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► **To cite this version:**

Alexandre Cugerone, Benedicte Cenki-Tok, Alain Chauvet, Elisabeth Le Goff, Laurent Bailly, et al.. Relationships between the occurrence of accessory Ge-minerals and sphalerite in Variscan Pb-Zn deposits of the Bossost anticlinorium, French Pyrenean Axial Zone: Chemistry, microstructures and ore-deposit setting. *Ore Geology Reviews*, 2018, 95, pp.1-19. 10.1016/j.oregeorev.2018.02.016 . hal-01842249

HAL Id: hal-01842249

<https://hal.science/hal-01842249>

Submitted on 3 Feb 2020

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Relationships between the occurrence of accessory Ge-minerals and sphalerite in Variscan Pb-Zn deposits of the Bossost anticlinorium, French Pyrenean Axial Zone: chemistry, microstructures and ore-deposit setting.

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Abstract

The presence of unique accessory Ge-minerals (containing up to 70 wt.% Ge) is a widespread phenomenon in Pb-Zn deposits of the Variscan Pyrenean Axial Zone (PAZ). Such a mode of occurrence is, however, rare worldwide with germanium more typically occurring as a trace component of sulfides, notably sphalerite (<3,200 ppm), or in coal deposits (<5,570 ppm). The PAZ Pb-Zn deposits are thus an excellent target to unravel the processes and key factors controlling formation of mineralization highly concentrated in Ge. Three Pb-Zn deposits are studied here: Argut-dessus; Pale Bidau; and Pale de Rase. All three are located in Late Ordovician rocks within the PAZ Bossost anticlinorium. The main mineralization (Type 2) is localized in epigenetic veins with different geometries relative to host rocks and deformation. Textural analysis of sphalerite mineralization shows evidence for both recrystallization and deformation. Sphalerite is associated with muscovite or graphite and is the unique host for the discrete Ge-minerals in the studied samples. Brunogeierite (GeFe₂O₄) and argutite (GeO₂) occur almost universally at sphalerite grain boundaries. Laser ablation inductively coupled plasma-mass spectrometry analysis of sphalerite and brunogeierite show that sphalerite is relatively depleted in Ge (mean ~13±3 ppm) and other trace elements such as Sb (~21±2 ppm), Cu (~153±23 ppm) and Ga (~127±10 ppm) compared to brunogeierite (29-30 wt.% Ge), which

is also richer in Ga ($\sim 2,406 \pm 270$ ppm) and Cu ($\sim 2,438 \pm 550$ ppm). Collectively, these observations on this exceptional example of Ge enrichment highlight the role of oxidizing, moderate temperature ($\sim < 450$ °C) metamorphic fluids on the partitioning of Ge between discrete Ge-minerals and their sulfide hosts. Comparison with other Ge-deposits worldwide supports the hypothesis that low grade metamorphism and deformation may play a key role in the genesis and concentration of Ge-mineralization, especially in low-grade metamorphic Kipushi-type deposits in which discrete Ge-minerals are located immediately adjacent to recrystallized sulfides.

Keywords: Germanium; Pyrenean Axial Zone; Sphalerite; Mineral chemistry; Sulfide textures

1. Introduction

Germanium (Ge) is one of twenty metals defined as critical by the European Union (European Critical Raw Materials Review, 2014). It is extensively used in the optical fiber and photovoltaic industries. Even though Ge-bearing deposits occur in various geological settings, the element is predominantly found in trace contents within zinc and coal deposits (up to $\sim 3,200$ and $\sim 5,570$ ppm respectively; Seredin and Finkelman, 2008; Saini-Eidukat et al., 2009). The largest Ge-deposits do not, however, exceed a few thousand tons of estimated metal resources, e.g., 2,160 t Ge for the Tsumeb deposit, Namibia (Lombaard et al., 1986), or 1,112 t Ge in the Yunnan coal province (Höll et al., 2007; Hu et al., 2009). Germanium has an average concentration of ~ 1.5 ppm in the continental crust (Smith and Huyck, 1999) which is significantly higher than estimates for elements such as molybdenum or silver (respectively, 1.1 ppm and 0.07 ppm; Laznicka, 2014). This paradox, i.e., the fact that Ge is relatively concentrated in the crust but does not appear as giant deposits, may explain why Ge deposits cannot be identified in a specific setting and instead occur in a diverse range of different environments.

Germanium mineralization may be linked to epigenetic or syngenetic ores even if (diagenetic)-epigenetic deposits hosted in sedimentary sequences typically provide for a greater enrichment (i.e., coal, Mississippi Valley Type (MVT) and Kipushi-type deposits). Germanium can readily partition

into sulfides, oxides, silicate minerals or organic matter, at a large range of concentration, from trace to major contents. Processes of Ge concentration remain poorly constrained but appear linked to low-temperature hydrothermal fluids (Höll et al., 2007). The source of Ge is still unclear in most of the Ge-deposits even if few Ge anomalies may be found in granites or black shales (Bélistont, 2016) associated with Ge ores. Post-mineralization processes, notably metamorphic recrystallization, can impact on Ge mineralization as Frenzel et al. (2016) showed that Ge concentration in sphalerite decreases with increasing metamorphic grade (<310 °C) affecting the Pb-Zn deposits.

In the Pyrenean Axial Zone (PAZ, Fig. 1a), the main metallic resources (Zn, Pb, Fe, Cu, Mn) are located in metasedimentary rocks of Paleozoic age (Fig. 1b; Vic and Billa, 2016), especially in Cambro-Devonian units that make up several metamorphic domes (Pierrefitte, Lys, Gavarnie; Pallaresa, Bossost etc.; Fig. 1b). Several events generating Pb-Zn mineralization in the PAZ have been proposed and continue to be debated, including Middle-Late Ordovician, Lower or Late Devonian, Carboniferous (Variscan) and Late-Triassic/Late-Jurassic ages (Marcoux et al. 1991; Nicol et al., 1997; Garcia-Sansegundo et al., 2014; Munoz et al., 2015). The two oldest events are considered as SEDEX-type by Bois et al. (1976) and Pouit (1985). More than 150 individual Pb-Zn deposits are identified in the French and Spanish parts of the PAZ within 40 different mineralized districts (Oudin et al., 1988). Production did, however, not exceed 300,000 tons of Zn in the French deposits (<http://sigminesfrance.brgm.fr/>).

The frequent and widespread occurrence of discrete Ge-minerals in the PAZ Pb-Zn deposits (Fig. 1b) is quite uncommon in comparison with other deposits worldwide. More usually, whenever Ge is present, it is enriched in the sphalerite (ZnS) lattice rather than as independent Ge-minerals (Reyx, 1973; Johan et al., 1983; Laforet et al., 1981; Bernstein, 1985; Cook et al., 2009, 2015). These Ge-minerals may be brunogeierite (GeFe_2O_4), argutite (GeO_2), Ge-chloritoid (carboirite, $\text{FeAl}_2\text{GeO}_5(\text{OH})_2$), rare briartite ($\text{Cu}_2(\text{Fe}, \text{Zn})\text{GeS}_4$), as well as Ge-bearing lepidomelane, titanite, garnet, zoisite, chlorite, quartz, allanite, and magnetite (Laforet et al., 1981; Johan et al., 1983; Bernstein, 1985; Pouit and Bois, 1986; Johan and Oudin, 1986). The formation of Ge-minerals in the

Pyrenean deposits is poorly documented until now except for Aye et al. (1978) and Johan and Oudin (1986) who suggested a possible link with regional metamorphism, based on paragenetic analysis.

