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# Behavior of critical metals in metamorphosed Pb-Zn ore deposits: example from the Pyrenean Axial Zone

Alexandre Cugerone<sup>1</sup> · Bénédicte Cenki-Tok<sup>1,2</sup> · Manuel Muñoz<sup>1</sup> · Kalin Kouzmanov<sup>3</sup> · Emilien Oliot<sup>1</sup> · Vincent Motto-Ros<sup>4</sup> · Elisabeth Le Goff<sup>5</sup>

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## Abstract

Rare metals (Ge, Ga, In, Cd) are key resources for the development of green technologies and are commonly found as trace elements in base-metal mineral deposits. Many of these deposits are in orogenic belts and the impact of recrystallization on rare metal content and distribution in sphalerite needs to be evaluated. Based on laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses, and micro-imaging techniques such as laser-induced breakdown spectroscopy (LIBS) and electron backscattered diffraction (EBSD), we investigate the minor and trace element composition related to sphalerite texture for three types of mineralization from the Pyrenean Axial Zone (PAZ). Vein mineralization (type 2b) appears significantly enriched in Ge and Ga compared to disseminated and stratabound mineralization (type 1 and type 2a, respectively). In vein mineralization, the partial recrystallization induced by deformation led to the remobilization of Ge, Ga, and Cu from the sphalerite crystal lattice into accessory minerals. We propose that the association of intragranular diffusion and fluid-rock reaction were likely responsible for the formation of patchy-oscillatory zoning in sphalerite, and the crystallization of Ge-rich accessory minerals. Chemical and textural heterogeneity is common in sphalerite from various world-class deposits and a full understanding of these heterogeneities is now crucial to assess the rare metal potential, and associated extraction processes of deformed base-metal ores.

## Introduction

Sphalerite (ZnS) commonly contains high amounts (up to a few 1000s of ppm) of rare metals such as germanium (Ge), indium

(In), gallium (Ga), or cadmium (Cd), which are currently extracted as by-products from zinc concentrates (Frenzel et al. 2014, 2016, 2017; Licht et al. 2015) and considered critical for the economy (European Commission 2017; U.S. Geological

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✉ Alexandre Cugerone  
alex.cugerone@gmail.com

Bénédicte Cenki-Tok  
benedicte.cenki-tok@umontpellier.fr

Manuel Muñoz  
manuel.munoz@umontpellier.fr

Kalin Kouzmanov  
Kalin.Kouzmanov@unige.ch

Emilien Oliot  
emilien.oliot@umontpellier.fr

Vincent Motto-Ros  
vincent.motto-ros@univ-lyon1.fr

Elisabeth Le Goff  
e.legoff@brgm.fr

<sup>1</sup> Géosciences Montpellier, Université de Montpellier, CNRS, Montpellier, France

<sup>2</sup> Earthbyte Research Group, School of Geosciences, University of Sydney, Sydney, NSW 2006, Australia

<sup>3</sup> Department of Earth Sciences, University of Geneva, Geneva, Switzerland

<sup>4</sup> Institut Lumière Matière Université Lyon 1, Villeurbanne, France

<sup>5</sup> BRGM, Bureau de Recherches Géologiques et Minières, Montpellier, France

33 Survey 2019). These high concentrations of trace elements are  
 34 generally related to undeformed sphalerite in the form of coarse  
 35 crystals originating from open-space crystallization or from  
 36 colloform-banded precipitates with fine-grained textures  
 37 (Cerny and Schroll 1995; Goffin et al. 2015; Henjes-Kunst  
 38 et al. 2017; Cugerone et al. 2018a). Undeformed sphalerite oc-  
 39 curs mainly in Mississippi Valley type (MVT) and polymetallic  
 40 vein deposits (Viets et al. 1992; Saini-Eidukat et al. 2009;  
 41 Murakami and Ishihara 2013; Belissont et al. 2014; Bonnet  
 42 2014; Bauer et al. 2018). However, the largest sphalerite de-  
 43 posits are found in orogenic domain (Lawrence 1973; Moore  
 44 et al. 1986; Kelley and Jennings 2004; Kampunzu et al. 2009;  
 45 Wilkinson 2013; Gibson et al. 2017). This reflects the fact that  
 46 the ores originally formed as sediment-hosted massive sulfide  
 47 (SHMS), volcanic-hosted massive sulfide (VHMS), or  
 48 carbonate-hosted deposits (Kipushi-type, more rarely MVT)  
 49 are more likely to have undergone metamorphism and recryst-  
 50 tallization during an orogenic event (Bernstein and Cox 1986;  
 51 Hughes 1987; Murphy 2004; Wagner and Monecke 2005;  
 52 Huston et al. 2006; Melcher et al. 2006; Monteiro et al. 2006;  
 53 Kamona and Friedrich 2007; Reiser et al. 2011; Ye et al. 2011).

54 In metamorphic environments, remobilization of minor and  
 55 trace elements related to dynamic recrystallization, annealing, or  
 56 even brecciation has been studied for various sulfide minerals.  
 57 The mobility of Au, As, Ni, Co, Pb, Bi, and Se has been exam-  
 58 ined in pyrite (Cook et al. 2009a; Large et al. 2009; Reddy and  
 59 Hough 2013; Velásquez et al. 2014; Dubosq et al. 2018;  
 60 Kampmann et al. 2018), arsenopyrite-löllingite (Tomkins and  
 61 Mavrogenes 2001; Wagner et al. 2007; Fougrouse et al. 2016)  
 62 and pyrrhotite (Vukmanovic et al. 2014). The dynamic recryst-  
 63 tallization assisted by metamorphic fluids in gold systems re-  
 64 leases invisible gold from the sulfide crystal lattice and subse-  
 65 quent crystallization of metallic gold (Fougrouse et al. 2016;  
 66 Dubosq et al. 2018). Lockington et al. (2014) studied sphalerite  
 67 mineralization from metamorphosed VHMS and SHMS de-  
 68 posits. Metamorphic recrystallization was shown to lead to re-  
 69 mobilization of minor and trace elements resulting in a loss of  
 70 compositional zoning, and homogenization of Cu distribution in  
 71 the crystal lattice of sphalerite, possibly associated to a depletion  
 72 in Pb, Bi, and Ag and an enrichment in Fe, Cd, Mn, and In.  
 73 These data were acquired in various deposits of different meta-  
 74 morphic grade and the role of primary enrichment for these  
 75 elements cannot be clearly established. In Neves-Corvos  
 76 (Iberian Pyrite Belt, Carvalho et al. 2018), indium is primarily  
 77 incorporated in high-temperature sphalerite and chalcopyrite,  
 78 but was not lost during recrystallization associated to hydrother-  
 79 mal re-working and/or low-grade tectonometamorphic over-  
 80 prints (Relvas et al. 2006; Carvalho et al. 2018). Nonetheless,  
 81 roquesite (CuInS<sub>2</sub>) locally occurs at sulfide grain boundaries. In  
 82 sphalerite from Neves Corvo, Ge is reported below ~ 100 ppm  
 83 Ge (Carvalho et al. 2018). In the Barrigão deposit (Iberian Pyrite  
 84 Belt), Reiser et al. (2011) and Belissont et al. (2019) suggested  
 85 late-stage remobilization of germanium associated to low-grade

metamorphism (260–300 °C) with germanium enrichments in  
 chalcopyrite and accessory phases localized in fractures.  
 Cugerone et al. (2018) showed evidence for redistribution of  
 Ge in partly recrystallized sphalerite from the Arre vein deposit  
 (Pyrenean Axial Zone). Recrystallized sphalerite is Ge-depleted  
 but correspond to textures where Ge minerals occur, compared  
 to dark domains in coarser grains which still contain up to  
 ~600 ppm Ge in the sphalerite lattice. Occurrences of rare metals  
 such as Ge, Ga, In, and Cd within deformed/metamorphosed  
 sphalerite ore remain poorly documented and their behavior in  
 such systems needs to be evaluated.

Sphalerite is ductile at relatively low temperature in various  
 experimental deformation studies (< 400 °C; Clark and Kelly  
 1973; Siemes and Borges 1979; Couderc et al. 1985; Cox  
 1987). No experimental study on the impact of sphalerite de-  
 formation on trace elements behavior is available.

Currently, the production of rare metals from base-metal de-  
 posits remains challenging. Germanium is generally extracted,  
 for example, by hydrometallurgy followed by various mass  
 transfer techniques (Ruiz et al. 2018). However, only a few  
 percent of the total rare metal content in sphalerite (at ppm level)  
 is recovered due to a negative effect which prevents the extrac-  
 tion of zinc (around ~ 3% of the Ge extracted; Ruiz et al. 2018;  
 U.S. Geological Survey 2019). Chemical extraction from highly  
 concentrated phases (with Ge contents > 1 wt%), previously  
 separated by magnetic or mechanic techniques, could prove to  
 be much more profitable (Cugerone et al. 2019).

This study aims to decipher the behavior of rare metals,  
 mainly Ge, Ga, In, and Cd, in sphalerite from different Pb-  
 Zn deposits and mineralization styles of the Pyrenean Axial  
 Zone (PAZ). The Pb-Zn deposits of the PAZ contain sphalerite  
 rich in rare metal (ppm level) and Ge-rich accessory min-  
 erals, such as brunogeierite GeFe<sub>2</sub>O<sub>4</sub>, briartite GeCu<sub>2</sub>(Fe, Zn)  
 S<sub>4</sub>, carboirite GeFeAl<sub>2</sub>O<sub>5</sub>(OH)<sub>2</sub>, or argutite GeO<sub>2</sub> (Laforet  
 et al. 1981; Johan et al. 1983; Bernstein 1985; Johan and  
 Oudin 1986; Pouit and Bois 1986; Julliot et al. 1987;  
 Cugerone et al. 2018a). We have investigated the textural  
 and chemical composition of different types of sphalerite min-  
 eralization in the Pyrenees using an in situ quantitative analy-  
 sis by LA-ICP-MS and micro-imaging techniques such as  
 EBSD and LIBS mapping. We show a detailed genetic model  
 at vein and granular scales for the partitioning of Ge and  
 associated trace elements between sphalerite and accessory  
 minerals. Finally, we present a comparison with other Ge-  
 enriched Pb-Zn deposits worldwide.

## Sampling and analytical methods

Oriented ore samples were collected from underground mines  
 or surface outcrops. We have studied polished sections (either  
 30 or 150 μm thick) from six Pb-Zn deposits of three miner-  
 alization types.

136 EBSD analysis is used to characterize the texture and the  
 137 grain size of the sphalerite. This technique requires a well-  
 138 polished surface. In order to eliminate surface defects, a last step  
 139 of polishing (0.25  $\mu\text{m}$ ) was performed using a Vibromet polish-  
 140 er with 150 g of pressure on a polyurethane layer with colloidal  
 141 silica. During this process, cleaning the frozen colloidal silica  
 142 was necessary to avoid scratches on sphalerite. EBSD maps  
 143 were performed with a Camscan Crystal Probe X500FE SEM-  
 144 EBSD at Geosciences Montpellier (CNRS-University of  
 145 Montpellier, France). Operating conditions were 20 kV and  
 146 5 nA, with a working distance of 25 mm under 2 Pa low vacu-  
 147 um. Sample surfaces were positioned horizontally at 20° to the  
 148 incident electron beam to improve the collection of the  
 149 backscattered electrons. Element distribution maps and  
 150 backscattered electron (BSE) images were simultaneously ac-  
 151 quired by measuring X-ray fluorescence with an EDS (energy-  
 152 dispersive spectrometer). The step size for 2D imaging was  
 153 below 5  $\mu\text{m}$ . EBSD mapping was preferentially performed on  
 154 sphalerite, indexed as a cubic crystal symmetry, while Ge min-  
 155 erals were localized by EDS maps. The EBSD indexation of  
 156 quartz, calcite, galena, and pyrite was also performed. Match  
 157 units used for sphalerite indexation were derived from published  
 158 crystallographic data from Villars and Calvert (1991). The lower  
 159 misorientation limit for grain boundary indexation is fixed at 20°  
 160 following careful investigation on misorientation boundary  
 161 maps superposed on orientation maps. Oxford Instruments soft-  
 162 wares AZtec and Channel 5 were used to generate maps using  
 163 the EDS (chemical maps) and EBSD (structural maps).

164 Electron probe micro-analyses were carried out using a  
 165 Cameca SX100 at the Service Inter-Régional Microsonde-  
 166 Sud (Montpellier, France). Major, minor, and trace elements  
 167 were measured with a beam current of 100 nA and accelerat-  
 168 ing voltage of 20 kV. The analytical procedure and detailed  
 169 settings for each elemental analysis are detailed in Cugerone  
 170 et al. (2018a). Zinc concentrations of sphalerite crystals were  
 171 used as an internal calibration for LA-ICP-MS analyses.

172 LA-ICP-MS was used to determine minor and trace ele-  
 173 ment concentrations in sphalerite. Type 1 sphalerite was ana-  
 174 lyzed in one sample from Bentaillou ( $n = 7$ ), type 2a sphalerite  
 175 in three samples from Bentaillou ( $n = 12$ ), Margalida ( $n = 9$ ),  
 176 and Victoria ( $n = 11$ ). Type 2b sphalerite was measured in  
 177 three samples from Arre ( $n = 36$ ), Anglas ( $n = 40$ ), and Pale  
 178 Bidau ( $n = 30$ ).

