Synsedimentary to early diagenetic rejuvenation of barite-sulfides ore deposits: Example of the Triassic intrakarstic mineralization in the Lodève basin (France)

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HAL Id: hal-02912521

https://hal.umontpellier.fr/hal-02912521

Submitted on 22 Aug 2022

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18 **Number of words of text (without abstract, bibliography and figure captions): 8632**

19 **Number of references:** 89

20 **Number of figures:** 15

21 **Number of tables:** 2

22 **Number of appendices:** 1

23 **Abbreviated title:** Synsedimentary to early diagenetic rejuvenation of barite-sulfides ore de-

24 posits

Abstract

The exhumed Lodève Basin (Hérault, France) provides a rich suite of outcrops showing diagenetic Ba-Pb-Fe-Cu fronts trapped in karst system in Cambrian dolomites during the Triassic post-rift exhumation of the basin. The sedimentological analysis on 10 sites in the basin reveals that barites-sulfides fronts formed during humid-arid climate fluctuations and the emplacement of a shallow lake environment. The fabric of ore deposits, the microthermometry of fluid inclusions entrapped within barites and the strontium/sulfur isotopic compositions of barite-sulfides associations reveal two distinct groups of mineralizations, Type I and Type II, which are contemporaneous but resulting from different processes. The synsedimentary mineralization of the Type I, the presence of only primary single-phase liquid fluid inclusions within barite crystals and the gradual increase of $\delta^{34}S$ for both barites and chalcopyrites with depth (from -7 to +18.9‰ V-CDT) suggest ore precipitation close to the vadose zone under bacterial sulfate reduction (BSR) in a confined sulfate-rich playa lake aquifer. The similar $^{87}Sr/^{86}S$ ratios between barites and the overlying Triassic evaporites indicate that the barium and strontium derived directly from the overlying sulfate-rich lake. For the Type II, the high homogenization temperature of fluid inclusion entrapped within barite (modal Th between 60 and 80°C) and the association with hydrocarbon markers, confirm the participation of deeper basinal brines in addition to downward percolating sulfate derived from the lake environment. The high positive values of $\delta^{34}S$ for both barites and sulfides are typical of a precipitation linked to the combined action between anaerobic oxidation of methane and sulfate reduction (AOM-SR) at the sulfate-methane transition zone (SMTZ) during hydrocarbon migration. Similar $^{87}Sr/^{86}Sr$ ratios between Middle Triassic barites and previous Late Permian barites confirm that the source of metals precipitated at the SMTZ originated from the dissolution of anterior ore deposits located in the sulfate-depleted zone. This study links very shallow metallogenesis processes to reworking of MVT ore deposits by the action of sulfate-reducing bacteria around hydrocarbon seeps in a karstic environment.

1. Introduction

A metallogenic cycle in a sedimentary basin can be summarized by four main key elements (Routhier, 1980): source, transport, deposition and remobilization of metals. If the three first steps are already well understood, the mechanism of remobilization needs to be better constrained. In particular, several questions remain concerning the nature of factors that control the redistribution of metals and its timing during the basin structuring (extension, compression, tectonic quiescence, etc...). If structural and stratigraphic controls are predominant in the formation of sulfur-rich sediment-hosted deposits such as Mississippi Valley-Type (MVT) or SEDimentary EXhalative (SEDEX) and often linked to the mature burial stage of sedimentary basin (topography-driven, sediment compaction, orogenic squeezing, overpressured reservoirs, thermal and density reflux drives; Leach et al., 2010), the rejuvenation of these ore deposits can occur during early diagenesis. In particular, barium-sulfides mineralization are known to form close to the sediment-water interface (SWI) due to metal remobilization (e.g. Torres et al., 1996; Riedinger et al., 2006). The cycle of barium is part of the debate about early diagenetic ore deposits rejuvenation, particularly linked to the formation of shallow diagenetic fronts related to the sulfate-methane transition zone (SMTZ) few meters under the SWI (e.g. Goldberg and Arrhenius, 1958; Brumsack, 1986; Torres et al., 1996). The SMTZ consists in a chemical boundary at the meeting place between downward diffusing sulfates coming from the overlying seawater and the upward circulating biogenic/thermogenic methane originated from deeper sources. This diagenetic transition results from a coeval activity of sulfate-reducing bacteria (bacterial sulfate reduction – BSR; Machel et al., 1995; Machel, 2001) and the methane-oxidizing Archaea (Anaerobic Oxidation of Methane – AOM; Reeburgh, 1976; Reeburgh, 1983) that consumes dissolved sulfates. Therefore, the SMTZ limits an underlying sulfate-depleted zone where primary barites are

79 dissolved (Barnes and Goldberg, 1976; Reeburgh, 1976; Borowski et al., 1999; Aloisi et al.,

80 2004; Rodriguez et al., 2000; Dickens, 2001; Niemann et al., 2006). The barium ions released

81 into the porewater then diffuse upward or can be moved with sedimentary brines along

82 permeable pathways (Kastner et al., 1990) up to a zone just above the SMTZ where SO_4^{2-} is

83 available, and precipitate to form authigenic barite-sulfides fronts (e.g. Torres et al., 1996;

84 Bréhéret and Brumsack, 2000; Aloisi et al., 2004; Arndt et al., 2006; Riedinger et al., 2006).

85 However, the role of SMTZ in the remobilization and precipitation of diagenetic barite-sulfide

86 fronts is only demonstrated in marine environment away from terrestrial influence, while

87 some continental depositional environments, such as playa lake, can led to similar chemistry

88 conditions. In addition, the major part of studies on SMTZ are mostly based on offshore 1D

89 core data (Torres et al., 1996; Aquilina et al., 1997; Riedinger et al., 2006; Snyder et al., 2007;

90 Borowski et al., 2013; Arning et al., 2015; Magnall et al., 2016; Hu et al., 2017) as very few

91 outcrop analogues have been evidenced that can give a 3D view of such shallow

92 metallogenesis (Zhou et al., 2015; Fernandes et al., 2017).

