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Rare metal concentration associated to recrystallization: example from the Pyrenean Axial Zone

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Abstract. Germanium is often found in trace concentration in non-deformed sphalerite (ZnS). However, locally in sphalerite from the Variscan Pyrenean Axial Zone, the presence of Ge-minerals (oxides, sulphides or chloritoids with up to 70% wt Ge) is remarkable. The rise question is thus what are the chemical and/or mechanical processes that control rare element contents of sulphides which have undergone deformation and metamorphism? In order to answer this question, we document microstructural and chemical heterogeneities in sphalerite, performed with EBSD (electron backscatter diffraction) coupled to LA-ICPMS *in situ* analysis. Deformation could induce recrystallization of primary sphalerite. Recrystallized domains contain low Ge contents (1-50 ppm Ge) whereas porphyroclastic sphalerite grains present higher Ge concentrations (up to 550 ppm Ge). Ge-minerals (up to 70 wt% Ge) are exclusively hosted in the Ge-poor recrystallized domains. We propose that Germanium was removed from the primary sphalerite crystal lattice during sulphide recrystallization and subsequently concentrated in Ge-minerals, leaving behind a Ge-depleted fine-grained recrystallized sphalerite matrix. Numerous sulphide ores enriched in rare elements similar to Pyrenean deposits may present recrystallization features like deformed Mississippi-Valley-Type, Kipushi-type or Volcanic-Hosted-Massive-Sulphide deposits. Consequently, the potential of this type of deposits shall be evaluated and we suggest that exploration methods must integrate precise textural and microstructural information coupled with trace element in situ and mapping techniques.

1 Introduction

Critical metals like Germanium (Ge), Gallium (Ga) or Indium (In) are often hosted in sphalerite lattice. These elements are presently exploited as by product in base metal deposits in low concentrations (up to several thousand of ppm ; Höll et al. 2007). These concentrations are observed in non-deformed sulphides (Cugerone et al., 2018a). But the largest concentrations of zinc sulphide are hosted in deformed/metamorphosed environments (Wilkinson 2013) and the presence of critical metals in these deposit-type has been poorly explored.

The impact of recrystallization on sulphide composition has been studied especially in pyrite or arsenopyrite (Cook et al. 2013; Dubosq et al. 2018) but only few studies are available for sphalerite. Lockington et al. (2014) compare diverse sphalerites which naturally endured different metamorphic imprints. A loss of trace elements like Pb, Bi, Ag is observed associated to a re-incorporation of Fe, Cd, Mn, In. Re-homogenization of Cu in the sphalerite lattice is observed but data for Ge in sphalerite are absent.

The studied sphalerites are located in the Pyrenean Axial Zone (PAZ) Pb-Zn district deposits. These Pb-Zn mineralizations were sampled from deposits exploited in the past and represent an interesting natural material for studying the impact of recrystallization on sphalerite texture and chemistry. The occurence of Ge-minerals hosted in sphalerite is reported in the Pyrenean Axial Zone (Johan et al. 1983; Cugerone et al. 2018a).like brunogeierite ($GeFe_2O_4$), briartite ($GeCu_2(Fe, Zn) S_4$) or carboirite ($GeFeAl_2O_5(OH)_2$).

Our study aims at investigating the role of recrystallization on trace elements composition of sphalerite, as well as the mode of formation of these hyper concentrated Ge-minerals. In this study, we have combined textural (EBSD) and chemical (EPMA and LA-ICP-MS) analyses.

2 Methods

Electron-BackScattered Diffraction (EBSD) maps were performed with a Camscan Crystal Probe X500FE SEM-EBSD at Geosciences Montpellier (CNRS-University of Montpellier, France). Condition of acquisition were 20 keV for the voltage, 5 nA for the probe current with a working distance of 25 mm under 2 Pa low vacuum. Samples were positioned horizontally and at the standard 70° angle of the EBSD detector. EDS maps were acquired simultaneously with electron backscatter pattern data. The measurement step was systematically below 5 µm. Oxford Instruments Aztec and Channel 5 softwares were used to generate EDS and EBSD grain size maps.