179 Analyses were carried out using an Excimer CompEx 102  
 180 coupled to a ThermoFinnigan Element XR at the OSU-  
 181 OREME AETE platform (University of Montpellier,  
 182 France). Laser ablation was performed using a constant 5 Hz  
 183 pulse rate at 140 mJ with a spot diameter of 26  $\mu\text{m}$ . Each  
 184 analysis comprises 180 s of background measurement and  
 185 60 s of sample ablation (signal measurement), followed by a  
 186 60-s retention time to ensure a proper cell washout. Data were  
 187 processed using the Glitter 4.0 software package (Van  
 188 Achterbergh et al. 2001). The following isotopes were

189 measured:  $^{29}\text{Si}$ ,  $^{34}\text{S}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{61}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{64}\text{Zn}$ ,  
 190  $^{69}\text{Ga}$ ,  $^{74}\text{Ge}$ ,  $^{75}\text{As}$ ,  $^{77}\text{Se}$ ,  $^{95}\text{Mo}$ ,  $^{105}\text{Pd}$ ,  $^{107}\text{Ag}$ ,  $^{111}\text{Cd}$ ,  $^{115}\text{In}$ ,  
 191  $^{118}\text{Sn}$ ,  $^{121}\text{Sb}$ , and  $^{208}\text{Pb}$ . MASS-1 reference material (Wilson  
 192 et al. 2002) was used as an external standard with a corrected  
 193  $57 \pm 1.75$  ppm value for Ge (Dr. Stephen Wilson, personal  
 194 communication). NIST SRM 610 (Pearce et al. 1997) was  
 195 used as secondary external standard to identify possible instru-  
 196 mental drift. Concentrations for Ni, As, Mo, Se, Pd, and Si  
 197 were below detection limits in all measurements. Several  
 198 time-integrated LA-ICP-MS spectra are reported in the  
 199 electronical supplementary material (ESM 1), illustrating the  
 200 time intervals used for the measurements. One standard devi-  
 201 ation is systematically indicated for median values.

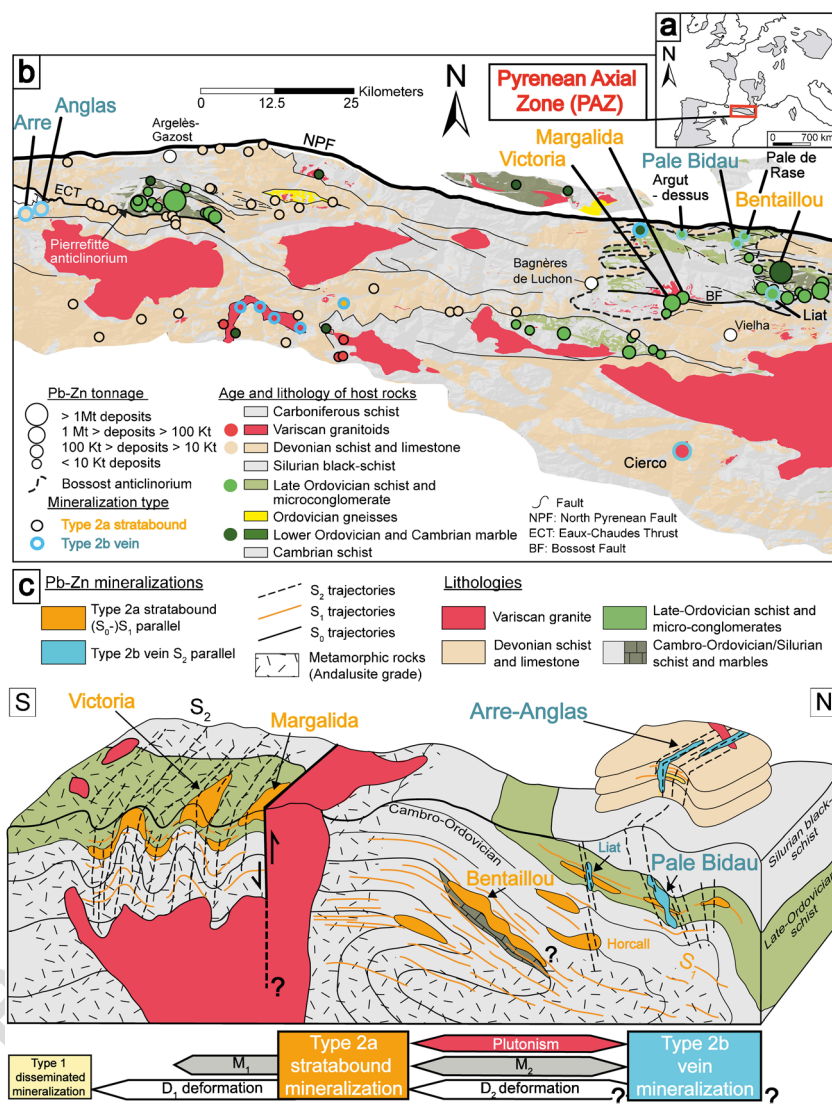
202 Laser-induced breakdown spectroscopy (LIBS) imaging  
 203 technique was used to highlight the distribution of Ge, Cu,  
 204 Ga, Zn, Si, Fe, Cd, Al, Mg, and Ti, in a highly zoned sphalerite  
 205 sample from Arre (ARR03 sample) to map metallic elements  
 206 at a micrometric spatial resolution, and with a sensitivity at the  
 207 ppm level (Sancey et al. 2014; Cáceres et al. 2017; Fabre et al.  
 208 2018). During the analysis, the sample surface is scanned,  
 209 through single laser pulses, in a pixel-by-pixel manner to in-  
 210 duce the breakdown of the material. The light radiation emit-  
 211 ted by the plasma is then collected by an optical system and  
 212 analyzed using a spectrometer. The sample was excited using  
 213 Nd:YAG laser with a pulse energy of about 600  $\mu\text{J}$  operating  
 214 at 100 Hz and a lateral resolution (i.e., distance between two  
 215 consecutive laser shots) of 13  $\mu\text{m}$ . The surface analyzed is  
 216 about 6  $\text{cm}^2$  (3.6 megapixels) and was measured in 6 h. The  
 217 spectrometer was configured in the spectral range 250–  
 218 330 nm to detect Ge (265.1 nm), Cu (324.7 nm), and Ga  
 219 (294.4 nm). Due to an interference with Al, the Ge line at  
 220 269.1 nm was used in the aluminosilicate phases.

## 221 Geological setting

222 The Pb-Zn ore deposits are hosted in the Variscan PAZ  
 223 (Fig. 1a) and exhumed during the Paleogene collision between  
 224 the Iberia and Eurasian plates (Zwart 1979; Carreras and  
 225 Druguet 2014). The PAZ is composed of Paleozoic  
 226 metasediments intruded by Ordovician and Late-Variscan  
 227 granite (Fig. 1b; Kleinsmiede 1960; Zwart 1963; Denèle  
 228 et al. 2014). The Pb-Zn deposits are concentrated in pluri-  
 229 kilometeric structures such as the Bossost or Pierrefitte  
 230 anticlinoria (Fig. 1b).

231 The Pb-Zn district of the PAZ was exploited in twentieth  
 232 century. It has produced ca. 400 kt of Zn and 180 kt of Pb  
 233 (BRGM 1984; Ovejero Zappino 1991). Three types of Pb-Zn  
 234 mineralization are described in Cugerone et al. (2018b). Type 1  
 235 is minor, disseminated, and laminated mineralization, probably  
 236 associated to sedimentation during Cambro-Ordovician and  
 237 Devonian times (Fig. 1c). Type 2a is a structurally controlled  
 238 mineralization parallel to  $S_0$ - $S_1$  (Fig. 1c), synchronous to

**Fig. 1** **a** Location of the Pyrenean Axial Zone in the Variscan belt of Western Europe. **b** Lithological and structural map of Central Pyrenean Axial Zone with location of Pb-Zn deposits (from Pouit 1985, Bureau de Recherches Géologiques et Minières [http://infoterre.brgm.fr], and Instituto Geológico y Minero de España [http://mapas.igme.es/Servicios/default.aspx]). **c** Structural 3D synthetic model with location of the studied Pb-Zn deposits in relation to lithology, structure, and metamorphic grade. Chronological interpretation from Cugerone et al. (2018b). Timing of mineralization for the type 2b vein mineralizations is unknown but deformation imprint is considered as Late-Variscan ( $D_2$ )



239 Variscan  $D_1/M_1$  regional deformation/metamorphism related to  
 240 crustal thickening (Zwart 1963, 1979; Mezger et al. 2004;  
 241 Laumonier et al. 2010) with a peak estimated at 580 °C and  
 242 0.55 GPa in the Bossost dome (Mezger et al. 2004). Type 2a  
 243 mineralization pre-dates Variscan  $M_2$  contact metamorphism,  
 244 culminating at ca. 525 °C and 0.2 GPa (Mezger and Passchier  
 245 2003; Mezger et al. 2004; de Hoym de Marien et al. 2019) in the  
 246 Victoria-Margalida area. In the field, type 2a mineralization ap-  
 247 pears in metric pull-apart type structures in Cambrian marble as  
 248 in Bentaillou (Fig. 1c) or folded by  $D_2$  deformation in Late-  
 249 Ordovician metasediments in Victoria (Fig. 1c). It can also be  
 250 associated to fault damaged zones in Late-Ordovician marble in  
 251 Margalida (Fig. 1b; Cugerone et al. 2018b).

252 Type 2b (Fig. 1) is epigenetic vein mineralization probably  
 253 late, or post-dating, the  $D_2/M_2$  deformation event (Cugerone  
 254 et al. 2018b). Pb-Zn mineralization is structurally controlled  
 255 and occurs as vertical decimetric-sized veins parallel to  $S_2$  cleav-  
 256 age, which locally intersect type 2a mineralization. No alteration

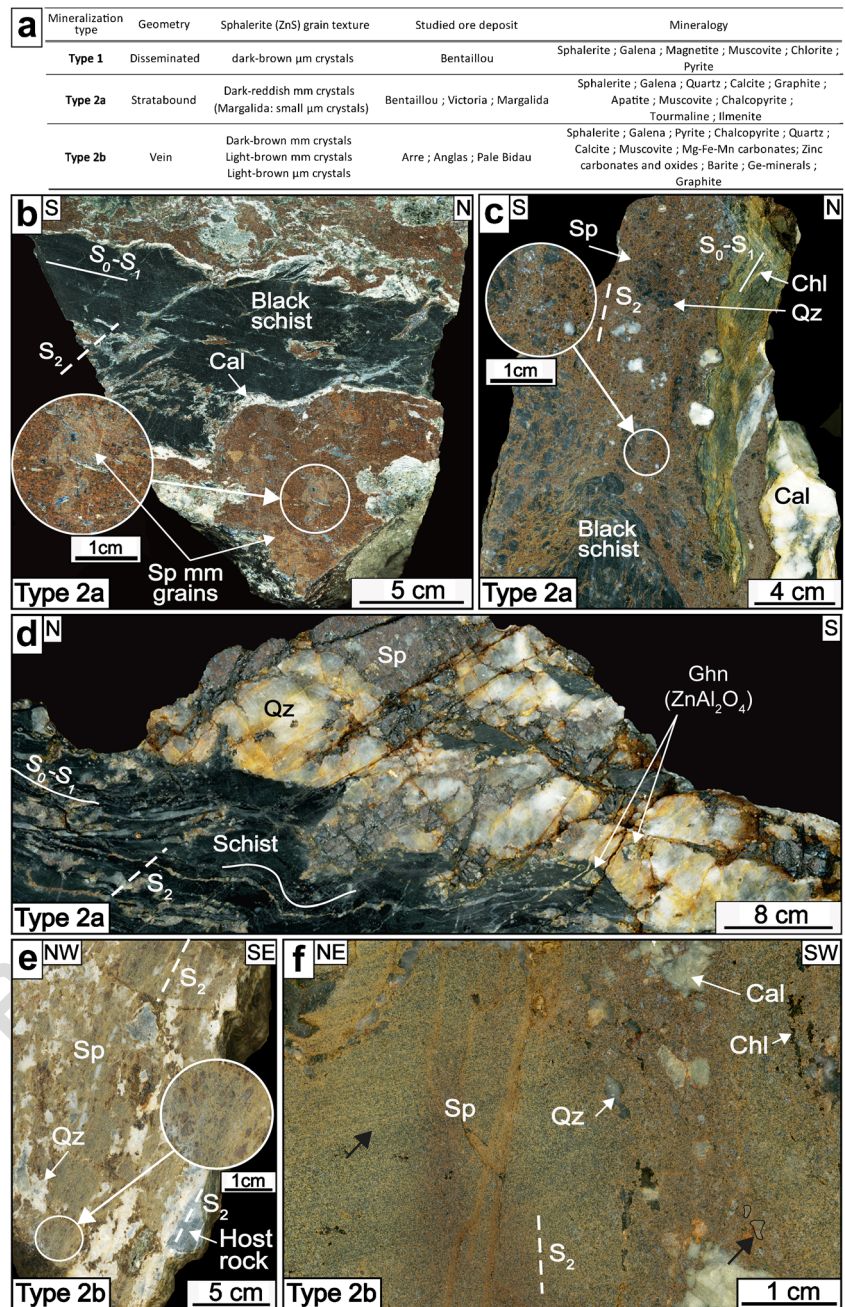
257 halo has been observed along the contact with the host-rock.  
 258 Type 2b mineralization cuts Late-Variscan aplitic intrusions  
 259 and is affected by a cleavage parallel to the Late-Variscan  $S_2$   
 260 cleavage in the host rock (Cugerone et al. 2018b). We have  
 261 studied samples from type 2b Pale Bidau, Arre, and Anglas  
 262 deposits hosted in calc-schists (Fig. 2b). A late  $D_3$  deformation  
 263 is reported in the literature (Carreras and Druguet 2014; Cochelin  
 264 et al. 2017) and corresponds to faults like the Bossost mylonitic  
 265 fault close to type 2a Margalida deposit.

