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# **Cu and Pb–Zn–Ba deposits in the Great Duchy of Luxembourg: role of brines penetrating the basement and place in the post-Variscan tectonic history of Western Europe**

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1 **Cu and Pb-Zn-Ba deposits in the Great Duchy of Luxembourg: role of brines**  
2 **penetrating the basement and place in the post-Variscan tectonic history of**  
3 **Western Europe**

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5  
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33 **Conflicts of interest**  
34

35 All authors declare that they have no conflicts of interest.

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39

40 **Abstract**

41 The Great Duchy of Luxembourg comprises a Variscan basement, part of the Ardennes-Rhenish  
42 fold-and-thrust belt and an unconformable Mesozoic sedimentary cover representative of the eastern  
43 [margin](#) of the Paris Basin. The basement hosts several vein-type ore deposits, which remain  
44 almosundocumented until now, except for a few geological and mineralogical descriptions. The  
45 Stolzembourg Cu-deposit and the Martelange and Soleuvre Pb-Zn-Ba deposits occur at the  
46 boundary of several ore deposit provinces in Belgium and Germany. By coupling the mineralogy of  
47 fracture infillings and P-T-X reconstruction thanks to a detailed fluid inclusion study, the primary  
48 fluid events and associated metal transfer and deposition are described and compared with other  
49 Mesozoic deposits in the nearby areas. At Stolzembourg copper-only deposit, the anisothermal  
50 mixing between two highly saline (a Ca-Na and a Na-only rich end-member) fluids of ca.27 wt %  
51 eq NaCl and low-salinity water resulted in the chalcopyrite-Fe-dolomite deposition. The process  
52 occurred at temperatures ranging from c. 160°C to c.140°C under hydrostatic conditions at a depth  
53 of around 3 km. By contrast, the quartz preceding and following copper deposition recorded a  
54 circulation of lower-temperature brines. The copper fluid event was thus related to a transient heat  
55 advection and brine convection. Such an event is likely the Mid-Cretaceous thermal event detected  
56 at the scale of Western Europe in response to the coeval openings of the Biscaye Bay (to the west)  
57 and Valaisan (to the east) oceanic tracts. This event occurred between 130 and 100 Ma and is  
58 synchronous with a series of ore deposits in Western Europe.

59 Similar to the Ardennes Pb-Zn deposits, the small Pb-Zn showings would probably have been  
60 formed simultaneously in the same conditions. The Hercynian basement in Luxembourg follows a  
61 similar history to other West-European Variscan massifs after peneplanation, particularly the  
62 penetration of brines, probably in part issued from Trias formations, during a series of stages linked  
63 to major Mesozoic geodynamic events.

64

65

66 **Keywords**

67 *fluid inclusion; Luxembourg; Ardennes Rhenish Massif; hydrothermal Cu-Pb-Zn ore deposits;*  
68 *brines*

69

70

## 71 **Introduction**

72

73 In recent years, a great deal of research work was performed on the ore deposits of the Ardennes-  
74 Rhenish Massif (Rheinisches Schiefergebirge), or the Vosges-Black Forest massifs (Fig. 1). Most  
75 of these deposits are considered Mississippi Valley-type deposits formed during the Mesozoic era  
76 and to a lesser extent in the Eocene-Miocene. Numerous mineralogical, fluid inclusion and isotope  
77 data are available (e.g., Dejonghe 1998; Götte and Richter 2003; Baatartsogt et al. 2007; Pfaff et al.  
78 2010; Staude et al. 2011, 2012a; Kirnbauer et al. 2012; Fusswinkel et al. 2013; Walter et al. 2016,  
79 2018b, 2020; Scharrer et al. 2021). The emerging picture is hydrothermal deposits that formed close  
80 to the basement-cover boundary due to repeated mixing events between surficial waters and deeper-  
81 sited calcic brines from the Jurassic to the Miocene, as documented in the French Massif Central to  
82 the west (Cathelineau et al. 2012).

83 Until now, however, the hydrothermal vein-type ore deposits and occurrences of the Grand Duchy  
84 of Luxembourg at the southeastern edge of the Ardennes-Rhenish massif (Fig. 1) remained  
85 undocumented, except from a geological and mineralogical point of view in a few cases (Philippo  
86 and Hanson 2007; Philippo and Krontz 2007; Philippo et al. 2007; Philippo and Hatert 2018). A few  
87 microthermometric results were obtained by Staudt (1977) for both quartz and dolomite, but  
88 unfortunately, without precise identification of their place in the paragenetic sequence.

89 These ore deposits are i) the Pb-Zn occurrences of Allerborn (Longvilly) and Martelange, which are  
90 part of the “Pb-Zn district of the Ardennes” as defined by Dejonghe (1998), ii) some small barite  
91 veins (Bivels, Soleuvre), similar to their counterpart in the Black Forest, and iii) the relatively  
92 uncommon Stolzembourg dominant copper deposit. The Stolzembourg deposit has only minor  
93 equivalents in some Black Forest districts, such as Wiesloch (Pfaff et al. 2010) or the Stavelot Massif  
94 in the Ardennes massif (Hatert 2005). Further comparison is nevertheless, up to now, hindered by a  
95 lack of data on the P-T-X conditions of ore formation.

96 In this paper we intend to get these data and on this basis, to place the Luxembourg deposits in the  
97 timing and geodynamic context of the Mesozoic and Tertiary ore deposition in Western Europe.  
98 Representative samples of Luxembourg deposits and occurrences were thus selected for a fluid  
99 inclusion study and comparisons of fluid chemistry and P-T conditions of fluid circulation with  
100 neighbouring areas.

101

## 102 **Geological setting**

103

104 In the Great Duchy of Luxembourg, the Variscan basement is partially covered by an unconformable  
105 Mesozoic sedimentary cover. The basement is part of the Ardennes-Rhenish Massif fold-and-thrust  
106 belt and mainly outcrops in the northern part of the Duchy (Eisleck). The Mesozoic cover, in the  
107 south (Guttland), is representative of the eastern edge of the Paris Basin, with, however, a small  
108 inlier of the Hunsrück Slate outcropping in the very southeastern corner of the Duchy (Schengen)  
109 (Fig. 1).

110 *The Luxembourg basement* (Konrad and Wachsmut 1973; Bornain 2003; Roth 2003) consists of  
111 Lower Devonian (Pragian-Emsian) siliciclastic metasedimentary rocks deposited in a rift formed  
112 onto the Baltica passive margin. Several thousand meters of turbidites accumulated, with a  
113 maximum in a trough presently represented by the Eifel synclinorium and its western prolongation  
114 in the High-Ardennes Slate Belt (including Eisleck), hereafter denominated as HASB. There, 6000  
115 to 8000 m of siliciclastic sedimentary rocks ( $\leq 4000$  m of Siegenian and  $\leq 4000$  m of Emsian) were  
116 deposited before the Late Devonian-Early Carboniferous carbonates and turbidites. They are only  
117 found nowadays on the northern limb of the Ardennes-Rhenish Massif. Peak metamorphic  
118 conditions (500°C, 400 Mpa) were attained during deep burial under extensional conditions at the  
119 end of the Devonian (Fielitz and Mansuy 1999). Starting in the Namurian (Asturian phase), the  
120 inversion of the rift led to the formation of a Variscan fold-and-thrust belt, with a main frontal thrust  
121 (the Midi-Aachen fault) and several secondary thrusts, such as the Siegen (Fig. 1). As everywhere  
122 in the Variscan belt, post-orogenic extensional tectonic conditions immediately succeeded, at c 270  
123 Ma in the Rhenish Massif (Nierhoff et al. 2011). According to Izart et al. (2016), in the nearby  
124 Lorraine coal basin, the basement exhumation occurred in three stages, each marked by significant  
125 erosion, at the beginning of the Stephanian, in the Late Permian and the Triassic.

126 *The unconformable cover*, as observed in the Luxembourg basin, comprises a thick sequence of the  
127 classical Buntsandstein red beds (~ 170 m), Muschelkalk marls (with gypsum) and carbonates  
128 (~ 180 m), Keuper marls and gypsum (~ 230 m) suite, followed by a thick Liasic pile (~ 650 m) of  
129 marls with intercalations of sandstones (~100 m of Hettangian “Grès du Luxembourg”, at the basis)  
130 and bituminous black shales (~ 150 m of Toarcian, at the top). The remnant of the pile is made by  
131 the ca. 180 m thick Dogger carbonates with formerly mined oolitic ironstones. The thickness of  
132 this cover, estimated at around 1.4 km, is a minimum owing to the Tertiary erosion. Indeed, Late  
133 Jurassic and possibly Early Cretaceous sedimentary rocks were probably present. A past study of a  
134 petroleum drill hole in the Metz area, south of Luxembourg, has revealed that the burial depth of  
135 the Toarcian hanging wall reached 750 m at the end of the Jurassic (Tissot 1967). In Luxembourg,  
136 an additional heap of about 570 m of Late Jurassic sedimentary rocks is likely, bringing the complete  
137 sedimentary cover to about 2 km. Such a thickness is comparable to the 1.9 km one estimated for

138 the Permian -Jurassic cover of the Black Forest (Staude et al. 2012 b). Moreover, in the nearby  
139 Lorraine basin, Izart et al. (2016) document erosion of the Upper Jurassic rocks in two Early  
140 Cretaceous erosion steps during Late Berriasian and Late Aptian. The Ardennes-Rhenish Massif  
141 area was still a source of clastic sedimentary rocks for the nearby basins at the end of the Trias  
142 (Durand 2014) and the beginning of the Lias (Thierry et al. 2014). Then, marine platform  
143 sedimentation (mainly carbonates) took place from the Toarcian to the end of the Malm. The  
144 exposure of the Tithonian-Berriasian boundary would explain the lack of more recent formations  
145 (Thierry et al. 2014). According to Stollhofen et al. (2008), a Muschelkalk cover would, however,  
146 have been present between the Brabant Massif (to the west) and the Rhenan Massif (to the east) in  
147 an N-S corridor, including our study area. Kirnbauer et al. (2012) state, "the thermo-chronological  
148 data suggest that large parts of the Rhenish Massif were covered by Triassic sedimentary rocks".  
149 Indeed, given the proximity to the present-day Mesozoic cover, it seems inescapable that Triassic  
150 and Jurassic sedimentary rocks were laid onto the Eisleck basement. Nevertheless, even admitting  
151 that the subsidence rate in the Ardennes-Rhenish Massif was similar to the nearby Luxembourg  
152 basin during the Middle-Late Jurassic, a thickness of 1 km seems the maximum possible. In the  
153 same way, according to apatite fission-track data (Karg et al. 2005), only several 100 m of  
154 sedimentary rocks covered the eastern Rhenish Massif. There, erosion of the Mesozoic cover did  
155 not occur before the Tertiary, beginning in the latest Oligocene (Ziegler and Dèzes 2007) and being  
156 achieved in the Burdigalian (Hautmann and Lippolt 2000; Kirnbauer et al. 2012).

157

## 158 **Luxembourg copper- deposits and lead-zinc-barite occurrences**

159

### 160 *The Stolzembourg copper deposit*

161 The Cu-bearing veins occur within the Stolzembourg Early Emsian schists as infillings of N150-  
162 170°E fractures roughly perpendicular to the synschistose hecto- to decametric folds (Philippo et al.  
163 2007). Although earlier workers thought there were up to seven distinct veins in the vicinity of the  
164 Stolzembourg mine, careful recent mapping and geophysical exploration suggest that there is only  
165 one vein, dilacerated by a series of ENE-WSW striking normal faults with a ~ 40° N dip (Philippo  
166 et al. 2007).

167 The Stolzembourg mine was active from 1717 to 1944, and, from the few production data at hand,  
168 more than 250 t Cu were extracted. Antun (1968) states that copper-bearing wastes contain gold (8  
169 g.t<sup>-1</sup>Au). Gold, however, could not be observed in the studied samples.

170 From old mine documents, the copper was mainly contained in subvertical and more or less  
171 interconnected ore shoots in a mineralised NNW-trending fault dipping 60° to 65° to the W, which

172 is thought to have a dextral component. Within the ore-shoots, several 10 cm-sized vein-like  
173 chalcopyrite masses (up to 40-50 cm thick) are embedded in a dolomite (so-called “ankerite”)  
174 matrix. The grades may reach 14 to 20 wt % Cu (up to 25%, and even 30% in the 18<sup>th</sup> and 19<sup>th</sup>  
175 centuries) (Antun 1968, Philippo et al. 2007). In contrast, in the intervening areas, only mm to cm-  
176 size pods of chalcopyrite are seen within the “ankerite”, forming a disseminated ore grading around  
177 2.2 wt % Cu. This ore is called “red ore” due to the thin coatings of hematite associated with quartz  
178 and “ankerite”. Only the ore-shoots were mined, and the remaining disseminated ore is thought to  
179 represent a significant resource of more than 100 kt Cu, according to the speculations of Antun  
180 (1968).

181

### 182 *The lead–zinc-barite occurrences*

183 A few uneconomic Zn-Pb vein-type occurrences occur in Luxembourg (Allerborn, Longvilly,  
184 Martelange (Fig. 1). They are part of a small district hosted in the Lower Devonian of the High-  
185 Ardennes Slate Belt, so-called the Pb-Zn district of the Ardennes (Dejonghe 1998), except for the  
186 Soleuvre deposit, which is hosted in the Bajocian cover. In Belgium, the richest veins are located in  
187 the low-grade domains of the belt (Rocheux-Oneux: 36.5 kt Zn and 27.7 kt Pb) (Dejonghe 1998).

188

### 189 **Materials and methods**

190

#### 191 *Samples*

192 Around thirteen samples come partly from the Luxembourg Museum of Natural History (LMNH)  
193 collections but also from new sampling, including nine samples from the Stolzembourg copper  
194 deposit (old addit), three samples from the Allerborn and Martelange Pb-Zn deposit (tailings), and  
195 one barite from Soleuvre quarry.

196

#### 197 *Micro-XRF mapping*

198 A Bruker-Nano M4 Tornado instrument was used to get chemical maps at the sample scale. This  
199 system has an Rh X-ray tube with a Be side window and polycapillary optics giving an X-ray beam  
200 with a diameter of 25-30  $\mu\text{m}$  on the sample. The X-ray tube was operated at 50 kV and 200  $\mu\text{A}$  and  
201 a 2 kPa vacuum. X-ray fluorescence was detected by a 30 mm<sup>2</sup> xflash® SDD with an energy  
202 resolution of <135 eV at 250,000 cps. Main elements such as Si, Ca, Fe, S, Cu and Ba were mapped,  
203 and composite chemical images were generated.

204

#### 205 *Scanning Electron microscopy*

206 After petrographic examination of the thin sections, an SEM study was conducted using a JEOL  
207 FEG7600 apparatus 7600F (hot cathode) equipped with an Oxford Instruments SDD-type EDS  
208 spectrometer to get BSE images and major element EDS analysis for the Stolzenbourg dolomite.

209

### 210 *ICP-MS*

211 Rare Earth Element (REE) contents of dolomite were determined using laser ablation inductively  
212 coupled plasma mass spectrometry (LA-ICPMS) at the GeoRessources laboratory. Fourteen REEs  
213 (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were analysed for each experiment.  
214 All data were acquired as raw counts (cps) using the time-resolved mode. For each analysis (external  
215 standard and unknown sample), the background was measured before ablation for 20 s, and its return  
216 to its initial value was checked before ablating a new zone. Signal intensity integration of 14 REE  
217 masses was carried out during the plateau regime. Signal acquisition of the sample was stopped after  
218 150 pulses (30 s at 5 Hz). The spot size was 60  $\mu\text{m}$ , and the acquisition time was 80 s, including 20  
219 s background acquisition and 30 s ablation. Reference materials are the certified glass standards  
220 NIST610 and NIST612 (Pearce et al., 1997). As determined by SEM-EDS, we used Mg as an  
221 internal standard (Mg). Data reduction was carried out following the standard methods of Longerich  
222 et al. (1996).

223

### 224 *Microthermometry*

225 Doubly polished thick sections (100  $\mu\text{m}$ ) were produced from representative samples across a cross-  
226 section through the central Stolzenbourg vein following the paragenetic sequence to determine the  
227 chronological sequence of fluid inclusion assemblages (FIA; Goldstein and Reynolds, 1994) by  
228 optical microscopy. Fluid inclusions (FI) could be studied in dolomite and quartz by  
229 microthermometry using a Linkam THSMG600 heating-freezing stage and an Olympus BX51  
230 optical microscope with a magnification of up to x800 (objective x80, ocular x10). The accuracy  
231 and precision of the measurements were assured by repetitive calibration of the stage. Calibration  
232 was made using nearly pure  $\text{CO}_2$  natural FI ( $T_{\text{m CO}_2}$  at  $-56.6^\circ\text{C}$ , using Camperio quartz, Switzerland)  
233 and synthetic aqueous FI of known ice melting temperatures ( $T_{\text{m ice}}$  at  $-21.2^\circ\text{C}$  and  $0.0^\circ\text{C}$ ). The  
234 accuracy is around  $\pm 0.2^\circ\text{C}$  for the low-temperature measurements. At high temperatures, the  
235 heating rate was  $5^\circ$  to  $10^\circ\text{C}\cdot\text{min}^{-1}$  up to temperatures close to  $T_{\text{h}}$  and then reduced to  $2^\circ\text{C}\cdot\text{min}^{-1}$ ,  
236 yielding an accuracy of around  $\pm 1^\circ\text{C}$ . As inclusions in calcite and sulphates quickly leak, severe  
237 precautions are needed (Ulrich and Bodnar, 1988) and were taken in the present work: (i) low-  
238 temperature glue was used to impregnate the samples before polishing, (ii) the largest inclusions  
239 were avoided, (iii) the inclusions were continuously monitored during the heating, to recognise

240 leakage or stretching, and (iv) freezing experiments were systematically conducted after heating, as  
241 “freeze-stretching” is possible. Also,  $T_h$  measurements were iterated for each inclusion and rejected  
242 if not reproduced at  $\pm 2^\circ\text{C}$ . Bulk salinity and the presence of volatile species were checked using  
243 micro-Raman analysis performed on a DILOR LABRAM Raman spectrometer at the  
244 GeoRessources laboratory (Nancy, France).