Microprobe analysis (EMPA) were carried out using a Cameca SX100 electron microprobe analyzer at the Service inter-regional Microsonde-Sud, Montpellier. Major, minor and trace elements were measured with a beam current of 100nA and accelerating voltage of 20 kV. 14 elements were analyzed: standards, spectral lines, and spectrometers were as follows: Zn (Zn, Lα, TAP); S (FeS_2,Kα, PET); Fe (Fe_2O_3,Kα, LLif); Cd (CdS, Lα, LPET); Ge (Ge, Kα, LLif); Sb (GaSb, Lα, LPET); Cu (CuS, Kα, LLif); Ga (GaSb, Kα, LLif); Ag (Ag, Lα, LPET); Mn (Mn, Kα, LPET); Sn (Sn, Lα, PET); Pb (Pb, Mα, PET); As (GaAs, Lα, TAP); Si ($CaSiO_3$,Kα, TAP). Peak counting times ranged from 30 to 240 s (240 s for Ge). Germanium is analyzed on 2 LLif monochromators. The limit of de- tection for Ge and Cu, calculated by internal Cameca procedures, is reduced to 84 ppm and 110 ppm respectively. Gallium, As, Ag, Pb, Sn, Sb, and Mn were below detection limit. Zinc contents in sphalerite measured with EMPA were used as internal calibration for LA-ICP-MS analysis.

Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) was used to determine trace elements concentrations in sphalerite. Analyses were carried out using an Excimer CompEx 102 coupled with a ThermoFinnigan Element XR available at the OSU-OREME AETE platform at the University of Montpellier.

Laser ablation was performed using a constant 5 Hz pulse rate at 140 mJ laser energy. Each LA-ICP-MS analysis comprises 180 s of background measurement and 60 s of sample ablation (signal measurement), followed by a 60 s retention time to ensure a proper cell washout. Data were processed using the Glitter 4.0 software package. The following isotopes were measured: ^{29}Si; ^{34}S; ^{55}Mn; ^{57}Fe; ^{59}Co; ^{61}Ni; ^{63}Cu; ^{65}Cu; ^{64}Zn; ^{69}Ga; ^{71}Ga; ^{74}Ge; ^{75}As; ^{77}Se; ^{95}Mo; ^{105}Pd; ^{107}Ag; ^{109}Ag, ^{110}Cd; ^{111}Cd, ^{115}In; ^{118}Sn; ^{119}Sn; ^{120}Sn; ^{121}Sb; ^{123}Sb and ^{208}Pb. MASS-1 reference was used as external standard (Dr. Stephen Wilson, personal communication) with a corrected 57 $\pm$ 1.75 ppm value for Ge. NIST SRM 610 was used as secondary external standard to identify possible instrumental drift. The elements Ni, As, Mo, Se, Pd and Si are in all analyses below the limits of detection. Only Ge and Cu contents measured in sphalerite will be discussed in this paper.

3 Samples

3.1 Pb-Zn deposits in Pyrenean Axial Zone

Pyrenean Pb-Zn deposits are hosted in the Variscan deformed (~ 325-290 Ma) Pyrenean Axial Zone exhumed during the collision between the Iberia and Eurasian plates since the Lower Cretaceous. Foliation trajectories exhibit a monotonous N080-N110°E trend with variable dip angles. Two main Variscan deformation events are recorded in the host-rock. A poorly expressed S_1 cleavage is often parallel to S_0 and is associated to regional M_1 Medium Pressure and Low-Temperature (MP-LT) metamorphic conditions. A well-expressed S_2 cleavage is sub-vertical and superimposed to the previous structures. S_2 axial planar

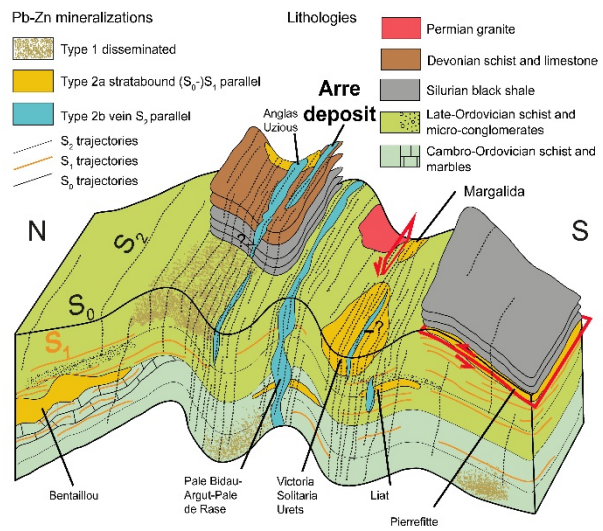

Figure 1: Schematic 3D sketch presenting the three main mineralization types which are typically observed in the studied area and related to each studied deposit. Type 2b vein mineralizations appear in intensely S_2 deformed domains. Location of Arre deposit is noted (modified from Cugerone et al., 2018b)

cleavage is associated to M_2 contact (HT-LP) metamorphic conditions, marked in the studied area with the appearance of cordierite.