The aim of this study is firstly to decipher the processes leading to genesis of Argut-dessus (AD), Pale Bidau (PB) and Pale de Rase (PR) Pb-Zn(-Ge) deposits located in the PAZ Bossost anticlinorium, and secondly, to compare their features with those of other Ge-occurrences worldwide. We focus on: (i) the structural setting of the three deposits within the regional tectonic framework; (ii) the mineralogy and micro-structures of 38 representative samples; and (iii) the chemistry of sphalerite and accessory Ge-minerals in order to highlight the role of metamorphism and deformation in ore genesis.

2. Geological and structural setting

The Pyrenean Axial Zone (PAZ) belongs to the West-European Variscan belt which was involved in the Pyrenean orogenic cycle (Fig. 1a). It is composed of Paleozoic metasedimentary rocks intruded by Ordovician granites which were metamorphosed and deformed during the Variscan orogeny (Aston, Hospitalet, and Canigou gneiss; Denèle et al., 2014). Two structural domains are present in the PAZ (Zwart, 1963, 1979): (i) the *Infrastructure* consists of high grade metamorphic rocks presenting moderately dipping foliation patterns. Numerous domes are present in the PAZ like the Bossost, Lys Caillaouas, or Aston, Hospitalet and Canigou (Fig. 1a; Zwart, 1979; Denèle, 2007; Denèle et al., 2008). Formation of these domes is associated with emplacement of late-Carboniferous granitoids (i.e., Lys, Maladeta, Bassies, Bossost; Kleinsmiede, 1960; Zwart, 1963a; Garcia-Sanseguno and Alonso, 1989; Mezger and Passchier, 2003; Mezger, 2005); (ii) the *Superstructure* is composed of low-grade metamorphic rocks and present steep folds and fabrics (Zwart, 1963; Cochelin, 2016). The main tectono-metamorphic events recorded in the PAZ are considered as Variscan (ca. 300-325 Ma, Evans et al., 1998; Denèle et al., 2014).

This study focuses on the Bossost anticlinorium (Fig. 1c). The study focuses on the northern part of the Bossost anticlinorium which is composed of Cambrian to Devonian rocks and is part of the Superstructure (Fig. 1b). The southern part of the anticlinorium forms the Aran valley synclinorium and the northern part is bounded by the North-Pyrenean Fault (Fig. 1b). It is composed of a late-

Variscan intrusive leucocratic muscovite-hornblende granite forming the core of a metamorphic dome (Infrastructure) within a larger anticlinorium of Cambro-Devonian metasedimentary rocks (Kleinsmiede, 1960; Zwart, 1963a; Garcia-Sanseguno and Alonso, 1989).

Four stages of deformation are recorded in the Superstructure of the Bossost anticlinorium. (1) A first Variscan deformation (D1) linked to formation of a discrete Pre-Upper Ordovician slaty cleavage (S1). D1 is poorly preserved due to superposition of intensive late events (Garcia-Sanseguno and Alonso, 1989). (2) D2 is expressed by F2 recumbent north-facing folds associated with a sub-horizontal axial planar S2 cleavage (Matte, 1969; Garcia-Sanseguno and Alonso, 1989). A regional metamorphism linked to MP/MT crustal thickening is synchronous with D2. Metamorphism is epizonal (Pouit, 1974; Johan and Oudin, 1986). (3) D3 is locally expressed with S3 cleavage and F3 crenulation folds (Aerden, 1994; Mezger and Passchier, 2003). At regional scale, Aerden (1994) describes D3 deformation patterns (which he named D2) as related to N-S compression and crustal thickening. A decollement is inferred at the base of Silurian black-shales (Zwart, 1979; Matte and Zhi, 1988; Mezger and Passchier, 2003) with tight north-vergent folds. (4) Alpine Upper Cretaceous to Miocene D4 deformation is locally present and essentially reactivates E-W Variscan faults like the Gavarnie Fault (Garcia-Sanseguno et al., 2014), the Merens mylonitic zone (Zwart, 1979; Mezger et al., 2012; Denèle et al., 2014) and in the area of interest here, the Bossost Fault (Zwart, 1979).

The three studied Pb-Zn(-Ge) deposits (Argut-Dessus, Pale Bidau and Pale de Rase). are located within the northernmost part of the Bossost anticlinorium (Fig. 2a). Sulfide mineralogy is dominated by sphalerite and galena. These deposits are relatively small with historical production of about 2,000 to 3,000 tons of Zn and less than 1,000 tons of Pb (Michard, 1966, 1969; Chaput and Michard, 1967; BRGM, 1984). The AD and PR deposits are hosted by schists, meta-siltstones and meta-conglomerates (Fig. 2b). The PB deposit is hosted by grey schists locally alternating with dm-scale siltstones that represent lower parts of the Late Ordovician (o5) compared to those of the AD and PR deposits (Fig. 2b; Pouit, 1974). These three deposits occur in Late Ordovician units affected by low-grade metamorphism with the appearance of sericite or muscovite and chlorite in the host schists (Chaput and Michard, 1967; Pouit, 1974; Johan and Oudin, 1986).

3. Methods

Samples were collected *in situ* in underground galleries, outcrops and rarely in mine dumps. 38 polished thin sections (30 and 100 μm) were studied. 21 of these contained sphalerite. One polished section from the BRGM collection (sample 32362 from the AD deposit) was included in the study.

Microanalysis was carried out using a FEI Quanta FEG 100 Scanning electron microscope (SEM) and a Cameca SX100 electron microprobe analyzer (EMPA) at the Service inter-regional Microsonde-Sud, Montpellier. Major, minor and trace elements were measured with a beam current of 100 nA and accelerating voltage of 20 kV. 14 elements were analyzed: standards, spectral lines, and spectrometers were as follows: Zn (Zn, $L\alpha$, TAP) ; S (FeS_2 , $K\alpha$, PET); Fe (Fe_2O_3 , $K\alpha$, LLif); Cd (CdS, $L\alpha$, LPET); Ge (Ge, $K\alpha$, LLif); Sb (GaSb, $L\alpha$, LPET); Cu (CuS, $K\alpha$, LLif); Ga (GaSb, $K\alpha$, LLif); Ag (Ag, $L\alpha$, LPET); Mn (Mn, $K\alpha$, LPET); Sn (Sn, $L\alpha$, PET); Pb (Pb, $M\alpha$, PET); As (GaAs, $L\alpha$, TAP); Si (CaSiO_3 , $K\alpha$, TAP). Peak count times ranged from 30 to 240s (240s for Ge). Germanium is analyzed on 2 LLif monochromators. The limit of detection for Ge, calculated by internal Cameca procedures, is reduced to 84 ppm. Gallium, As, Ag, Pb, Sn, Sb, and Mn were below detection limit and are not reported in the data tables.

Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) was used to determine trace elements concentrations in sphalerite and brunogeierite. Analyses were carried out using an Excimer CompEx 102 coupled with a ThermoFinnigan Element XR available at the OSU-OREME Montpellier. Analytical setting is modified from BéliSSont et al. (2014). Laser ablation was performed with a constant 5 Hz pulse rate at 90 mJ laser energy. Ablation was performed with different spot diameters: 26 μm for sphalerite and 5 μm for brunogeierite. Total acquisition time was limited to 300s including 180s of background measurement (laser off) followed by 60s of signal acquisition and 60s of washout time. Zinc or Fe contents measured with EMPA were used as internal calibration for sphalerite or brunogeierite, respectively. MASS 1 (synthetic polymetallic sulfide) with a Ge concentration of 57.8 ± 2.6 ppm (S. Wilson, pers. comm.) was used as external standard. The following isotopes were measured: ^{64}Zn ; ^{34}S ; ^{55}Mn ; ^{57}Fe ; ^{59}Co ; ^{61}Ni ; ^{118}Sn ; ^{75}As ; ^{63}Cu ; ^{69}Ga ; ^{74}Ge ; ^{107}Ag ; ^{110}Cd ; ^{115}In ; ^{121}Sb ; and ^{208}Pb . Data were processed using the Glitter 4.0 software package (Van Achterbergh

et al., 2001). Twenty-nine spot analyses were made on sphalerite from three different samples, one from each of the three deposits (14 spots on PB sample PB08; 9 spots on AD sample AD12; 6 spots on PR sample PR01). Three spot analyses were made on brunogeierite (sample PB08). The mean minimum detection limit for Ge was ~1.1 ppm for sphalerite and 170 ppm for brunogeierite.

4. Structural and petrological study of the PAZ Pb-Zn(-Ge) deposits

4.1. Structural study

In the three studied deposits, two main cleavages are present. Both cleavages are roughly oriented N090-120°E (Fig. 2a) across the entire study area and exhibit various dip angles (Fig. 2c). A first cleavage (here termed S1) is weakly developed and transposes the stratification S0. It is observed within most outcrops except when a second cleavage overprint (S2) is strong. According to the NNE-SSW cross-section (Fig. 2b), S0-1 cleavage is affected by cm- to dm-scale E-W trending asymmetric F2 folds (Fig. 3a). S2 cleavage is always strongly dipping or vertical (Figs. 2c and 3a), intensively developed and locally erases all pre-existing structures. Regional structuration is essentially related to south-verging asymmetric F2 folds. This D2 deformation is the D3 deformation described in Garcia-Sansegundo and Alonso (1989). In contrast, Silurian black-shale in the north of the Bossost anticlinorium display north-vergent E-W trending F2 tight folds (Fig. 2b) and may be considered as a decollement layer with the Silurian level as suggested by Zwart (1979) and Matte and Zhi (1988).

4.2. Macroscopic description of the mineralization

Two types of mineralized structures are observed. The first (type 1) consists of μm - to cm-scale disseminated sulfides within the stratigraphic sequence. This type occurs especially at PB and AD but is minor in PR. The second mineralization type (type 2) consists of dm- to m-scale veins and represents the main exploited orebodies in PB and AD. These are particularly well-developed within the lithologies affected by D2 deformation. Geometries of these veins vary and can be sub-parallel to

S0-1 and affected by S2 (Fig. 3b-d), or sub-parallel to S2 and cross-cutting S0-S1 (Fig. 3e, f). Mineralization appears larger and better developed when crossing competent, relatively coarse beds such as siltstone-conglomerates (PR and AD) or siltstones (PB) and tends to be parallel to S2 in this case. In AD, and especially PB, mineralization is essentially sub-parallel to S2 in coarse beds, or parallel to S0-1 in schists (Fig. 3c). This sulfide-rich mineralization forms veins up to several tens of cm thick (Fig. 3e, f). The vein gangue is composed of quartz and carbonate with local brecciated domains (Fig. 3e) Erosive box-work structures are often present in sphalerite or pyrite mineralization with the formation of cubic cavities (Fig. 3c, d) in quartz gangue. It evidences macro-overgrowth structures of sphalerite in gangue minerals (seen in section in Fig. 3c). These box-work structures and associated mineralized bodies are preferentially located within the dm-scale levels of siltstone. In AD, type 2 mineralization is locally composed of sphalerite boxwork (in schist-siltstone levels; Fig. 3c), or present in N040-trending fractures (Table 1). PR deposit contains type 2 mineralization essentially observed parallel to stratification (Fig. 3b), which is deformed by the S2-corridor. This mineralization may be offset by barren normal faulting (Fig. 3b). Minor sphalerite mineralization is also present in N050-trending fractures (Table 1).

4.3 Micro-structure, mineralogy and texture of mineralization

4.3.1. Mineralogy

Type 1 (stratiform) mineralization is essentially composed of an assemblage of disseminated pyrite and brown sphalerite (Fig. 4a, b; MEL-1; AD01; AD03).

Type 2 (vein) mineralization (samples PB08, PR01, MEL-1, AD06, AD12, AD16, AD20, and AD32362) is mainly composed of massive brown sphalerite ($\cong 80\%$), galena, minor pyrite, and arsenopyrite (Fig. 4a, c, d). Pyrrhotite, chalcopyrite, tennantite-tetrahedrite, Pb-Bi-sulfosalts and magnetite occur rarely (Fig. 5). The presence of graphite, chlorite and frequent metamorphic muscovite associated with sphalerite is noteworthy. Germanium oxides (brunogeierite and rare argutite) can be observed only in the PB and AD samples. Gangue minerals are composed of quartz and carbonate minerals (Fig. 5).

4.3.2. Textures

Quartz and *carbonates* display comb textures in type 2 vein mineralization. Brecciated textures are locally present in vein mineralization (PB). Generally, carbonates are present as coarse (>2 mm) grains that are intensely fractured with curved continuous thick twins, and locally filled with sphalerite. Two generations of quartz are recognized. The earlier one occurs as coarse deformed grains, and is affected by stylolites, whereas the second occurs as overgrowth at the contact with sulfide minerals. Early quartz is rounded or presents comb textures. Stylolites are locally filled with sulfide mineralization. Muscovite is associated with sphalerite at grain boundaries, or as inclusions (Fig. 6a).

Two different *pyrite* textures are present: Py1 appears in beds or as disseminated xenomorphic dull yellow crystals (Fig. 6b) compared to shiny automorphic Py2 in vein structures. Intervals containing Py1 are folded and graded beds of pyrite are present (Figs. 4b and 6c); pressure shadows appear locally. Locally, rare isolated and elongate Py1 crystals parallel to S0-S1 are present. Framboidal cores are apparent in Py1. Py2 appear often orientated perpendicular to vein boundaries (Fig. 6c).

Galena occurs systematically at sphalerite grain boundaries. It exhibits rounded-lensoid habit or foamy texture (Fig. 6d) after etching with HCl-thiourea solution (composition in Brebrick and Scanlon, 1957). Triangular cleavage pits from polishing are locally curved.

In the three different deposits, *sphalerite* from vein mineralization (type 2), as well as disseminated mineralization (type 1), appears as fine grains (<50 μm ; Fig. 6a, d-g). Sphalerite in veins is generally late compared to quartz and carbonate gangue. After etching sphalerite with hypochlorous acid HClO, two intimately associated textures appear in type 2 mineralization from the three deposits: (1) fine grains (<50 μm) frequently exhibit polygonal aspects or foam texture with dihedral 120° angles and equidimensional size (Fig. 6a, d-g). Regular twinning in these grains shows no apparent deformation (Fig. 6e, f). (2) coarser grains (>80 μm) with irregular shape frequently display deformed folded twins (Fig. 6e; coarse grain in image center). Sphalerite can be dark or light brown. The difference in color is due to variable Fe content in PB deposit (see section 5.2).