245

## 246 **Results**

### 247 ***Stolzembourg***

#### 248 *Field observations*

249 Accessible galleries still allow observing the dolomite-“ankerite” vein system. The carbonates fill  
250 en-echelon tension joints or veins, indicating a normal faulting component (Fig. 2a, b). Matrix-  
251 supported breccias (hydraulic fracturing) are also present, usually parallel to the veins. The main  
252 veins run in the N160°-170° E60°-70°E direction, and local observation of oblique striation at the  
253 fault walls yields a dextral-normal behaviour, as already stated by Mosar (1992).

254 In exploration workings (Fléssen and Riedgerbësch galleries), the copper vein is associated with a  
255 parallel barite vein. A barite vein, without associated copper mineralisation, is known at the close  
256 vicinity of Bivels. There, outcropping veins of the barite system observed along with a road cut  
257 [CR355, GPS coordinates: 81894-113208] display an organisation similar to that at Stolzembourg,  
258 with the main veins running at N170°E and being offset by pull-apart jogs along the N10°-20°E  
259 direction, indicative of a dextral-normal setting.

#### 260 *Observations at the sample scale*

261 At the outcrop and sample scales, both brecciation and repetitive fracture opening and filling are  
262 observed (Fig. 2, 3 and 4). Vein filling starts with quartz, typically featuring a comb texture (Fig.  
263 4c), followed by thick dolomite. Late quartz (locally known as “diamond quartz”) occupied  
264 incompletely filled, open vugs (Fig. 3b, c).

265 Breccias may either occupy the whole vein or, in the ore shoots, are located in the vein wall rock.  
266 All breccias are matrix-supported, typical of hydraulic fracturing. The clasts are fragments of the  
267 wallrocks, varying in size from a few cm to a few mm, typically reddened (Fig. 3b, 4a). Wallrocks  
268 are typically reddened on distances ranging from several centimetres to metres from the boundary.  
269 Clasts featuring the reddening border are present in the breccias (Fig. 4a), indicating that the  
270 reddening preceded the brecciation.

271 The breccia matrix is formed either by coarse-grained dolomite (Fig. 3b, 4a) or by fine-grained  
272 quartz aggregates reddened by association with hematite (“red ore”) (Fig. 3a).

273 Chalcopyrite is later than dolomite (Fig. 3c, f), which may have been dilacerated (Fig. 4b).

274 Although not observed in present-day accessible galleries, barite was observed in some samples  
275 from the LMNH collections, where barite appears earlier than the quartz-ferroan dolomite  
276 association (Fig. 4d).

### 277 *Paragenetic succession*

278 A synthetic paragenetic succession may be constructed by combining sample-scale and microscopic  
279 observations, excluding supergene associations. Three stages are distinguished (Fig. 5): a first stage  
280 corresponding to the emplacement of the dolomite veins, a main mineralising stage with  
281 chalcopyrite deposition, and a late stage marked by euhedral quartz deposition (so-called “diamond  
282 quartz”). The expression of the different stages varies from one vein to the other: dolomite is the  
283 dominant mineral of the early stage in the Stolzembourg vein, while it is quartz in the Riedgerbësch  
284 occurrence.

285 *The early stage* consists of quartz (Q1 and Q2) and saddle dolomite (Dol1). The first quartz  
286 generation (Q1) occurs as microcrystalline quartz in the breccia matrix. It currently contains fine-  
287 grained hematite (Hm1) and relicts of tiny barite prisms (Fig. 6a), containing up to 5.6 wt % Sr.  
288 Uncommon, small ( $\leq 1 \mu\text{m}$ ) inclusions in Q1 are found by EDS to be mainly composed of Cl, C and  
289 Pb, with minor As and Cu, suggesting that the included mineral is phosgenite  $\text{Pb}_2(\text{CO}_3)\text{Cl}_2$ . Q2  
290 quartz is euhedral and forms overgrowth on Q1 aggregates but comb ribbons at the vein selvages  
291 (Fig. 4c). Dolomite Dol1 (Fig. 7a) usually crystallises onto Q2 quartz but may be directly  
292 overprinting Q1. Pyrite1 preceded the dolomite and occurred at the Q2-Dol1 boundary. A unique  
293 observation shows a complicated history, with a pyrite “nodule” filled with skeletal barite, Dol1 and  
294 pyrite. Most pyrite, however, is found as euhedral crystals within chalcopyrite and could, therefore,  
295 be related to the main ore stage, being a pyrite2. Dolomite Dol1 is saddle dolomite, commonly  
296 exhibiting a plumose texture (Fig. 7b-d). Dol1 is locally internally complex, displaying irregular  
297 zoning patterns under SEM and  $\mu\text{-XRF}$  examination (Fig. 6d). Zoning is caused by slight variations  
298 of the Fe content with compositions varying from  $\text{CaMg}_{0.6}\text{Fe}_{0.3}\text{Mn}_{0.1}(\text{CO}_3)_2$  to  
299  $\text{CaMg}_{0.5}\text{Fe}_{0.4}\text{Mn}_{0.1}(\text{CO}_3)_2$ . As already noted by Filippo et al. (2007), these compositions lie indeed  
300 outside the ankerite field. However, the saddle crystals of Stolzembourg were called “ankerite” for  
301 a long time by successive collectors. According to Filippo et al. (2007), other carbonates (calcite,  
302 siderite) may also be found at Stolzembourg, but their paragenetic position remains obscure.

303 *The main mineralisation stage* followed a renewal of tectonic opening, marked by the second  
304 generation of comb ribbon quartz (Q3), preceding the chalcopyrite deposition in the quartz-rich  
305 portions of the system (Fig. 4c, 6c). The second generation of dolomite (Dol2) is observed,  
306 commonly as mm-size overgrowths on Dol1, and also as small euhedral Dol2 crystals (down to 20-  
307 30  $\mu\text{m}$ ) incorporated into chalcopyrite and found under SEM examination to contain tiny hematite

308 prisms (Hm2, up to 1-5  $\mu\text{m}$ ). Dol2 dolomite is ferroan, although less than Dol1, with a composition  
309  $\text{CaMg}_{0.7}\text{Fe}_{0.3}(\text{CO}_3)_2$  practically devoid of manganese. Philippo et al. (2007) state that rare cubanite,  
310 sporadic galena, and sphalerite are associated with chalcopyrite.

311 The *late stage* is represented by the “diamond quartz” Q4 (Fig. 4c, 7e-f), which displays growth  
312 zoning with internal plumose textures (Fig. 7f). Q3 may be absent, and chalcopyrite expression is  
313 highly reduced, and in such cases, Q4 seems to lie directly on the Dol2 dolomite (Fig. 6e-f).

314  
315 *REE profile of Stolzembourg dolomite*

316 All generations of Stolzembourg dolomite display identical chondrite-normalised REE distribution  
317 patterns with a typical bell-like disposition (Fig. 8). Such MREE-enriched patterns are rarely  
318 encountered in hydrothermal carbonates, except in a few instances, such as the dolomite from U-  
319 deposits found around unconformities in Saskatchewan, Canada (Richard et al., 2010). A few  
320 similar MREE-enriched patterns are presented in Fig. 8, A, some for ankerite from the nearby Black  
321 Forest deposits (Staude et al. 2012a), others more exotic: siderite from cold methane seeps in the  
322 Niger delta (Rongemaille et al. 2011) and calcite from a Carlin-type gold deposit in China  
323 (Shuiyidong: Su et al. 2009), the latter being by far the closest to the Stolzembourg carbonates.

324  
325 *Fluid inclusions study*

326 *FI petrography:* Fluid inclusion assemblages (FIAs) for all petrographic types were interpreted  
327 and classified according to their relative age in the paragenetic sequence. FIs are abundant in  
328 dolomite (Dol1, Dol2) and are primary, as they distribute along crystal growth zones. Studiable  
329 FIAs follow some dolomite growth bands, as shown in Fig. 9a, where they are particularly abundant;  
330 the last growth band of Dol2 is generally devoid of FI (Fig. 9a). In the growth zone, FIs are grouped  
331 as clusters (Fig. 9b). Their morphology is elongated, frequently parallelipedic and their distribution  
332 in dolomite is geometrically controlled by the geometry of the crystal with Fi edges parallel to the  
333 growing face and cleavage (Fig. 9 c and d). FIs are scarce in quartz except in localized clusters of  
334 primary inclusions (Q2, Q4) in some growth zones, as shown in Fig. 9 e. Q1 was not studied as too  
335 microcrystalline. FIs exhibit irregular and angular shapes, as shown in Fig. 9 f; some small-size  
336 healed cracks can be considered pseudo-secondary as they are not transgranular. No evidence of  
337 boiling was observed in the investigated samples.

338 As almost all FIs are primary, the relative chronology of the fluid inclusions follows the succession  
339 of the paragenetic sequence: quartz 2, dolomite (mostly II) characterized by large crystals, and  
340 euhedral quartz Q4.

341 *Microthermometry:* Most FIs are small ( $\leq 10 \mu\text{m}$ ), thus making difficult the observation of ice  
342 melting in dolomite. A few ice melting measurements were, however, possible. When observed, the  
343 first apparent melting temperature of ice ( $T_e$ ) is usually low and close to or lower than  $-40^\circ\text{C}$ ,  
344 indicating the presence of divalent cations in the fluid compositions. In such a case, observing  
345 hydrohalite and ice melting behaviour is a prerequisite for interpretation in the  $\text{CaCl}_2\text{-NaCl-H}_2\text{O}$   
346 model system (Bodnar 2003). Hydrohalite was the first to melt at a temperature comprised between  
347  $-35^\circ$  and  $-25^\circ\text{C}$  when its observation was possible. Ice melting ranges from  $-13$  to  $-24^\circ\text{C}$  in quartz  
348 and from  $-11$  to  $-28^\circ\text{C}$  in dolomite (Fig. 10 and 11, Table 1). All the FI are 2-phase, and bulk  
349 homogenisation is in the liquid phase. For a given sample, results are usually very homogeneous.  
350 Based on  $T_{m \text{ ice}}$  measurements, salinity is high (Fig. 10), and the  $T_h$  range from  $100^\circ$  to  $150^\circ\text{C}$  (Fig.  
351 11).

352 *Fluid composition and evolution:* Based on the hydrohalite melting temperatures, the  
353  $\text{CaCl}_2/(\text{CaCl}_2+\text{NaCl})$  ratio estimated in the  $\text{H}_2\text{O-CaCl}_2\text{-NaCl}$  model system (Bodnar 2003) ranges  
354 from 0.49 and 0.86. The Stolzembourg fluids are, therefore, highly calcic brines (Fig. 10). Using  
355 the Na/ Ca ratio, the bulk salinity was estimated from the ice melting temperature using diagrams  
356 from Steele-MacInnis et al. (2011) and ranges from 15.1 to 25.0 wt% eq ( $\text{CaCl}_2+\text{NaCl}$ ). Raman  
357 spectrometry using the  $\text{H}_2\text{O}$  band (Dubessy et al. 2002) confirmed the validity of this chlorinity  
358 range. Thus, on the sample ZA074 FIs, the chlorine content estimate issued from Raman  
359 spectrometry data (3 to 3.8 mole Cl) is similar to the estimate from microthermometry (15 to 18%  
360 wt eq ( $\text{NaCl}+\text{CaCl}_2$ )).

361 The  $T_h\text{-}T_{m \text{ ice}}$  diagram in Fig. 11 shows two distinct trends, one more characteristic of the  
362 dolomite-hosted FI (trend 1) and the other of the quartz-hosted FI (trend 2). As some FI are  
363 secondary, it is unsurprising that some FIs from either the dolomite or the quartz are associated with  
364 opposite trends (group 2 for dolomite, group 1 for quartz). On the one hand, most of the dolomite-  
365 hosted FI (comprising all the possible primary FI), while exhibiting the highest  $T_h$  (ranging between  
366  $130$  and  $150^\circ\text{C}$ ), display an inverse  $T_h\text{-}T_{m \text{ ice}}$  relationship. Such a trend could correspond to a more  
367 or less isobaric anisothermal mixing trend. Interestingly, the data from Staudt (1977) coincide with  
368 trend 1 (Fig. 11), extending the high salinity to up to 26.5 wt % eq. ( $\text{CaCl}_2+\text{NaCl}$ ). On the other  
369 hand, the quartz-hosted FIs are characterised by a more dispersed behaviour, with lower  $T_h$  in the  
370  $120^\circ$  to  $100^\circ\text{C}$  range and a salinity range as in the previous trend. Salinity is, however, restricted to  
371 the 17.4 and 23.2 wt % eq ( $\text{CaCl}_2+\text{NaCl}$ ) range. This second group may consist of several more or  
372 less parallel trends (trends 2, Fig. 11), thus recording isothermal fluid mixing under fluctuating  
373 pressure conditions. Such an interpretation would be consistent with the textures testifying for  
374 hydraulic fracturing and crack seal in quartz (see above § 4.1.2).

375

376 ***The lead–zinc–barite occurrences***

377 *Martelange Ba-Pb*

378 The mineralised system is no more visible at the outcrop, but sampling is possible in the old mine  
379 wastes. The mineralisation occurs in Late Pragian slates (“ardoises”). Barite, siderite, pyrite and  
380 galena are hosted by old (late Variscan) quartz veins reworked at the mineralisation stage deemed  
381 to be Mesozoic. The Martelange samples of the same generation presented in the Luxembourg  
382 Museum only show sulphide mineralisation, dominated by pyrite: stockworks of pyrite veins  
383 (apparently formed through hydraulic fracturing) are reworked (dissolution-recrystallisation), and  
384 late cubic pyrite followed by cuboctahedral galena crystallised in the resulting vugs. A small quartz  
385 vein with barite was studied for FIs, but the only FIs found were in the quartz and appeared to be  
386 late Variscan metamorphic fluids, as shown by the density of volatile components.

387 *Allerborn - Longvilly Pb-Zn*

388 The Allerborn Pb-Zn showings are hosted in Variscan quartz veins in the regional NE-trending  
389 Wardin fault (Fielitz and Mansy 1999). These quartz veins are boudinaged, and primary FI are  
390 naturally decrepitated and could not be studied. When these quartz host Pb-Zn ores, secondary fluid  
391 inclusion as FIPs are present. They are very small ( $\leq 10 \mu\text{m}$ ) 2-phase FI, with an ice melting  
392 temperature ranging between  $-6^\circ$  and  $-2^\circ\text{C}$ , yielding a bulk salinity of 3.4 to 9.2 wt% eq NaCl in the  
393 NaCl-H<sub>2</sub>O model system (Bodnar 2003)). These FIs homogenise in the liquid state at temperatures  
394 between 210 and 300°C, with however two modes at ca. 230-250°C and 270-290°C, the latter  
395 suggestive of a post-trapping re-equilibration process (stretching?). The sphalerite contains a few  
396 small ( $< 10 \mu\text{m}$ ) FI, in which no melting temperatures were observed, but only one bulk  
397 homogenisation temperature (95°C).

398 *Soleuvre barite*

399 Unfortunately, as is often the case in the Black Forest deposits (e.g. Staude et al. 2012a), most barite  
400 crystals in Luxembourg occurrences lack measurable FI. Only in a barite vein in the Bajocian cover  
401 at Soleuvre were some FI visible. They are small ( $\leq 10 \mu\text{m}$ ) regular 2-phase inclusions  
402 homogenising into the liquid phase. Unfortunately, owing to both the scarcity in FI and the very  
403 brittle behaviour of barite, only one  $T_{\text{m ice}}$  ( $-8.5^\circ\text{C}$ ) and one  $T_{\text{h}}$  ( $100^\circ\text{C}$ ) could be measured. Salinity  
404 estimated in the NaCl-H<sub>2</sub>O system is ca. 11 wt % eq. NaCl.

405

406 **Discussion**

407 ***The Stolzembourg vein system and its relationships with the barite vein systems***

408 Our proposed paragenetic succession is consistent with the paragenetic sequence presented, as a  
409 synthesis of earlier works and new observations, by Filippo et al. (2007), the main differences lying  
410 in our introduction of early (Q1) and late (Q4) quartz generations on the one hand, and the barite  
411 position, on the other. Barite was considered younger by all previous workers. Yet, in our copper-  
412 bearing samples from the Stolzenbourg mine, the only barite we found was in the earliest Q1 quartz,  
413 where it was replaced, leaving only relicts (with up to 5.6 wt % Sr). Moreover, some samples from  
414 mineral collections at the Stolzenbourg or Luxembourg museums and labelled as coming from the  
415 main copper mine, display the relationships between large euhedral barite crystals and a quartz-  
416 dolomite association (very reminiscent of the Q2-Dol1 succession), with clear evidence of  
417 overprinting of the former by the latter (Fig. 4d). Also, Filippo et al. (2007) report that on the  
418 occasion of piercing a drain adit for the Our hydroelectric plant, euhedral barite crystals were  
419 collected from the Bivels barite vein, and that euhedral chalcopyrite crystals overgrew them. A stage  
420 of barite deposition thus clearly preceded the main mineralisation stage.

421 In the Bivels outcrops, however, barite was later than the ferroan carbonate and, therefore, than the  
422 copper episode, although associated with the same dextral-normal structural pattern. Yet, the Bivels  
423 and Stolzenbourg (Fléssen and Riedgerbësch veins) barites contain some strontium, as does the  
424 earliest barite from the Stolzenbourg copper ore, although in lesser quantity (3.2 wt% Sr at Bivels,  
425 2.7% at Fléssen and 1.8% at Riedgerbësch: Filippo et al. 2007). One might be tempted to see the  
426 indication of a penecontemporaneity between these different barite occurrences, but we do not think  
427 this is very conclusive. In conclusion, although the question of the relative timing between the  
428 chalcopyrite and barite vein systems cannot be considered definitively settled, it may be tentatively  
429 proposed that the dolomite-chalcopyrite vein system at Stolzenbourg was intercalated between two  
430 barite vein systems: an early one represented by the Fléssen and Riedgerbësch veins (and the  
431 remnants in the Stolzenbourg Q1 quartz) and a later one represented by the Bivels system.