266 **Results**

267 **Mineralization types and textures**

268 The three types of mineralization are mainly composed of  
 269 sphalerite and galena, with minor pyrite, chalcopyrite, arseno-  
 270 pyrite, and gangue of quartz-carbonate (Fig. 2a).

**Fig. 2** Polished samples of type 2a and type 2b mineralization (Cal: calcite; Chl: chlorite; Ghn: gahnite; Qz: quartz; Sp: sphalerite). **a** Characteristic of the three mineralization types: type 1, type 2a, and type 2b. **b** Sample with millimetric coarse-grained sphalerite (dark brown reddish), associated to calcite (white), and black-schist (Bentaillou deposit). **c** Pluri-micrometric small-grained sphalerite (dark brown reddish). A brecciated texture can be observed with clasts of quartz, calcite, and black-schist (Margalida deposit). **d** Folded ( $F_2$ ) coarse-grained sphalerite and quartz mineralization. Gahnite crystals are reported in schists and in the mineralization (Victoria deposit). **e** Light to dark brown zonation in sphalerite crystals associated to quartz and calcite host rock. Set shows coalescence of coarse millimetric and small micrometric crystals appear (Arre deposit). **f** Light to dark brown sphalerite associated to quartz, calcite, and chlorite. Dark brown vertical bands are visible on the sample. Sphalerite grains are locally visible as shown by the black arrow at bottom right (Pale Bidau deposit)

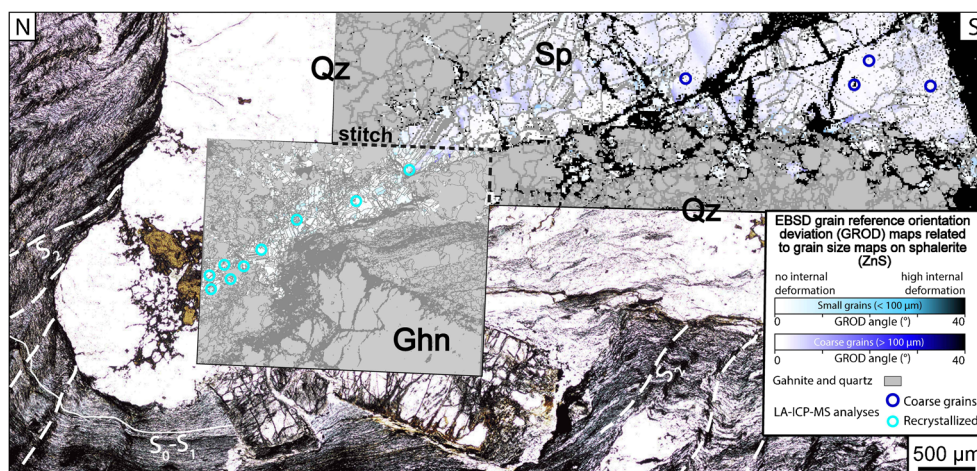


271 Type 1 is composed of micrometric-size disseminated sulfide  
 272 crystals. This mineralization is crosscut by type 2a veins  
 273 (Bentaillou deposit; Cugerone et al. 2018b). It consists of  
 274 pluri-micrometric euhedral dark brown crystals.  
 275 Type 2a sphalerite shows undeformed millimeter-size  
 276 twinned crystals and polygonal shape that is dark-red in  
 277 polished slabs (Fig. 2b). The texture is different at Margalida  
 278 (Fig. 2c), which presents micrometer-scale dark brown sphalerite  
 279 grains and forming the matrix of a durchbewegung breccia  
 280 composed of quartz, calcite, and schist clasts. Sphalerite is  
 281 folded in Victoria (Fig. 2d) and cross-cuts metamorphic  
 282 centimeter-scale gahnite (Fig. 3; Cugerone et al. 2018a).

Sphalerite exhibits recrystallized textures in  $F_2$  fold hinges (Fig. 3).

The mineral assemblages of types 2a and 2b veins (Cugerone et al. 2018b) are distinct with the presence of apatite, ilmenite, and tourmaline in type 2a and Ge-minerals, graphite, and Mg-Fe-Mn-Zn carbonates in type 2b. Sphalerite crystals of type 1, 2a, and 2b mineralizations do not contain chalcocopyrite inclusions.

Type 2b sphalerite is light to dark brown in transmitted-light and with heterogeneous grain size resulting from a superimposed cleavage (considered to be  $S_2$ ) parallel to the vein contact (Fig. 2e and f). In the Arre, Anglas, and Pale Bidau



**Fig. 3** EBSD-grain reference orientation deviation angle component (GROD) maps related to grain size superimposed onto a transmitted-light microphotograph of type 2a sphalerite-quartz mineralization hosted in schist deformed by  $F_2$  fold hinge from Victoria deposit. The GROD maps allow to visualize intragranular microstructures and represent the misorientation deviation for each pixel compared to the

mean misorientation deviation of the entire sphalerite grain (steps of measurement of 4 and 10  $\mu\text{m}$  for the left and right EBSD maps respectively). In the GROD calculation, twin boundaries are considered as grain boundaries to exclude their large misorientation ( $55\text{--}60^\circ$ ) (Ghn: gahnite; Qz: quartz; Sp: sphalerite). LA-ICP-MS spot analyses in type 2a coarse and recrystallized sphalerite are indicated

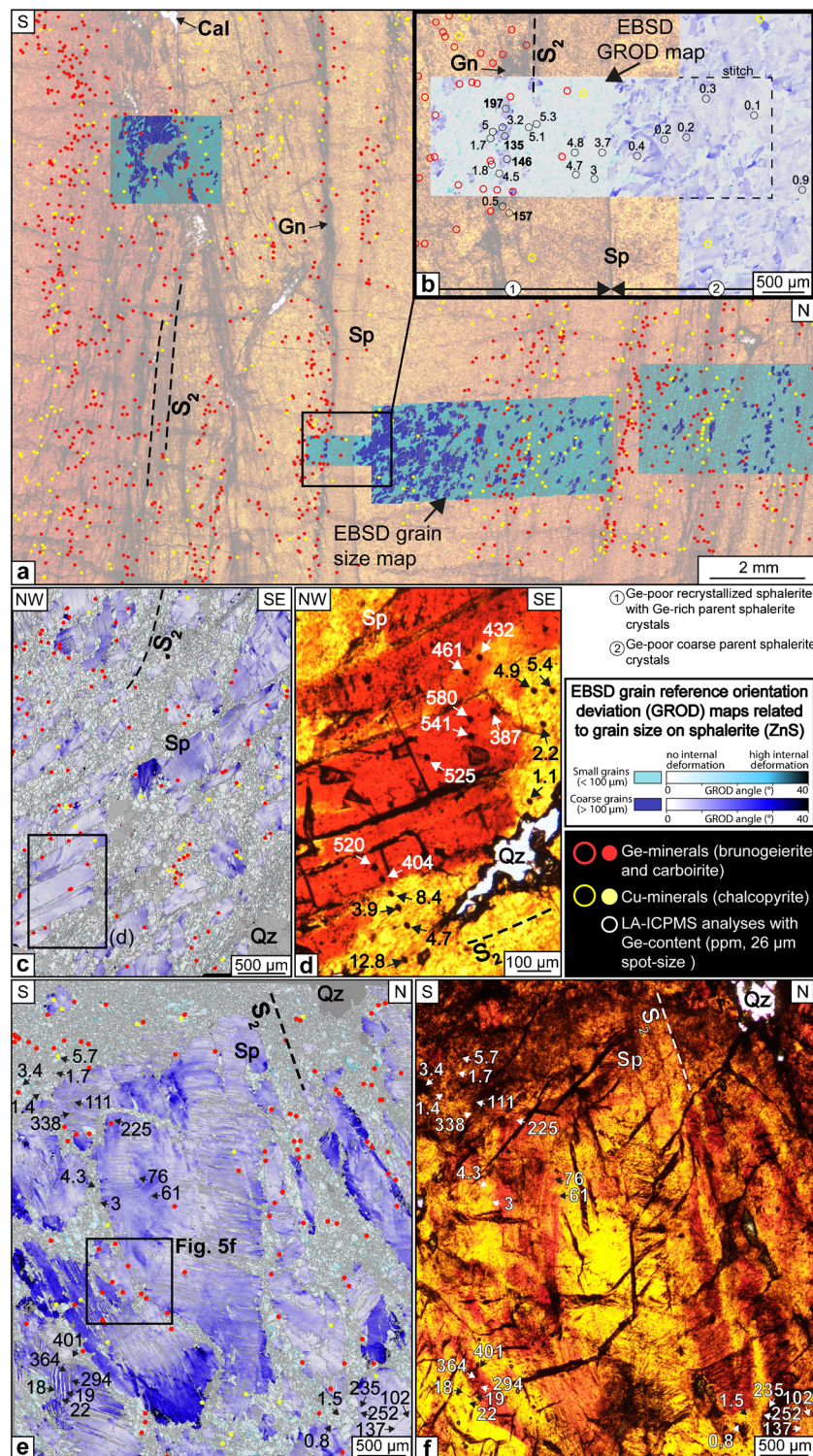
295 Bidau deposits, sphalerite crystals exhibit various colors from  
 296 dark brown zones in coarse, millimetric grains, to light-brown  
 297 zones in coarse millimetric, or fine micrometric, grain frac-  
 298 tions (Figs. 2e and 3f). Quartz and carbonate show comb tex-  
 299 tures with the occurrence of cockade breccia mainly in Arre  
 300 and Anglas type 2b veins. EBSD-grain reference orientation  
 301 deviation (GROD) maps and transmitted-light microphoto-  
 302 graphs are superposed in Fig. 4. Coarse grains ( $> 100 \mu\text{m}$ )  
 303 and small recrystallized grains ( $< 100 \mu\text{m}$ ) are colored in shad-  
 304 ed of dark and light blue, respectively. Blue colors are more  
 305 pronounced where internal deformation is more intense. Three  
 306 types of sphalerite textures appear in type 2b mineralization:  
 307 coarse grains with dark brown domains, coarse grains with  
 308 light-brown domains, and recrystallized light-brown crystals.  
 309 Sub-vertical fine recrystallized fraction domains appear most-  
 310 ly in white color in the GROD maps (Fig. 4a) which attests to  
 311 poor internal deformation and commonly mark the cleavage,  
 312 for example in PB (Fig. 4a and b). Coarse crystals ( $> 100 \mu\text{m}$ )  
 313 with color zones from light to dark brown are reported in the  
 314 Arre and Anglas samples (Fig. 4c–f) and commonly contain  
 315 ductile deformation attested by intense dark-blue color mainly  
 316 close to grain boundaries (Fig. 4e). In the EBSD-GROD and  
 317 the grain size maps, it is possible to discriminate between  
 318 recrystallized and light-brown coarse grains while these two  
 319 fractions show the same light-orange color in transmitted light  
 320 (Fig. 4). Sphalerite from the Pale Bidau deposit exhibits  
 321 blurred color domains with progressive variations from light  
 322 to dark brownish tints and no intragranular color zonation is  
 323 observed, especially in coarse grains.