Three Pb-Zn mineralizations types are present in the PAZ and fully described in Cugerone et al. 2018b. In Figure 1, schematic 3D sketch is shown and describe the major mineralization types. Type 1 corresponds to minor disseminated mineralization, probably syngenetic and from an exhalative source. (II) Type 2a is a stratabound mineralization, epigenetic and synchronous to the Variscan D_1 regional deformation event and (III) Type 2b is a vein mineralization, epigenetic and supposed synchronous to the late Variscan D_2 regional deformation event.

Herein, we will only focus on the Type 2b Ge-rich mineralization and more precisely on Arre deposit (Cugerone et al. 2018b). Type 2b is an epigenetic sub-vertical vein-type mineralization (Fig. 2A) which has endured at least one deformation event, probably Variscan in age (D_2 in Cugerone et al. 2018b). These veins are composed of sphalerite and galena, with a small amount of pyrite, chalcopyrite, arsenopyrite and gangue of quartz-carbonate (Fig. 2B). Numerous Type 2b deposits are present in the Axial Zone (Cugerone et al. 2018b) and in this paper, we will only focus on the Arre deposit. This Pb-Zn(-Ge) mineralization is hosted in Devonian calc-schist and marble rocks. Veins are oriented N070 E with sub-vertical dip (Fig. 2A).

3.2 Macrotextures and microtextures

EBSD has been performed on several Type 2b mineralizations and especially in Arre sphalerite (Fig. 3A and 3B) to obtain textural and microstructural information. Sphalerite appear with diverse grain size (from 10 µm to > 1 mm). Coarse grained are considered as parent grains are internally deformed Smaller grains (< 100µm) are located around the parent grains locally

in twin boundaries. Three different texture in sphalerite are distinguished: dark domains and light domains in coarse grains and recrystallized small grains.

On the same area, EDS chemical mapping is performed during EBSD acquisition, and location of Ge-minerals is noted in Figure 3A. Ge-minerals are essentially composed of brunogeierite ($GeFe_2O_4$) and carboirite ($GeFeAl_2O_5(OH)_2$). Ge-minerals are preferentially hosted in the small recrystallized sphalerite fraction or close to twin boundaries.

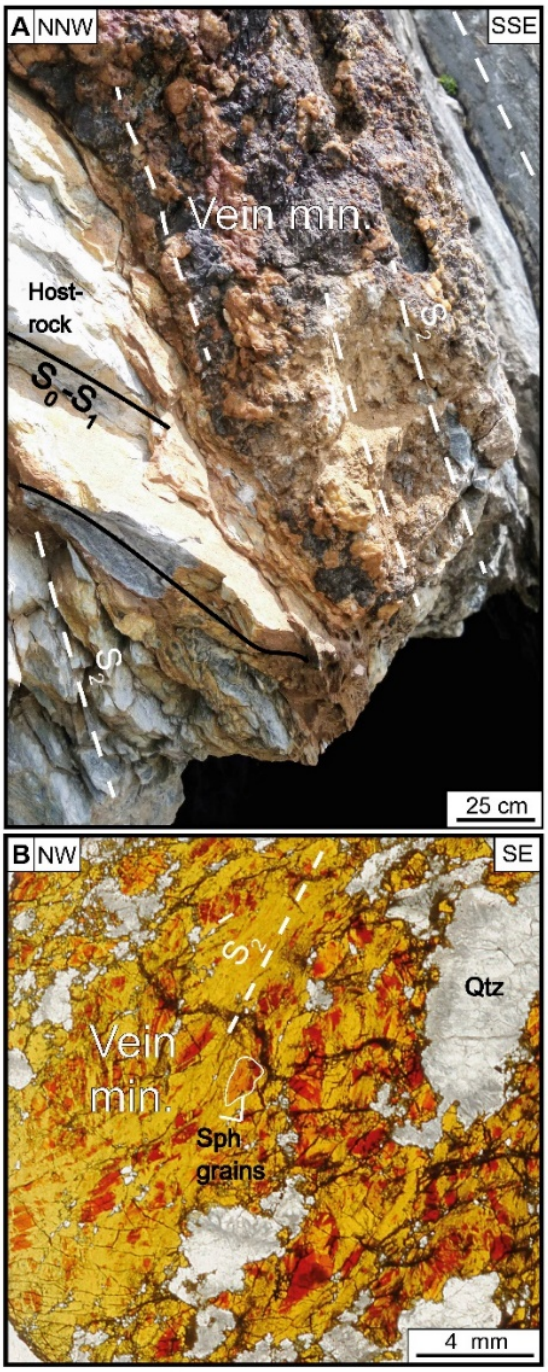

Figure 2: A: Pb-Zn Type 2b Vein mineralization in Arre deposit. B: Typical Pb-Zn Type 2b ore mineralization with color zonation in sphalerite and presence of superimposed S_2 cleavage (modified from Cugerone et al., 2018b, S_0-S_1: S_0-S_1 foliation; S_2: S_2 foliation; Qtz: quartz; Sph: sphalerite.