432

### 433 ***P-T-X evolution***

#### 434 *Fluid compositions and evolution at Stolzenbourg*

435 The Stolzenbourg fault infillings result from two events of brine circulation and mixing: a low-  
436 temperature one, mostly recorded in pre- and post-mineralisation quartz, and a higher-temperature  
437 one, recorded in saddle dolomite and, in particular, in syn-chalcopyrite Dol2 dolomite. The latter is  
438 characterised by the anisothermal mixing of a  $\geq 150^{\circ}\text{C}$  (higher recorded  $T_h$ ),  $\geq 27$  wt eq %  
439  $(\text{CaCl}_2+\text{NaCl})$  brine L1 with a lower salinity ( $\leq 10$  wt % eq  $\text{CaCl}_2+\text{NaCl}$ ) and slightly lower  
440 temperature ( $\geq 130^{\circ}\text{C}$ ) aqueous fluid L2 (Fig. 11). A complication arises however when the Ca  
441 content is taken into consideration: it appears that the L1 brines display the full range of measured

442 Na/Ca ratios for the same bulk salinity, meaning that “L1” would indeed be itself a mixture of two  
443 brines, one (L1a) far more calcic ( $\text{Na/Ca} \leq \sim 0.2$ ) than the other (L1b,  $\text{Na/Ca} \geq \sim 1.1$ ) (Fig. 10).  
444 Hydrohalite melting temperature was, unfortunately, difficult to measure in lower salinity FI. Still,  
445 the few obtained data suggest that the diluting L2 fluid is close to pure water (Fig. 10).

446 The low-temperature brines may represent the “regional” fluid circulations during copper  
447 mineralisation. Trend 1 records the local invasion by a hotter brine, yielding to the dolomite  
448 deposition as carbonates have a retrograde solubility and, most probably, chalcopyrite deposition.

#### 449 *P-T conditions at Stozembourg*

450 Isochores were constructed for representative FIs (Fig. 12). As presented above, FIs in quartz record  
451 mixing events at various pressures. As far as this may be considered as due to crack-seal processes,  
452 it may be hypothesised that this variation consisted of switches from litho- to hydrostatic pressure  
453 conditions (Fig.11). Under this assumption, it is possible to retrieve a pressure estimate at the time  
454 of quartz deposition by considering two extreme isochores, the one with the lesser slope ( $T_h$  120°C)  
455 supposed to represent trapping under hydrostatic conditions, the steeper one ( $T_h$  100°C) taken as  
456 representative of lithostatic conditions. With the assumption of isothermal mixing at the  $T_0$   
457 temperature, the two pressures obtained by the intersection of the  $T_0$  isotherm with the lithostatic  
458 and hydrostatic isochores,  $P_0^L$  and  $P_0^H$ , respectively, must be such that  $P_0^L = \rho \cdot P_0^H$ , where  $\rho$  is the  
459 mean density of the superincumbent rocks. This condition is attained by an iterative “trial-and-error”  
460 method. The method is not very sensitive to the density value, the results being very similar for  
461  $\rho=2.6$  and  $\rho=2.7$  (Fig. 12): the condition is met for  $T_0 = 132^\circ\text{C}$  and  $P_0^H = 28$  MPa, i.e., at a depth of  
462 2.8 km. This depth is compatible with regional estimates, such as those proposed for the southern  
463 Black Forest district: 2.5 to 3 km depth, according to Walter et al. (2015). Given that formation  
464 depth, the anisothermal but isobaric mixing between the two L1 and L2 brines involved in the  
465 dolomite-chalcopyrite cycle is seen in Fig. 12 to proceed between 162°C, or more (L1) and 142°C,  
466 or less (L2). The corresponding geothermal gradient is estimated at  $\sim 48^\circ\text{C.km}^{-1}$ , pointing to an  
467 anomalous thermal regime in the Luxembourg crust at the time of copper deposition.

468

#### 469 *Nature and source of fluids in the regional context*

470 In the Ardennes-Rhenish Massif, as well as the Vosges and the Black Forest, deposits are  
471 characterised by the circulation of brines at relatively low temperatures (FI  $T_h$  comprised between  
472 50° and 150°C or more) (Dubois et al. 1996; Heijlen et al. 2001; Muechez et al. 2005; Baatartsogt et  
473 al. 2007; Pfaff et al. 2010; Staude et al. 2011, 2012b; Fusswinkel et al. 2013, Walter et al. 2018a)  
474 (Fig. 13). In the Black Forest, a clear-cut difference is observed between the Jurassic-Cretaceous  
475 and post-Cretaceous deposits when the brine compositions are considered: as seen in Fig. 13, the

476 former is characterised by higher salinity, and more calcic composition of the brines, compared to  
477 the later (Pfaff et al. 2010, Walter et al. 2015). On this basis, Fig. 13 demonstrates that based on the  
478 composition of the fluid inclusions, it would appear the Luxembourg deposits are members of the  
479 Jurassic-Cretaceous family.

480 All the above-cited workers on the Black Forest or Ardennes deposits concur in admitting the  
481 existence of several fluids and their mixing as a cause of ore deposition (Fig. 13).

482 The nature of these fluids is, however, discussed. In the Black Forest, post-Variscan deposits  
483 resulted from the “large scale mixing of a basement-derived saline NaCl-CaCl<sub>2</sub> brine with meteoric  
484 water”, according to Schwinn et al. (2006), as indeed well seen in the T<sub>h</sub>-T<sub>m ice</sub> diagram (Fig. 13).

485 The deep brine would be therefore both metal- and S-rich (likely as sulphate ions, thus raising the  
486 question of the reducing agent at the locus of deposition). However, as demonstrated by Fusswinkel  
487 et al. (2013) and emphasized by Walter et al. (2015), two types of brines are involved in the  
488 formation of Jurassic-Cretaceous deposits: a NaCl-dominated brine and a Ca-rich brine, and this is  
489 also the case for the Stolzembourg Cu deposit in Luxembourg (Fig. 10). In a detailed survey of the  
490 Jurassic hydrothermal veins in the Black Forest, Walter et al. (2017) demonstrated that the brine  
491 salinity and Ca/Ca+Na ratio were apparently under the dependence of the nature of the former  
492 Triassic cover (halite-bearing or not). According to Staude et al. (2011), for the Black Forest  
493 deposits, the two participating brines are: i) a deep one (rooted at 7 to 8 km depth), the Na-rich brine,  
494 the basement brine, and ii) “stagnant formation water” the Ca-rich (Ca-Na exchanged) brine derived  
495 from the cover reservoirs. The reservoir for this “formation water” component is usually considered  
496 the Permo-Trias red beds from the cover: “red bed-derived fluids”. According to Staude et al. (2012  
497 b), although ore components may be derived from various sources, including magmatic and  
498 metamorphic rocks and red-beds sedimentary rocks, the latter are “the most probable ones”. Where  
499 such red-beds were not deposited onto the southern Black Forest basement, the Muschelkalk  
500 carbonate platform is thought to have acted as the reservoir (Walter et al. 2015). By FI microanalysis  
501 of a south Black Forest vein, Fusswinkel et al. (2013) also demonstrate the mixing between a calcic  
502 brine with Na/Ca ≤ two and a sodium-dominated brine. They consider that the latter, with elevated  
503 Cl/Br ratios, came from halite dissolution (i.e., from a Triassic evaporite reservoir), with some Ca  
504 enrichment by Na-Ca exchange reactions along the flow path through the uppermost parts of the  
505 basement. In contrast, the calcic brine, with typically low Cl/Br ratios, was a bittern brine, having  
506 resided in a basement reservoir. Moreover, the microanalysis concluded that the metal-rich brine  
507 was the basement brine, the halite dissolution brine being, by contrast, metal-depleted but S-rich. In  
508 the same way, Walter et al. (2016) conclude their regional study of the Jurassic-Cretaceous fluids  
509 in the Black Forest deposits by identifying an “older” bittern, which was stocked in the basement

510 and suffered a long-term fluid-rock interaction (the calcic brine), and a “younger” sodic brine  
511 evolved by halite dissolution in the cover, and Walter et al. (2018a) conclude to “multi-component  
512 fluid mixing processes” implying several reservoirs.

513 The basement bittern brines are usually thought to come from the Mid-Triassic evaporites initially  
514 and then have penetrated deep into the basement during early Mesozoic extensional episodes. Such  
515 an origin is demonstrated in the Black Forest (Bons et al. 2014; Walter et al. 2016) or the western  
516 French Massif Central (Boiron et al. 2002; 2010; Cathelineau et al. 2012). For the Belgium Pb-Zn  
517 deposits, however, in an area where Triassic evaporites were never deposited, Dejonghe (1998),  
518 Heijlen et al. (2000), Dewaele et al. (2004) and Muchez et al. (2005) consider the late-Variscan  
519 infiltration in the deeper crust of brines derived from Carboniferous evaporites, which are well  
520 known (by drilling) in the autochthonous Viséan in front of the fold-and-thrust belt. This early  
521 infilling of deep reservoirs able to be remobilised at different times is consistent with the diversity  
522 of the hydrothermal events in the considered areas, which, as underlined by Pfaff et al. (2009),  
523 supposes that “through time, the same fluid source was repeatedly involved in the formation of  
524 hydrothermal vein deposits”.

525 The deposition mechanism may be the following succession: old bittern fluids having reached a  
526 significant depth where they resided a long time, **received** their calcium content, **then** scavenged  
527 metals, and rapidly ascended to the surface when pressure was released. There, they developed  
528 hydrofracturing and encountered younger shallow-level fluids with which they may **have mixed**  
529 (Staupe et al. 2009; Bons et al. 2014; Walter et al. 2016). However, the residing time would be  
530 several 10 Ma (up to 100 Ma: Muchez et al. 2005). There is, in conclusion, a consensus on the  
531 participation of a “basement brine”.

532 Such sequestration in the long term of basin-derived brines in a deep basement in relation to the  
533 development of continental crust permeability (Gleeson and Yardley 2002; Ingebritsen et al. 2010)  
534 is indeed well documented. In the Åspo Scandinavian basement, brines **were** trapped for more than  
535 1.5 Ma (Louvat et al. 1999). More significantly, the residence time of the brines observed at 4 km  
536 depth and more in the KTB continental-drill hole is **longer** than 30 Ma (Fehn and Snyder 2005).  
537 These fluids are indeed thought to have been trapped in a deeper reservoir during the Mesozoic and  
538 remobilised to their present position in the late Cretaceous (Lodemann et al. 1998; Möller et al.  
539 2005).

540 In the SE margin of the French Massif Central, Aquilina and de Dreuzy (2011) came to the  
541 conclusion that present-day fluids trapped in the **micropores** of the Permian reservoir (at a 634 m  
542 depth) resulted from the early to middle Jurassic (200-160 Ma) circulation of brines laterally derived  
543 from the Triassic evaporites in the subsiding SE Basin. In the same way, Boiron et al. (2002) and

544 Cathelineau et al. (2004) document, on the NW margin of the Aquitaine Basin, the deep penetration  
545 in the Variscan basement of brines issued from the basin at ca. 120 Ma and the sequestration of  
546 these brines in the **micropores** of the granites up to nowadays. Brine residence times in the basement  
547 of 50 Myr and more are equally demonstrated in the U.S. midcontinent (Thornton and Wilson 2007).  
548 A far longer sequestration time may be observed when formation brines trapped in shale aquicludes  
549 are directly dated, as the brines of the Ordovician age are presently found at 860 m depth below the  
550 Michigan Basin in Canada (Clark et al. 2013).

551 The two brines observed at Stolzembourg match well the “basement/cover” brine model proposed  
552 for the Black Forest deposits (Fig. 11): the two brines both represent the hot end-members of the  
553 anisothermal mixing process and, indeed, must be considered as “basement” brines, mixed on their  
554 way to the deposition locus. Still, dilution by a less saline and colder fluid is also implied (Fig. 11  
555 and 13).

556

#### 557 ***Copper transport and precipitation: the need for an oxidising fluid***

558 Copper is transported in solution in the Cu(I) valence state, mainly as a  $(\text{CuCl}_2)^-$  complex (Xiao et  
559 al. 1998; Mei et al. 2013), and is then found under the same valence state in copper sulphides (Goh  
560 et al. 2006). No redox change would thus be needed a priori for copper deposition. However, under  
561 reducing conditions and relatively low temperatures ( $< 250^\circ\text{C}$ ), copper solubility as a Cu(I) chloride  
562 complex is so low that it precludes significant copper transportation unless conditions are unusually  
563 oxidized (Xiao et al. 1998). In the Stolzembourg case, an oxidising fluid was needed to transport  
564 copper to the deposition site at temperatures between 150 and  $200^\circ\text{C}$ . Indeed, at Stolzembourg, the  
565 transient presence of oxidising fluids is marked by the wall-rock reddening and the hematite  
566 occurrences, including the tiny hematite in the Dol2 rhombohedra, immediately preceding the  
567 chalcopyrite. The source of the oxidising fluid could have been an Early Cretaceous regolith (see  
568 below). Reduced fluids were, however, necessary to provide iron to the locus of hematite and  
569 chalcopyrite deposition, and fluid mixing is therefore required, as observed in the fluid inclusion  
570 record.

571 Chalcopyrite deposition also requires the presence of reduced sulphur. Reduced sulphur could have  
572 been present in one of the involved fluids (but not the copper-bearing one!) or have resulted from  
573 sulphate reduction. In the latter case, reducing the sulphur could have been related to a TSR process  
574 producing reduced sulphur from brine sulphate ions, driven, for instance, by methane. The process  
575 demands, however, the former presence of  $\text{H}_2\text{S}$  as a catalyser (Truche et al. 2014). If the reduction  
576 had occurred near the deposition site, BSR could have fulfilled this prerequisite at the lower  
577 temperature of fluid circulation attested before the chalcopyrite event. It remains speculative in the

578 absence of C isotope data at Stolzembourg to prove the methane intervention. Nevertheless, in the  
579 Ardennes belt, the FI homogenisation temperatures are consistently between 110° and 150°C, and  
580 low  $\delta^{13}\text{C}$  in calcite, together with most  $\delta^{34}\text{S} > 10\text{‰}$  are data in favour of methane-driven TSR for  
581 the origin of the sulphur for the sulphides (in Dejonghe 1988). The source of sulphate is thought to  
582 have been the thick anhydrite beds known by drilling in the autochthonous Visean (Muechez et al.,  
583 1995). The methane could have been produced by interaction with organic matter of the deep and  
584 hot fluids, somewhere on their path from the deep reservoir, or even through their equilibrium with  
585 basement graphite, as proposed for the deepest fluids from the Black Forest by Staude et al. (2012  
586 a). By directly observing hydrocarbons trapped in sulphides from the Pb-Zn deposits in the nearby  
587 Rhenish Massif, Jochum (2000) argues the local heating of kerogen by the hot Mesozoic basement  
588 fluids.

589 In general, copper deposition may be triggered by decreased temperature,  $f\text{O}_2$  and bulk salinity, and  
590 increased pH (Xiao et al. 1998). At Stolzembourg, all these conditions were met, notably the  
591 chlorinity decrease at the time of ore deposition: the FI data indicate temperature and bulk salinity  
592 decrease. The inferred existence of reducing fluids ( $\text{Fe}^{2+}$  transportation, production of  $\text{HS}^-$ ) may be  
593 taken as evidence for a lowering of  $f\text{O}_2$ . This conjunction of favourable factors might have allowed  
594 the formation of a significant deposit even if the bulk copper content of the mineralising fluids was  
595 not high. However, such conditions are not infrequently encountered in many Pb-Zn deposits and  
596 cannot explain why copper-only deposits are so scarce in the Mesozoic record of Western Europe.

597

## 598 ***Sources of metals and trace elements***

### 599 *Significance of REE data*

600 At Stolzembourg, the REE pattern in the syn-ore dolomite is a possible direct insight into the source  
601 area(s). According to Rongemaille et al. (2011), there is no REE fractionation during the carbonate  
602 deposition; thus, an REE spectrum is representative of the forming fluids. On the other hand, the  
603 total REE abundance, controlled mainly by the mineral growth rate and the fluid flow rate (Möller  
604 et al. 1991), does not directly depend on the REE source. The observed pattern at Stolzembourg  
605 shows a moderate bulk REE enrichment and a strong MREE enrichment relative to both the highly  
606 depleted LREE and the HREE (“bell-shaped” or “hat-shaped”) (Fig. 8). In addition, no europium  
607 anomaly is found. As seen in Fig. 8, although ankerites from the Black Forest deposits display  
608 contrasted profiles, they are in general much different from the Stolzembourg “ankerite” (some even  
609 exhibiting an inverse behaviour, as at Wittichen), with the noticeable exception of the Waldkirch  
610 ankerite (Staude et al. 2012a), which shows an MREE-enriched pattern. The Waldkirch ankerite is  
611 intergrown with chalcopyrite and is enriched in copper (up to 270 ppm Cu) (Staude et al. 2012a).