324 Minerals in which Ge is a major element have been identified  
 325 by optical microscopy and EDS maps as brunogeierite  
 326 ( $\text{GeFe}_2\text{O}_4$ ), carboirite [ $\text{FeA}_{12}\text{GeO}_5(\text{OH})_2$ ], briartite [ $\text{Cu}_2(\text{Fe},$   
 327  $\text{Zn})\text{GeS}_4$ ], and argutite ( $\text{GeO}_2$ ). Briartite is the main Ge-

328 mineral in Arre sphalerite but is rare in Anglas and Pale Bidau  
 329 sphalerite. Carboirite, brunogeierite, and more rarely argutite are  
 330 the common Ge-minerals in the Anglas and Pale Bidau de-  
 331 posits. These minerals are preferentially hosted along grain  
 332 boundaries of recrystallized sphalerite grains. In Figs. 4 and 5,  
 333 Ge-minerals occur as small crystals ( $< 100 \mu\text{m}$ ; see yellow dots  
 334 in Fig. 4) and are preferentially aligned in the  $S_2$  cleavage.  
 335 Similarly, micrometric chalcopyrite is preferentially aligned in

**Fig. 4** Microphotographs associated to EBSD-grain reference orientation deviation angle component (GROD) maps related to sphalerite grain size. The GROD maps allow to visualize intragranular microstructures. Small grains contain low internal misorientation compared to coarse grains, which confirm the presence of dynamic recrystallization. Grain boundaries are represented in all maps except in **b** and chemical contents acquired with LA-ICP-MS are reported (Gln: galena; Qz: quartz; Sph: sphalerite). **a** Scanned microphotograph of sphalerite with superposition of four EBSD-grain size maps (Pale Bidau deposit; step of measurements between 1.5 and 4  $\mu\text{m}$ ). Germanium and Cu minerals observed with EDS map are reported. Location of **b** is indicated. **b** Enlargement of **a** showing the location of LA-ICP-MS spot analyses with Ge contents essentially on two EBSD-GROD maps. Occurrence of Ge and Cu minerals are reported with empty yellow and blue circles to highlight relationships between Ge-Cu minerals and sphalerite (step of measurement of 1.5 and 4  $\mu\text{m}$  for the left and right EBSD maps respectively). **c** EBSD-GROD map with location of Ge- and Cu-rich phases (Arre deposit). These minerals are preferentially located in the recrystallized sphalerite domains. Location of **d** is represented (step of measurement of 2.5  $\mu\text{m}$ ). **d** Enlargement of **c** in transmitted-light with LA-ICP-MS spot analyses associated to Ge contents. Note that the color zonation correspond in part to variations in Ge content. **e** EBSD-GROD map with location of Ge- and Cu-rich minerals in recrystallized sphalerite (Anglas deposit). LA-ICP-MS spot analyses are located with their corresponding Ge contents (step of measurement of 3  $\mu\text{m}$ ). **f** Enlargement of **e** in transmitted-light (150  $\mu\text{m}$  of thickness) with color zonation between light and dark brown. LA-ICP-MS spots are indicated with black or white arrows corresponding to **e**



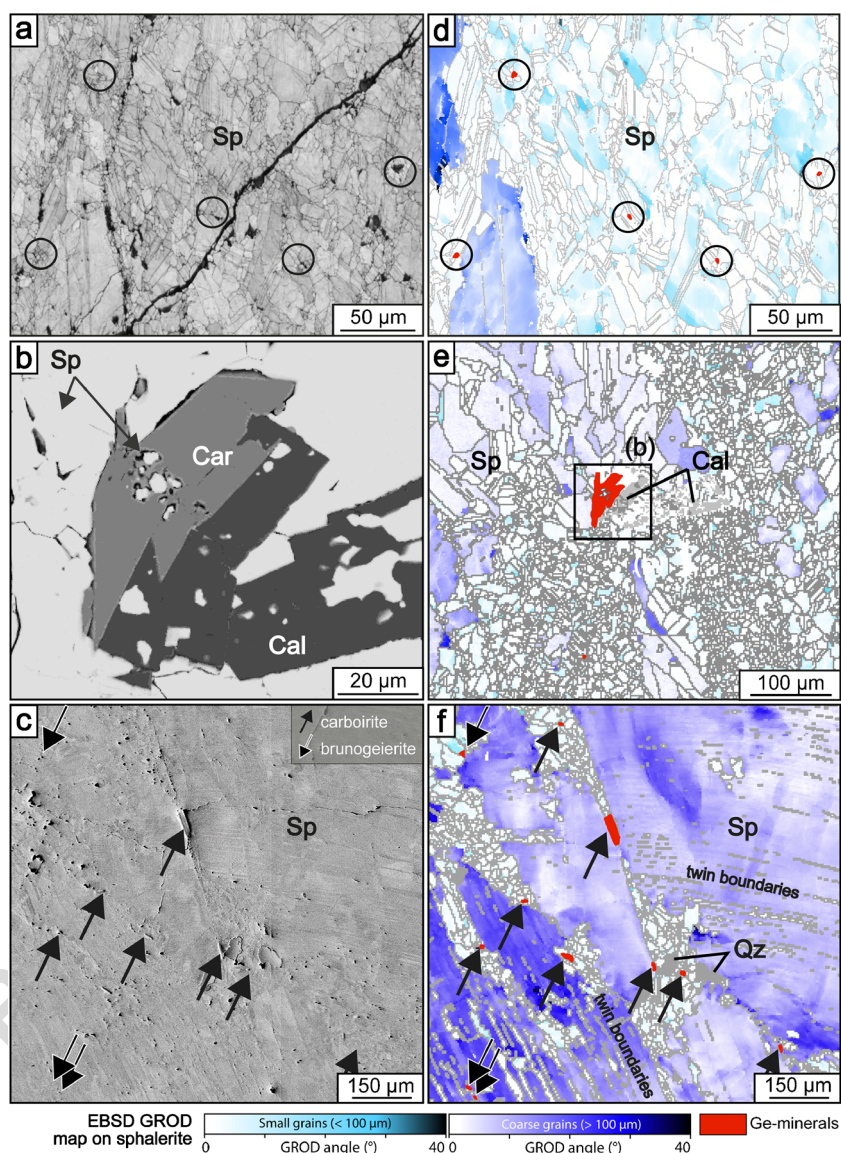


336 the same recrystallized areas (Fig. 4). These minerals are detected in all type 2b samples (Fig. 4c and e). Carboirite crystals are coarser (from 10 to 100 μm) compared to brunogeierite, argutite, and briartite (5 to 20 μm in size; Fig. 5). Figure 5a–c shows three representative examples of Ge-minerals occurrence characteristic of type 2b mineralization. Two sphalerite grain

size fractions (below and above 100 μm) are considered for the GROD maps (Fig. 5d–f). These maps show that Ge-minerals are only hosted between recrystallized sphalerite grains (< 100 μm, Fig. 5d and e) in areas with low GROD angle, at the contact or between coarse-grained sphalerite crystals or in twin boundaries (Fig. 5f).

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**Fig. 5** Images of Ge-minerals hosted in the interstices between recrystallized sphalerite grains (Cal: calcite; Qz: quartz; Sp: sphalerite). **a** Five brunogeierite crystals from the Arre deposit (in the black circle; BSE image). **b** Carboirite crystals with in sphalerite and calcite from the Pale Bidau deposit (SEM image) **c** Nine Ge-minerals hosted between sphalerite grains from the Anglas deposit. **d–f** EBSD-GROD maps related to grain size for **a**, **b**, and **c**, respectively (step of measurement of 0.5, 3, and 3  $\mu\text{m}$  for the three EBSD maps, respectively)

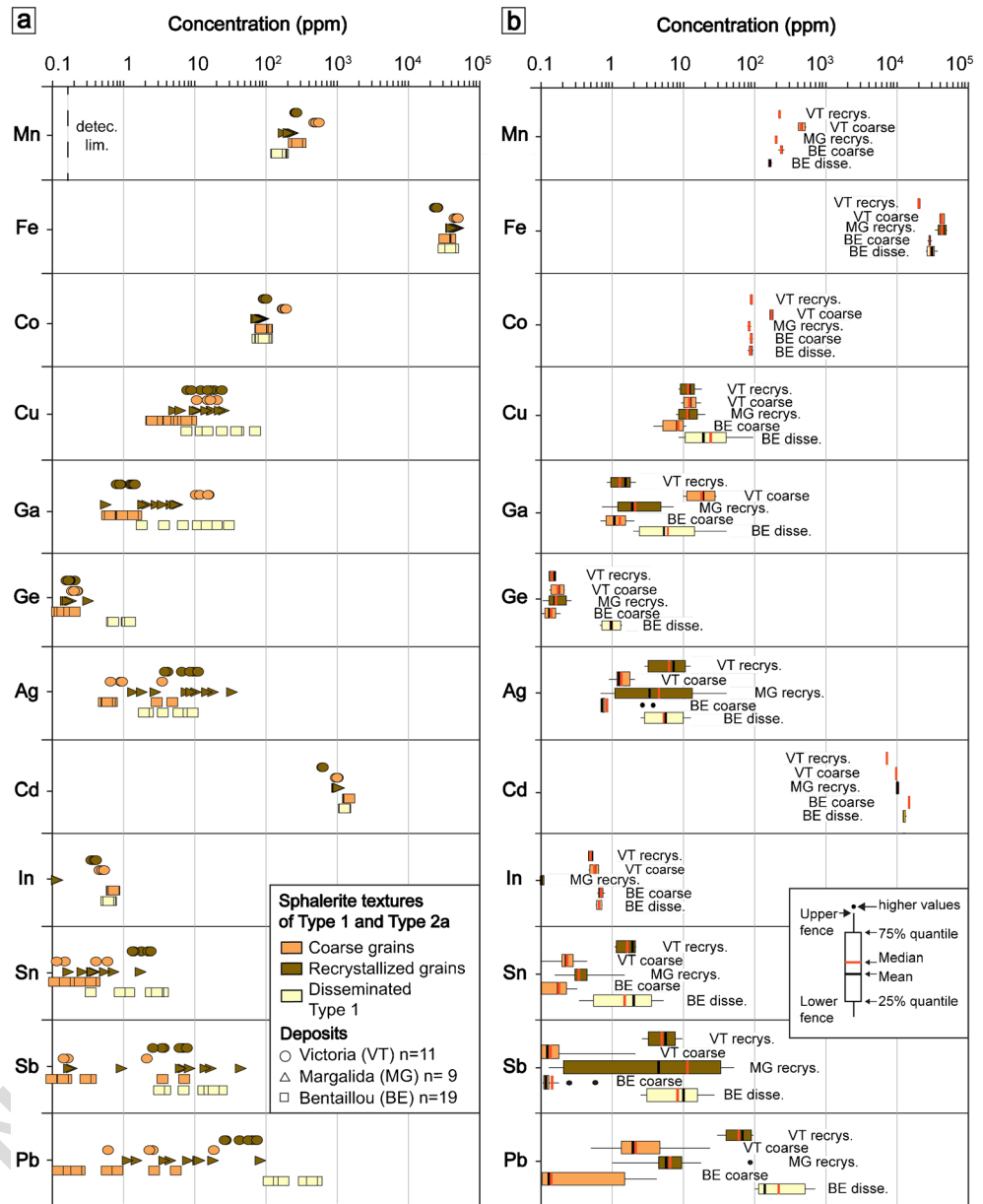


348 **Chemical composition of sphalerite**

349 The distribution of trace elements for type 1, 2a, and 2b mineralizations is plotted in the Figs. 6 and 7 (see dataset in ESM  
 350 1). The main characteristic of type 1 and type 2a sphalerite mineralizations is the small amount of Ge, mostly below  
 351 1 ppm (Fig. 6). In type 1 disseminated grains from Bentaillou, Fe median content is  $2.5 \pm 0.2$  ppm, and the concentrations of Cu and Ga are low with median values of  
 352  $24 \pm 22$  ppm and  $12 \pm 1$  ppm, respectively (Fig. 6). Variations in concentration are relatively large in Cu, Ga,  
 353 Ag, Sn, Sb, and Pb compared to Fe, Co, Ag, or Cd with only minor disparities (Fig. 6).  
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In type 2a, Fe median content is higher than that in type 1, with median value of  $5.4 \pm 0.5$  ppm. Copper and Ga contents are generally low with values below 70 and 30 ppm and median contents of  $11 \pm 13$  ppm and  $1.4 \pm 6$  ppm, respectively (Fig. 6). Recrystallized grains in Victoria type 2a mineralization show lower median contents in Mn, Fe, Co, Ga, and Cd but higher median values in Ag, Pb, Sb, and Sn, compared to coarse grains in the same sample from Victoria (Fig. 6; analyzed spot locations are reported in Fig. 3). Recrystallized grains from Victoria and Margalida have similar Mn, Co, and Cu contents (Fig. 6) but Fe and Cd median values are distinct with  $2.6 \pm 0.1$  wt% and  $952 \pm 20$  ppm for