Brunogeierite and *argutite* are abundant and exclusively associated with sphalerite. Carboirite has been previously reported from the AD deposit (Oudin, 1982) but the phase was not observed in our samples. Brunogeierite and argutite grains are rounded, dark grey, <20 µm in size, and mainly located at sphalerite grain boundaries (Fig. 6f). Sixty-six Ge-minerals were detected with SEM (63 brunogeierite and 3 argutite) in thin sections from PB and PR deposits. Among these, 36 appear at sphalerite grain boundaries (Fig. 6f, g, bru2) with size ranging between 5 and 20 µm. Twenty-four are close to sphalerite grain boundaries (Fig. 6g, bru1) in intermediate position and 6 (\cong 5 µm) are included within sphalerite grain cores. Argutite was found in AD sphalerite (sample AD12) as grains smaller than 3 µm in diameter. In the PB samples (PB08), 10 aligned brunogeierite inclusions were observed within dark brown sphalerite close to the light brown sphalerite, and aligned parallel to S2.

4.3.3. Micro-structures

In thin section, S0-S1 is readily identified because of lithological changes and superposition of S1 on S0 is marked by elongate oxide disseminations (Fig. 6h). When cross-cutting fine-grained beds, type 2 vein-mineralization tends to disappear or become parallel to S0-S1. But like at the macroscopic scale, when crosscutting coarser beds, the veins are typically larger, and mineralization tends to be parallel to S2 (Fig. 4b, c). Continuous veins can appear with both geometries (Fig. 4a) and present deformational imprint, but many are exclusively parallel to S2 cleavage (Fig. 4b-d). Figure 4d shows that, within zones in which S2 is dominant, S0-1 is vertical and parallel to S2, as a response to folding.

5. Mineral chemistry

5.1 Germanium minerals

EMPA analysis was performed on 28 <15 µm-sized brunogeierite grains from AD (AD05, n=3; AD06, n = 5, AD12, n=10) and PB (PB08, n=10) (Table 2a). Due to small grain size, two attempts to obtain analyses of argutite were unsuccessful. No visible compositional zoning in these minerals was observed.

The chemistry of major and minor elements in brunogeierite is summarized in Table 3a. In one sample from PB and three from AD, GeO_2 and FeO vary in the range of a few wt.% (Fig. 7). A slight depletion in GeO_2 can be noticed within grains in intermediate position with a mean of 38.7 ± 0.3 wt.% GeO_2 compared to grains at sphalerite grain boundaries (mean 40.5 ± 0.4 wt.% GeO_2). Low FeO contents for brunogeierite in intermediate positions is linked to a relative enrichment in ZnO (up to 1.6 wt.% ZnO).

LA-ICP-MS analyzes on 3 brunogeierite crystals from PB (PB08) are given in Table 2b. Mean Ge content is 28.0 ± 3.0 wt.% Ge (40 ± 4 wt.% GeO_2). For Co, Cu, Ga, Ag, Sn, Sb, and Pb, results are not in agreement with the EMPA data which showed these elements to be below detection limits. This may be either a matrix effect (use of the MASS-1 sulfide standard to analyse brunogeierite), or more likely indicative of the presence of micro- to nanoscale inclusions carrying these elements below the surface, which are intercepted during ablation. The higher Cu content may, for example, be explained by the presence of Cu-rich inclusions in sphalerite in textural contact with brunogeierite which can be observed by SEM.

5.2 Sphalerite

Forty-nine EMPA (Table 3a) and twenty-nine LA-ICP-MS (Table 3b) analyses were performed on type 2 sphalerite crystals from the three studied deposits.

Principal component analyzes (PCA) applied to the entire dataset of LA-ICP-MS analyzes show element distributions and spot representations in the PC1 and PC2 plane (Fig. 8). PCA helps to highlight inter-element correlations (Bélistont et al., 2014; Frenzel et al., 2016). Each arrow represents a variable or an element. The length of the arrow gives an indication of the elemental representivity in the dataset and the small angle between arrows indicates a correlation between these elements. The PC1–PC2 space carries 63% of the total dataset variance. Figure 8 reveals the high depletion in all elements except for Cd, Fe and In within sphalerite from the PR deposit compared to PB and AD. The PB and AD deposits display larger variations in Cd ($1,980 \pm 420$ to $3,105 \pm 410$ ppm Cd) and In (below

limit of detection to 1.9 ± 0.5 ppm In) compared to PR with Cd contents ranging from $2,650\pm 522$ to $3,096\pm 510$ ppm Cd, and In contents ranging from 1.09 ± 0.4 to 1.17 ± 0.4 ppm In.

The entire dataset shows a positive correlation between Sb and Ag, and another correlation between Ge and Sn in sphalerite. No correlation between Ge and Ga is observed. Correlations between Pb and Cu, Ag, Sb are remarkable, and are almost certainly related to the small inclusions that can be observed on the time-resolved LA-ICP-MS depth spectra (Fig. 9a).

Variability in Fe and Ge within the entire dataset is explored in Fig. 9b and is detailed for each deposit. PB deposit contains brown dark and light zones in sphalerite (Fig. 4). LA-ICP-MS analyzes show enrichment in Fe ($\sim 5.8\pm 0.3$ wt.%) within dark domains compared to lighter ones ($\sim 4.0\pm 0$ wt.%). In this sphalerite, the light brown domains show greater variation in Ge than the darker zones (Fig. 9b) with concentrations ranging between 0.75 ± 0.4 to 80 ± 1 ppm Ge. Germanium concentrations in dark brown domains concentrations are consistently $<10\pm 1$ ppm. These large variations of Ge in sphalerite appear localized and seem associated with the presence of Ge- and Ge-Sn-Cu-bearing inclusions (Fig. 9, b). Small inclusions of Pb-Ag-Sn-Sb are also often recognizable on the time-resolved LA-ICP-MS depth spectra (Fig. 9a).

In the AD samples, no color differences are visible in brown sphalerite in plane-polarized light; these are depleted in Fe (3.68 ± 0.2 wt.% Fe). Similarly, larger variations in Ge (Fig. 9b) appear in sphalerite with concentration ranging from 0.5 ± 0.6 to 102 ± 1 ppm Ge. These variations are systematically associated with small inclusions of Ge-minerals, and locally associated with Sn and/or Cu. Compared to PB, sphalerite from the AD deposit has lower mean concentrations of Co, Ga, and Pb, and higher mean concentrations of Ag, Sb, Mn and Ge.

In the PR samples, sphalerite appears red-brown in plane-polarized light and has the highest Fe content (7.67 ± 0.5 wt.% Fe). Sphalerite from PR does not contain accessory Ge-minerals (sample PR01). It is significantly depleted in all analyzed elements relative to AD and PB (Table 3a, b) and especially so in Ge with contents below the minimum limit of detection (1.1 ppm).

6. Discussion

6.1 Genetic model for the three studied deposits and formation of Ge-minerals

6.1.1 Structural context of the studied mineralization

Relationships between structures and mineralization are represented on the schematic diagrams shown as Figures 10 and 11 (at macroscopic and microscopic scales, respectively). The location and characteristics of each deposit with respect to deformational structures are indicated taking the specific lithologies that host the mineralization into account. In all three studied deposits, mineralization is present essentially within type-2 veins dominated by Zn- and Pb-sulfides (Fig. 10), with different geometries linked to rock competence and S2 cleavage. The lithological and structural control on vein geometry is strong (Fig. 11). Disseminated mineralization within the Late-Ordovician stratigraphic sequence (type 1) is rare in the studied samples (Fig. 10).