612 Compared to other ankerites from the Black Forest, it also displays an exceptionally heavy  $\delta^{13}\text{C}$   
613 signature, supposed to dismiss the influence of basement brines in its genesis (Staude et al. 2012a).  
614 However, the reason for such a conclusion is somewhat unclear. As shown in Fig.8, several fluorites  
615 of the Black Forest (Schwinn and Markl 2005) equally show MREE-enrichment, with, however,  
616 less depleted HREE and, above all, LREE. At the world scale, only a few carbonate samples  
617 (indifferently, ankerite, siderite or calcite) display the typical “bell-shaped” pattern of Stolzembourg  
618 (Fig. 12 d). The most similar profiles are those of the mid-proterozoic Saskatchewan carbonates,  
619 which also have bell-shaped REE profiles close to  $\text{UO}_2$  profiles. These carbonates were formed by  
620 mixed Na-Ca brines close to the unconformity at around 200°C (Richard et al., 2003). The calcite  
621 from the Shuyindong Carlin-type deposit in China (Su et al. 2009), the siderite from the present-day  
622 methane-seeps in the Niger Delta (Rongemaille et al. 2012), and, to a lesser extent, the calcite from  
623 the world-class Xikuhangshan Sb deposit (Peng et al. 2003), also present bell shape profile when  
624 normalized to chondrite. Unfortunately, most authors do not propose an explanation of the MREE-  
625 enriched patterns. For the Black Forest fluorites, however, these patterns are interpreted as recording  
626 “a basement source” (Schwinn and Markl 2005).

627 Based on a bibliographic review, Hecht et al. (1999) consider that “upward convex or roof-shaped  
628 REE patterns of hydrothermal fluids seem to be typical for crustal fluids that have interacted with  
629 **pelitic metasedimentary rocks** most probably under acid conditions”. On the other hand, to explain  
630 the observed MREE-enrichment of acid and hypersaline groundwaters found in arid areas of  
631 Australia and Texas, Johannesson et al. (1996) invoke the preferential leaching of detrital Fe-Mn  
632 oxide-hydroxides which are known to concentrate the MREE (e.g., Bayon et al. 2004; Négrel et al.  
633 2006). Unfortunately, in these oxide-hydroxides, the LREE are often more concentrated than the  
634 HREE, and their leaching is, therefore, unable to yield the desired “bell-shaped” pattern (which is  
635 not observed in the just mentioned hypersaline groundwaters when chondrite-normalized). By acid  
636 leaching of Fe hydroxides from Eifelian and Givetian siliciclastic sedimentary rocks in the  
637 northeastern Rhenish Massif, Zwing et al. (2009) obtain relatively flat REE patterns, which,  
638 although slightly MREE enriched, cannot, however, better match the Stolzembourg pattern (Fig. 8).  
639 Finally, “bell-shaped” profiles have been observed in the solute load from the acidic Vosges rivers  
640 (Tricca et al. 1999) and in experimental (acid) leachates obtained from Paleozoic anchizonal meta-  
641 turbidites (Ohr et al. 1994) (Fig. 8). In both cases, the MREE-enrichment is interpreted as due to the  
642 preferential leaching of apatite: it is well known that apatite concentrates the REE at an early  
643 diagenetic stage (Lev et al. 1998) and that, in particular, the biogenic apatites display typical “hat-  
644 shaped” REE patterns (Grandjean-Lecuyer et al. 1993). Also, dissolution experiments demonstrate  
645 that apatite dissolution is far faster under acid conditions than other REE-bearing minerals, such as

646 monazite or florencite (Köhler et al. 2005). Moreover, these experiments demonstrate that in the  
647 first steps of the dissolution, the LREE remain sequestered in the residue due to the re-precipitation  
648 of rhabdophane (Köhler et al. 2005). As pointed out by Debruyne et al. (2016), such a retention  
649 effect is the most convenient explanation for such a highly depleted LREE pattern as observed at  
650 Stolzembourg (and in very few other occurrences, see Fig. 8d), which indeed contrasts with much  
651 of the published “bell-shaped” patterns, in which LREE are currently less depleted than the HREE  
652 (Fig. 8).

653 Alternatively, the REE could have been leached from a combination of phosphates and Fe-Mn  
654 oxides in a regolith. Indeed, In the kaolin clay deposits of the Rhenish Massif, Dill et al. (1995)  
655 report the presence of both LREE- and HREE-rich alumino-phosphates (florencite-goyazite and  
656 gorceixite, respectively); the clays are supposed to be Tertiary, and supergene K-Mn oxides from  
657 the southern Rhenish Massif were dated from the late Tertiary (25-1 Ma,  $^{40}\text{Ar}/^{39}\text{Ar}$ : Hautmann and  
658 Lippolt 2000). Such an alternative would, however, imply a Tertiary age for the Stolzembourg  
659 deposit, which is considered unlikely (see below). There is, unfortunately, no published information  
660 on the possible presence of REE-bearing minerals (other than the Fe-Mn oxy-hydroxides) in the  
661 lower Cretaceous regolith, which would otherwise be an appealing alternative. To conclude,  
662 although a contribution of the dissolution of Fe-Mn oxy-hydroxides cannot be ruled out, it seems  
663 most likely that the REE pattern of the Stolzembourg “ankerite” records the dissolution of apatite  
664 in the Lower Paleozoic turbidites from the HASB, i.e., points to sourcing of at least part of the ore-  
665 forming brines in the basement.

666 On the other hand, the lack of any positive europium anomaly (Fig. 8a) does not favour a Ca to Na  
667 exchange process with the feldspars in the basement to explain the Ca-enrichment of one of brines  
668 at Stolzembourg. Consequently, the Na-rich brine could have been the basement brine derived from  
669 a brine coming laterally from the Keuper evaporites in the nearby Luxembourg basin. This brine  
670 deeply infiltrated during the Early Jurassic extensional events and was sequestered until the early  
671 Cretaceous. A similar process of long-term sequestration of brines in the basement is invoked by  
672 Heijlen et al. (2003) for Silesian deposits, where Triassic brines were the pristine brines. During the  
673 same event, the calcium-rich brine could come from the locally overlying Muschelkalk cover  
674 (gypsum-bearing marls) and could have interacted with Permian red beds (see below).

### 675 *5.2. Source of copper*

676 In line with the findings of Fusswinkel et al. (2013), showing that in the Black Forest hydrothermal  
677 systems, the metal-rich brines were sourced in the basement, it may be asked if the HASB basement  
678 could have been a copper source. Although leaching of ordinary basement rocks in cataclastic zones  
679 is experimentally demonstrated to yield metals to the solution, the copper contents of minerals in

680 “ordinary” basement rocks are so low as to preclude the formation of a brine significantly enriched  
681 in copper (Burisch et al. 2016). Thus a specific source is likely needed. Paleoplacers are known in  
682 the Ardennes Upper Famennian (Bocq valley), concentrating Fe-Ti oxides and chromite of mafic  
683 magmatism derivation (Goemaere and Hurford (1997). According to Ganssloser (1999), most of the  
684 Rhenish metagreywackes of Frasnian to Visean age contain a chromian spinel as a minor component  
685 of the heavy mineral spectra, deemed, however, to be sourced in far-sited Alpine-type peridotites.  
686 Yet, according to Oncken et al. (1999), this spinel is no longer found to the west of the Rhine graben.  
687 Indeed, compared to the east, the western part of the Rhenish massif is characterised by its scarcity  
688 in early magmatism, a fact thought by Muechez et al. (2005) to explain the poor endowment in ore  
689 deposits of the western Rhenish massif. Although such characteristics would suggest the possibility  
690 of some Late Devonian to Carboniferous metasediments containing detrital material that could act  
691 as a leachable source of copper (for instance, in Fe-Ti oxides from mafic rocks), it remains that at  
692 the erosion level attained in Luxembourg at the onset of Mesozoic sedimentation, all these rocks  
693 had already disappeared, thus precluding their potential as source rocks for the copper  
694 mineralisation. In the northern Rhenish Massif, low concentrations of stratabound sulphides  
695 (interpreted as sedimentary-exhalative) are documented in Lower Carboniferous black shales, and  
696 copper, as chalcopyrite, is known at Marsberg and would amount there to about 55 kt Cu, at 1.3 to  
697 1.6% Cu (Stribny et al. 1988). Such a source was eroded at the time of copper deposition and cannot  
698 be considered a source for Stolzembourg copper. In the HASB, a small Cu-Mo occurrence is known  
699 at Helle, in the Stavelot Massif, as chalcopyrite-molybdenite dissemination and veins within a sill  
700 of quartz diorite to tonalite intruded at  $381 \pm 16$  Ma into the Cambrian siliciclastic rocks (Dejonghe  
701 2003). In the Lower Ordovician chloritoid-bearing schists, quartz veins with bornite-chalcopyrite-  
702 chalcocite mineralisation are known in the Stavelot Massif. They are interpreted as formed at  $350^\circ$ -  
703  $300^\circ\text{C}$  at the end of the Variscan metamorphism (Hatert 2005). Thus, the Cambro-Ordovician series  
704 of the Caledonian basement to the Luxembourg lower Devonian siliciclastics is a possible copper  
705 source. This series lies around 1 to 2 km below the copper deposition site, which, given the estimated  
706  $45^\circ\text{C.km}^{-1}$  gradient, would have reached a temperature close to  $230^\circ\text{C}$  necessary to dissolve copper.  
707 For the Wenzel deposit in the Black Forest, Staude et al. (2007) also propose the remobilisation of  
708 older basement-hosted mineralisations as a source for the Mesozoic ores.  
709 On the other hand, the classic view that copper was sourced in the overlying red-beds, as supported  
710 in the Black Forest by Staude et al. (2011), is best consistent with the need for oxidising fluid for  
711 copper transportation. Yet, to be a valuable source, the red-beds series must include volcano-  
712 sedimentary components (bimodal magmatism in rifted areas) or at least a detrital component issued  
713 of such series. Yet, LA-ICP-MS analysis of FI in carbonates and fluorite from a deposit (Sailauf,

714 Spessart Crystalline Complex in Germany), where red-bed sourced fluids are documented, failed to  
715 find high copper contents in the fluids (Fusswinkel et al. 2014). Such red beds are present in the  
716 Vosges and Black Forest districts. Still absent in Luxembourg, the closer area with bimodal  
717 components is the Permian Saar-Nahe basin, with its southwestern prolongation beneath the  
718 Mesozoic cover, or the Permian Malmédy Graben, in the nearby Stavelot massif (Fig. 1). Presently,  
719 the latter is a small structure, 22 km long and 0.5 to 2.5 km wide, with no more than 240 m thick  
720 red conglomerates unconformably resting onto the Cambro-Ordovician series of the Stavelot  
721 Massif, and fed in detritus by the Devonian of the Eifel massif (Bultynck et al. 2001). These red  
722 beds may have reworked some of the potential copper sources in the basement. Finally, although  
723 large-scale circulation, possibly through a network of basement faults, is needed, Permian red beds  
724 could have constituted the copper source for Stolzenbourg.

725

### 726 *Age of the Stolzenbourg deposit*

727 Stolzenbourg is hosted in Lower Pragian rocks, as seen in Fig. 1, at a depth of 2.5 and 1.8 km under  
728 the Mesozoic unconformity. Thus, to achieve the 2.8 km depth estimated for the copper deposition  
729 at Stolzenbourg 300 and 1,000 m of sedimentary cover are required at the time of the mineralisation.  
730 This width is roughly consistent with the stratigraphic data. As the final erosion of the cover did not  
731 begin before the Miocene, this would imply an earlier date for the mineralising event.

732 Due to the lack of datable material, the age of the Stolzenbourg system can be indirectly bracketed  
733 because the intense hematization event must have been related to the deep penetration of surface-  
734 derived oxidising water allowing “reddening at great depth along basement fractures”, as described  
735 by Cathelineau et al. (2012) on the Poitou High. Deep weathering mantles were frequently  
736 developed in Western Europe, starting from the Early Triassic. They show a trend from a  
737 kaolinite/ferrallitic style in the Mesozoic to a gussic style in the Tertiary (Migon and Bergström  
738 2002). The first event was Permian, in relation to the post-Variscan unconformity. In that  
739 Luxembourg area presently corresponding to the Eisleck, where no red-bed deposition of this age  
740 seems the rule, such an origin of the wall rock reddening at Stolzenbourg may be excluded. A  
741 second event, dated from the Early Triassic, is recorded in emerged areas south of Luxembourg, in  
742 Swiss (“Vindelician cordillera”: Gisler et al. 2007). Still, at that time, the sedimentary pile was not  
743 thick enough to meet the above-discussed requirements. During the Early Cretaceous, in association  
744 with major “wavelength deformation” events recorded at the Early Berriasian, and at the end of the  
745 Barremian (Guillocheau et al. 2000), a third set of ferricrete was developed. The extensive erosion  
746 of the Jurassic limestone platforms on the eastern margin of the Parisian Basin may be attributed to  
747 such continent-scale warping and produced kaolinite saprolites and ferricretes, the latter being dated

748 by palaeomagnetism of the Barremian ( $130\pm 10$  Ma, Thiry et al. 2006, Théveniaut et al. 2007). The  
749 formation of the calamine zinc deposits from the Ardennes and the northern Rhenish massif can be  
750 related to this event. They were formed by oxidation at the expense of former Pb-Zn sulphide veins  
751 during the development of an erosion surface with a kaolinite-bearing regolith (Dejonghe and Boni  
752 2004), the latter having been dated by Yans (2003) from the Barremian-Aptian ( $135\pm 15$  Ma and  
753  $126\pm 10$  Ma, i.e., ca 130 Ma). This event is recorded in the western FMC (Innocent et al. 2019), east  
754 of Luxembourg, and Bavaria (c. 125 Ma kaolinite saprolite: Gilg 2000).

755 The wall rock reddening at Solzembourg could thus be related to this third ferricrete event, and early  
756 Cretaceous age (Barremian, c 130 Ma) for the Stolzembourg copper mineralisation may, therefore,  
757 be proposed with a certain degree of confidence.

758

### 759 ***Putting the Luxembourg mineralisation in a time and geodynamic context***

760 There is a wealth of absolute chronological data allowing the establishment of a time framework for  
761 the fluid circulation events and the related mineralizing episodes, first at the scale of the Upper  
762 Rhine graben (taken as a proxy for Luxembourg), then expanded at the western Europe scale: a  
763 compilation of available data, in the sedimentary basins and their basement (Appendix A1), and the  
764 ore deposits (Appendix A2-3), is summarized in Figure 14.

#### 765 *Evidence for a pulsed activity*

766 Based on illite K/Ar and Ar/Ar dating (Appendix A1) and the evidence for remagnetisation based  
767 on palaeomagnetism data (Schott and Peres 1987; Henry et al. 2001; Kechra et al. 2003; Ricordel  
768 et al. 2007), it appears that episodic hydrothermal fluid circulation occurred at the same times in the  
769 whole of the west European domain, at the boundary between the basement and Permo-Triassic  
770 detrital formations (Fig. 14): in the Early and Late Triassic; in the Jurassic during the Lias, then the  
771 Malm; in the Cretaceous, during the Neocomian, then the Albo-Aptian, and finally, the Late  
772 Cretaceous; at the Cretaceous-Paleogene boundary; and eventually during the Eocene (the latter,  
773 only in the Upper Rhine graben). In parallel, the dating of ore deposits, based on various methods  
774 and minerals (Appendix A2-3), reveals a pulsed mineralizing activity in broad coincidence with the  
775 fluid circulation pattern (Fig. 14).

776 In the best-documented area (the Black Forest, representative of the Upper Rhine graben), after a  
777 minor Early Triassic event, three main periods may be distinguished: (i) Jurassic-early Early  
778 Cretaceous (Neocomian) for a series of fluorite-barite-quartz-(carbonates) with several substages of  
779 Pb-Zn-Ag-Ni-Co-Bi-(Cu) mineralisation, (ii) late Early Cretaceous-Late Cretaceous, for quartz-  
780 barite-calcite-(fluorite) with again Pb-Zn-(Cu) and (iii) terminal-Cretaceous-Miocene for barite and  
781 Cu-Bi-Pb-Zn mineralisation. These element associations, including Pb-Ag-Bi-Cu, are notably close

782 to that found in the rare luxembourgitite ( $\text{AgCuPbBi}_4\text{Se}_8$ ), described in association with siderite,  
783 dolomite and arsenopyrite at Our electric station close to Stolzenbourg (Philippo and Henson, 2007).  
784 When other deposits in western Europe are considered, a broadly coincident partition is revealed,  
785 with some differences, notably the presence of a limited number of Late Triassic deposits and the  
786 minimal occurrences of post-Paleocene deposits (Fig. 14).

787 A very significant fact is the existence of a widespread hydrothermal event in the Late Jurassic (at  
788 c 160-145 Ma), with mainly Pb-Zn deposition, which is proved to have coincided with a significant  
789 thermal event by fission-track measurements on zircon (Black Forest: Timar-Geng et al. 2004).  
790 Everywhere well identified by the radiometric dating, this major event is documented by indirect  
791 evidence in areas such as the Ardennes and Rhenish massifs (evidently relevant for comparison with  
792 Luxembourg), where the mineralisation is not dated. Thus, the numerous vein-type Pb-Zn deposits  
793 and occurrences in the HASB (Fig. 1) are probably related to this Malm event: at least in the Dinant  
794 Synclinorium, they pre-date the Cretaceous (Dejonghe 1998; Heijlen et al. 2001). In the northern  
795 Rhenish Massif, the Devonian- and Carboniferous-hosted Pb-Zn veins are sealed by “deep phreatic  
796 cavities filled with Lower Cretaceous sedimentary rocks” (Drozdowski et al. 1998, in Götte and  
797 Richter 2003). Non-sulphide (calamine) zinc deposits from the Ardennes and the Rhenish massif  
798 were formed by oxidation at the expense of former Pb-Zn sulphide veins and related to the  
799 development of the Early Cretaceous erosion surface with a kaolinite-bearing regolith (Dejonghe  
800 and Boni 2004). It is, therefore, highly probable that the Luxembourg Pb-Zn showings were formed  
801 during this Late Jurassic hydrothermal event, as a first barite event as documented at Stolzenbourg  
802 (cf supra § 5.1).

803 In the Ardennes, paleontologic evidence may be added to the radiometric data. Indeed, the Fleurus  
804 barite deposit in the Verviers syncline is dated from the Albian-Aptian by a palynoflora (Demaiffe  
805 and Dejonghe 1990, Dejonghe et al. 1987). This is likely to give even more confidence to the  
806 attribution of this age to the Stolzenbourg copper deposit. A consequence of this attribution is the  
807 existence in Luxembourg of the second generation of barite deposition (such as the Biwels system)  
808 likely of Cretaceous age as in the Upper Rhine graben. These data equally support the existence of  
809 a well-defined Early Cretaceous hydrothermal activity.