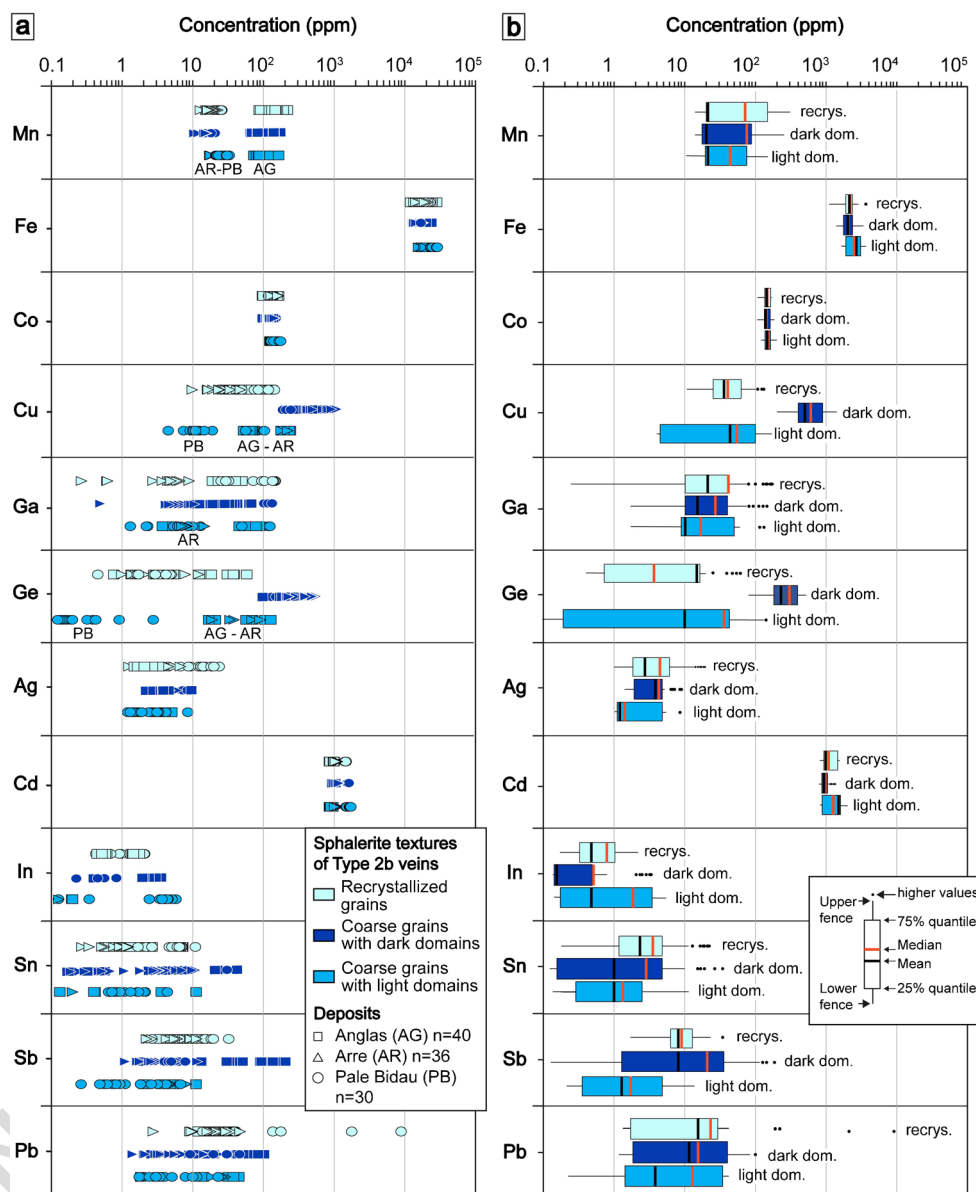
**Fig. 6** LA-ICP-MS data for type 1 and 2a sphalerite, showing trace element concentration in three different textures and for the Bentailou, Victoria, and Margalida deposits (dataset in ESM 1). **a** Individual analyses. **b** Box plots



373 Victoria recrystallized grains and  $5.0 \pm 0.4$  wt% and  
 374  $1946 \pm 42$  ppm for Margalida recrystallized grains (Fig.  
 375 6). Silver, Sn, Sb, and Pb concentrations are similar be-  
 376 tween Victoria and Bentailou coarse grains compared to  
 377 Mn, Co, Cu, Ga, and Cd contents that show large varia-  
 378 tions (Fig. 6). For Bentailou coarse grains, median  
 379 values are  $282 \pm 19$  ppm for Mn,  $3.8 \pm 0.2$  wt% for  
 380 Fe,  $94 \pm 7$  ppm for Co,  $1 \pm 0.3$  ppm for Ga, and  
 381  $2246 \pm 35$  ppm for Cd. Manganese content is generally  
 382 high in Victoria and Bentailou coarse grains (Fig. 6)  
 383 with median values of  $289 \pm 100$  ppm. Cobalt content

is high in Victoria coarse grains with a median value of  
 384  $172 \pm 10$  ppm compared to the grains analyzed in other  
 385 textural position that yield a median value of  
 386  $89 \pm 8$  ppm. Cadmium is highly variable according to  
 387 deposit and texture. Recrystallized Victoria coarse grains  
 388 show the lowest contents with a median value of  
 389  $956 \pm 20$  ppm (Fig. 6). Victoria coarse grains present  
 390 higher Cd content with  $1504 \pm 28$  ppm. But recrystal-  
 391 lized grains from Margalida contain similar Cd values  
 392 with median contents of  $1557 \pm 37$  ppm. Indium content  
 393 is generally below detection limit, when detected the  
 394

**Fig. 7** LA-ICP-MS data for type 2b vein sphalerite, showing trace element concentration in three different textures and for the Arre, Anglas, and Pale Bidau deposits (dataset in ESM 1). **a** Individual analyses. **b** Box plots



395 median value is  $0.8 \pm 0.4$  ppm. Silver, Sn, Sb, and Pb  
 396 contents are generally higher in recrystallized grains (and  
 397 in type 1 disseminated crystals) than in coarse grains  
 398 (Fig. 6). In addition, Ag contents are relatively low with  
 399 total median value of  $7 \pm 3$  ppm but locally, Ag can reach  
 400 43 ppm in Margalida sphalerite (Fig. 6). The same range  
 401 of concentrations is observed for Sb, with median value  
 402 of  $7 \pm 2$  ppm with contents up to  $45 \pm 15$  ppm. Tin  
 403 content is low with a median value of  $1 \pm 0.2$  ppm.  
 404 Lead is below 100 ppm for most of the studied sphalerite  
 405 types except for type 1 sphalerite which shows higher  
 406 content with a median value of  $267 \pm 37$  ppm.

In type 2b, Fe content ranges from 1.3 to 5 wt% Fe  
 but no systematic difference is observed between de-  
 posits or textures (Fig. 7). In Pale Bidau, a progressive  
 zonation in color is observed (Fig. 4a and b), and high  
 Fe contents are reported in dark brown sphalerite zones  
 with values up to 5 wt% Fe. High Mn median values are  
 reported for Anglas ( $151 \pm 10$  ppm), comparatively to  
 Pale Bidau and Arre ( $24 \pm 4$  ppm and  $18 \pm 2$  ppm, re-  
 spectively). Conversely, low median Cd values are pres-  
 ent in Anglas ( $970 \pm 38$  ppm) and higher median values  
 for Pale Bidau and Arre ( $1500 \pm 75$  ppm and  
 $1110 \pm 43$  ppm, respectively). No correlation between

419 grain size or color and the contents in Fe, Mn, or Cd has  
 420 been established. Cobalt content is homogeneous be-  
 421 tween the three textures (Fig. 7) with a median value  
 422 of  $143 \pm 11$  ppm. Low In content is measured in these  
 423 sphalerite types reaching a maximum of 6.2 ppm (Fig. 7)  
 424 and median value below 1 ppm. Indium content is slight-  
 425 ly higher light coarse grains from Pale Bidau with a  
 426 median value of  $4.1 \pm 0.2$  ppm.

427 Gallium content is generally below 100 ppm in the sphal-  
 428 erite samples (Fig. 7) but exhibits relative large dispersion in  
 429 concentrations between 0.3 and 156 ppm Ga which is not  
 430 clearly related either to the type of grain or the deposit.  
 431 Silver, Sn, Sb, and Pb contents are commonly below  
 432 100 ppm. Some Pb-(Sb-Sn-Ag) micrometric inclusions are  
 433 recognized in LA-ICP-MS spectra (ESM 2) preferentially in  
 434 recrystallized domains with Pb values reaching up to  
 435 9420 ppm. Except for the presence of micro-inclusions, no  
 436 clear difference between textures (Fig. 7) and deposits can  
 437 be defined.

438 Germanium and Cu contents show generally large varia-  
 439 tions from 102 to 580 ppm for Ge and from 209 to 1265 ppm  
 440 for Cu. These contents correlate with the type of texture (Fig.  
 441 4) and are detailed below.

442 In dark domains of coarser grains, Ge and Cu are typically  
 443 high in the three deposits with median value of  $290 \pm 19$  ppm  
 444 and  $610 \pm 61$  ppm, respectively (Fig. 7). In Pale Bidau, only  
 445 few dark domain relicts ( $n = 4$ ) are reported and analyzed with  
 446 median values of  $152 \pm 20$  ppm for Ge and  $233 \pm 45$  ppm for  
 447 Cu. Arre samples show the highest Ge and Cu contents with  
 448 median contents of  $433 \pm 21$  ppm and  $1012 \pm 75$  ppm,  
 449 respectively.

450 In light domains of coarse grains, Ge and Cu contents are  
 451 lower with median values of  $20 \pm 2$  and  $60 \pm 8$  ppm, respec-  
 452 tively (Fig. 7). Pale Bidau shows the lowest median contents,  
 453 with  $0.7 \pm 0.1$  ppm for Ge and  $29 \pm 4.5$  ppm for Cu compared  
 454 to Arre and Anglas which show median contents of respec-  
 455 tively  $38 \pm 1$  and  $61 \pm 3$  ppm for Ge, and  $102 \pm 7$  and  $191$   
 456  $\pm 13$  ppm for Cu.

457 In recrystallized grains, Ge and Cu are systematically low  
 458 like in light domains of coarse grains, with median contents of  
 459  $4.3 \pm 1$  ppm and  $49 \pm 10$  ppm, respectively (Fig. 7). In Pale  
 460 Bidau, recrystallized grains may contain similar or larger en-  
 461 richment in Ge and Cu than in light color domains of coarse  
 462 grains, with respectively  $4.1 \pm 0.5$  ppm and  $102 \pm 19$  ppm.

463 **Spatial distribution of trace elements in sphalerite**

464 Figure 8 shows Ge, Cu, and Ga spatial distribution obtained  
 465 from LIBS mapping of Arre type 2b sphalerite. Sphalerite is  
 466 zoned in color in transmitted-light (Fig. 8a), correlating with

the concentration of these trace elements. Germanium and Cu  
 contents are heterogeneous in sphalerite, with patchy zoning,  
 and locally oscillatory zoning (Fig. 8) with numerous Ge- and/  
 or Cu-bearing minerals (Fig. 8b and c), some of them with Fe  
 correspond to briartite  $\text{GeCu}_2(\text{Fe}, \text{Zn})\text{S}_4$  (ESM 2). Localized  
 Ge-Cu minerals are preferentially found in sphalerite Ge-Cu-  
 poor domains (ESM 2). Nonetheless, some of them occur in  
 Ge and Cu-rich dark domains and are sub-parallel to  $\text{S}_2$  cleav-  
 age (Fig. 8b and c).

Mass-balance calculations are performed, based on LIBS  
 mapping (see dataset in ESM 1). The bulk Ge concentration  
 hosted in the Ge-rich minerals is 4.72 wt% Ge, based on  
 25 wt% Ge. Light and dark domains present 0.1 and  
 2.07 wt% Ge, respectively, considering Ge-poor and Ge-rich  
 sphalerite with 20 and 400 ppm Ge, respectively. Germanium  
 mass fraction is two times higher in Ge minerals than in sphal-  
 erite. The total Ge mass is equivalent to a sphalerite with  
 690 ppm Ge uniformly distributed in the structure without  
 Ge minerals.

Gallium in sphalerite shows zoned distribution on LIBS  
 maps. Gallium-rich areas are located in dark domains in trans-  
 mitted light, correlating with relatively high Cu and Ge con-  
 tents (Fig. 8d and ESM 2). Gallium-bearing mineral phases  
 have not been detected. Other elements such as Fe and Cd  
 show a homogeneous distribution in sphalerite (ESM 2).