93 The continental Lodève basin contains several Ba-F-Cu-Pb-Fe ore deposits infilling karst

94 systems and fault zones affected Cambrian dolomites. Exceptional outcrop conditions allowed

95 to evidence a main mineralizing event during Late Permian syn-rift burial identified as a

96 MVT ore deposit (Laurent, 2015; Laurent et al., 2017). In addition, polymetallic deposits are

97 entrapped within meteoric karsts developed very close to the Middle Triassic post-rift

98 unconformity of the basin and sealed by evaporitic marls (Lopez, 1992). The question here is

99 whether the post-rift episode of barite and sulfide mineralization is related to a hydrothermal

100 fluid circulation, as for the Late Permian metallogenesis, or a diagenetic remobilization of the

101 previous ore deposits? We propose here a detailed study of the depositional environment and

102 karst dynamics during the post-rift mineralizing event supplemented by a multi-scale analysis

103   of textures, mineralogy, fluid inclusions and radiogenic/stable isotopes (sulfur and strontium)

104   on mineralized markers. The objectives of this study will be to (i) constrain the link between

105   the sedimentary infill of meteoric karsts and ore trapping (ii) define the diagenetic

106   transformations, the different fluid events and associated stages of mineralization that follow

107   the post-rift exhumation of the basin, and (iii) understand the origin of metals as well as the

108   sulfur cycling in the system and its role in the timing and location of polymetallic deposits. *In*

109   *fine*, this multidisciplinary approach allows us to propose an integrated model of economic

110   metals trapping few meters below the SWI and to discuss the interconnection between karst

111   dynamics, playa lake environment and hydrocarbon dysmigration.

112

113

114   **2. Geological settings**

115   **2.1   Geodynamic evolution of the Lodève Basin**

116   The Lodève Basin, located 50km northwestern of Montpellier in the south of the

117   French Massif Central, is a 180 km² cuvette-shaped half graben (Fig.1A). The half-graben

118   geometry of the basin is linked to a gravitational collapse along the Hercynian mountain chain

119   from Late Carboniferous to Late Permian (Echtler and Malavieille, 1990). The series shows

120   an overall 15-20° southward dipping continental infilling bounded in the south by a north

121   dipping listric normal fault related to an inversion of a main thrust during the Late Hercynian

122   collapse (Lopez et al., 2008) (Fig.1B). During this phase, the progressive tilting of the basin

123   was accommodated at the hinge of the roll-over anticline by the development of an E-W

124   trending synthetic and antithetic fault corridor (Lopez, 1992; Wibberley et al., 2007; Laurent

125   et al., 2017; Fig.1A and 1B). Middle Triassic terrestrial deposits unconformably seal an

126   erosive surface truncating both the Late Carboniferous-Permian half graben and its basement

127   at the southern and northern basin margins (Fig. 1B). This post-rift unconformity marked the

128   end of the Late Hercynian tectonics followed by a major regional erosion during which at

129   least 1500m of Permian deposits where eroded, representing a gap of 15Myr (Lopez, 1992;

130   Laurent, 2015). The Mesozoic period corresponds to a major change of the tectonic regime

131   with the opening of the South-East basin, where the Lodève area corresponds to the western

132   continental high margin controlled by NE-SW trending faults. The complete sealing of the

133   residual Paleozoic reliefs is then linked to the overall extension of shallow marine carbonate

134   deposits during Jurassic. Jurassic series are today preserved on the Causse du Larzac plateau,

135   which was uplifted during the Cenozoic with the regressive entrenchment of the river

136   networks.

137

138   **2.2   Stratigraphy of the Lodève Basin**

139   *The Hercynian basement*

140   In the northern margin of the basin, the Stephano-Permian series onlap unconformably

141   the large wavelength folded and partly thrusted Cambrian basement at the hinge point of the

142   roll-over anticline (Lopez, 1992). The major part of the Cambrian deposits corresponds to

143   thick massive dolomite interbedded with thin calcschist layers. These carbonates are

144   intensively fractured and suffered a severe karstification and canyon entrenchment during the

145   Late Hercynian subaerial exposure.

146

147   *Syn-rift deposits (Stephano-Permian series)*

148   The Stephanian sedimentary deposits, which are only visible in the westernmost part

149   of the basin (Graissessac sub-basin) and evidenced at depth by older exploration drillholes

150   (Lod 2 projected drillhole in Fig.1B), are composed of thick coarse alluvial fan deposits at the

151   base, passing upward to coarse fluvial sandstones and muddy swamp to peat clay formations.

152   Above Stephanian series, the Permian deposits have been divided into two large

153   megasequences: the Autunian Group and the Saxonian Group (Gand et al., 1997). The

154   Autunian Group is composed of a 700m-thick isopachous series of deltaic sandstones

155   evolving upward into deep anoxic lacustrine black shales with high potential source rock for

156   hydrocarbon (Laurent, 2015) and interlayered with laterally continuous volcanic ash layers

157   (Odin, 1986). The Saxonian Group lies unconformably on the Autunian deposits and displays

158   a clear divergent pattern that marks the main southward tilting of the Hercynian basement

159   along the south bordering listric fault. The thickness of the Saxonian Group is estimated to

160   3000m at present day but has certainly reached 5000m during the syn-rift subsidence of the

161   basin (Laurent, 2015). It shows alluvial fan conglomerates passing rapidly to thick floodplain

162   red pelites interbedded with thin blue-green playa lake mudstone deposits.