#### 810 *Geodynamic constraints on the calendar of hydrothermal activity*

811 As seen in Figure 14, a series of continental-scale tectonic events punctuated the post-Variscan  
812 history of Western Europe. They appeared to have coincided broadly with the hydrothermal events  
813 they may have monitored. Working at the European plate scale, Burish et al. (2022) concluded that  
814 “the formation of Mesozoic vein-hosted and MVT ore deposits is a local expression of geological

815 processes that happen on a continental scale”, and they stressed the importance of rifting to trigger  
816 the fluid mixing processes that control ore deposition.

817 Thus, the Mesozoic events were monitored to a large extent by the rifting and drifting events in both  
818 the northern Atlantic and the Tethyan oceanic realms (e.g., Handy et al. 2010, and references  
819 therein).

820 First, the Late Triassic to Liassic events may be correlated with the initiation of the proto-North  
821 Atlantic rift system (Sibuet et al. 2012). During the Late Triassic, extensional tectonics were  
822 documented in several basins (Dumont 1988), and, at the Trias-Lias boundary, was formed the  
823 Central Atlantic Magmatic Province (CAMP), a basaltic LIP developed between 202 and 192 Ma  
824 and peaking at c 201 Ma (Marzoli et al. 2018). Indeed, the focus of the responsible mantle plume  
825 for the CAMP was located far to the South (between Florida and Senegal). Still, Late Triassic  
826 basaltic volcanism is recorded in southern Europe, at the Norian-Rhaetian boundary (c 210 Ma) in  
827 the Dauphinois (Dumont 1988) and the Betic belt (Perez-Lopez et al. 2010) and c 200 Ma in Sicily  
828 (Cirrincione et al. 2014), meaning that the lithosphere was thermally disturbed much further north  
829 than the core zone of the CAMP. The CAMP and related tectonics forecasted the rifting event, active  
830 from the Sinemurian to the Early Bajocian (190-170 Ma: Labails et al. 2010).

831 The major Malm hydrothermal event is related to both the “dramatic change” registered from the  
832 Kimmeridgian to the Tithonian in the opening of the Central Atlantic Ocean (Labails et al. 2010)  
833 and the coeval North Sea active mantle-driven rifting (Underhill and Partington 1993; Cowie et al.  
834 2005), and the simultaneous opening of the Liguria-Piemont Tethyan oceanic tract starting from the  
835 Oxfordian (e.g., Liati et al. 2005; Masini et al. 2013).

836 The Early Cretaceous hydrothermal events are related to a significant Early Cretaceous extensional  
837 event in western Europe (Muechez et al. 2005), which was driven by the westward propagation of  
838 oblique hyperextension (up to magma-starved oceanic tracts: Stampfli et al. 2002; Beltrando et al.  
839 2013) along a major transform fault (Handy et al. 2010), from the Valaisan domain to the east (rifting  
840 starting at ca 130 Ma: Liati and Froitzheim 2006; Stampfli et al. 2009; Loprieno et al. 2011), to the  
841 Pyrenees and the Bay of Biscay to the west (opening beginning as early as 125 Ma, with a peak in  
842 the Albian-Cenomanian at 110-95 Ma: Gong et al. 2008; Stampfli et al. 2002; Calvet et al. 2021).  
843 Such extensional tectonics could explain the heat input recorded by the FIs in the Stolzembourg  
844 deposit, a further argument for the proposed c 130 Ma for the formation of the deposit. The  
845 transtensional nature of the Stolzembourg vein system is equally consistent with such an extensional  
846 context.

847 From the very Late Cretaceous onwards, the West European stress state was controlled by the  
848 development of the Pyrenees-Alps orogenic wedges. The first Santonian to Maastrichtian

849 (“Laramide”) phase of Pyrenean orogenesis (84-68 Ma: Calvet et al. 2021) was apparently of minor  
850 importance when hydrothermalism is concerned (Fig. 13). By contrast, the main “Pyreneo-  
851 Provençal” phase spanning the Eocene and starting from 55 Ma (Calvet et al. 2021) exerted a  
852 considerable influence: compressional stresses exerted on continental Europe by the evolving  
853 orogens caused lithospheric buckling and basin inversion up to 1700 km to the north of the Alpine  
854 and Pyrenean deformation fronts. This deformation was accompanied by the injection of melilite  
855 dykes, reflecting a plume-related increase in the temperature of the asthenosphere beneath the  
856 European foreland. Fluid circulation at the continental scale was one of the consequences (Fig. 14).  
857 Starting from the Oligocene, the development of the West European rift system was under the  
858 control of the ongoing orogenesis in the Alpine domains (“impactogene rifting”: Merle and Michon  
859 2001). Despite the significant thermal impact revealed by the Tertiary volcanic provinces in the  
860 French Massif Central and the Rhenish Massif (Wilson and Downes 2006), the consequences of  
861 hydrothermal circulation and mineralizing events were quite limited, being essentially present in the  
862 Upper Rhine graben (Fig. 13).

863

#### 864 *Thermal regimes*

865 An inventory of published data on the Black Forest, Vosges and Ardennes deposits show that during  
866 the Mesozoic, recorded fluid temperatures were constantly changing: as shown in Figure 13, fluid  
867 mixing occurred at temperatures higher than  $T_h$  ranging from 160°C and more, attained for instance  
868 at Stolzembourg (this work), Wiesloch (Pfaff et al. 2010), and other Black Forest deposits  
869 (Baatartstogt et al. 2007) down to 40°-60°C, recorded for instance by ferroan dolomites occurring  
870 in N20°-N30°E extension veins from the Namur Syncline (Muechez et al. 1995), with many  
871 carbonates (Nielsen et al. 1998; Walter et al. 2015) and the Pb-Zn in Belgium (Heijlen et al. 2001)  
872 being characterised by intermediate temperatures. At a depth of mineralisation of c. 3 km  
873 (Stolzembourg: this work, southern Black Forest: Walter et al. 2015) to 1 km (northern Black Forest:  
874 Walter et al. 2015), the expected wall rock temperatures would have continuously been lower than  
875 100°C owing to the maximal 35°C.km<sup>-1</sup> geothermal gradients commonly affecting the European  
876 crust. The temperatures recorded by the ferroan dolomites from the Namur Syncline (FI  $T_h$  between  
877 40° and 60°C: Muechez et al. 1995) would be representative of the circulation of fluids thermally  
878 equilibrated with their host rocks, as would also be many carbonates from the Black Forest, as well  
879 as several barite deposits, and the Pb-Zn showings from Luxembourg at temperatures below 100°C  
880 (Fig. 13, lines C and L). Temperatures above 210°C ( $T_h$ ) recorded in most Pb-Zn, and CaF<sub>2</sub> (and Cu  
881 at Stolzembourg) deposits suggest either the transient implementation of abnormal heat flows or the  
882 implication of deep fluids, equilibrated under the “normal” thermal gradient but at greater depths,

883 or both. Indeed, combining geochemical thermometry and thermodynamic approaches, it is often  
884 proposed that these fluids were initially at temperatures as high as 300°C or more: Deloule (1982)  
885 for the Tarn fluorites in French Central Massif, formed at ca 180°-210°C (Munoz et al. 2005), or  
886 Pfaff et al. (2010) for the Wiesloch deposit in the Black Forest, formed at  $T_h \leq 210^\circ\text{C}$ . Along the  
887 normal gradients, such temperatures would be reached at 9-10 km depth or more. According to  
888 Lodemann et al. (1998), the calcic brines found at around 4 km depth in the KTB continental drill  
889 hole were transferred into their modern setting from a deeper reservoir at about 9 km depth. There  
890 are, however, arguments in favour of transient perturbations of the geothermal gradients.

891 Anisothermal mixing is often observed and records the advection of hot fluids into colder reservoirs,  
892 as the model requires. As proposed in Figure 13 (lines S1 and A), this could be a general process,  
893 at least for the hotter hydrothermal systems. For instance, in the Wiesloch deposits (late Cretaceous-  
894 Paleogene) in the Black Forest, Pfaff et al. (2010) argue for mixing a deep brine equilibrated with  
895 the basement at temperatures possibly as high as 300°C but cooled down to ca. 150°C at the  
896 deposition site. There, the formation water, initially at no more than 100°C and equilibrated with  
897 carbonates, would have been alkaline (pH ca. 8). However, given that the deposit is hosted in the  
898 Muschelkalk cover, the temperature of ca 100°C reached by the “low temperature” component  
899 requires a high geothermal gradient. In the same way, at Stolzembourg, the colder fluid in the mixing  
900 is at c. 140°C, which, if in thermal equilibrium at the estimated c. 3 km depth, would require a  
901  $48^\circ\text{C.km}^{-1}$  geothermal gradient. It may be observed, by contrast, that the lower  $T_h$  recorded by the  
902 FI in pre- or post-ore quartz would correspond, under lithostatic conditions, at the same c. 3 km  
903 depth, to a temperature of c. 90°C (Fig. 12), yielding, in turn, a less pronounced gradient of  $35^\circ\text{C.km}^{-1}$ .  
904 It, therefore, seems that a transient increase of the regional geothermal gradient characterised the  
905 Stolzembourg area at the time of ore formation. Such a conclusion could be extended to the Black  
906 Forest deposits and would agree with the extensional context associated with the ore-forming events.

907

## 908 **Conclusions**

909

910 1. The small Pb-Zn showings in Luxembourg are thought to be equivalent to the Ardennes Pb-Zn  
911 deposits. They would consequently have been formed during the Late Jurassic hydrothermal event,  
912 associated with the North Atlantic and Ligurian-Piemontese (Thethysian) ocean opening at the  
913 Western Europe scale.

914 2. The Stolzembourg copper-only deposit is a likely product of the Mid-Cretaceous thermal event,  
915 which affected Western Europe in response to the coeval openings of the Biscaye Bay (to the west)  
916 and Valaisan (to the east) oceanic tracts between 130 and 100 Ma. As recorded by fluid inclusions

917 in syn-chalcopyrite Fe-dolomite, copper ores resulted from the anisothermal mixing from 165°C or  
918 more down to 135°C, between two highly saline (ca.27 wt % eq NaCl), brines, one Ca-Na and the  
919 other Na-only rich, and low-salinity water. Hydrostatic conditions at an estimated depth of around  
920 3 km are most probable. By contrast, the quartz, which precedes and follows copper deposition,  
921 records circulation of lower-temperature brines, interpreted as the result of regional fluid circulation  
922 under “normal” geothermal gradients. The copper depositing event thus appears related to a  
923 localised transient heat advection produced by the upward migration of brines from a deeper  
924 reservoir.

925 3. Some barite showings in Luxembourg, which post-dated the Stolzembourg ore deposition, must  
926 be ascribed to the Late Cretaceous hydrothermal events.

927 4. Finally, although of little economic importance, the Luxembourg mineral district appears as a  
928 missing link between the mineralisation of the Ardennes-Rhenish massifs, on the one hand, and the  
929 Upper Rhine graben districts of the Vosges and the Black Forest, on the other.

930

931

932

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934

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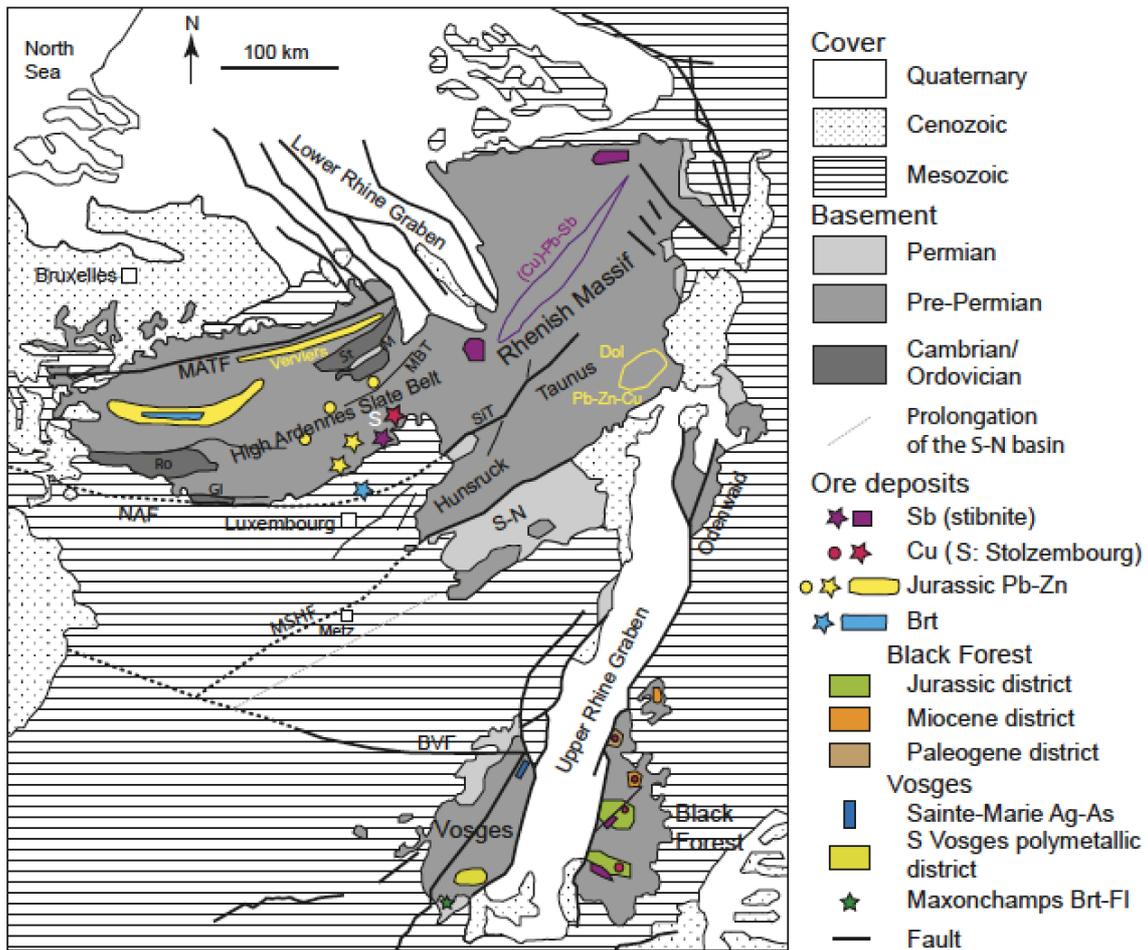
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1406 **Figure captions**



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Figure 1. Luxembourg ore deposits and occurrences in their regional context. Geology adapted from

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France 1/1 000 000 geological map (BRGM), Timar-Geng et al. (2006), Sintubin et al. (2008)

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and Pryvalov et al. (2015). The Sb deposits are taken from Baatartsogt et al. (2007) (Black

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Forest) and Wagner and Cook (2000) (Hunsrück). Pb-Zn-(Cu) deposits from the Hunsrück

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are taken from Kirnbauer et al. (2012), while Pb-Zn-Ba deposits from the Ardennes (Verviers

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syncline, etc.) are taken from Dejonghe (1998). The Black Forest Pb-Zn-F-Ba and

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polymetallic districts are taken from Baatartsogt et al. (2007), Staude et al. (2009) and Ströbele

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et al. (2012). Vosges deposits are from Fluck and Weil (1975). Pre-Devonian inliers in the

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Ardennes belt: Gi Givonne, Ro Rocroi, St Stavelot. Permian basins: M Malmédy, S-N Saar-

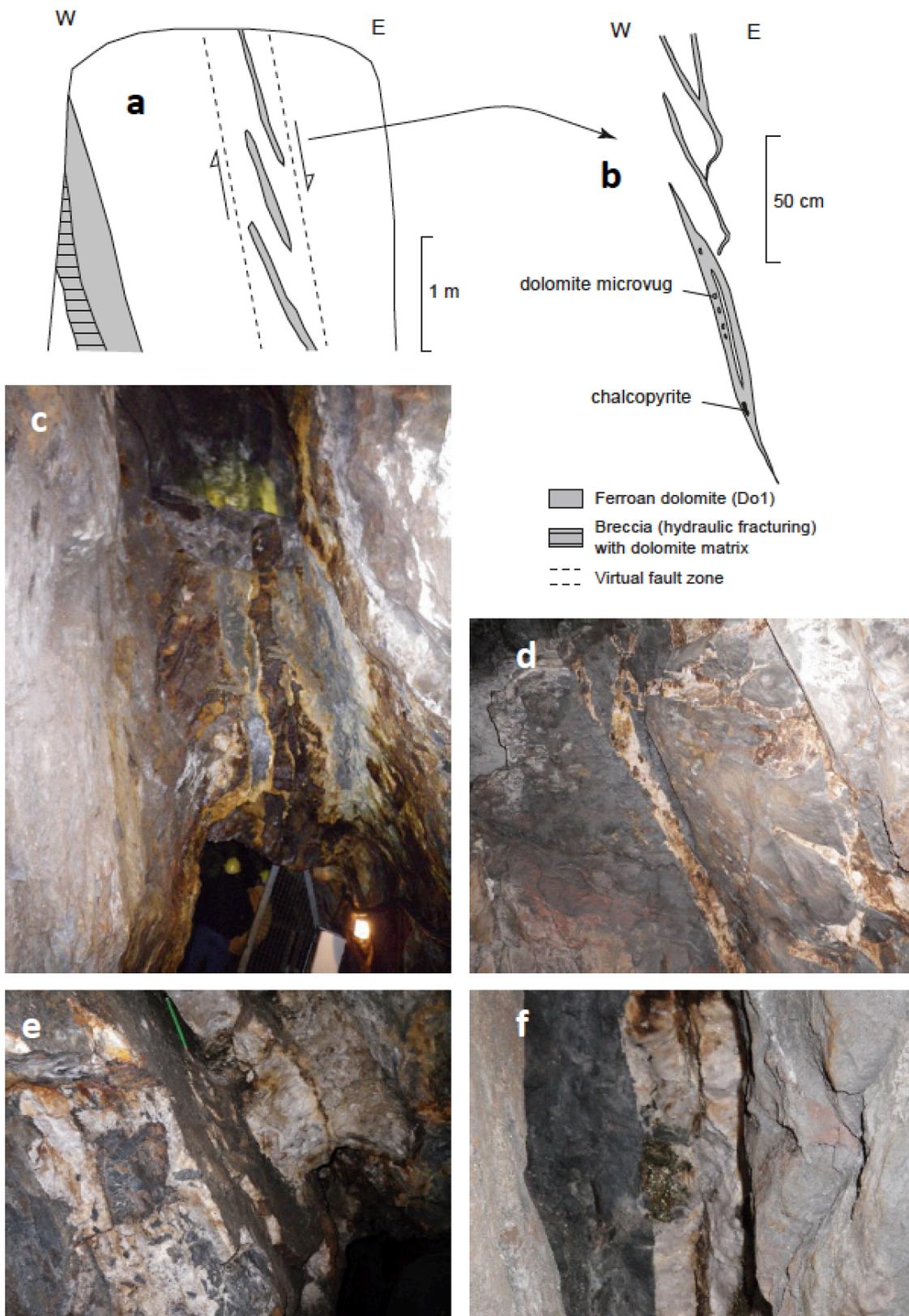
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Nahe. Faults: BVF Bray-Vittel fault, MBT Malsbenden back thrust, MFAT Midi Fault-