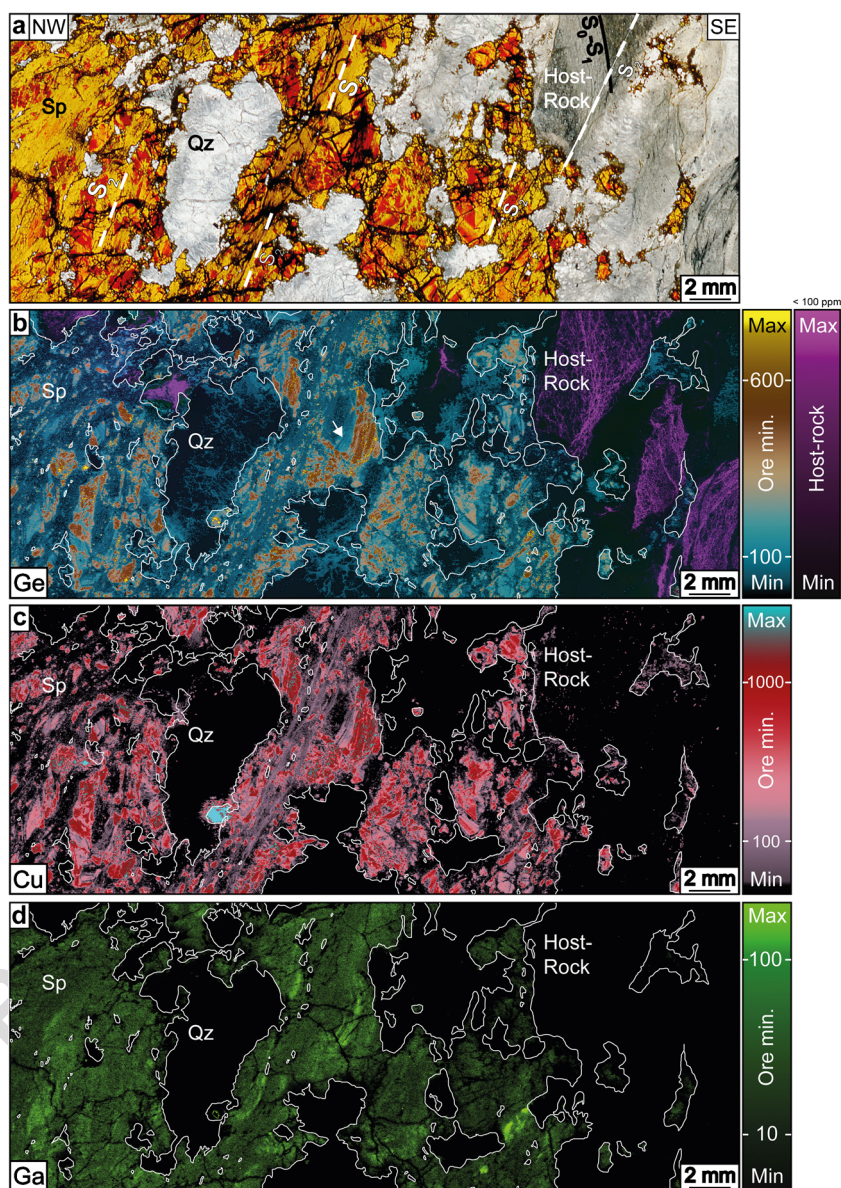
Trace element distribution in quartz spatially associated  
 with sphalerite is reported in Fig. 8. Several areas in quartz  
 show enrichment in Ge, up to  $\sim 75$  ppm (Fig. 8b). Copper and  
 Ga have not been detected in quartz (Fig. 8c and d). In the host  
 rock, a few Cu-bearing micrometer size grains are identified,  
 and Ge is detected in structures parallel to  $\text{S}_0$ - $\text{S}_1$  or  $\text{S}_2$  (Fig. 8b)  
 and correlate with the higher Al contents (ESM 2), which  
 correspond to muscovite.

**Discussion**

**Substitution mechanisms of rare metals in sphalerite**

The mechanism of Ge incorporation in sphalerite has been  
 studied by Cook et al. (2009b) who deduced from the  
 apparent lack of correlation with other trace elements that  
 Ge could be present in a divalent form and substitute for  
 Zn in the sphalerite structure ( $\text{Zn}^{2+} \leftrightarrow \text{Ge}^{2+}$ ). Later, Cook  
 et al. (2015) reported a XANES study performed on Tres  
 Maria Ge-Fe rich acicular sphalerite, demonstrating  $\text{Ge}^{4+}$   
 in sphalerite and proposed substitution of  $\text{Ge}^{4+}$  and a vac-  
 ancancy for  $\text{Zn}^{2+}$  or  $\text{Fe}^{2+}$  (i.e.,  $2\text{Zn}^{2+} \leftrightarrow \text{Ge}^{4+} + []$ ). In  
 Central and East Tennessee, Bonnet et al. (2017) showed  
 $\text{Ge}^{2+}$  and  $\text{Ge}^{4+}$  in the same sphalerite crystal, which was

**Fig. 8** LIBS mapping on Arre type 2b (abbreviations: Qz: quartz; Sp: sphalerite). **a** Microphotograph (thick section, transmitted-light) of Arre sphalerite associated to quartz and calc-schist host-rock. **b** Ge map in sphalerite, quartz, and host-rock. Ge is also shown in purple color in the host rock (calc-schist) because it is measured on a different spectral line due to Al interferences. White arrow indicates specific Ge zones. **c** Cu map in sphalerite, quartz, and host-rock. **d** Ga map in sphalerite, quartz, and host-rock

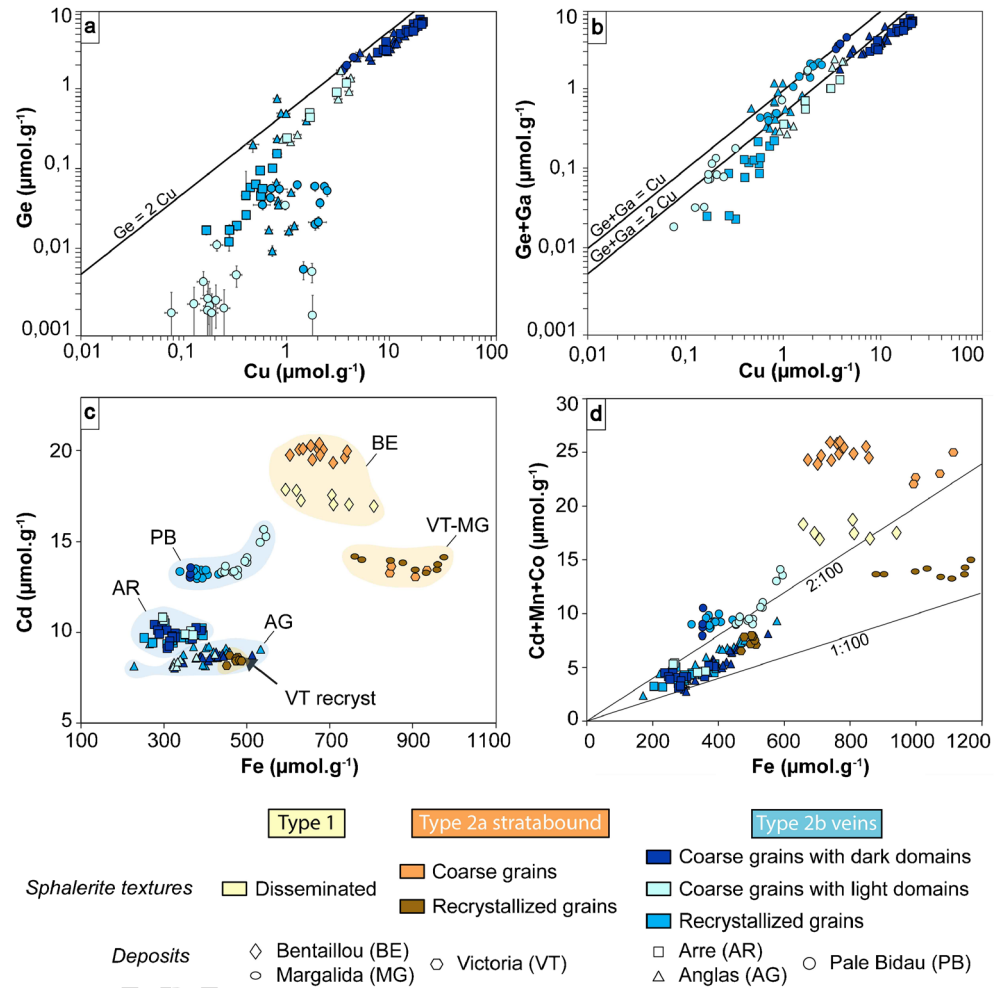


513 interpreted as due to a difference in  $S_2$  and  $O_2$  fugacities. 514 Bauer et al. (2018) demonstrated a coupled substitution 515 between  $Ge^{4+}$  and  $Ag^+$  in low-temperature ( $186 \pm 36$  °C) 516 Ge-rich sphalerite. Johan (1988) suggested a coupled substitution 517 between tetravalent Ge and combination of monovalent and divalent Cu (i.e.,  $4Zn^{2+} \leftrightarrow 2Cu^+ + Cu^{2+} + Ge^{4+}$ ) on low-temperature Ge- and Cu-rich sphalerite 518 from Saint-Salvy. Belissont et al. (2016)  $\mu$ -XANES study 519 on the same sphalerite confirmed the exclusive occurrence 520 of  $Ge^{4+}$  in sphalerite, showing correlation with monovalent 521  $Cu^+$ , supporting the hypothesis of a coupled substitution 522 mechanism involving monovalent copper. This substitution 523  $3Zn^{2+} \leftrightarrow 2Cu^+ + Ge^{4+}$  is consistent with the PAZ 524 525

sphalerite  $2Cu-Ge$  correlation in Fig. 9a. Coarse grains 526 follow this substitution mechanism; however, the recrystallized 527 grains as well as some of the coarse grains with light domains 528 do not plot along the correlation line. For these two Ge-poor 529 domains, such a deviation to the regression line may be explained 530 by the incorporation of Cu coupled to an additional substitution 531 involving Ga (Fig. 9b). Gallium in sphalerite is considered to be 532 trivalent (Cook et al. 2009b; George et al. 2016; Wei et al. 2018) 533 and its incorporation occurs following the coupled substitution 534  $2Zn^{2+} \leftrightarrow Cu^+ + Ga^{3+}$ . 535 536

Divalent cations such as  $Cd^{2+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ , or  $Fe^{2+}$  are 537 incorporated by direct substitution with  $Zn^{2+}$  ( $X^{2+} \leftrightarrow$  538

**Fig. 9** Content of elements for type 1, 2a, and 2b sphalerite. In coarse grains within dark domains, analyses are close to the Ge–2Cu line. **a** Ge vs Cu contents. Recrystallized grains and light domains in the coarse grains do not lie on the correlation line. Pale Bidau coarse grains within light domains contain very low Ge contents. **b** Ge + Ga vs Cu contents. All the points lie closely to the substitution Ge + Ga=1Cu or 2Cu depending on the dominant element in the sphalerite lattice (Ge or Ga). **c** Cd vs Fe contents. Note that each deposit forms a cluster. Recrystallized grain concentrations from Victoria deposit are close to Anglas deposit. **d** Cd + Mn + Co vs Fe contents. Note the correlated enrichment between Cd + Mn + Co and Fe contents. Recrystallized grains recompositions from Victoria deposit are close to Anglas deposit

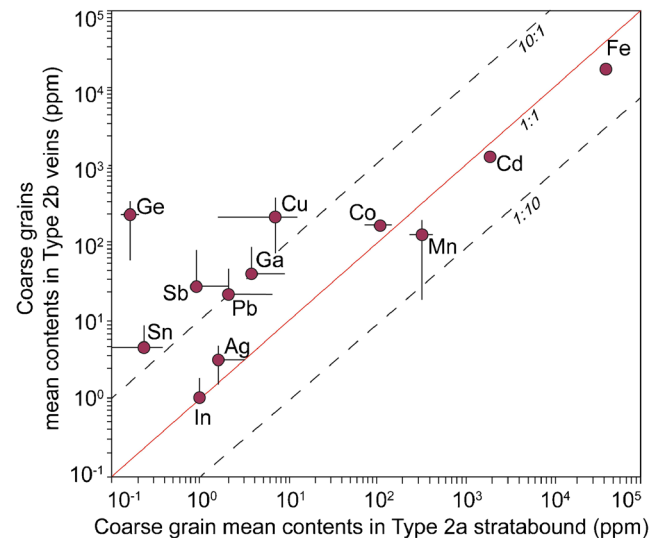


539  $Zn^{2+}$ , Cook et al. 2009b; George et al. 2016). No clear  
 540 correlation is observed between  $Cd^{2+}$  and  $Fe^{2+}$  (Fig. 9c),  
 541 but the Cd-Fe values are mainly varying according to the  
 542 deposit, indicating poor mobility during vein recrystalliza-  
 543 tion. In Fig. 9d, Fe is significantly correlated with Cd+  
 544 Mn+Co at low values, which attests for their coupled in-  
 545 corporation in sphalerite.

**Relationship between sphalerite texture, chemical composition, and formation temperature**

548 Crystallization temperature of vein assemblages is diffi-  
 549 cult to assess, but we use relative field chronology to  
 550 place vein formation in the regional tectonometamorphic  
 551 framework.  $M_1$  peak is estimated at 580 °C and  
 552 0.55 GPa, and  $M_2$  peak at 525 °C and 0.2 GPa  
 553 (Mezger and Passchier 2003; Mezger et al. 2004). The  
 554 three sphalerite mineralization types show significant  
 555 differences in trace element signatures. Types 1 and 2a  
 556 have low Ge content (<0.5 ppm), as well as Cu, Ga,  
 557 and Ag, Sb, Sn, Pb but higher Fe, Mn, and Cd contents  
 558 (Fig. 10). Type 1 disseminated mineralization from

Bentailou is considered pre-metamorphic and has been 559  
 affected by Variscan  $M_1$  regional and  $M_2$  contact meta- 560  
 morphism (Cugerone et al. 2018b). 561



**Fig. 10** Trace element comparison of coarse sphalerite grains between type 2b and type 2a crystals

562 Type 2a sphalerite from Bentaillou, Victoria, and  
563 Margalida is syn- $M_1$  and prior to  $D_2$  associated with  $F_2$   
564 folds (Fig. 3) and  $M_2$  metamorphism. During metamor-  
565 phism, sphalerite can incorporate Fe, Mn, and Cd and in  
566 a lesser extent Pb, Bi, Ag, Sn, and Sb (Lockington et al.  
567 2014) during static recrystallization. Accordingly, type  
568 2a sphalerite that was statically (coarse-size fraction)  
569 and subsequently dynamically recrystallized (small-size  
570 fraction) in Victoria deposit shows respectively high  
571 and low Fe, Cd, and Mn contents (Figs. 6 and 8c, d).  
572 The geothermometer based on Ga-Ge-In-Mn-Fe concen-  
573 trations in sphalerite lattice (GGIMF, Frenzel et al. 2016)  
574 was applied for type 1 and 2a sphalerite (see dataset in  
575 ESM 1) and yields temperatures below 150 °C.  
576 Sphalerite underwent static recrystallization at tempera-  
577 tures, likely above 400 °C, and in some areas subsequent  
578 dynamic recrystallization, which affect the reliability of  
579 the GGIMF geothermometer (Frenzel et al. 2016), such  
580 that, this temperature is not that of mineralization or  
581 deformation.