163

164   *Post-rift deposits (Middle Triassic series)*

165   The Middle Triassic deposits seal respectively the Permian in the southern and

166   western part of the basin and the Cambrian and Precambrian basement in the northern part

167   (Fig.2A and 2B). It consists of a 250m-thick pile composed of sandstone, mudstone and

168   evaporite deposits, topped by mixed siliciclastic-carbonate facies at the transition with the

169   Early Jurassic series. The series can be subdivided into four main formations according to

170   their facies assemblage (Lopez and Mader, 1992; Fig.2C). The Lower Formation corresponds

171   to the first 120m and shows typical Buntsandstein facies reported to the period from Anisian

172   to Ladinian. It is mainly composed of fluvial sandstones passing to playa lake mudstone and

173   evaporite deposits and vice-versa in a symmetrical megacycle. The Middle and Upper

174   Formation (about 40m-thickness each one) show the same Keuper facies assemblage with a

175 basal 3-5 m-thick dolomite layer (key beds [a] and [b] in Fig.2C) capped by mudstones and

176 gypsum/anhydrite/dolomite interbeddings developed in shallow littoral sabkhas. The Rhaetian

177 Formation on top of the Triassic pile (Upper Norian) is characterized by mixed siliciclastic-

178 carbonate facies (Lower Unit in Fig.2C) passing upward to pure ooidal and bioclastic

179 grainstone-packstone deposits related to a shallow subtidal platform environment (Upper Unit

180 in Fig.2C).

181

182 **2.3   Metallogenesis of the basin**

183   The Lodève basin was the site of two episodes of barite-sulfide ore deposition, the first

184 during the Late Permian syn-rift structuring (Laurent et al., 2017) and the second following

185 the post-rift exhumation during the Middle Triassic. During the syn-rift phase, the Lodève

186 Permian basin experienced a long period of differential subsidence that led to a northward

187 basinal fluids migration at the interface between Cambrian dolomites and the Lower Permian

188 unconformity (Lopez, 1992; Laurent et al., 2017). Metal-rich dewatering fluids sourced in the

189 Autunian blackshales and ash layers and moved under thermal and pressure gradient below

190 the Early Permian seal to be accumulated at the hinge point of the roll-over anticline in the

191 northern part of the basin (Lopez, 1992; Laurent, 2015; Laurent et al., 2017). Fluids were

192 released and trapped along the active E-W compensation fault network, leading to

193 polymetallic barite-sulfide (Pb, Cu, Zn) veins in fault zone and paleokarst cavities (Lopez,

194 1992; Laurent et al., 2017). During Late Permian, the Autunian blackshales of the deepest part

195 of the basin reached the oil window and led to hydrocarbon migration according to the same

196 pathway and hydrodynamical conditions than prior metal-rich fluids (Laurent, 2015). Several

197 oil seeps are still visible at the contact between the Early Permian series and the Cambrian

198 basement (Lopez and Petit, 2003). This fluid event was characterized as a typical MVT ore

199 deposits linked to sediment dewatering during basin burial (Laurent et al., 2017).

200 Close to the post-rift unconformity marking the general exhumation of the entire basin,

201 different barite-sulfide deposits were identified in the rejuvenated Cambrian paleoreliefs

202 sealed by evaporitic marls in the northern part (Fig.2B and 2C; Lopez, 1992; Lopez, 1993).

203 These ore deposits which may result from a distinct mineralizing episode than the syn-rift

204 mineralizations are the focus of this paper.

205

206

207 **3. Materials and methods**

208 **3.1   Geological mapping and field studies**

209 The main work was conducted in the hanging wall of the Olmet normal fault on the

210 right bank of the Lergue River in the northern part of the basin where the lower formation of

211 the Middle Triassic onlaps unconformably the Cambrian basement (Fig.1, 2A and 2B). A de-

212 tailed geological map of the studied area was first carried out for the purpose of locating and

213 clarifying the main ore deposits and facies distribution along the major post-rift unconformity

214 (Fig.2A and 2B). Ten main ore deposits (identified by the name of the place and letter from a

215 to j in Appendix A) have been recognized and studied in this area. All these sites were care-

216 fully studied and sampled in order to characterize the lithology of the studied site, the sedi-

217 mentological assemblage and the fabric of the mineralized deposits. 4 main outcrops are de-

218 scribed in detail in this paper (in bold characters on Appendix A).

219 Complementarily, Triassic evaporitic gypsum and anhydrite were sampled at the near-

220 est accessible sites where this formation is accessible at outcrop (see Fig.1A for the location

221 of samples).

9

222

3.2 Petrography

224   Textures and mineralogy of ore deposits have been observed from polished thin sec-
225 tions using a Zeiss Scopa A1 optical microscope in transmitted and reflected lights at the Uni-
226 versity of Montpellier (France). These observations were supplemented by Scanning Electron
227 Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS) with a FEI Quanta 200
228 Field Emission Gun of Schottky type.