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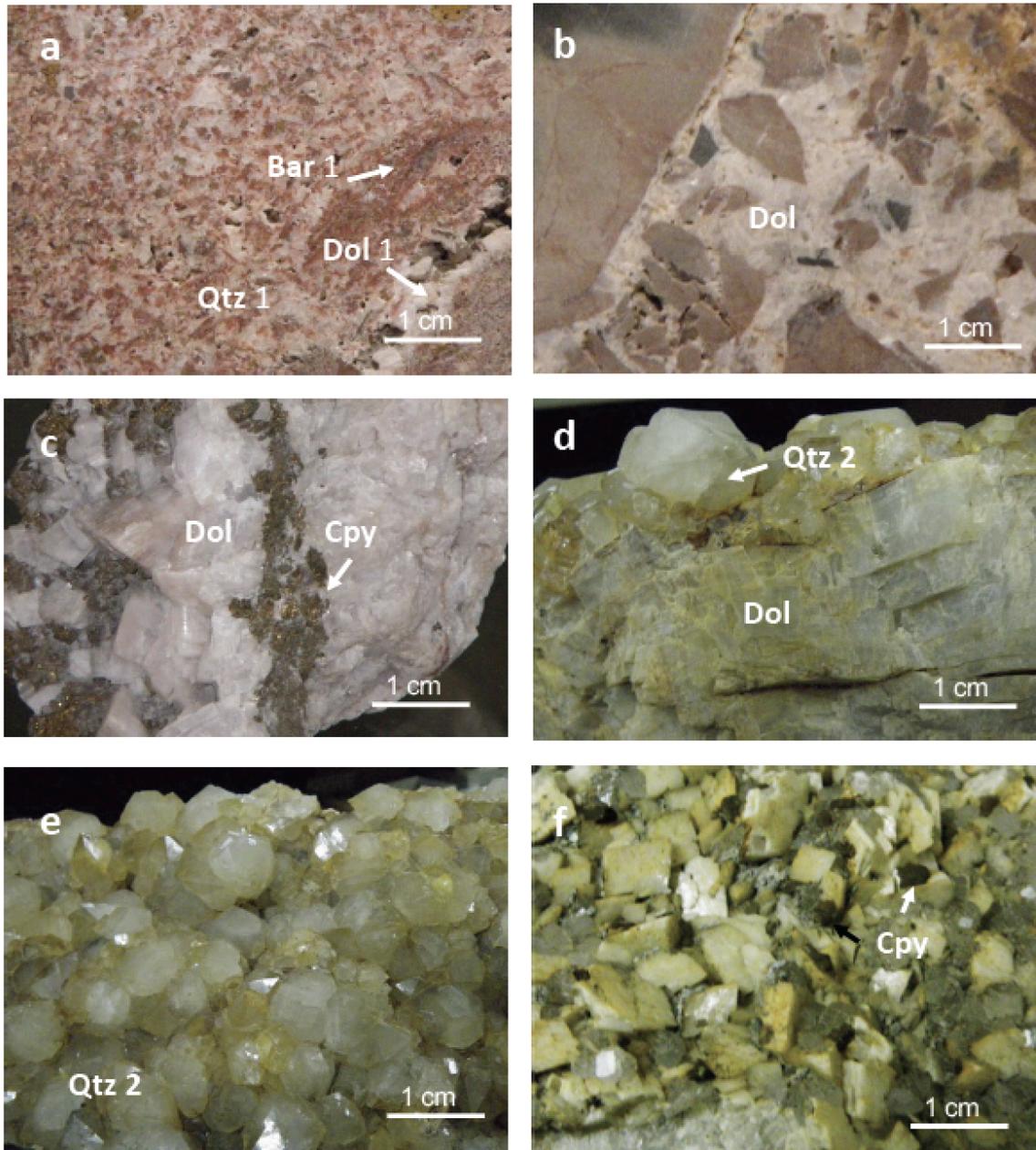
Aachen thrust, MSHF Metz-South Hunsrück fault, NAF North Artois fault, SiT Siegen thrust.

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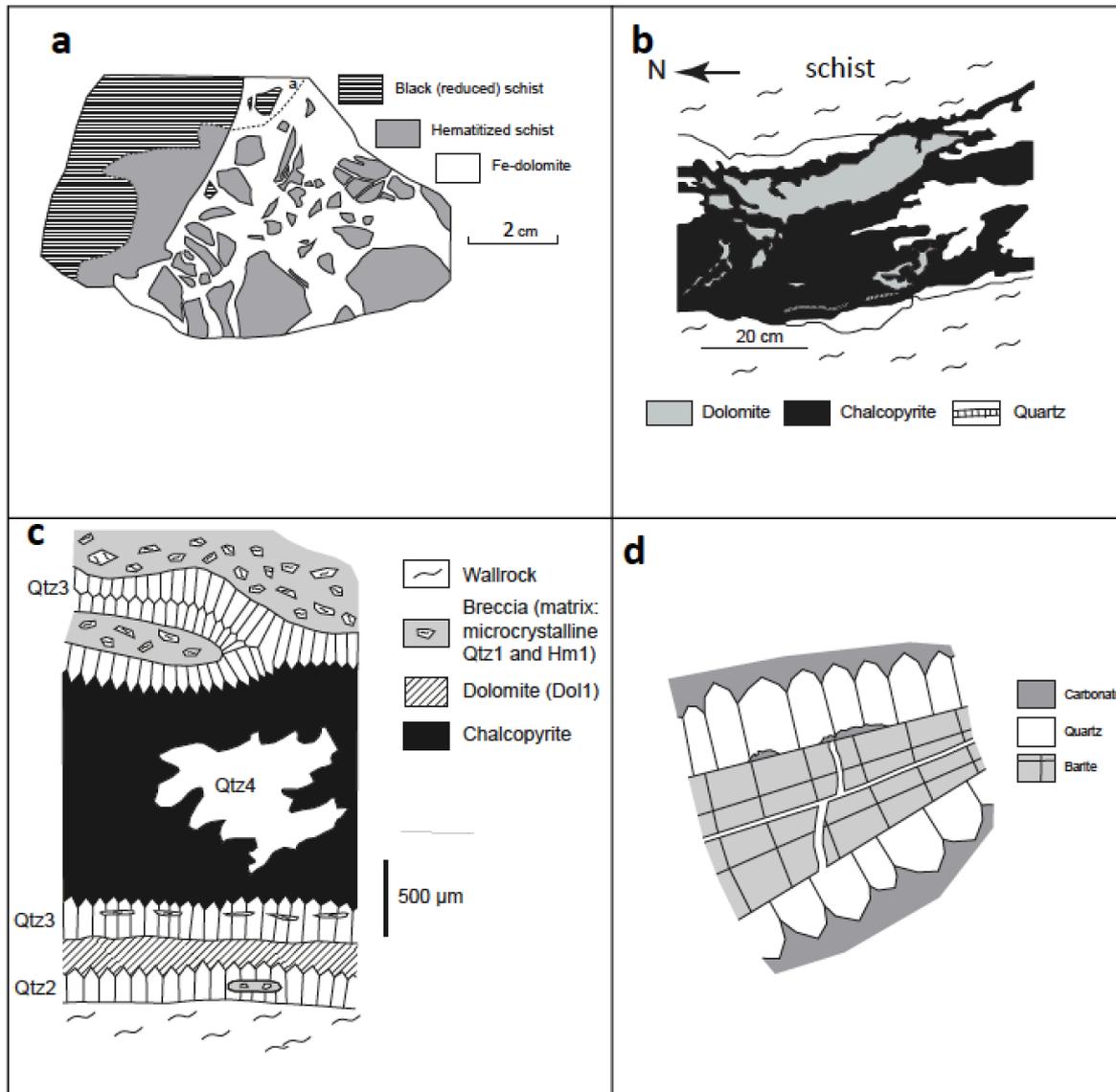


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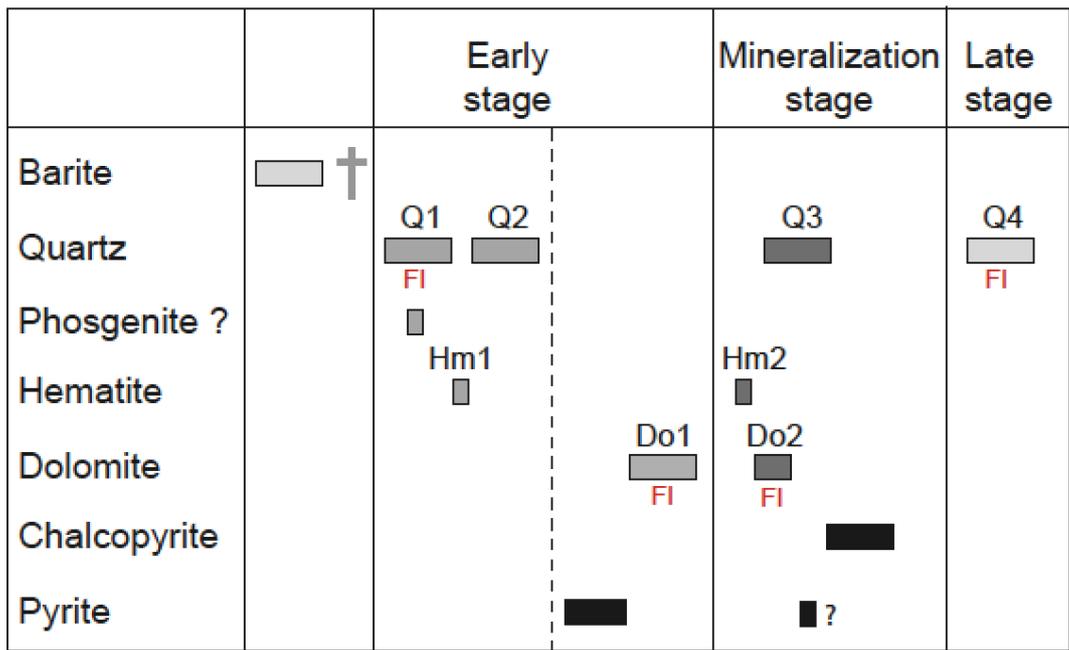
Figure 2. a, b: Carbonate veins structure at Stolzenbourg, drawing from the level 1 gallery. c, d: photographs of the level 1 addit; e,f details of the vein infilling: e: breccia cemented by dolomite, f: chalcopyrite in a subvertical dolomite infilling.



1424  
 1425 Figure 3: Macrophotographs of ore samples. a: red ore with quartz (Qtz1), dolomite (Dol 1) and  
 1426 barite (Bar1); b: breccia cemented by dolomite; c: large dolomite crystals and chalcopyrite; d:  
 1427 Dolomite covered by euhedral bi-terminated euhedral quartz crystals (Qtz2), e: late infilling  
 1428 of euhedral quartz (Qtz2), f: euhedral dolomite crystals covered by chalcopyrite nodules.



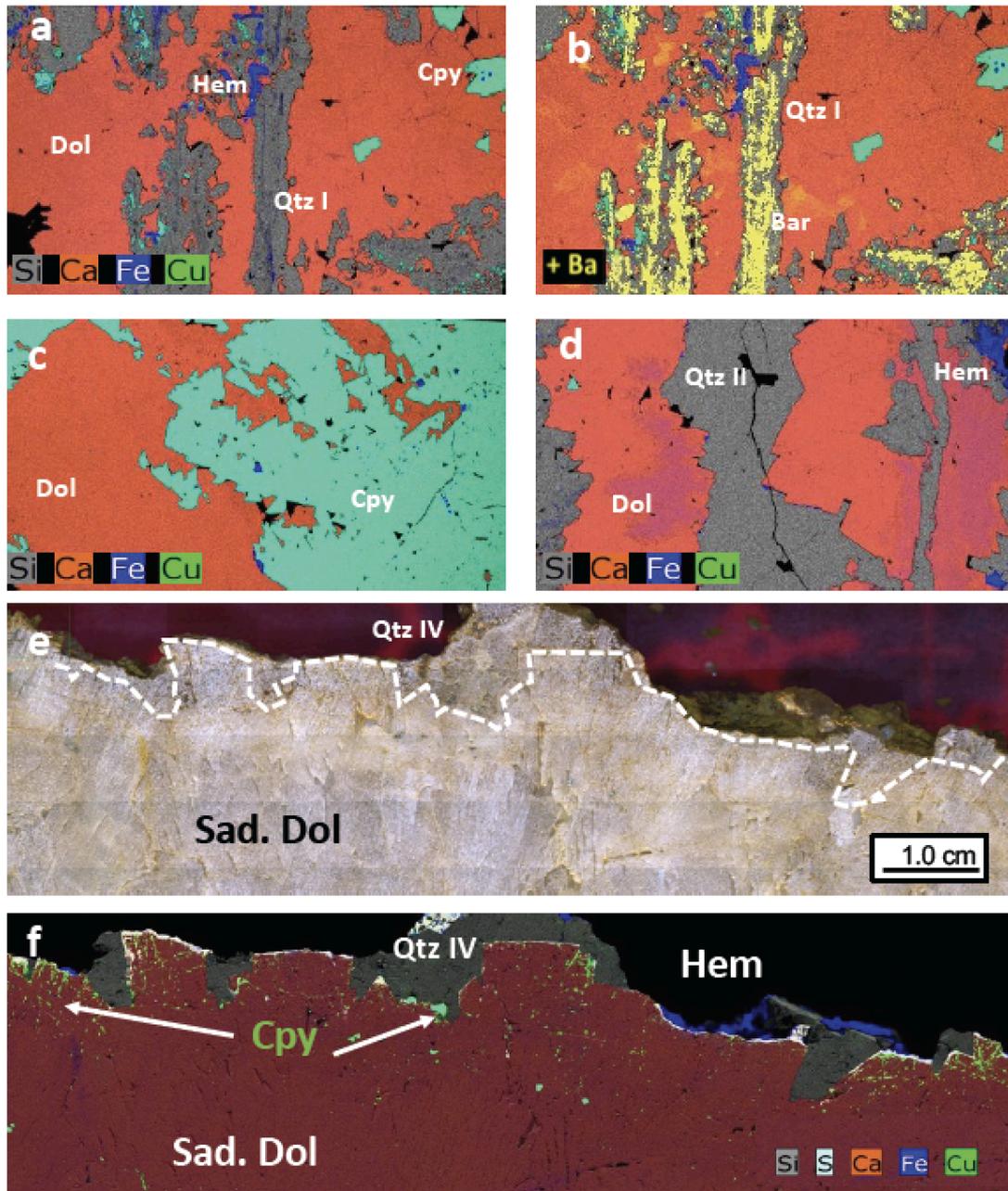
1429  
 1430 Figure 4. a) Drawing of a Stolzenbourg mine sample from the MnhnL collection (ZA109),  
 1431 illustrating the early reddening of the country-rock schists before hydraulic fracturing and the  
 1432 formation of the dolomite-cemented breccia. The dotted line “a” marks the boundary between  
 1433 reduced and oxidised schists as established before the inception of hydraulic fracturing. b) Ore  
 1434 texture at the vein scale in the Stolzenbourg mine, at level 1 (redrawn from Filippo et al.  
 1435 2007). c) Sketch drawing of a mineralized vein from the Riedgerbäsch exploration drive at  
 1436 Stolzenbourg. d) Drawing of a thin section in a barite sample (ZA094) from the Stolzenbourg  
 1437 mine.  
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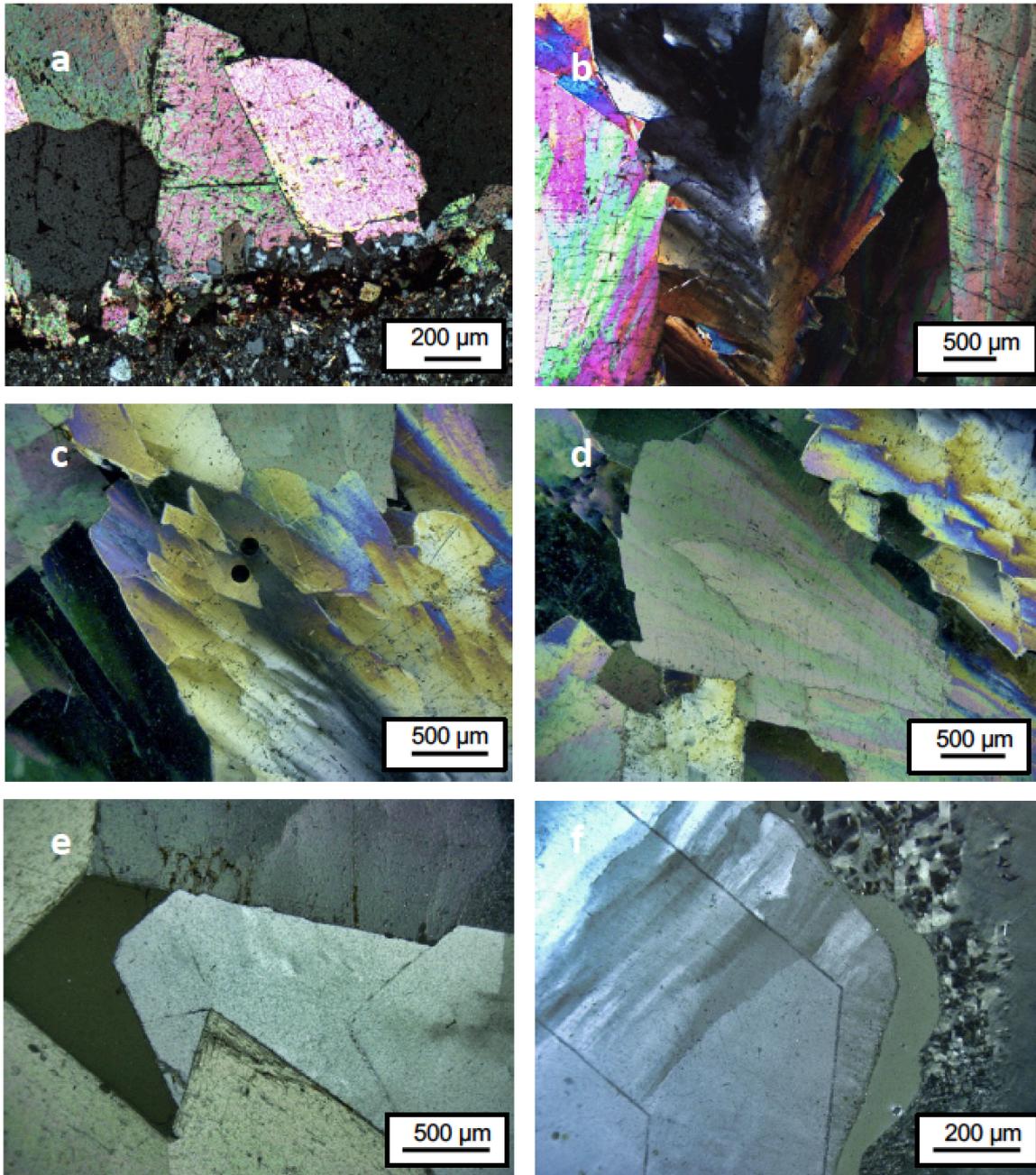
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1440 Figure 5 Paragenetic succession at the copper mine of Stolzembourg.