582 The chemical composition of type 2b sphalerite from the  
583 Anglas and Arre deposits is heterogeneous. Germanium, Cu,  
584 and locally Ga are enriched in coarse grains with dark do-  
585 mains (Fig. 8) but depleted in recrystallized grains and coarse  
586 crystals with light domains (Cugerone et al. 2020). At Pale  
587 Bidau, no strong chemical zonation is observed in sphalerite,  
588 except some color bands that highlight contrasts in Fe contents  
589 (Cugerone et al. 2018a). However, Ge-poor coarse crystals  
590 can be found (Fig. 4b), the latter being interpreted as inherited  
591 Ge-poor domains.

592 Type 2b mineralization has low Cd and Fe contents.  
593 Variations in Cd content between the Arre-Anglas and  
594 Pale Bidau deposits might be linked to differences in  
595 the fluid source or in the bulk host rock composition.  
596 The Arre and Anglas deposits are hosted by similar  
597 Devonian sequences in the same mining district, contrary  
598 to Pale Bidau which is hosted by Late-Ordovician calc-  
599 schists (Cugerone et al. 2018b, Fig. 1). Cadmium content  
600 in type 2b mineralization is generally not affected by  
601 recrystallization. Nonetheless, type 2a recrystallized and  
602 coarse sphalerite grains from the Victoria deposit present  
603 differences in Cd concentrations, as well as in Fe, Mn,  
604 and Co. Recrystallized grains from Victoria have similar  
605 low Cd-Fe concentrations to type 2b sphalerite from the  
606 Anglas deposit. A likely hypothesis is that type 2b min-  
607 eralization resulted from remobilization of early type 2a  
608 mineralization in  $D_2$  structures, such as Victoria  $F_2$  fold  
609 hinge (Fig. 3). However, this hypothesis is restricted by  
610 the lack of Ge minerals in recrystallized sphalerite and  
611 by the relatively low Ge, Cu, or Ga contents in the type

612 2a mineralization. Late Ge-Cu(-Ga)-rich fluids circulating  
613 in  $S_2$  cleavage plane during type 2b mineralizing event  
614 may have been the main Ge-carrier.

615 If type 2b primary sphalerite had the same chemical  
616 composition as coarse grains, the estimated temperature,  
617 using GGIMF, is about 250 °C, with large variations of  
618  $\pm 50$  °C due to chemical heterogeneity between dark and  
619 light domains. This geothermometer may be applied in  
620 dark domains of the coarse grains, if we consider no  
621 change in composition after the primary mineralizing  
622 stage. However, in light domains, composed of recrystal-  
623 lized grains and some part of the coarse grains, the tem-  
624 perature recorded is inconsistent. Deformation and re-  
625 crystallization of the sphalerite lattice have contributed  
626 to the redistribution of the elements used in GGIMF  
627 thermometry. Germanium-rich veins are commonly  
628 formed at low temperatures, below 200–250 °C (Munoz  
629 et al. 1994; Höll et al. 2007; Belissont et al. 2014;  
630 Frenzel et al. 2016; Bauer et al. 2018). There is no fluid  
631 inclusion study yet for the PAZ mineralization to com-  
632 pare with the GGIMF. Johnson et al. (1996) have inves-  
633 tigated fluid inclusions in the Cierco deposit where Pb-  
634 Zn veins similar to the PAZ type 2b veins appear (Fig.  
635 1b). At Cierco, some Ge-minerals have been identified in  
636 recrystallized sphalerite hosted in Late-Variscan granodi-  
637 orite. This likely indicates that at least a part of the  
638 mineralization, belongs to type 2b (Johnson et al.  
639 1996). Primary or pseudo-secondary fluid inclusion  
640 microthermometry in quartz and sphalerite yield temper-  
641 ature between 150° and 200 °C with salinities between 3  
642 and 29 wt% NaCl equivalent. Pressure is assumed to be  
643 negligible (Johnson et al. 1996). No clear petrographic  
644 relationship or evidences between fluid inclusions and  
645 host-minerals is described and their primary or pseudo-  
646 secondary origins are questionable in a largely deformed  
647 environment.

648 In our samples, pressure-temperature conditions of de-  
649 formation events, which are syn- or post-mineralization,  
650 are difficult to assess. Experimental studies on carboirite  
651 bracket its stability field between 340 and 600 °C and  
652 0.75 to 2 MPa whereas brunogeierite is reported above  
653 510 °C at 2 MPa (Julliot et al. 1987). Quartz crystals  
654 appear only slightly deformed, preserving original cock-  
655 ade textures and no alteration halo is observed along the  
656 vein contacts. Partial recrystallization of the Pyrenean  
657 sphalerite is localized in bands associated to a pro-  
658 nounced cleavage, parallel to the  $S_2$  cleavage of the host  
659 rock (Figs. 4 and 8). Such a partial recrystallization  
660 might occur at temperatures below 400 °C and low pres-  
661 sure in comparison with experimental studies on

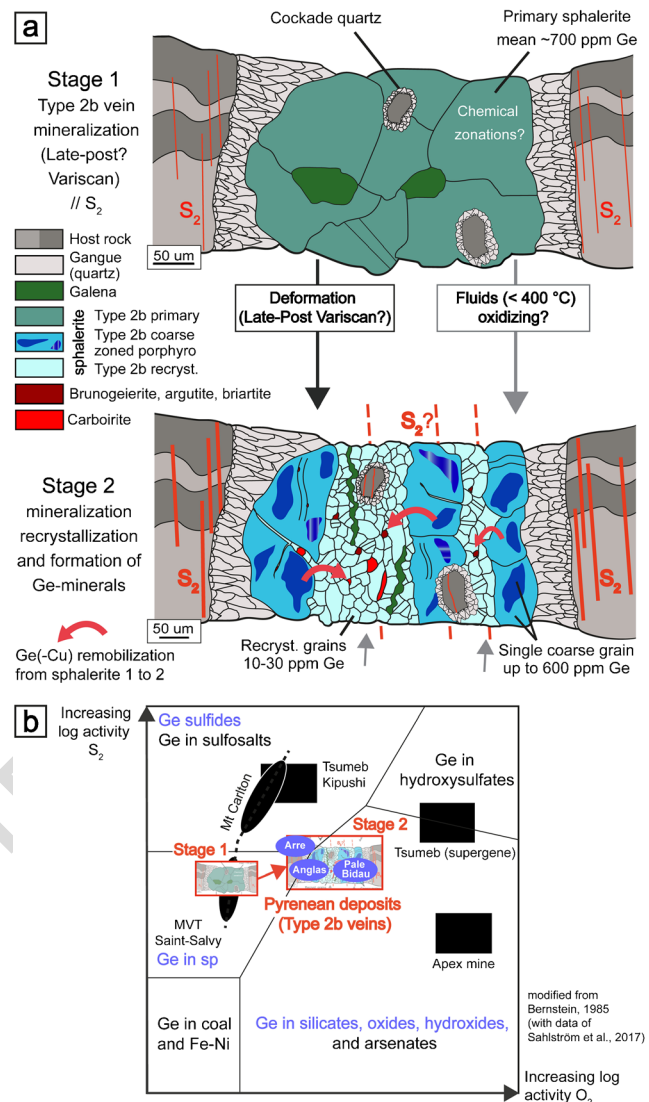


662 sphalerite that evidence dynamic recrystallization of  
 663 sphalerite at low-metamorphic grade (Clark and Kelly  
 664 1973; Siemes and Borges 1979; Couderc et al. 1985;  
 665 Cox 1987). Recrystallization of sphalerite at higher-  
 666 metamorphic grade will result loss of parent grains in  
 667 favor of recrystallized grains.

668 **Mechanisms of formation of accessory minerals**

669 Germanium minerals are exclusively located in type 2b veins  
 670 which have been affected by subgrain rotation recrystalliza-  
 671 tion or in close association with weak structures such as twin  
 672 boundaries (Fig. 8b; Cugerone et al. 2020). Figure 11a shows  
 673 a genetic model of their formation. Stage 1 represents the  
 674 primary type 2b mineralization hosted in an undeformed vein  
 675 and Ge is in the sphalerite lattice. Stage 2 is characterized by  
 676 dynamic recrystallization of sphalerite related to subgrain ro-  
 677 tation mechanism (Cugerone et al. 2020) and the formation of  
 678 Ge-minerals. Ge-minerals are not included in sphalerite and  
 679 are commonly located at sphalerite triple junctions (Fig. 5d  
 680 and f). They rim the grain boundaries of recrystallized sphal-  
 681 erite, which attests of their late formation.

682 Occurrence of intragranular oscillatory zonation (Plümper  
 683 et al. 2012) may inform on diffusion mechanisms (Fig. 8 and  
 684 ESM 2) within sphalerite coarse grains in dark to light do-  
 685 mains. Intragranular diffusion is comprised of different mech-  
 686 anisms such as volume, high diffusivity pathway, or  
 687 dislocation-impurity pair diffusion (Klinger and Rabkin  
 688 1999; Reddy et al. 2007; Plümper et al. 2012; Vukmanovic  
 689 et al. 2014). In addition, hydrothermal fluids might have per-  
 690 colated and extract Ge, Cu, and Ga from the sphalerite lattice  
 691 along grain boundaries, and twin cleavage planes which con-  
 692 stituted nucleation sites as Ge(-Cu) minerals are abundant in  
 693 such locations (Fig. 5). In hydrothermal fluids, Ge is  
 694 transported as a Ge(OH)<sub>4</sub> complex, and its solubility increases  
 695 with temperature (up to 400 °C; Pokrovski and Schott 1998;  
 696 Pokrovski et al. 2005). In the Arre deposit, direct correlation  
 697 between Ge and Cu in sphalerite lattice and in accessory min-  
 698 erals (briartite; Fig. 8b and c) attests to the similar behavior of  
 699 these two elements during remobilization. It could be linked to  
 700 similar ionic radius (Shannon 1976) or specific conditions  
 701 enhancing the extraction and coupled incorporation in acces-  
 702 sory phases. In the Pale Bidau and Anglas deposits (Fig. 4a, b  
 703 and e, f), Ge-minerals such as carboirite and brunogeierite do  
 704 not contain high Cu contents which may indicate possible  
 705 differences in Ge and Cu behavior. Gallium is only found in  
 706 coarse grains (< 100 ppm Ga), mostly correlated to Ge- and  
 707 Cu-rich areas in the sphalerite lattice (Fig. 8), but no Ga en-  
 708 richment occurs in Ga-bearing phases which may be due to  
 709 loss of this metal or to low primary content in sphalerite (Fig.



**Fig. 11** a Two stage genetic model of the formation of Ge-minerals and sphalerite textures and chemical composition in type 2b Pb-Zn mineralization. Stage 1 represents the mineralization before D<sub>2</sub>/M<sub>2</sub> Variscan deformation. Stage 2 is the mineralization after deformation. b Behavior of Ge in different geologic environments and minerals according to fO<sub>2</sub> and fS<sub>2</sub> for the two type 2b stage described in a. Experimental data were acquired between 27 and 327 °C (300 to 600 K) and 0.1 MPa (modified from Bernstein 1985 with values of Sahlström et al. 2017). Stage 2 is plots in three different fields according to the deposit: sulfide, sphalerite, and oxide fields. The Arre deposit is restricted to the “Ge-sulfides” field due to abundance of briartite and rare carboirite and brunogeierite. The Anglas and Pale Bidau deposits contain both carboirite and brunogeierite but briartite is rare. Germanium in sphalerite lattice occurs quasi exclusively in Arre and Anglas. Ge-hosts in blue represent the Ge-carrier in the PAZ Pb-Zn deposits

8). No impact of recrystallization on Cd concentrations is 710  
 detected in sphalerite (ESM 2). Cadmium is mainly 711  
 transported as chloride water complexes in hydrothermal 712

713 fluids ( $20 \leq T \leq 450$  °C; Bazarkina et al. 2010) whereas hydroxyl complexes generally transport Ge ( $[\text{GeOH}]_4$ );  
 714 Pokrovski and Schott 1998) and more rarely Cu ( $[\text{CuOH}]$ );  
 715 Hack and Mavrogenes 2006) at low pressure ( $< 500$  MPa). Hydroxyl complexes might be the main rare metal-bearing  
 716 complexes in hydrothermal fluid during the remobilization  
 717 stage.