4 Ge and Cu in sphalerite

LA-ICP-MS analyses were all performed associated to EBSD grain size map to link in situ chemistry to the type of texture ablated, on the surface at least. Figure 3A

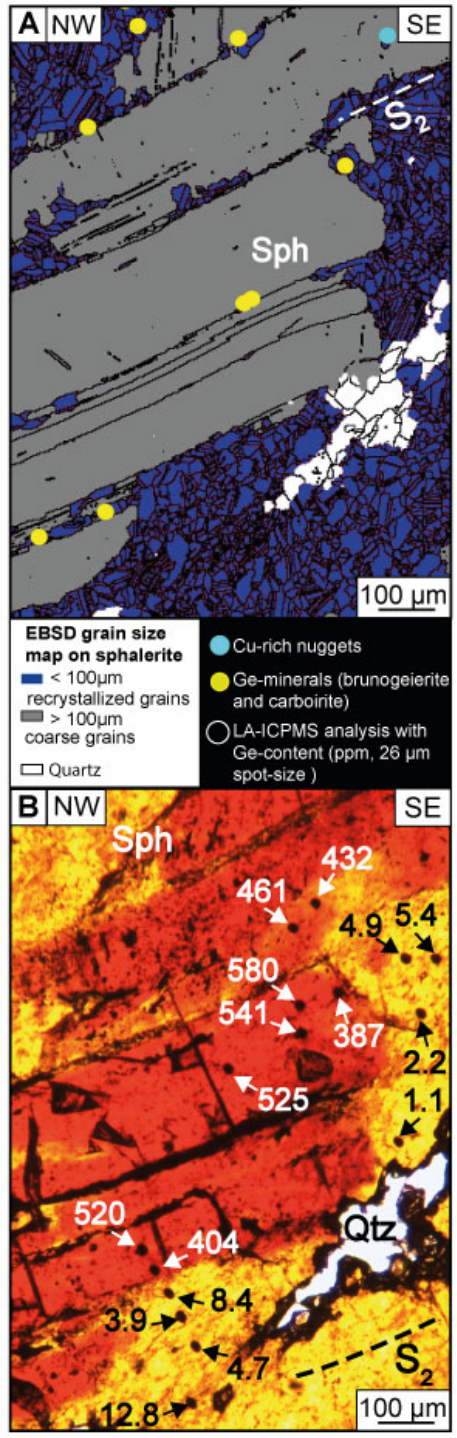

Figure 3. A: EBSD grain size map in sphalerite (Arre sample) with location of Ge and Cu rich phases. These minerals are preferentially preferentially located in the recrystallized sphalerite domains. B: Corresponding area in transmitted light with LA-ICP-MS spot analyses associated to Ge-contents (in ppm). Note the color zonation which is corresponding to variations in Ge content. (S_2: S_2 foliation; Qtz: quartz; Sph: sphalerite). This figure is from Cugerone et al., in prep.

shows EBSD grain size map on sphalerite ore. LA-ICP-MS spots are visible in Figure 3B associated to their Ge-contents with a sphalerite observed in transmitted light. Germanium appear highly zoned. In dark and light domains, median content reach 433 $\pm$ 21 ppm and 46 $\pm$ 2 ppm respectively. In recrystallized domains, Ge content is typically low with median Ge concentrations of 4 $\pm$ 2 ppm. Heterogeneous Ge in sphalerite is positively correlated to Cu, especially in the dark and light domains in Arre deposit with Cu median content of 1012 $\pm$ 75 ppm and 102 $\pm$ 7 ppm respectively. Cu is lower in recrystallized grains with median values of 29 $\pm$ 9 ppm.

Calculation of Ge content in the sphalerite compared to Ge-minerals shows that Ge concentration in Ge-minerals is equivalent to a supposed primary non-deformed sphalerite with mean content of 700 ppm Ge (Cugerone et al., in prep).