According to Bois et al. (1976) and Pouit (1985), pre-Silurian mineralization events for Ordovician-hosted ores are considered of SEDEX-type. The Pb-Zn ores are considered syngenetic with concordant mineralization, or epigenetic for discordant ore (Bois et al., 1976) and are only weakly remobilized. In the three deposits, only the minor type 1 disseminated mineralization is syngenetic and strictly concordant with stratification. This study shows that type 2 vein mineralization sub-parallel and oblique to stratification must be linked to an epigenetic hydrothermal event. Vein geometry is linked to rock grain size and the presence of S0-S1 and S2 deformation imprints. Ore concordant to S0-S1 is often present in schists but tends to be discordant to S0-S1 and parallel to S2 cleavage in coarser rocks (siltstones to conglomerates, Figs. 10 and 11). These observations clearly indicate a post-Ordovician vein-like emplacement of type 2 Pb-Zn-(Ge) mineralization.

6.1.2 The role of metamorphism and recrystallization in the genesis of Ge-minerals

This study shows that Ge mineralization is concentrated in accessory Ge-minerals in the three deposits. Ge-minerals are widespread in the PAZ deposits with more than 44 deposits known to contain independent Ge-minerals (Oudin, 1982). Such minerals are, however, absent in the Aulus-Les

Argentieres deposit (Oudin, 1982) which has been recently associated with a post-Variscan mineralization event (Munoz et al., 2015). In most deposits, sphalerite is depleted in many trace elements, particularly in Ge (mean value $<13\pm 1$ ppm), and shows evidence of deformation and recrystallization (Figs. 6d, e, 7 and 13). These recrystallization/deformation textures seem widespread in PAZ deposits (Nicol et al., 1997), and in Basque Massifs (Pesquera and Velasco, 1989, 1993). PR sphalerite is even more depleted in Ge and other trace elements (except for Fe, Cd and In) than the other two deposits. No Ge-mineral is reported in this sphalerite. Bulk chemistry was probably primarily poor in these elements, as PR presents the same mineralization type and sphalerite texture as the two other deposits.

Fe-rich zones in a set of sphalerite crystals are present (darker sphalerite, Fig. 4c) but no compositional zoning at crystal scale is reported as in Ge-minerals. Nevertheless, higher values of Ge and elements like Sn or Cu appear locally in rare nano-inclusions within sphalerite or attached to brunogeierite. Dark brown domains in PB08 which host the majority of brunogeierite grains (Fig. 4c) do not display large variations in the concentrations of these elements and have a consistently low Ge content ($<1.1\pm 1$ ppm, Fig. 9b). The presence of Ge(-Cu) nano-inclusions in an otherwise Ge-poor sphalerite is reported from the Kipushi Cu-Zn-(Ge-Pb) deposit, D.R. Congo (Bélistont et al., 2016). PAZ Germanium-minerals like brunogeierite (~30% Ge), or argutite (~70% Ge), are only hosted in sphalerite and preferentially located at sphalerite grain boundaries.

The observed sphalerite-dominant mineral assemblage in host metasedimentary rocks dominated by graphite, muscovite and chlorite. This assemblage corresponds to a pressure-temperature paragenesis characteristic of the greenschist facies (ca. 300–450 °C) as inferred by Pouit (1974) and Johan and Oudin (1986). Recent work on metamorphic conditions of the PAZ Superstructure indicates that maximum metamorphic temperatures were 350–400 °C (Cochelin, 2016) concordant with greenschist facies conditions. Low temperature processes are considered to account for Ge-enrichment in sulfides such as sphalerite (Belissont, 2016; Frenzel et al., 2016). Above 150–200 °C, Germanium incorporation in sphalerite decrease with increase in temperature (Belissont, 2016). Metamorphic conditions above 300 °C seem to affect and reduce the Ge (and Ga) concentrations in sphalerite

(Frenzel et al., 2016). Chemical analyses in this study show a generally depleted sphalerite which is coherent with greenschist facies conditions (300-450 °C).

Formation of independent Ge-minerals (spinel as brunogeierite and oxides as argutite in the PAZ deposits) is likely triggered by low-grade metamorphic processes. During metamorphic recrystallization processes, Germanium would be expelled from the ZnS lattice, and concentrated into Ge-minerals preferentially nucleating at sphalerite grain boundaries. Trace element remobilization during low grade-metamorphism and recrystallization is well-documented for many elements in sphalerite (Au, Ag, Cu, Mn, etc.; Brugger and Giere, 2000; Pitcairn et al., 2010; Zheng et al., 2013; Taylor et al., 2010; Lockington et al., 2014) and proposed for Ge-mineralization in Morales-Ruano et al. (1996). Syn-metamorphic recrystallization and release of trace elements may be responsible for formation of diverse accessory minerals parageneses (Cook, 1996; Cook et al., 1998; Hofmann and Knill, 1996; Marshall et al., 1998; Eremin et al., 2007; Taylor et al., 2010). fO_2 and fS_2 conditions may play a key role as well in the remobilization of element like Ge, as this will control which Ge-mineral crystallizes. High fO_2 (and low fS_2) has an essential impact on remobilization of Ge in sphalerite to form Ge oxide, which is thermodynamically stable under highly oxidizing conditions (Johan and Oudin, 1986; Bernstein, 1985). The impact of fO_2 on the stability of brunogeierite has been explored by Hariya and Wai (1970). They confirmed the stability of brunogeierite at high fO_2 above the wüstite-magnetite buffer ($fO_2 = >10^{-15}$ at 800 °C). Bernstein (1985) describes a phase diagram with GeO_2 stable at high fO_2 and shows a widening of the GeO_2 stability field when temperature decreases. On the contrary, high fS_2 would rather stabilize Ge-sulfides, as in Kipushi type deposits. For example, Melcher et al. (2006) showed that ore formation in Khusib Springs Ge-deposit (Kipushi type) is linked to highly saline hot fluids (up to 370 °C) with high fS_2 .

Therefore, in the present case, it is expected that Ge would originate from primary trace level enrichment in sphalerite associated with strong Ge partitioning into independent Ge-minerals during sulfide recrystallization under greenschist facies conditions that renders the recrystallized sphalerite depleted in Ge. Semi-quantitative evaluation shows that the proportion of Ge by mass in accessory Ge-minerals is seven times that of Ge in the sphalerite host (PB08, Fig. 4c). For this evaluation, nineteen

brunogeierite grains (30 wt.% Ge) were considered with an average diameter of 10 μm , and the rest of the thin section is considered as pure sphalerite with a mean content of 30 ppm Ge. A density of 5.2 $\text{g}\cdot\text{cm}^{-3}$ is assumed for sphalerite and 4.1 $\text{g}\cdot\text{cm}^{-3}$ for brunogeierite (spinel group). Considering the same sphalerite volume and a closed system, a primary (pre-recrystallization) Ge content in sphalerite can be estimated. A maximum amount of Ge in PB08 sphalerite is 227 ppm.