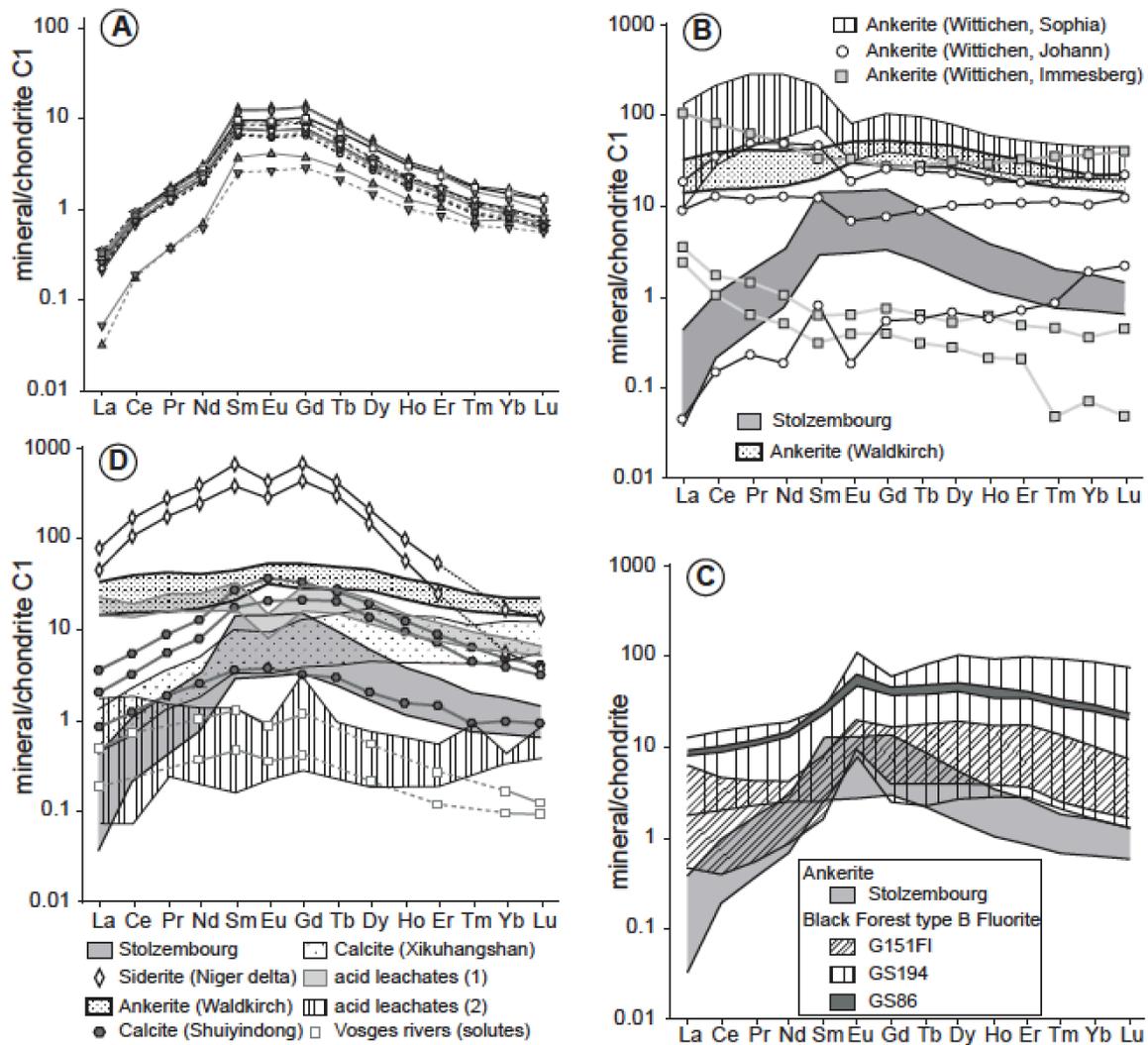
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1442  
 1443 Figure 6: MicroXRF maps of element distribution. a) red ore: association quartz (Qtz 1), dolomite  
 1444 (Dol 1), chalcopyrite, hematite; b) barite partly replaced by quartz, included in dolomite; c)  
 1445 relationships between dolomite and chalcopyrite, d: dolomite with microdomains enriched in  
 1446 iron (same sample as c); d) euhedral dolomite and quartz (Qtz3) infillings; e: macrophotograph  
 1447 of saddle dolomite covered by euhedral quartz Qtz 4; f: microXRF image of the same sample  
 1448 showing chalcopyrite grains in the late growth band and below Qtz4.  
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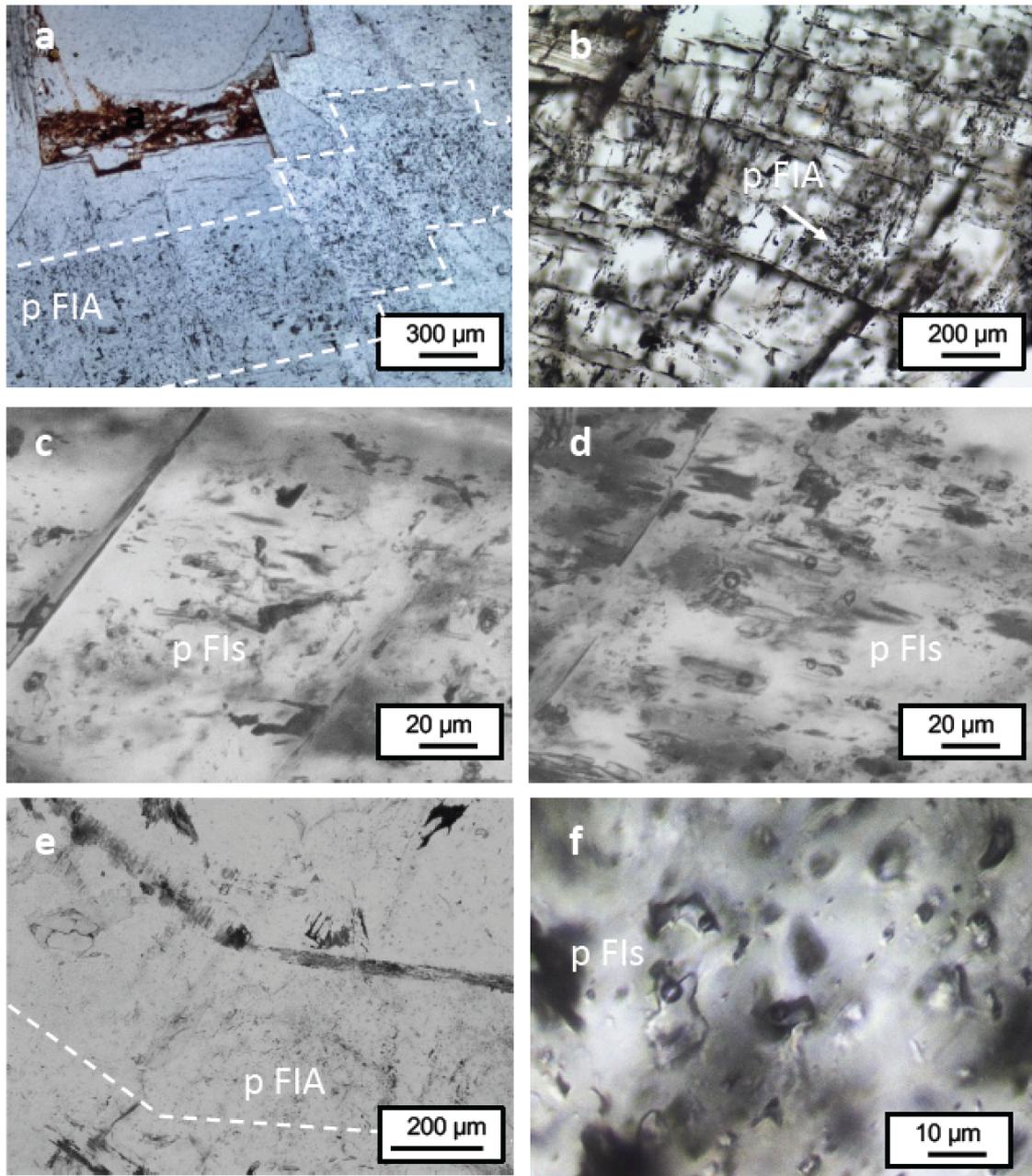


1450  
 1451 Figure 7. Microphotographs of quartz-dolomite assemblage. a: quartz (Qtz 2) preceding dolomite  
 1452 (Dol 1), b: plumose dolomite crystals, saddle dolomite 2, c: saddle dolomite 2 with craters of  
 1453 LA-ICP-MS analyses (black dots), d: saddle dolomite crystals, e: euhedral quartz Qtz 4 over  
 1454 saddle dolomite 2, f: quartz growth bands of Qtz 4.  
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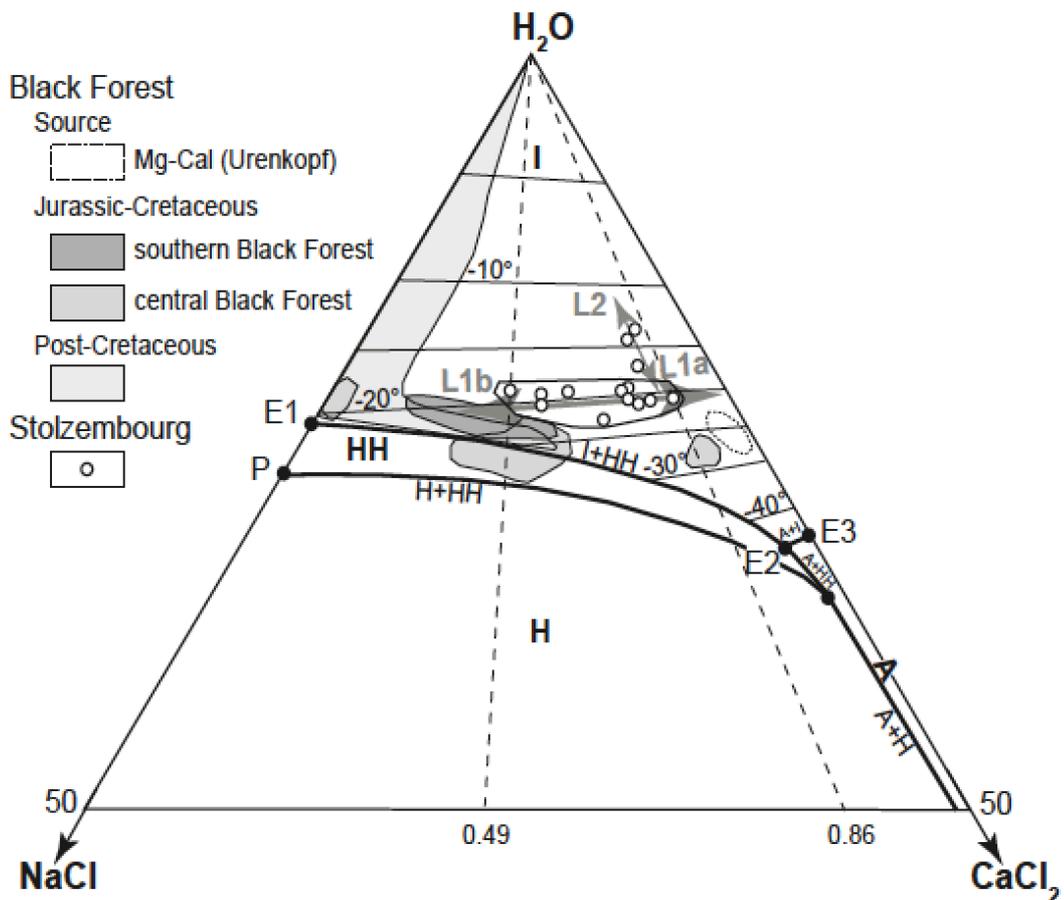


1456  
 1457 Figure 8. REE data for the Stolzembourg dolomite and comparison with a selection of similar data.  
 1458 A: REE spidergrams of the Stolzembourg dolomites. B: comparison of the Stolzembourg REE  
 1459 patterns with a selection of Black Forest ankerites (data from Staude et al. .2012 a). C:  
 1460 comparison of the Stolzembourg REE pattern with a selection of Black Forest fluorites (data  
 1461 from Schwinn and Markl 2005). D: Comparison of the Stolzembourg REE patterns with a  
 1462 selection of carbonates from other deposits worldwide (data from Peng et al. 2003; Shu et al.  
 1463 2009; Rongemaille et al. 2011) and with the results of experimental (Ohr et al. 1994) and  
 1464 natural (Tricca et al. 1999) leaching. The dolomite REE contents are normalized to the C1  
 1465 chondrite (Anders and Grevesse 1989).