720 Fields of stability of Ge in different minerals according to  
 721  $f\text{O}_2$  and  $f\text{S}_2$  indicate potential  $f\text{O}_2$  increase during formation of  
 722 Ge-minerals during the stage 2 (Fig. 11b). Increasing of  $f\text{O}_2$   
 723 may enhance the release of Ge from sphalerite lattice by cir-  
 724 culation of low-temperature fluids which significantly change  
 725 and diversify the Ge-mineral paragenesis (silicates, oxides,  
 726 hydroxides, sulfide). It is important to note that hydrothermal  
 727 fluids responsible for Ge remobilization during deformation  
 728 do not need to be rich in Ge, if we consider a primary sphal-  
 729 erite with uniform  $\sim 700$  ppm Ge content (Fig. 11a and ESM  
 730 1). These arguments allow to demonstrate that a primary Ge-  
 731 rich sphalerite (and other sulfides) impacted by low-grade  
 732 deformation below 400 °C with significant increase in  $f\text{O}_2$   
 733 (Fig. 11b) are potential indicators of Ge-mineral rich deposit.

734 **Comparison with world-class Ge-rich deposits**

735 Type 2b sphalerite vein mineralization from the PAZ present  
 736 chemical and textural similarities with world-class Pb-Zn(-  
 737 Ge) districts. In many SHMS, VMS, or other Pb-Zn(-Cu)  
 738 deposits, metamorphism and deformation may have reworked  
 739 the mineralization (Bodon 1998; Large et al. 2005; Huston  
 740 et al. 2006; Wilkinson 2013; Vikentyev et al. 2016) as shown  
 741 by partly dynamically recrystallized sphalerite at the world  
 742 class George Fisher (Chapman 2004; Murphy 2004) or in  
 743 the Currawong deposits (Bodon and Valenta 1995).  
 744 However, too few chemical analyses of rare metals have been  
 745 performed in these deposits. As an example, Fig. 12 reports a  
 746 compilation of Ge and Cu contents in sphalerite analyzed in  
 747 Pb-Zn(-Cu) deposits worldwide. These deposits are mostly  
 748 related to low-temperature hydrothermal fluids ( $\sim 100$ –  
 749  $250$  °C) with no- or only low-grade deformation. Numerous  
 750 studies on Pb-Zn(-Cu) deposits deformed or metamorphosed  
 751 at higher grades ( $> 400$  °C) do not report significant rare  
 752 metals contents in sphalerite or in accessory Ge-minerals  
 753 and may be related, in some cases, to insufficient textural  
 754 and chemical investigation. Nonetheless, in all Pb-Zn deposits  
 755 affected by high-grade metamorphism, Ge was lost from  
 756 sphalerite during high-grade metamorphic processes ( $>$   
 757  $400$  °C) and recrystallization has potentially concentrated Ge  
 758 in accessory minerals. This assumption is likely for the gran-  
 759 ulite facies Broken Hill deposit (Spry et al. 2008; George et al.  
 760 2016) where Ge is not reported in sphalerite, while the Ga and

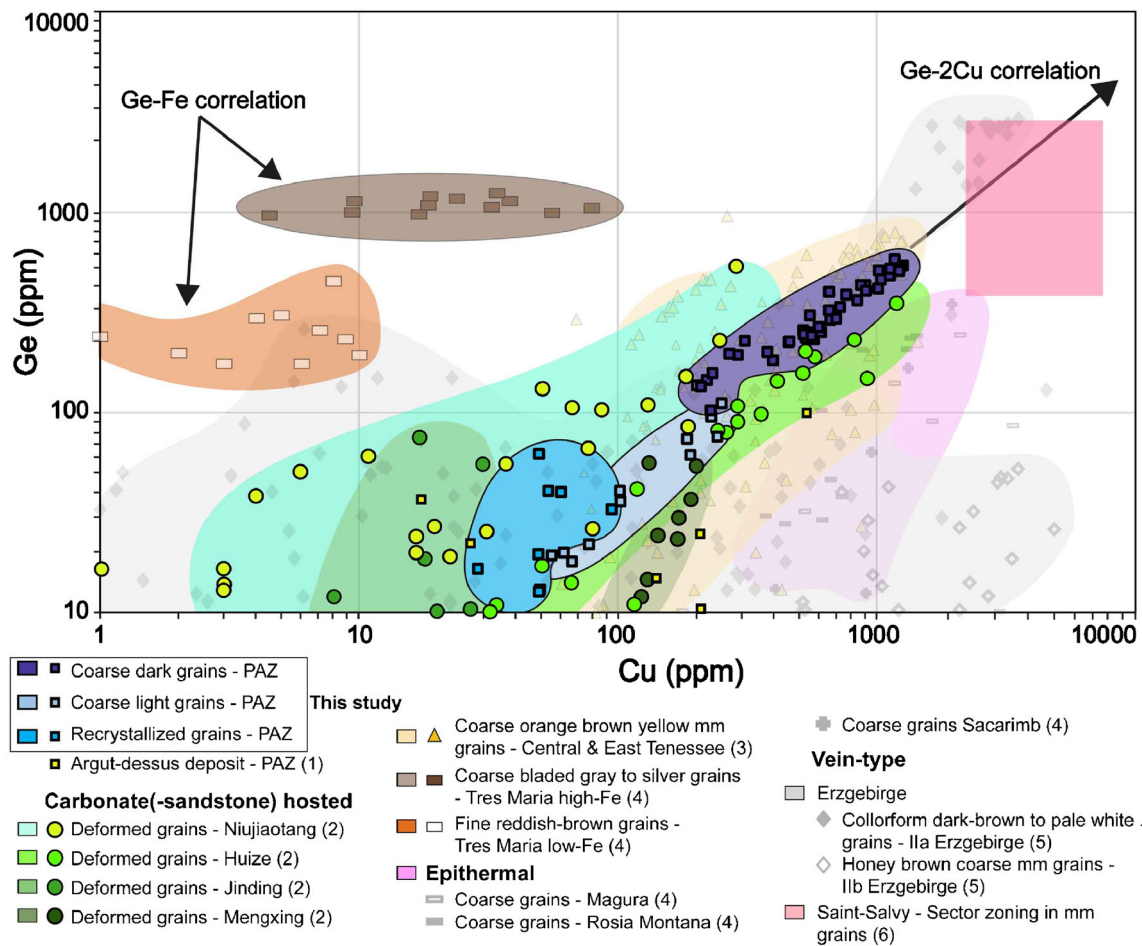
In contents are low, suggesting that these rocks should be  
 761 revisited for accessory minerals rich in rare metals. 762

763 Examples of Ge-rich sphalerite in the Saint-Salvy deposit,  
 764 Montagne Noire (France), in the Erzgebirge district  
 765 (Germany), and in MVT deposits from the Central and East  
 766 Tennessee indicate that Ge is in bands within a single crystal  
 767 (Bonnet 2014; Bauer et al. 2018) or in sector zones (Belissont  
 768 et al. 2014) and may reach up to  $\sim 3000$  ppm Ge (Fig. 12) with  
 769 no Ge minerals reported.

770 In Ge-rich sphalerite, a correlation between Ge and Cu is  
 771 observed except with the Tres Maria deposit where Ge is  
 772 mainly correlated to Fe (Fig. 12). Wurtzite, a non-cubic zinc  
 773 sulfide, is inferred in the zinc ore at Tres Maria (type I miner-  
 774 alization; Cook et al. 2009b, 2015; Saini-Eidukat et al. 2009)  
 775 due to an acicular habit, similar to the wurtzite observed in the  
 776 Kokanee range by Beaudoin (2000).

777 Rare elements (Ge, Ga, In, Cd) are reported in deformed  
 778 sulfide deposits such as Barrigão, a remobilized Cu-rich  
 779 VHMS deposit. Germanium-rich chalcopyrite with heteroge-  
 780 neous contents and Sn-Ge-rich phases (Reiser et al. 2011) are  
 781 probably a result of Ge remobilization during deformation  
 782 (Belissont et al. 2019). In China, Pb-Zn deposits, considered  
 783 to be deformed MVT deposits, contain abundant deformed  
 784 sphalerite mineralization as in Huize (Han et al. 2006),  
 785 Niujiaotang (Ye and Tiegeng 1999; Ye et al. 2012),  
 786 Mengxing (Ye et al. 2011), Jinding (Xue et al. 2007) and  
 787 Lehong (Wei et al. 2019). Germanium and Cu contents from  
 788 these deposits are plotted in Fig. 12 and show that the chemi-  
 789 cal composition of these deposits is similar to that of the PAZ  
 790 deposits, but with a wider dispersion along the Ge-Cu arrow.  
 791 Wei et al. (2019), focusing on the carbonate-hosted Lehong  
 792 deposit, described dark brown Ge-rich sphalerite and light-  
 793 brown Ge-poor sphalerite with Ge content similar to  
 794 Pyrenean vein mineralization with up to 536 ppm and  
 795 118 ppm in dark and light-brown domains, respectively.  
 796 However, no detail on the texture of these sphalerite grains  
 797 is provided, and Ge-minerals are not reported. Another exam-  
 798 ple of deformed sphalerite mineralization is reported by  
 799 Monteiro et al. (2006) in the carbonate-hosted Fagundes Pb-  
 800 Zn deposit, where large variations in Ge (up to 2390 ppm Ge)  
 801 were measured. Based on similarities with our observations,  
 802 this heterogeneity in Ge content may be related to differences  
 803 in sphalerite texture such as type 2b sphalerite in the PAZ.

804 Germanium minerals were reported in the Kipushi-type  
 805 deposits (Emslie 1960; Francotte et al. 1965; Ottemann and  
 806 Nuber 1972). Belissont (2016) describes highly variable Ge  
 807 contents, from 0.2 to 5930 ppm, in sphalerite from the Kipushi  
 808 mine that presents evidence of dynamic recrystallization  
 809 (Hughes 1987). At the Black Angel deposit, Greenland  
 810 (Horn et al. 2018), sphalerite is depleted in Ge and Cu, and



**Fig. 12** Germanium vs copper contents comparison between Pyrenean sphalerite (including Argut-dessus deposit; Cugerone et al. 2018a) and others sphalerite in the world. A lower Ge limit of 10 ppm is set to compare Ge-rich sphalerite. Germanium and copper measurements generally follow the line Ge=2Cu when Ge is enriched in the sphalerite lattice, with the exception of the Tres Maria zinc sulfide. 1—Niujiaotang,

Huize, Jinding, and Mengxing deposits: 2—Ye et al. (2011); 3—Central and East Tennessee deposits: Bonnet (2014); 4—Tres Maria, Magura, Rosia Montana, Sacarimb deposit: Cook et al. (2009a, 2009b); 5—Erzgebirge deposits: Bauer et al. (2018); 6—Saint-Salvy deposit: Belissont et al. (2014)

811 the occurrence of briartite is reported. In the Eastern-Alpine  
 812 base-metal sulfide ores, a LA-ICP-MS study indicates Ge-rich  
 813 mineralization in carbonate-hosted Pb-Zn deposits (Melcher  
 814 and Onuk 2019). The analyses reveal that the Ge content in  
 815 sphalerite is highly variable (from < 1 up to 3700 ppm).  
 816 Moreover, renierite  $(Cu,Zn)_{11}(Ge,As)_2Fe_4S_{16}$  is reported as  
 817 inclusions in bornite from one of these deposits.

818 **Conclusions**

819 Type 2a stratabound mineralization in the PAZ was affected  
 820 by static recrystallization and local dynamic recrystallization  
 821 during  $M_2$  metamorphism. In such mineralization, sphalerite  
 822 is largely depleted in Ge, Cu, and Ga, but generally enriched

823 in Cd. However, Cd content has been found to be variable  
 824 depending on the type of deposit and the texture, with sub-  
 825 stantial depletion during dynamic recrystallization.

826 Type 2b mineralization, interpreted as dynamically recrystallized  
 827 Pb-Zn vein mineralization, shows chemical heterogeneity in  
 828 sphalerite, particularly in terms of Ge and Cu contents,  
 829 which are related to deformation at relatively low-temperature  
 830 (< 400 °C) associated with a possible increase in  $fO_2$ . Gallium  
 831 is depleted in the recrystallized fraction and recrystallization  
 832 does not have significant impact on Cd concentrations. The  
 833 interplay between diffusion and dissolution processes in  
 834 sphalerite may account for large variations in Ge and Cu con-  
 835 tents and the precipitation of Ge minerals.

836 Textural and chemical heterogeneity is frequent in Pb-Zn  
 837 deposits around the world. Understanding the coupling

838 between microstructures and chemistry has major implica-  
 839 tions on evaluating rare element potential of deposits. In  
 840 this study, we show that exploration for rare and critical  
 841 metals (Ge, Ga, In) must integrate micro-textural and in  
 842 situ chemical analyses of sulfides. In cases of dynamic  
 843 recrystallization of sphalerite, we show in situ analysis by  
 844 LA-ICP-MS is not sufficient to provide a good screening of  
 845 critical metals. In such case, these elements will be accu-  
 846 mulated in discrete solid phases that can be found using  
 847 chemical maps. These small minerals can be often respon-  
 848 sible for the high dispersion of bulk and in situ chemical  
 849 data. Dynamic recrystallization of sphalerite appears to be  
 850 widespread in all orogenic fields. The recognition of these  
 851 textures is essential in a first stage to locate enrichment of  
 852 rare metals in specific mineral phases. Numerous deformed  
 853 Pb-Zn(-Cu) such as in SEDEX, MVTs, or Kipushi-type  
 854 deposits should be further explored for their contents of  
 855 rare metal.

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871

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