229

3.3 Fluid inclusion microthermometry

231   Fluid inclusion microthermometry was performed on 100μm-thick double polished
232 section using Linkam heating/freezing stage, mounted on a Leica microscope. The stage was
233 calibrated according to synthetic fluid inclusions (Sterner and Bodnar, 1984) at temperatures
234 of -56.6°C, 0.0°C and 374.1°C. The primary, pseudo-secondary and secondary nature of fluid
235 inclusions assemblages were identified according to the criterion defined by Roedder (1984)
236 and Bodnar (1985). In our study, only primary fluid inclusions were analysed reflecting the
237 P/T/χ properties of the mineralizing fluids such as (i) the homogenization temperature (Th), (ii)
238 the first apparent melting temperature at which liquids first co-exist with solids related to
239 eutectic temperature (Te) and (iii) the final ice-melting temperature (TmIce), when solids
240 completely disappeared. The McFlincor program (Brown, 1989) was used to calculate the salt
241 composition, the salinity and the density of the initial fluids (Bodnar, 1993; Duan et al., 1992).
242 Finally, fluorescence X and Raman spectroscopy were used to identify potential hydrocarbon-
243 rich fluid inclusions.

244

3.4   Strontium concentration and isotopic composition

Strontium isotopic composition of barites has been measured at Isotope Laboratory of BRGM (Orléans, France). Around 30-50mg of barite powder was partly dissolved in beaker with a solution of 10ml of 8N HCl which was heated at 100°C during 12 days. After centrifugation, the liquid is separated from the solid residue and the latter is dried and weighted. 5 to 15% of barite was dissolved. The liquid is then evaporated to recover the dry residue then mixed up with 0.3ml of 41N HNO_3 and diluted with ultrapure water. Normalized on the Sr content in samples, 2µg of Sr was dried and submitted to the purification chain. A chemical separation is then performed with the purification of the Sr using an ion-exchange resin (Sr-Spec) before mass analysis according to a method adapted from Pin and Bassin (1992) (total blank <1ng). For the analysis of $^{87}Sr/^{86}Sr$ ratios, 150ng of Sr was loaded onto a tungsten filament with tantalum activator and analysed with a Finnigan MAT262 multi-collector solid source mass spectrometer. The internal precision obtained during the analyses is around ±10ppm ($2\sigma_m$) according to repeated analyses of the NBS987 standard to test the reproducibility, with a mean value of $^{87}Sr/^{86}Sr$ of 0.710246 ± 0.000010 (2σ, $n = 18$). Sample ratios are normalized to the certified value of the NBS987 ($^{87}Sr/^{86}Sr= 0.710240$).

The strontium concentration have been measured using the in situ laser ablation method LA-ICPMS (Laser ablation – Inductively Coupled Plasma Mass Spectrometry) on 100µm-thick double polished sections, at Geosciences Montpellier (France). We used a Compex 102 excimer laser (LambdaPhysik) operating in the deep-UV, which is periodically infilling by an ultrapure ArF gas excited by 28 kV electric shock in order to associate the fluor with argon to form the ephemerian molecule ArF. As this molecule is unstable, the liberation of fluor atom induced a photonic ray with a wavelength of 193nm. The particles issued from the interaction between the laser and the samples are directed to the ICP-MS torch by a He

269 flux and then mix to argon. The ablation by He enhanced the sensibility of the mass

270 spectrometer and reduced the interelementary variations (Günther and Heinrich, 1999). The

271 quantification of elementary concentration of samples was realized through the repeated

272 measurements on a silicate glass (NIST 612) containing around 40ppm of most trace elements.

273 The control of the accuracy and precision of the analyses was based on natural reference

274 materials of BIR (basaltic glass) and artificial type of MACS3 (carbonate pellet). Signals are

275 analysed by a magnetic sector mass spectrometer Element XR (Thermofinnigan). Finally,

276 signal processing and concentration calculations were performed using GLITTER software

277 (GEMOC – Van Achterbergh et al., 2001).

278

279 **3.5 Sulfur isotopes**

280 Sulfur isotopes analyses of barites, gypsum and anhydrite were performed at the

281 Institute of Earth Surface Dynamics of the University of Lausanne (Switzerland) using a

282 Carlo Erba 1108 elemental analyser (EA, Fisons Instruments, Milan, Italy) connected to a

283 Thermo Fisher (Bremen, Germany) Delta V isotope ratio mass spectrometer (IRMS) that was

284 operated in the continuous helium flow mode via a Conflo III split interface (EA-IRMS). The

285 stable isotope composition of sulfur is reported in the delta (δ) notation as the per mil (‰)

286 deviation of the isotope ratio relative to known standards: $\delta = [(R_{sample} - R_{standard})/R_{standard}] \times 1000$, where R is the ratio of the major heavy to light sulfur isotopes

287

288 ($^{34}S/^{32}S$). The sulfur standard is the Vienna Cañon Diablo Troilite (V-CDT). Preparation of

289 samples have been made according to the method presented in Spangenberg et al. (2010). The

290 reference SO_2 gas was calibrated against the IAEA-S-1 sulfur isotope reference standard

291 (Ag_2S) with $\delta^{34}S$ value of -0.3‰. The overall analytical reproducibility of the EA-IRMS

292 analyses, assessed by replicate analyses of three laboratory standards (synthetic cinnabar, with

293 a working $\delta^{34}S$ value of +15.5‰; barium sulfate, +12.5‰; pyrite Ch, +6.1‰; pyrite E, −7.0‰)

294 is around ±0.2‰ (1 SD). The accuracy of the ^{34}S analyses was checked periodically by

295 analyses of the international reference materials IAEA-S-1 and IAEA-S-2 silver sulfides (0.3‰

296 and +22.7 ±0.2‰, respectively, values from IAEA-Catalogue and Documents) and NBS-123

297 sphalerite (+17.09 ±0.31‰, value from NIST-Catalogue and Documents).