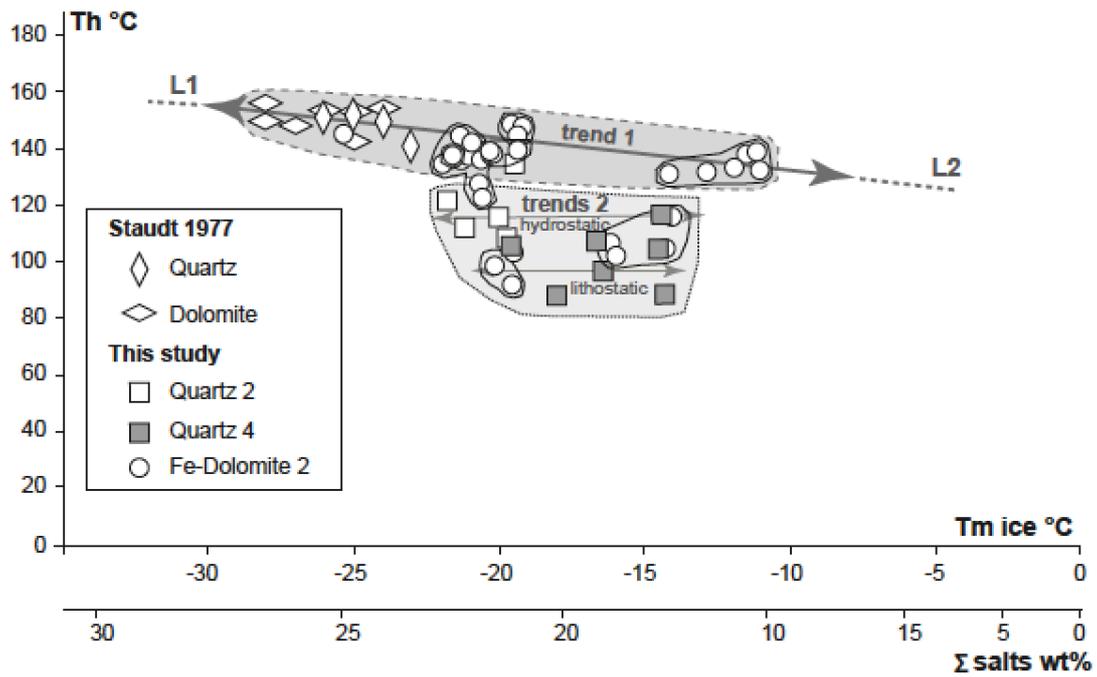
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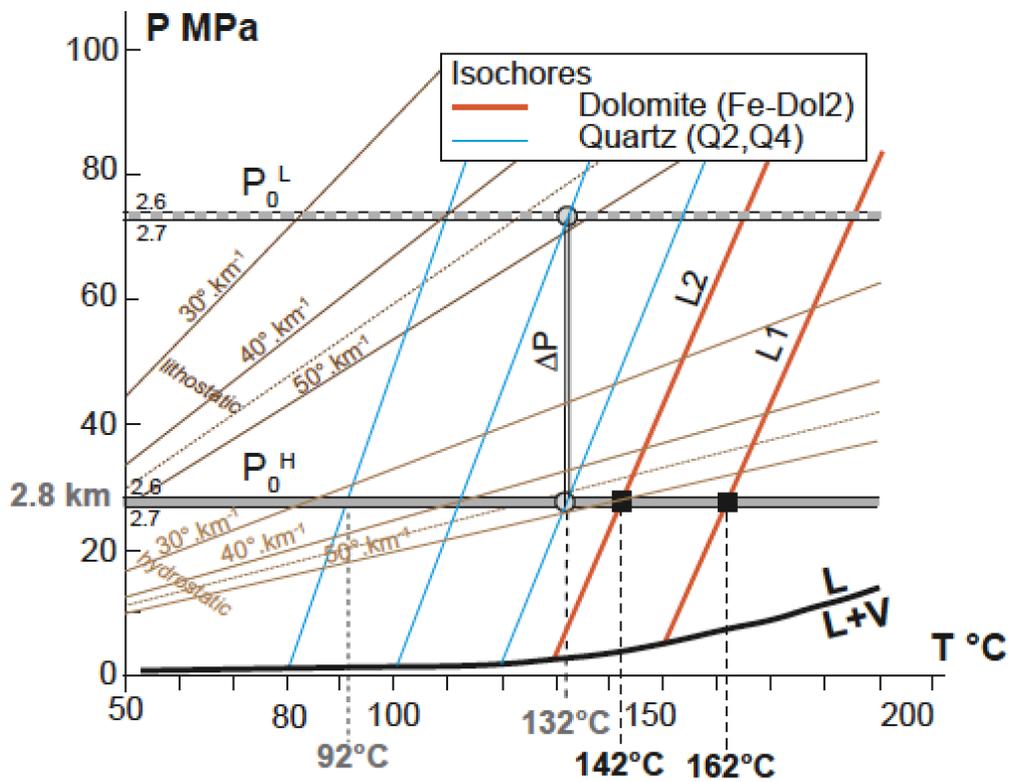
1467  
 1468 Figure 9: Fluid inclusions assemblages in quartz and dolomite from the main Stolzembourg  
 1469 vein. a: distribution of primary FIA (p FIA) in growth bands of saddle dolomite; b: location  
 1470 of p FIA in dolomite growth bands; c: two-phase FIA, Lw in dolomite; d: two-phase FIA, Lw  
 1471 in dolomite showing elongated shapes with edges subparallel to the main crystallographic  
 1472 orientation; e: growth band in quartz Q2 with primary FIs cluster (p FIA); f: primary two-  
 1473 phase FIs in quartz Q4.  
 1474



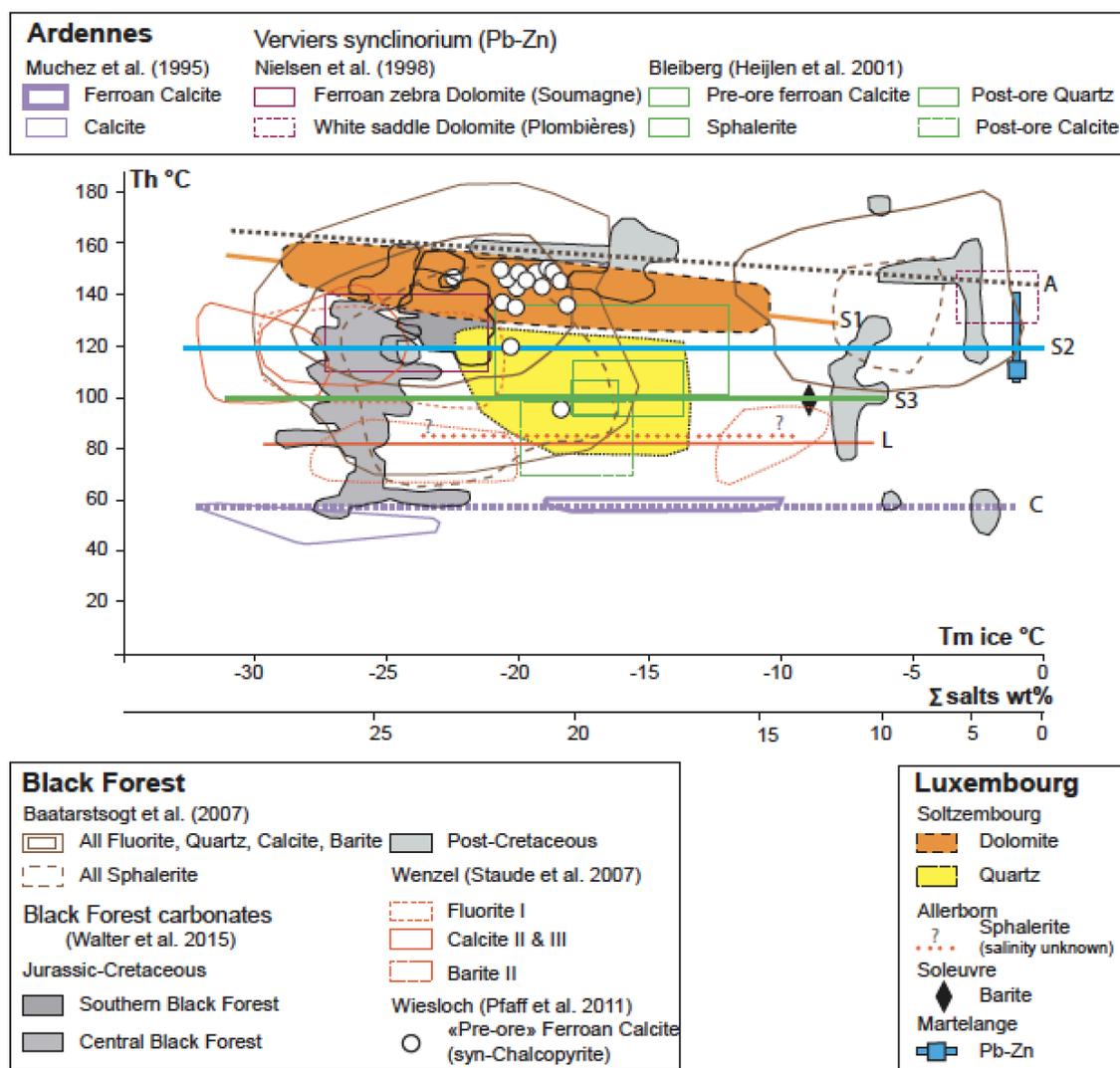
1475  
 1476 Figure 10: Estimated compositions of the Stolzembourg brines from dolomite and quartz, in the  
 1477 H<sub>2</sub>O-NaCl-CaCl<sub>2</sub> system (phase diagram adapted from Bodnar 2003). Phase fields and  
 1478 cotectic labelling: A antarcticite, H halite, HH hydrohalite, I ice; eutectic points: E1 H<sub>2</sub>O-  
 1479 NaCl-CaCl<sub>2</sub>, E2 H<sub>2</sub>O-NaCl, E3 H<sub>2</sub>O-CaCl<sub>2</sub>; P: H<sub>2</sub>O-NaCl peritectic point. Most hydrohalite  
 1480 melting temperatures ( $T_{m\ hh}$ ) were obtained for high salinity FI (with similar low  $T_{m\ ice}$  around  
 1481  $-20^{\circ}\text{C}$ ), displaying evidence (very variable Na to Ca ratios) for a mixing trend between two  
 1482 fluid poles (L1a and L1b). The few  $T_{m\ hh}$  measured in lower salinity FI suggest the existence  
 1483 of a trend toward the H<sub>2</sub>O pole, possible evidence for a mixing trend between the L1 brines  
 1484 and a low-salinity L2 fluid.  
 1485



1486  
 1487 Figure 11.  $T_h$ - $T_{m\text{ ice}}$  (bulk salinity) diagram for the Stolzenbourg fluid inclusions in Stolzenbourg  
 1488 quartz and dolomite. Individual FIs are plotted. Two trends may be defined based on the main  
 1489 host for the FI, either the Fe-dolomites (trend 1) or the quartz (trend 2). These trends may be  
 1490 interpreted as mixing trends. See the text for an explanation.

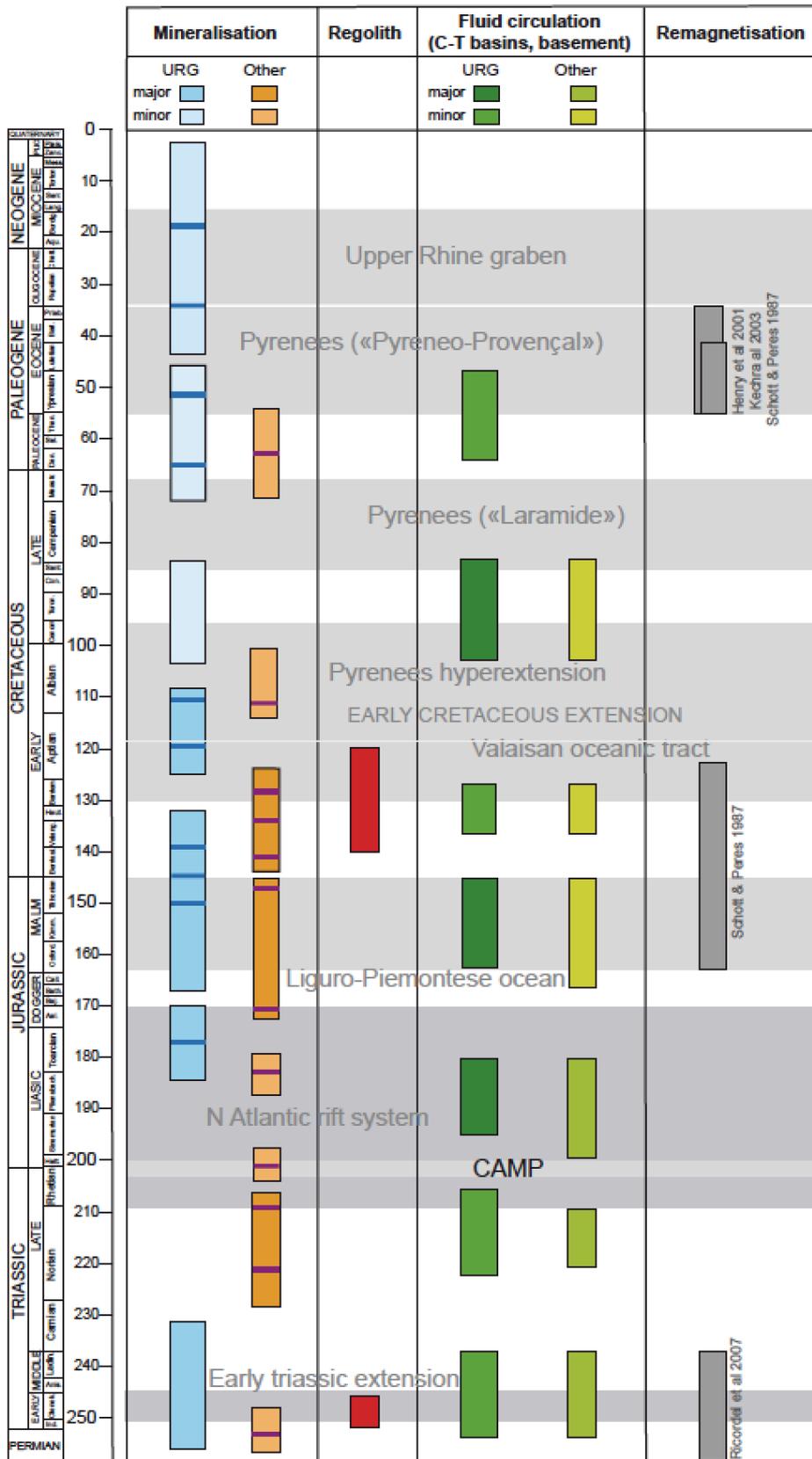


1491  
 1492 Figure 12. Isochores of the Stolzenbourg fluid inclusions and estimation of the P-T trapping  
 1493 conditions.  $P_0^H$ : estimated hydrostatic pressure during copper ore formation;  $P_0^L$ :  
 1494 corresponding lithostatic pressure. See the text for an explanation.



1495  
 1496 Figure 13. Comparison of Luxembourg fluids with mineralizing fluids from various districts in the  
 1497 Ardennes and the Black Forest in a  $T_h$ - $T_{m\ ice}$  (or bulk salinity) diagram. When necessary, bulk  
 1498 salinity in published diagrams was converted into  $T_{m\ ice}$ . All these fluids are Ca-rich, but as  
 1499 the Ca/Na ratio usually remains unknown (due to a lack of pertinent microthermometric data),  
 1500 the bulk salinity- $T_{m\ ice}$  bijection was calculated from Steele-MacInnis et al. (2011) for an  
 1501 arbitrary 0.5 value of the  $XCaCl_2$  parameter. The mixing trends observed at Stolzembourg  
 1502 lines S1 to S3 in the figure are seen to be representative (i) of some other Luxembourg deposits  
 1503 and (ii) of many deposits from both the Ardennes and the Black Forest; in particular, the  
 1504 Wesloch deposit data appear to fit the S1 trend associated with Cu deposition. A line A drawn  
 1505 parallel to S1 seems to be able to explain the highest  $T_h$  measured in several deposits. The line  
 1506 L, drawn close to the measured temperature at Allerborn, is also possibly representative of a

1507 series of Black Forest data. Finally, a low-temperature mixing trend (line B) is present in the  
1508 Ardennes and the Black Forest.  
1509



1512 Figure 14. A synthetic time framework for the fluid circulations in sedimentary basins and their  
1513 basements and the associated mineralizing episodes at the Upper Rhine graben (URG) and  
1514 western Europe scales. Explanations in the text; see Appendix A2-3 for more details. Data are  
1515 from: Aldega et al. (2016); Alderton et al. (2016); Brockamp et al. (2003, 2011, 2015);  
1516 Cathelineau et al. (2004, 2012); Clauer et al. (1996, 2008); Efimenko et al. (2014); Gigoux et  
1517 al. (2000); Grandia et al. (2000); Hagedorn et al. (1993); Heijlen et al. (2003); Henry et al.  
1518 (2001); Jowett et al. (1987); Kechra et al. (2003); Mertz et al. (1991); Muchez et al. (2022);  
1519 Munoz et al. (2005); Navarro-Ciurana et al. (2018); Piqué et al. (2000); Ricordel et al. (2007);  
1520 Schaltegger et al. (1995); Schlegel et al. (2007); Schleicher et al. (2006); Schärer et al. (1999);  
1521 Schneider et al. (1999, 2003); Schott and Peres (1987a, b); Symons et al. (2009, 2011); Thiry  
1522 et al. (2006); Timar-Geng et al. (2004, 2006); and Yans (2003).  
1523

Nature	Sample	Type	Size	T <sub>m hh</sub> (°C)	T <sub>m ice</sub> (°C)	T <sub>h</sub> (L) (°C)	Raman salinity wt.% eq. NaCl
<b>Stolzembourg</b>							
dolomite (Dol2)	ZA014	primary Lw	10-20 µm		-19.6; -20.2	90-105 (16)	
dolomite (Dol2)	ZA074	primary Lw	10-20 µm		-14/-11 (5)	130.8-142 (17)	15
dolomite (Dol2)	ZA092-1	primary Lw	10-20 µm	-25.4	-11.2	145-95 (6)	
dolomite (Dol2)	ZA092-2	p-secondary Lw	10-20 µm		-12	131.1-141 (4)	
dolomite (Dol2)	ZA031-1	primary Lw	10-20 µm		nd	139.5-146	
dolomite (Dol2)	ZA031-2	primary Lw	10-20 µm		-21.3	140-146	
dolomite (Dol2)	ZA031-3	primary Lw	10-20 µm	-37/-28 (7)	-22/-20.6 (13)	144.5-122.5 (13)	
dolomite (Dol2)	STOL1-1	primary Lw	20 µm		-15.7/-12.8 (3)		
dolomite (Dol2)	STOL2-1	primary Lw	10-20 µm	-26; -26	-20.3; -19.4	139; 140	
dolomite (Dol2)	STOL4	primary Lw	10-20 µm	-33/-25 (4)	-21/-19.2 (4)	148.6-141.9 (4)	
quartz Q2	ZA031-qtz	primary Lw	5-20 µm	-43/-31 (4)	-19.6/-14.3 (13)	116.5-84.3	
quartz Q2	ZA074-qtz	primary Lw	5-20 µm	-31; -30	-23/-19.1 (5)	107.3-134.5 (5)	
quartz Q4	STOL-Qtz-4	primary Lw	5-20 µm	-31	-22/-17	108-134	
<b>Allerborn</b>							
quartz	ZE120	secondary Lw	10 µm		-6/-2 (3)	211-220 (277*) (5)	
sphalerite	ZE60	primary Lw	10 µm		nd	93	
<b>Soleuvre</b>							
barite	ZM127	primary Lw	10-20 µm		-8.5	100	
<b>Martelange</b>							
quartz	ZE004	secondary Lw	10 µm		metastable (1.5)	107-130 (3)	1.5

Table 1: Microthermometric data obtained on fluid inclusions from Stolzenbourg, Allerborn, Soleuvre and Martelange. Several sub-samples were studied in some samples. T<sub>m hh</sub>: hydrohalite melting temperature, T<sub>m ice</sub>: ice melting temperature, T<sub>h</sub>: bulk homogenization temperature to the liquid state.