5 Discussion and conclusions

The studied sphalerites from Arre deposit show remarkable heterogeneous sphalerite texture and related chemistry. Formation of Ge-minerals is intimely associated to the deformation (supposed Variscan D_2) and recristallization due to their preferentially occurence in recrystallized fraction (Fig. 3a). Germanium was probably removed from the primary sphalerite crystal lattice during recrystallization and subsequently concentrated in Ge-minerals, leaving behind a Ge-depleted fine grained recrystallized sphalerite matrix (Cugerone et al., in prep).

Several textural and chemical analogues to these sphalerites may be present in deformed-MVT deposits (Ye et al. 2011), in Kipushi deposits (Belissont et al. 2016; Horn et al. 2018) but also in other sulphides like chalcopyrite from VHMS deposit (Reiser et al. 2011). These studies present recrystallized textures and, in some cases reported Ge-minerals. Ores affected by recrystallization are likely to contain accessory minerals that can be potentially enriched in rare metals.

This study will integrate Laser induced breakdown spectroscopy (LIBS) mapping on these ore samples to better understand the trace element heterogeneities in sphalerite. It is an excellent technique to map Ge because there is no interference with another element in sphalerite, contrary to WDS or µ-XRF mapping.

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References

Belissont R, Munoz M, Boiron MC, Luais B, Mathon O (2016) Distribution and oxidation state of Ge, Cu and Fe in sphalerite by u-XRF and K-edge u-XANES: Insights into Ge incorporation, partitioning and isotopic fractionation. Geochim Cosmochim Acta 177:298–314. doi: 10.1016/j.gca.2016.01.001

Cook NJ, Ciobanu CL, Meria D, Silcock D, Wade B (2013) Arsenopyrite-Pyrite Association in an Orogenic Gold Ore : Tracing Mineralization History from Textures and Trace Elements. Econ Geol 108:1273–1283

Cugerone A, Cenki-Tok B, Chauvet A, Le Goff E, Bailly L, Alard O, Allard M (2018a) 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 Geol Rev 95:1–19. doi: 10.1016/j.oregeorev.2018.02.016

Cugerone A, Oliot E, Chauvet A, Gavald J, Le Goff E (2018b) Structural Control on the Formation of Pb-Zn Deposits: An Example from the Pyrenean Axial Zone. Minerals 8:1–20. doi: 10.3390/min8110489

Dubosq R, Lawley CJM, Rogowitz A, Schneider DA, Jackson S (2018) Pyrite deformation and connections to gold mobility : Insight from micro-structural analysis and trace element mapping. Lithos 310–311:86–104. doi: 10.1016/j.lithos.2018.03.024

Höll R, Kling M, Schroll E (2007) Metallogenesis of germanium-A review. Ore Geol Rev 30:145–180. doi: 10.1016/j.oregeorev.2005.07.034

Horn S, Dziggel A, Kolb J, Sindern S (2018) Textural characteristics and trace element distribution in carbonate-hosted Zn-Pb-Ag ores at the Paleoproterozoic Black Angel deposit, central West Greenland. Miner Depos 1–18. doi: 10.1007/s00126-018-0821-5

Johan Z, Oudin E, Picot P (1983) Analogues germanifères et gallifères des silicates et oxydes dans les gisements de zinc des Pyrénées centrales, France; argutite et carboirite, deux nouvelles espèces minérales. TMPM Tschermaks Mineral und Petrogr Mitteilungen 31:97–119. doi: 10.1007/BF01084764

Lockington JA, Cook NJ, Ciobanu CL (2014) Trace and minor elements in sphalerite from metamorphosed sulphide deposits. Mineral Petrol 108:873–890. doi: 10.1007/s00710-014-0346-2

Reiser FKM, Rosa DRN, Pinto ÃMM, Carvalho JRS, Matos JX, Guimaraes FMG, Alves LC, de Oliveira DPS (2011) Mineralogy and geochemistry of tin- and germanium-bearing copper ore, Barrigao re-mobilized vein deposit, Iberian Pyrite Belt, Portugal. Int Geol Rev 53:1212–1238. doi: 10.1080/00206811003683168

Wilkinson JJ (2013) Sediment-Hosted Zinc-Lead Mineralization: Processes and Perspectives: Processes and Perspectives, Treatise on Geochemistry, Second Edition. Elsevier, H Holland, K Turekian (ed), Amsterdam, Netherlands 219–249. doi: 10.1016/B978-0-08-095975-7.01109-8

Ye L, Cook NJ, Ciobanu CL, Yuping L, Qian Z, Tiegeng L, Wei G, Yulong Y, Danyushevskiy L (2011) Trace and minor elements in sphalerite from base metal deposits in South China: A LA-ICPMS study. Ore Geol Rev 39:188–217. doi: 10.1016/j.oregeorev.2011.03.001