298   In addition, in situ sulfur isotope measurements on 23 chalcopyrites were made by

299 Secondary Ion Mass Spectrometry (SIMS) equipped with a cesium source on CAMECA

300 IMS5F at the University of Montpellier (France). The internal precision as well as the

301 reproducibility of results was checked on laboratory standards of three chalcopyrites whose

302 $\delta^{34}S$ signatures are respectively 4.4 ±1.6‰, 3.47 ±0.42‰ and 2.29 ±0.2‰, giving an

303 analytical error inferior to ±1‰.

304

305

306 **4. Results**

307 **4.1 Architecture, mineralogy and texture of Middle Triassic ore deposits**

308 **4.1.1 The Roche Percée paleo-pothole**

309   The site of Roche Percée is located close to the right bank of the Soulondres River in

310 the western suburb of Lodève city (b in Fig.2A and Appendix A). The outcrop consists of an

311 isolated dyke of mineralized and silicified breccias, largely exhumed from the surrounding

312 rocks, and rooted into the Cambrian basement. Here the Triassic cover has been totally erod-

313 ed.

314   The mineralized dyke displays a subvertical east-west trending wall of 40 m-long, 4m-

315 wide and 8 to 12m-high entrenched parallel to the stratigraphic contact between beige massive

316 dolosparite in the southern border and blue-grey calcschists in the northern side (Fig. 3A).

317   The dyke infill is bounded by a silicified wall penetrating both the Cambrian dolomites and

318   the calcschists on a thickness of about 10 to 20cm and even reaching 4m in the northwestern

319   slab (Fig. 3B and 3C). Moreover, angular centimetre to pluri-decimetre-size blocks of silici-

320   fied wall are visible in the dyke infill, indicating that the major stage of silicification preceded

321   the mineralization. Three main facies, called respectively RP1, RP2 and RP3, have been ob-

322   served in the dyke infill:

323   **- RP1 Facies:** this facies consists of a black organic matter- and silica-rich pyrite bear-

324   ing mudstone forming the northward inclined slab in the northwestern part of the outcrop

325   (Fig. 3A and 3B). This facies is thinly laminated with lighter fine siltstone laminae alternating

326   with dark organic-rich and highly silicified mudstone laminae;

327   **- RP2 Facies:** composing the main dyke infill, the RP2 Facies is a well stratified pluri-

328   centimetre- to decimetre-thick barite-rich beige siltstone forming undulated bedsets with mul-

329   tiple low-angle truncations (Fig.3B, 3C, 4A and 4B). Perpendicular sections of the dyke show

330   a clear concave shape pattern of the bedsets attesting to a collapse during the phase of infil-

331   ling. In thin section, the RP2 Facies shows a particularly remarkable stacking of millimetre- to

332   centimetre-thick graded couplets including a silt and sand-size grains with discrete barite

333   crystals plates, passing upward to brown dolomitic siltstone (Fig.4C). Barite plates are often

334   broken and corroded (Fig.4D). Plates are progressively more abundant to the top forming

335   massive barite laminae of millimetre- to centimetre-size fibro-radiated spherules. Locally,

336   speckles and blebs of galena, chalcopyrite and gray copper are dispersed in barite (Fig.4E).

337   **- RP3 Facies:** the RP2 Facies is overlaid or passes laterally to massive mud-supported

338   breccia, composing the RP3 Facies (Fig.3B and 3C). The breccia consists in centimetre- to

339   pluri-decimetre size angular clasts of calcschists, dolomites and silicified surrounding rocks

340   floating into barite-rich siltstone to fine sandstone (upper part of Fig.4A). In some places, both

14

341 the RP2 and RP3 Facies display centimetre-size craters linked to gypsum-anhydrite dissolu-

342 tion (Fig.4A).

343

4.1.2 The Olmet Road paleo-lapiaz network

345 Along the Olmet Road (f in Fig.2A and Appendix A), an outcrop consists in a fault-

346 controlled Cambrian paleorelief partly onlapped by sandstones and marls belonging to the

347 Lower Formation of the Middle Triassic (Fig.2C and 5A). The main outcrop forms an

348 irregular 2.5 to 6m-high and 45m-long ENE-WSW trending escarpment. The vertical

349 succession shows in the upper part of the outcrop massive to roughly bedded Cambrian

350 dolomites with a general dip of about 80° to the south, unconformably onlapped by bluish

351 evaporitic marls and fine to very fine yellowish sandstones moulding the karstified paleorelief

352 (Fig. 5A). The intermediate part of the outcrop is characterized by a blurred and very irregular

353 orange to dark brown colored interval partly masking the surface of unconformity because of

354 the intense impregnation by limonites, goethite and hematite. This oxidized front has a

355 thickness ranging from about 1 to 4m according to the depth of karstification. Careful

356 observation of this interval shows that the beige-colored Cambrian dolosparites progressively

357 assumes upward a brown color with an increase in iron carbonate and silica content. In

358 parallel to paleo-lapiaz infill, silicified sulfide-impregnated subvertical bed-controlled bands

359 develop locally several meters below the paleosurface. The western part of the outcrop is

360 crossed by a NW-SE trending normal fault showing a throw of about 4m toward the North-

361 East.

362 Barite-sulfides mineralizations are covered by alternations of bluish gypsum-rich

363 marls and fine partly silicified sandstones (Fig.5A and 5B). Three types of mineralizations

364 have been observed below the unconformity surface, from the base of the outcrop to the

365 paleosurface: (i) pluri-centimetre-thick massive barite veins, without sulfides, dispersed in the

366 Cambrian dolomites with a random distribution; (ii) connected to the paleosurface, subvertical

367 pluri-decimetre-thick partly oxidized bed-parallel pyrite veins and sulfide-rich impregnations

368 of the Cambrian dolomites (Fig.5B); and (iii) the main ore facies consists in a complete

369 mineralized sedimentary infill all along the irregular karstic paleosurface affected by paleo-

370 lapiaz. In the central part of the outcrop, this main ore facies forms a laminated sulfide-rich

371 bluish vadose silty claystone including brown patches of iron oxides associated with barite

372 pockets (Fig.5A and 5C). This mineralized interval is capped by a 1m-thick brown sulfide-

373 rich siltstone to very fine sandstone, partly silicified sealing the karstic Triassic unconformity.