Two additional hypotheses of formation may be considered: Is it only an enrichment of primary accessory minerals or a complete neof ormation of Ge-minerals, both processes assisted by metamorphic fluids? Bernstein (1985) and Otteman and Nuber (1972) report solid solution between brunogeierite and magnetite because of frequently observed enrichment in Ge within magnetite. In Ga-bearing magnetite close to brunogeierite crystals, Ge is reported from Pyrenean deposits with concentrations exceeding 4,000 ppm (Johan et al., 1983). In addition, a large paragenesis of Ge-minerals is described (Johan et al., 1983; Oudin et al., 1988). These observations could indicate that PAZ Ge-minerals result from the enrichment of a primary mineral (magnetite in the case of brunogeierite). Nevertheless, Ge-mineral neof ormation associated with metamorphic fluids may also play a key role with formation of Ge-minerals like argutite (70 wt.% Ge) in high oxidizing conditions.

6.2 Comparison with other Ge occurrences worldwide

6.2.1 Chemistry

Sphalerite from the studied deposits is largely depleted in Ge with mean concentration of 13 ± 1 ppm (Fig. 12). Classically in sulfide-rich environments, Ge is found as traces in sphalerite, as presented in Figure 12. These well-known and documented Pb-Zn(-Ge) deposit-type are MVT deposits (< 3,200 ppm Ge in Tres Marias, Mexico, Saini-Eidukat et al., 2009), SEDEX (<723 ppm Ge in Anarraaq, Graham et al., 2009) or in polymetallic vein deposits (up to 2,576 ppm Ge in Saint-Salvy, Bélistont et al., 2014). In such deposits, fluid temperature is generally low and below 200 °C (Viets et al., 1992; Leach et al., 2004; Kelley and Jennings, 2004; Bonnet, 2014; Bélistont et al., 2014).

In Ge-rich environments, sphalerite depleted in Ge can be found in Kipushi type deposits (0.3 ppm Ge, main mode in Kipushi deposit, Bélistont, 2016; Fig. 12). Also, similar to PAZ deposits, discrete Ge-minerals are reported from Kipushi-type deposits (De Vos et al., 1974; Lombaard et al., 1986; Melcher et al., 2006). These are, however, mostly Ge-sulfides such as germanite (9.1% Ge), renierite (6.58% Ge), or briartite (18.6% Ge), even if brunogeierite has been reported from the Tsumeb (Kipushi-type) deposit (Lombard et al., 1986). The occurrence of Ge-sulfides is also reported from a range of other deposit types, including epithermal deposits (Fig. 13; Kouzmanov, 2001; Bailly et al., 2005; Putz et al., 2006; Yun et al., 1993) and VHMS deposits (Fig. 13; Tourigny et al., 1993; Komuro and Kajiwara, 2004; Wagner and Monecke, 2005; Vikentyev et al., 2016). Fluid temperatures associated with the mineralization event are relatively moderate, between 250 and 400 °C (Lombaard et al., 1986; Bailly et al., 2005; Melcher et al., 2006; Kampunzu et al., 2009) and are similar to the temperatures of metamorphic fluids in studied PAZ deposits (300-450 °C). Nevertheless fS_2 is clearly higher than in the PAZ deposits (Bernstein, 1985; Melcher et al., 2006). High fS_2 controls formation of Ge-sulfides rather than Ge-oxides which are thermodynamically stable under high oxidizing conditions. Even though they share many similarities, variability in redox conditions may explain the difference between Kipushi and PAZ deposits (crystallization of Ge-sulfides rather than Ge-oxides, respectively).

6.2.2 Tectono-metamorphic setting

Figure 13 shows the large diversity of settings for Ge-bearing deposits and locates the PAZ studied deposits. According to their structural-lithological settings, the three studied have some similarities with either reworked SEDEX, vein type, or Kipushi-type deposits. Sedimentary-exhalative (SEDEX) Pb-Zn (and Ge) mineralization is linked to circulation of syngenetic to diagenetic fluids in continental crust (Fig. 13; Wilkinson, 2013). The studied veins are clearly epigenetic and cannot be associated with syn- to diagenetic mineralization of SEDEX type. The three studied deposits are structurally closer to Ag-Pb-Zn(-Cu) vein type deposits which intersect meta-sedimentary or magmatic basement (Fig. 13) in various tectonic settings (Schwarz-Shampera and Herzig, 2002; Munoz et al., 1994; Höll et al., 2007). Despite this, the deformational-metamorphic imprint recorded in the studied PAZ

deposits, has not been reported for polymetallic sulfide vein mineralization (Fig. 12). In Kipushi-type deposits, micro-textures of the mineralization tend to display a similar recrystallization and deformation imprint on sphalerite (Fig. 12; Hughes, 1987; Chabu, 1990; Kamona and Friedrich, 2007; Heijlen et al., 2008). Nevertheless, from a structural point of view, Kipushi-type mineralization is different from the studied deposits because the orebodies are polymetallic, characteristically pipe/tube-like or tabular, and are hosted in carbonate rocks (Fig. 13; Höll et al., 2007).

7. Conclusions

This study highlights the unique occurrence of Ge-minerals in three representative PAZ deposits and shows the major role played by recrystallization processes associated with low-grade metamorphism and deformation, on the formation of the Ge-minerals. During Variscan regional metamorphism, primary sphalerite underwent recrystallization and Ge was expelled from the ZnS lattice under the presence of highly oxidizing metamorphic fluids and moderate temperature (~300-450 °C). Probable enrichment of pre-existing accessory minerals (e.g. magnetite for brunogeierite), and neof ormation of minerals (argutite) leading to the observed Ge-mineral parageneses. The fact that certain minerals like argutite or Ge-chloritoid (carboirite) are described only from the Pyrenees testifies a unique mode of formation. The three studied PAZ mineralizations share some similarities with Kipushi-type mineralization (Fig. 12) including the occurrence of Ge-minerals, similar recrystallization-deformation imprint under greenschist facies conditions, and the presence of sphalerite which is depleted in Ge. The occurrence of Ge-sulfides parageneses in Kipushi may be linked to fluid composition with higher fS_2 and medium fO_2 compared to PAZ deposits.

Finally, the likely source of Ge is still largely unresolved for Ge-deposits (Bélistont, 2016). This issue may be potentially addressed by a study of organic-rich levels within the associated Late-Ordovician or Silurian rocks. Furthermore, a variety of ages are reported for different deposits in the PAZ, ranging from Middle-Late Ordovician, through Lower or Late Devonian and Carboniferous (Variscan), to Late-Triassic/Late-Jurassic. A detailed study of other PAZ deposits displaying different tectono-

metamorphic imprints and occurrence of Ge mineralization would be essential to understand the hydrothermal mobility of strategic metals during the Variscan orogeny.

Acknowledgments

The authors thank the French Geological Survey (Bureau de Recherches Géologiques et Minières; BRGM) for funding through the national program “Référentiel Géologique de France” (RGF-Pyrénées). We acknowledge Christophe Nevado and Doriane Delmas for thin section preparation, Bernard Boyer and Olivier Bruguier for respectively, their involvement in EMPA (Service inter-régional Microsonde-Sud, Montpellier) and LA-ICP-MS analysis (Plateforme AETE, OSU-OREME, Montpellier). The authors are thankful for the editorial handling of Cristiana L. Ciobanu and for the constructive comments of five anonymous reviewers.

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Figure Captions

Fig. 1: a) Location of the Pyrenean Axial Zone (PAZ) within the Hercynian belt of Western Europe (modified from Denele et al., 2007)); b) Main Pb-Zn deposits in Paleozoic rocks of the Central PAZ, with the location of the studied Pb-Zn deposits (modified from Zwart, 1979). Location of the cross-sections shown in Figs. 1c and 2b; c) N-S cross-section of the Bossost dome (from Mezger and Gerdes, 2016).

