clear quartz (right).

eq. They concluded that the sulphide deposition resulted from a mixture of an upwelling hydrothermal fluid from the Paleozoic basement and a marine or meteoric water, near the margin of the subsiding basin. Cardellach et al. (2002) concluded that the formation of the Berta F-



**Fig. 14.** Diagram for the H<sub>2</sub>O–NaCl–CaCl<sub>2</sub> fluids found at the Terramonte orebody. The dots represent hydrohalite and the ice last melting temperatures observed in a fluid inclusion assemblage (dots on the right correspond to temperatures observed during microthermometry of inclusion shown in Fig. 13a–e).

Pb-Zn vein system in NE Spain resulted from mixtures of a saline brine (up to 23% NaCl eq.) with a less saline fluid. The high salinity was interpreted as derived from leaching of the crystalline basement. Lourenco (2002) studied the fluid inclusions of a Pb–Zn paragenesis in the Panasqueira mine and concluded that the fluids were CaCl<sub>2</sub>-dominant (up to 22 wt.% eq. CaCl<sub>2</sub>) and with Th in the range 99–147 °C. He suggests that the fluids were formed from reactions of an H<sub>2</sub>O-NaCl fluid (derived from evaporated Devonian seawater that percolated the basement) with the metasediments (locally albite-rich, as a reaction product). Subías and Fernández-Nieto (1995), Subías et al. (1997, 1998, 2010), Fanlo et al. (1998) and Billström et al. (2003) studied several Pb-Zn-F-(Ba) vein deposits in the Pyrenees and concluded that they formed at low temperature (100-200 °C) from high-salinity fluids derived from basinal brines or basement leaching, and that deposition was caused by one or more of the following mechanisms: cooling, changes in the pH/oxidation state of the fluid, mixing of different fluids and interactions with reactive lithologies. Marques de Sá and Noronha (2011) studied the Braçal Pb-Zn-Ag vein (Aveiro, Portugal) and concluded that the ores were probably deposited following a mixture of high salinity aqueous fluids (up to 23% wt.% eq. NaCl), which they suggest could have come from a basin origin.

In the Central Iberian Zone, the circulation of meteoric waters was important during the later stages of Variscan orogeny (D3) and also probably later, during the Cretaceous period. It is known that saline beds constitute an average of 3% of the world sedimentary record and that brines circulating through the upper crust are not rare. Times



Fig. 15. Plot of salinities versus homogenization temperatures of fluid inclusions from the Terramonte orebody, and histograms for Ths and salinities. Areas corresponding to the low-salinity fluids, mixtures and high-salinities found on samples.

before or soon after the breakdown of continents are the periods most conducive to formation of confined basins that could accumulate salts by evaporation, as is the case of the Hetangian salt deposits in the Lusitanian Basin. The existence of saline brines in crystalline basement rocks is a well-documented phenomenon of many stable regions (e.g., Frape and Fritz, 1987; Moller et al., 1997). Fluids flow downwards when fractures in brittle basement rocks have low pore fluid pressure relative to fluid pressure in stratigraphically younger sequences located above. The variable fluid density in a fluid inclusion assemblage suggests that fluid was not continuous, but occurred sporadically, probably in association with seismicity. Studies of deep drilling show that the upper crust is essentially dry, except along fractures where fluid pressures are lesser than hydrostatic pressure (Moller et al., 1997). This permits the downward movement of fluids during periods of extension. With decreasing temperature, this fluid became progressively richer in salts, probably as a result of prolonged low temperature fluid-rock interaction (e.g., Fritz and Frape, 1982; Frape and Fritz, 1987).

According to our data, the Terramonte ores were formed by the mixing of a highly saline fluid with a fluid almost absent in salt (Fig. 16). The first fluid acquired the salinity in one of two possible ways: seawater evaporation, or percolation of halite-bearing beds.

This fluid circulated from above and/or laterally and leached the metals from country rocks. These precipitated from the fluid following an abrupt fall in solubility caused by mixing with a very low salinity fluid that could have come from above along faults or fractures and convectively circulated to deeper and hotter levels of the crust. A small part of the saline fluid could have circulated close to (or in) the nearby granite contact and acquired there a Ca-rich signature following the albitization of the country rock, a phenomenon studied by Davisson and Criss (1996), and observed in other areas (e.g., Frietsch et al, 1997; Engvik et al., 2008). Couto et al. (1999) described veins of acid igneous rocks with albitization and brecciation in an area near the granitic contact, 2 km from Terramonte. However, we have not found any significant metasomatic change in the studied Terramonte samples. Pulses of a low salinity low temperature fluid after the main high-salinity fluid input are suggested by the existence of trails of low salinity fluids crossing the hyaline quartz crystals where NaCl(-CaCl<sub>2</sub>) occurs. The observation of different types of fluids in the core of the quartz and quartz zonation and ore textures (Figs. 12, 13) suggests that the hydrothermal deposition was recurrent, possibly during seismic episodes. The process known as seismic pumping (Sibson et al., 1975) is a hydrothermal fluid transport mechanism. Its effectiveness as a mineralizing process



**Fig. 16.** Conceptual model for the ore formation at the Terramonte orebody. The genesis of the deposit has resulted from metal leaching of the country rocks and Variscan mineralization by hyper saline fluids coming from surface brines and / or leaching of salt beds with an occasional minor contribution of  $Ca^{2+}$  ions removed from rocks. The precipitation mechanism was triggered by seismic activity and occurred by mixing of this fluid with meteoric waters practically devoid of salts. The granite that certainly exists at depth had a passive action in the deposit formation.

(Sibson, 1987, 1990) has been documented in many hydrothermal mineral deposits around the world.

The origin of the Terramonte Pb-Zn-Ag quartz vein may be associated with faulting due to extensional tectonics related to the opening of the Atlantic ocean and consequently is of Alpine age, as suggested by other authors (e.g., Medeiros, 1964; Thadeu, 1977; Couto, 1993) and, according to the opinion of several French geologists (e.g., Moëlo, 1983; Marcoux et al., 1988) for similar to ore deposits in the Central French Massif. Therefore, the origin of this vein cannot be related to a magmatic process resulting from crustal melt, because the S-type granites from the area are Variscan, ranging from 310 to 305 Ma (Carvalho et al., 2012). The host metasediments are the most likely source for fluids to leach Pb, Zn, Ag, As, Sb and Cu, because they were the source for As, Au, Pb and Sb of Sb-Au quartz veins, as the Pb isotope compositions of stibnite suggested (Neiva et al., 2008). However, a mixture of host metasediments with some nearby previously formed ore (Sb-Au) deposits may have been the source, as in the case of Pb-Zn-Ag and barite Alpine vein deposits in the Iberian Range, NE Spain (Subías et al., 2010).

## **Conflict of interest**

There is no conflict of interest.

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