374 This facies is several meters-thick and fills completely the karstic cavities in the eastern and

375 western part of the outcrop. The mineralized suite include dispersed blebs and speckles of

376 galena, sphalerite and grey copper filling the intergranular porosity and forming thin veins or

377 platings associated to secondary copper and lead carbonates, barite and bitumen blebs. As this

378 facies is really representative to the Middle Triassic mineralizing event, we name this deposit

379 OR Facies in the following.

380

381 **4.1.3   The Montifort Road planar cavities string**

382   This ore deposit is located along the Montifort road to Olmet village in the south sub-

383 urb of Lodève city (a in Fig.2A and Appendix A). Here the Cambrian blue-grey calcschists

384 dip 75° to the south and are unconformably covered by the Middle Triassic deposits (Fig.6A).

385 The Triassic unconformity is clearly irregular with decimetre-large potholes sealed in onlap

386 by very fine brown sandstones and evaporitic marls interbeddings. About 1 to 1.5m below the

387 unconformity, the calcschists are intersected by superposed strings of interconnected planar

388 cavities parallel to the unconformity surface and partly filled with barite and brown fine

16

389   grained silts (Fig.6A and 6B). The size of the planar cavities is comprised between a few cen-

390   timetre to a few decimetre. They are surrounded by a sub-vertical fracture network developed

391   in bedding planes, enlarged by karstification process and sometimes infilling by vadose sedi-

392   ments. As observed in the Roche Percée paleo-pothole, the planar cavities string and associat-

393   ed veins are accompanied by an intense silicification of the surrounding calcschists penetrat-

394   ing the walls from about 10 to 20cm with red-coloured chalcedony development (4 in Fig.

395   6B). The planar cavities display a geopetal fabric with carbonate granules and siltstone sealed

396   locally by barite blocky cement (Fig. 6C and 7AD). The granules infilling the cavities show a

397   particularly relevant reverse grading with a size ranging from 100µm at the base to a few mil-

398   limetre at the top (Fig. 6B and 6C). Granules are rounded and composed of dolomudstone-

399   supported silts (Fig.7A). Laterally within the infilling, granules pass to more homogeneous

400   sediments constituting mud with curved cracks. In thin section, the fine-grained sediment and

401   associated granules are mainly composed of dolomudstone-supported silt including quartz and

402   iron oxides. Very fine-grained silt (20 to 100µm) partly fills the intergranular space with a

403   geopetal pattern. On cross polarized light microscopy, the granules show a partial penetrative

404   silicification with the development of quartzine spherolites tending to evolve into microquartz

405   (Fig.7A). The residual intergranular voids are upholstered with drusy megaquartz that can

406   close completely the remaining space (Fig.7B).

407   The barite and accessory sulfide cement developed discontinuously above the granule-

408   siltstone infill. The contact is erosional with a very irregular sharp and underlined by pluri-

409   millimetre-thick brown ankerite (Fig.6C, 7B, 7C). This mineralized facies is mentioned as

410   MR1 Facies in the following. Fluorescence X observations reveal a high content of organic

411   matter-rich patches within and along crystal faces of ankerite at the contact with barite crys-

412   tals (Fig.7D). Locally, the intrakarstic sedimentary infill is brecciated and incorporated as re-

413 sidual clasts or blocks in the barite cement. The barite develops as fan shaped cockade clus-

414 ters corresponding to the growing of large slats in an open space (Fig.6C and 7C). Close to the

415 contact with barites, pyrites, galena and sphalerite patches are present, always cemented by a

416 late sparitic calcite (Fig.9E) and often associated with bitumen bubbles and blebs trapped in

417 residual voids.

418 Two hundred meters north-eastward along the main road, the Cambrian dolomites are

419 unconformably onlapped by the basal conglomerate of the Early Permian dipping 25° to the

420 North (outcrop j on Fig.2A and Appendix A). The conglomerates are themselves capped hori-

421 zontally by the Middle Triassic sandstone and marl alternations. Here the Cambrian dolomites

422 and basal conglomerates are crossed by multiple barite and grey copper/chalcopyrite veins

423 and hydraulic breccia without any link with the overlying Triassic unconformity. This miner-

424 alized fabric, called here as MR2 Facies, is similar to the Late Permian MVT ore deposits de-

425 scribed by Laurent et al. (2017).

426

427 **4.1.4   The Belbezet karstic mine**

428 This site corresponds to an old mining work exploited during the roman period for

429 copper and silver. The main mining gallery is carved in the mineralized interval along the

430 basal unconformity on the flank of a paleorelief between the Cambrian dolomites at the

431 footwall and a debris-flow conglomerate at the hanging wall (e in Fig.2A, Fig.8A and 8B).