Fig. 2: a) Regional structural map for the northern part of the Bossost anticlinorium (compiled from the geological map and our own data). Structural positions of Argut-dessus (AD), Pale Bidau (PB) and Pale de Rase (PR) deposits are indicated in red. Location of the cross-section shown as Fig. 2b is indicated; b) NNE-SSW structural cross-section near Melles in Cambro-Silurian rocks. c) Pole figures of S0-S1 and S2 measurements.

Fig. 3: Outcrop photographs from the three studied PAZ deposits: a) Folded Late Ordovician (o5) grey schists in the northern Bossost anticlinorium; b) Stratiform type 2 mineralization in Pale de Rase (PR); c) Type-2 vein mineralization (boxworks) parallel to S0-S1 in Argut-dessus (AD); d) Boxworks in Pale Bidau (PB) preferentially within Late Ordovician (o5) siltstone bed; e) Type-2 vein mineralization parallel to S2 in Pale Bidau (PB) gallery; f) Type-2 vein mineralization in Pale Bidau (PB) with position of sample PB08.

Fig. 4: Microphotographs of different structures in thin section a) Relationships between lithologies, S2 cleavage and mineralizations (TB: thin beds; CB: coarse beds); b) Relationships between pyrite mineralization, S0-S1 and S2 cleavages. Note that S0-S1 and S2 are perpendicular; c) Location of grains of brunogeierite in sphalerite (sp) with galena (gn) and Fe-carbonates (cb) also present (Pale Bidau, sample PB08). Numbers associated with brunogeierite crystals refer to the LA-ICP-MS analyses given in Table 2; d) Relationships between vein mineralization, S0-S1 and S2 cleavages. S0-S1 and S2 are parallel.

Fig. 5: Paragenetic succession of ore and gangue minerals in stratiform and vein mineralizations in the three PAZ studied deposits.

Fig. 6: Microphotographs showing characteristic textures in sulfide mineralization. a) Microtexture of sphalerite (sp) associated with muscovite (ms) and quartz (qz). Sphalerite grains present rounded habitus (crossed nicols, sample AD06). b) Different textures of pyrite: bright and automorphic texture preferentially in vein and dull yellow, less automorphic texture preferentially in host rock with the presence of framboidal cores (sample AD03). c) Different textures of pyrite : bright and automorph texture in vein and dull yellow less automorph texture in host rock with the presence of framboïdal cores (sample AD03). d) Rounded small grains of galena (gn) associated with polygonal sphalerite (sp) (etched with HCl-thiourea solution, sample AD12). e) Sphalerite grains with recrystallized (small and undeformed twins) and deformed (deformation twin in coarser grain, in the center of the picture) textures (etched with HClO; 32362 from AD; SEM). f) Brunogeierite (bru) at sphalerite grain boundary (etched with HClO; AD12; SEM color inverted). g) Two brunogeierite (bru1 and bru2) and one magnetite inclusions in sphalerite. Bru2 is in boundary position in sphalerite, bru1 is in intermediate position. Magnetite has a low Ge-content (<600 ppm GeO_2) (sample AD12). Minerals abbreviations from Whitney and Evans (2010). h) Relationships between S0 stratification, S1 cleavage observed locally with elongated iron-oxide grains, and S2 main cleavage parallel to mineralization (quartz, carbonates and iron-oxides) (sample PB10).

Fig. 7: Diagram showing GeO_2 and FeO contents in 28 brunogeierite grains from the three different deposits (EMPA data) and in different textural position according to sphalerite grains. 1σ errors are represented for each data point. Blue - brunogeierite located at sphalerite grain boundaries; orange - brunogeierite in intermediate position. Low FeO content for brunogeierite in intermediate position is linked to a corresponding enrichment in ZnO.

Fig. 8: Principal component analysis of the LA-ICP-MS log-transformed dataset of trace element contents in sphalerite from the Pale Bidau, Argut-dessus and Pale de Rase deposits. Circle of correlation and related covariance biplots. Arrow length is important to correlate element; if the arrow is short, the representation is poor (loadings close to 0) but if arrow is long (close to circle line), the representation is good (loadings close to -1; 1). The second parameter is the angle between two arrows. It is related to the covariance between the concentrations of elements: if the angle is close to

0°, element concentrations correlate positively. If it is close to 90°, these do not correlate, and if it is close to 180° they are negatively correlated.

Fig. 9: a) Representative single-spot LA-ICPMS spectra for selected elements in sphalerite. Nuggets or small inclusions can be detected for elements like Ge-Sn(-Cu) or Pb-Ag-Sn-Cu. b) Comparison of Ge and Fe wt.% contents in sphalerite from the three studied deposits. For PB deposit, analyzes in dark and light domains in sphalerite are presented. 1σ errors are represented for each data point.

Fig. 10: Schematic N-S regional sketch of structural relationships between mineralization, bedding and cleavage at macroscopic scale.

Fig. 11: Schematic sketch showing relationships between host-rocks, type-1 and 2 mineralizations at microscopic scale. Ge-bearing minerals are represented in the insert.

Fig. 12: Synthesis of the characteristics of the four main Ge-bearing deposit-types and PAZ deposits (red frame) based on several criteria: deposit-setting, ore texture (sphalerite), metamorphic imprint, and main Ge-concentration. Abbreviations: YBS: yellow-brown sphalerite; EBS: early-brown sphalerite; sp: sphalerite; gn: galena; tn: tennantite, rn: renierite, cp: chalcopyrite, brt: baryte.

Fig. 13: Geodynamic sketch diagrams showing the geologic environments of the main Ge-bearing ore deposits worldwide: high- and low-sulfidation epithermal; VHMS; SEDEX; polymetallic Ag-Pb-Zn veins (Saint-Salvy); MVT; Kipushi-type; coal (Lincang) deposits; and the studied PAZ deposits.

Table captions:

Table 1: Geological characteristics of the three studied Pb-Zn deposits and the two types of mineralizations.

Table 2: a) EPMA analyzes of 28 brunogeierite (GeFe_2O_4) crystals in weight-oxide % (structural formula normalized to 4 oxides). b) LA-ICP-MS analyzes of 3 brunogeierite (GeFe_2O_4) crystals in weight % for different elements (Co, Cu, Ga, Ge, Ag, Sn, Sb, Pb) (PBO8 sample).

Table 3: a) EPMA analyzes of sphalerite (ZnS , n=49) in weight %. Mean limit of detection for Ge is 84 ppm for the entire dataset. b) LA-ICP-MS analyzes of sphalerite (ZnS , n=29) in weight ppm or % for different elements (Mn, Fe, Co, Cu, Ga, Ge, Ag, Cd, In, Sb, Sn, Pb).

Table 1. Geological characteristics of the three studied Pb-Zn deposits and the two types of mineralizations.

Locality		AD (Argut-dessus)	PR (Pale de Rase)	PB (Pale Bidau)
Host rocks		Conglomerates/siltstone/schists		siltstones-calc-schists
Type 1	Structure/Deformation	parallel to S0-1 deformed with asymmetric E-W folds	parallel to S0-1 deformed with asymmetric E-W folds	only boxworks
	Samples	AD01, AD03, MEL4	/	PBO3-PB10
	Mineralogy	Py + Sp		
Type 2	Structure/Deformation	parallel to S2 or S0-S1, N040 fractures	parallel to S2 or S0-S1, N050 fractures	parallel to S2, minor parallel to S0-S1
	Samples	AD06, AD12, AD17, AD20	PR01, PR02, PR03, PR04	PBO3, PB08, PB10
	Mineralogy Mineralization	Sp + Gn + Py + Ccp + Po + Apy +/- Ms +/- Gr + Ge mineralization	Py +/- Ms +/- Chl +/- Gr	Sp + Gn + Py + Chl + Ge mineralization +/- Ms +/- Chl

				+/-Gr
	Gangue	Qz + (Ca-Fe-Mg) Cb	Qz + (Ca-Fe-Mg) Cb	Qz + (Ca-Fe-Mg) Cb

Mineral abbreviations : Sp : sphalerite ; Gn : galena / Py : pyrite / Ccp : chalcopyrite / Po : pyrrhotite / Apy : arsenopyrite / Ms : muscovite / Chl : chlorite / Gr : graphite / Qz : quartz / Cb : carbonate

Table 2: a) EPMA analyzes of 28 brunogeierite (GeFe₂O₄) crystals in weight-oxide % (structural formula normalized to 4 oxides). b) LA-ICP-MS analyzes of 3 brunogeierite (GeFe₂O₄) crystals in weight % for different elements (Co, Cu, Ga, Ge, Ag, Sn, Sb, Pb) (PBO8 sample).

Brunogeierite (GeFe₂O₄) EMPA		SO₂	ZnO	FeO	Ga 2O 3	GeO 2	As₂ O₃	SiO₂
Pale Bidau (PB, n=10) PBO8	n	10	8	10	4	10	10	10
	Mean (wt-ox%)	0.25	0.49	56.8 0	0.0 4	39.8 3	0.19	0.12
	SD (wt-ox%)	0.11	0.20	0.32	0.0 2	0.68	0.03	0.01
	LOD (ppm)	442	1579	392	354	676	410	104
Argut- dessus (AD, n=18)	n	18	12	18	6	18	18	18
	Mean (wt-	0.50	0.78	56.2 0	0.0 1	39.9 6	0.17	0.12

AD05-AD06-AD12	ox%)							
	SD (wt-ox%)	0.14	0.33	0.33	0.03	0.58	0.04	0.01
	LOD (ppm)	331	1609	379	547	683	435	100

	Brunogeierite (GeFe₂O₄) LA-ICP-MS	Co (ppm)	Cu (ppm)	Ga (ppm)	Ge (%)	Ag (ppm)	Sn (ppm)	Sb (ppm)	Pb (ppm)
PB08 - 1	Contents	3965.8	2907	3018.9	26.7	225.4	256.2	327.3	1717
	SD	1152	850	402	2.9	146	383	125	297
PB08 - 2	Contents	4511.4	1906.6	1788.7	27.4	195.7	114.8	30.8	423.1
	SD	1124	534	223	3.2	38	362	41	66
PB08 - 3	Contents	4257	2502.3	2412	30	214	214	122	570
	SD	1202	586	325	3.1	84	349	69	75
Mean		4244.7	2438.6	2406.5	28	211.7	195	160	903.4
LOD		340	369	72	383	73	90	12	9

n: number of measurements with higher contents than the limit of detection

LOD: Limit of detection ; SD: Standard Deviation

Sphalerite (ZnS) EMPA		S	Zn	Fe	Cu	Ge	Cd	Si
Pale Bidau (PB) (n=14)	n	14	14	14	3	2	14	14
	Mean (wt%)	33.1	61.1	4.0	0.0	0.01	0.2	0.05
		4	5	3	2		0	
	SD (wt%)	0.57	0.97	0.0	0.0	0.01	0.0	0.00
				4	2		1	3
	LOD (ppm)	483	2266	342	541	84	110	32
Argut-dessus (AD) (n=24)	n	24	24	24	2	5	24	24
	Mean (wt%)	34.1	59.2	5.5	0.0	0.01	0.1	0.06
		8	1	3	1		7	
	SD (wt%)	0.12	0.27	0.3	0.0	0.37	0.1	0.01
				2	2		3	
	LOD (ppm)	342	1529	347	487	88	426	107
Pale de Rase (PR) (n=11)	n	11	11	11	1	0	11	11
	Mean (wt%)	33.8	58.9	5.7	0.0	<	0.1	0.07
		6	9	4	3	LOD	8	
	SD (wt%)	0.57	0.95	0.1	0.0	<	0.0	0.01
				2	5	LOD	4	
	LOD (ppm)	484	2313	348	544	84	422	106

Sphalerite (ZnS) LA-ICP-MS	Mn (ppm)	Fe (%)	Co (ppm)	Cu (ppm)	Ga (ppm)	Ge (ppm)	Ag (ppm)	Cd (ppm)	In (ppm)	Sb (ppm)	Sn (ppm)	Pb (ppm)	
Argut-dessus (AD12 ; n=9)	Mean	51.5	3.7	79.1	206.7	75.3	32.1	165.7	234.7	0.8	29.4	11.4	174.0
	Median	59.1	3.8	72.7	112.9	45.6	11.9	55.1	217.0.7	0.8	33.1	<L	32.6
	Min	23.6	0.9	25.3	<L	10.9	2.3	11.1	211.9.1	0.3	2.4	<L	22.7
	Max	78.3	6.4	154.2	619.4	320.9	102.2	418.4	290.6.4	1.6	54.7	20.9	523.7
	1 σ	16	0.2	11	41	18	14	33	395	0.5	4	6	76
Pale Bidau (PB08; n)	Mean	33.2	5.2	181.4	184.5	206.3	11.8	27.6	257.5.9	0.5	19.9	19	203.6

n=14)	M edi an	31. 9	5. 5	171 .8	167 .5	244 .1	4.8	25. 7	267 1.5	0.3	17. 7	16. 8	46. 8
	Mi n	19. 8	2. 8	86. 9	51. 2	30. 5	0.8	6.6	198 0.7	0.2	4.5	5.2	11. 1
	M ax	51. 7	6. 6	235 .6	653 .4	332 .5	80. 5	51. 1	310 5.2	1.9	44. 7	47. 8	229 7.0
	1 σ	6	0. 3	19	42	47	32	6	432	0.5	3	4	130
Pale de Rase (PR01 ; n=6)	M ea n	42. 9	7. 7	38. 7	17. 9	17. 3	<L OD	10. 5	277 4.5	1.1	9.8	<L OD	4.7
	M edi an	49. 1	8. 5	43. 1	16. 9	10. 8	<L OD	4.4	269 2.6	1.1	2.3	<L OD	1.4
	Mi n	7.7	3. 6	16. 2	7.5	5.1	<L OD	3.2	265 1.4	1.1	1	<L OD	0.6
	M ax	63. 7	10 .1	48. 5	36. 4	44. 1	1.1	41. 1	309 6.1	1.2	46. 3	1.3	21. 3
	1 σ	5	0. 5	4	4	4	1	2	465	0.4	0.4	2	2
Mean (total)	40. 1	5. 2	121 .6	153 .2	127 .5	13	65. 0	254 6	0.7	20. 6	13. 9	153 .3	
Detection limite (mean)	4.4 6	0. 04	1.6 4	2.7 9	0.5 1	1.1 3	0.1 5	3.7 8	0.1	0.2	3.6	0.0 6	

n: number of measurements with higher contents than the limit of detection

LOD: Limit of detection ; SD: Standard Deviation