432 The stratigraphical contact shows a general dip of about 35° to the South-West. The debris-

433 flow conglomerate is about 2m-thick and includes numerous pebble-sized dolomite blocks

434 floating into a sandy matrix. It is capped by blue-green marls alternating with thin very fine

435 sandstone layers including pseudomorphs after anhydrite. The paleosurface includes metric

436 paleo-potholes associated with an open-fracture network descending several decimetres to

18

437 several meters below the unconformity and including pluri-decimetres blocks brecciated in

438 situ and intrakarstic infill.

439   The mineralized interval (BM Facies) fills the cavities network with a very variable

440 thickness. It is composed of sulfide-barite-rich silty-clayey matrix packing within

441 heterometric Cambrian blocks (Fig.8B and 8C) and passing upward to massive white barite

442 (Fig.8A and 8B). Barites are locally highly sheared and also injected by grey copper sulfides,

443 chalcopyrites and abundant bitumen droplets and heavy oil that totally stain the barite in grey

444 (Fig.8D).

445

446 4.2   **Fluid inclusion petrography and microthermometry in barites**

447 **4.2.1   Petrography of fluid inclusions**

448   The fabric of primary fluid inclusions in barite within the MR2 Facies, from the

449 northern part of the Montifort Road outcrop, displays a two-phase assemblage with an oblong

450 geometry positioned along growth zones and a size between 10 and 40µm. We have

451 intentionally excluded fluid inclusions close to the cleavage planes as barite is very sensitive

452 to post-crystallization deformation (Ulrich and Bodnar, 1988). The Rv (ratio between vapor

453 and vapor+liquid) is ranging between 10 and 20%.

454   Entrapped within blocky barites of the MR1 Facies from the Montifort Road planar

455 cavities string, we observed two generations of primary fluids inclusions: two-phase

456 inclusions with Rv of 20 to 30% close to the centre of the crystal and stable single-phase

457 liquid inclusion along the external face (Fig.9A). Secondary inclusions are also identified with

458 a higher Rv, between 50 and 60%, a larger size, and evidences of post-trapping deformation

459 such as necking-down. Very few and small hydrocarbon-rich fluid inclusions were identified

460 by fluorescence X despite the fact that oil and bitumen is clearly visible in the mineralized

461 facies. Raman analyses were not discriminating, because of the high fluorescence of the

462 samples linked to the important content of oil impregnations in barites.

463   Fluid inclusions entrapped within the rhythmic infilling of the Roche Percée paleo-

464 pothole (RP2 Facies) and the barite from the Olmet Road paleo-lapiaz (OR Facies) are

465 essentially stable single-phase liquid inclusions and very small in size considering the fine

466 barite crystallites (Fig.9B). Even during cooling of samples, no gas bubbles have nucleated in

467 these inclusions. Consequently, no microthermometry have been performed on these

468 mineralized facies.

469

470 **4.2.2 Microthermometry**

471   The results of microthermometry (Te, TmIce and Th) for all selected ore facies are

472 presented on Table 1 and Figure 10.

473   The primary fluid inclusions in the MR2 Facies of Montifort Road show a majority of

474 homogenization temperatures in the range of 180-200°C. The Te are between -30 and -20°C,

475 for an average of -24°C, indicating that the mineralizing fluid is an H_2O-NaCl brine with a

476 low proportion of Ca^{2+} (from -22.9°C: Crawford, 1981; from -21.2°C: Borisenko, 1977). The

477 TmIce are characterized by a wide distribution of values for an average of -8.77°C,

478 corresponding to a salinity of 12.6 wt%eq.NaCl (Brown and Lamb, 1989) and a density of

479 0.987 (Bodnar, 1994).

480   For the MR1 Facies within the Montifort Road planar cavities string, primary two-

481 phase inclusions have lower homogenization temperatures, mostly in the range of 60 to 80°C

482 for a mean value of 77°C. The modal values of Te and TmIce are between -25/-20 °C and -

483 12/-10°C respectively, corresponding to an average salinity of 13.56 wt% eq.NaCl and a

484 density of 1.069.

485

4.3   Sulfur and strontium geochemistry

487   Strontium concentration and strontium isotopes (^{87}Sr/^{86}Sr) analyses on barite of the

488   three main textural facies (RP2, MR1 and BM) were performed associated to sulfur isotopes

489   (^{34}S/^{32}S) measurements on both barites and chalcopyrites evidenced within a same facies.

490   Similar sulfur isotopes analyses have been made on chalcopyrites in a fourth sample of

491   mineralization from the Olmet Road (OR Facies) and also in evaporites belonging to the

492   Middle to Upper Triassic formations (EV1 and EV2 Facies). A comparison with the isotopic

493   signatures of Late Permian barites and sulfides presented in Laurent et al. (2017) was also

494   carried out in order to determine a potential geochemical inheritance (Table 2).

495

4.3.1   Ba-Sr concentration and strontium isotopes in barites

497   The Sr concentration in barites close to the Triassic post-rift unconformity ranges from

498   4400 and 11800ppm, far away from the barites attributed to the Late Permian in Laurent et al.

499   (2017) that ranges from 19500 to 43803ppm (Table 2).

500   Figure 11 shows the ^{87}Sr/^{86}Sr values as a function of strontium concentration for

501   Middle Triassic barites compared to the signature of the three ore generation of Late Permian

502   barites identified in Laurent et al. (2017). The strontium isotopic signature of the barites

503   composing the RP2 Facies is significantly lower than all other barites with a value of 0.70888,

504   but very close to the general value of Triassic evaporites which ranges between 0.70745 and

505   0.70795 after Koepnick et al. (1990) and up to 0.7086 after Song et al. (2015). The ^{87}Sr/^{86}Sr

506   values between 0.71139 and 0.71142 for BM and MR1 Facies respectively are close to the

507   signatures of the first and second generations of Late Permian barites.

508

509   **4.3.2   Sulfur isotopes of barites, chalcopyrites, evaporitic gypsum and anhydrite**

510   As chalcopyrites are often associated with barites in all ore facies studied in this paper,

511   we use the difference of $\delta^{34}S$ between barite and associated chalcopyrites in a same facies

512 $\delta^{34}S_{barite}$ - $\delta^{34}S_{chalcopyrite}$, annotated $\varepsilon^{34}S$, which may be representative of the fractionation of

513   sulfur isotopes during the precipitation of the barite-sulfide front. All results of sulfur isotopic

514   composition are synthetized in Table 2.

515   We obtained values of $\delta^{34}S$ of +13.7 and +14.79‰ V-CDT for the Triassic evaporitic

516   gypsum (EV1 Facies) and of +14.6 and +14.9‰ V-CDT for the Triassic evaporitic anhydrite

517   (EV2 Facies).

518   For the Middle Triassic barites, the $\delta^{34}S$ of OR and RP2 Facies ranges between +15.7

519   and +16.2‰ V-CDT and are slightly superior for the mineralizations corresponding to the

520   MR1 and BM Facies with $\delta^{34}S$ values between +16.2 and +18.5‰ V-CDT. For all Middle

521   Triassic barites, $\delta^{34}S$ values are higher than the Triassic evaporites but mostly similar to the

522   Late Permian barites which signatures range between +15.6 and +18.4‰ V-CDT (Laurent et

523   al., 2017).

524   The $\delta^{34}S$ for Middle Triassic chalcopyrites is different from Late Permian sulfide de-

525   posits ($\delta^{34}S$ between -15 and -5‰ V-CDT; Laurent et al., 2017) with two distinctive domains:

526   (i) negative $\delta^{34}S$ values for RP2 and OR Facies, ranging respectively from -2.1 to -

527   1.4‰ V-CDT and from -7.2 to -1.7‰ V-CDT. For these facies, the difference of $\delta^{34}S$ be-

528   tween barite and chalcopyrites $\varepsilon^{34}S$ ranges between +17.1 and +23.4‰ V-CDT, representing

529   an important fractionation of sulfur isotopes during the precipitation.

530   (ii) positive $\delta^{34}S$ values in BM and MR1 Facies. The BM Facies shows $\delta^{34}S$ varying

531   between +11.9 and +17.1‰ V-CDT, close to the Triassic evaporites signatures, and are char-

532   acterized by a very week $\varepsilon^{34}S$ ranging from +4.8 to -0.9‰ V-CDT. The MR1 Facies has a

533 δ^{34}S of +18.9‰ V-CDT, for a ε^{34}S of -0.4 and -2‰, thus close to 0‰ if we consider the ana-

534 lytical error of around 1‰ for SIMS measurements.

535   Even though some chalcopyrites are considered to be synchronous with barites accord-

536 ing to the petrographic study, we did not consider an isotopic equilibrium between these two

537 phases. Indeed, the temperatures calculated according to the Rye and Ohmoto (1974) and

538 Ohmoto and Lasaga (1982) equations give aberrant precipitation temperature values (superior

539 to 250°C) in comparison with those obtained by microthermometry.

540

541

542 **5.**   **Discussion**

543 **5.1**   **Timing and origin of mineralizaing fluids**

544   Field observations supported by fluid inclusions microthermometry and

545 sulfur/strontium isotopes analyses clearly indicate two main types of mineralization trapped in

546 the Cambrian paleokarst just below the Middle Triassic unconformity (Fig.11).

547   The early mineralization includes anhedral sulfides (pyrite, chalcopyrite, galena and in

548 less proportion sphalerite and tetrahedrite) that precipitated into void spaces of sheaf-like and

549 massive barite composing the intrakarstic sediments of the Roche Percée paleo-pothole (RP2

550 and RP3 Facies) and of the exokarst observed in the Olmet Road outcrop (OR Facies). The

551 alternation of barite and intrakarstic sediments in karstic cavities and the presence of

552 allochtonous corroded and broken barite crystals in the RP2 Facies indicates their

553 synsedimentary precipitation origin and hydrodynamic transportation during water table

554 fluctuation in the karst. For convenience, we named this event Type I mineralization.

555   A second type of barite-sulfides deposits has been observed associated with

556 hydrocarbon and mineralized few meters below the water table in endokarst network. They

557 were particularly observed at the Montifort Road outcrop and Belbezet Mine and include

558 euhedral sulfides (pyrite, chalcopyrite and galena) trapped into cockade-shaped barite for the

559 first area (MR1 Facies) and disseminated into a silty clayey matrix from the second zone (BM

560 Facies). The ore deposits related to this event is called Type II mineralization.

561   Complementarily, the barite of the MR2 Facies, sampled in a sub-vertical vein distant

562 from the post-rift unconformity, are characterized by higher homogenization temperature

563 (between 139 and 195°C) of primary fluid inclusions than for the Type I and Type II

564 mineralizations (between 49 and 102°C) (Fig.10 and Table 1). Such fluid characteristics are

565 very similar to the ore facies described for the Late Permian MVT episodes by Laurent et al.

566 (2017). Consequently, we attributed these veins as a prior mineralizing event regarding the

567 Middle Triassic mineralizing episodes.

568   Knowing that strontium isotopes do not fractionate below 400°C (Matter et al., 1987),

569 the ^{87}Sr/^{86}Sr of barites reflects the strontium isotopic composition of the source. In our case,

570 strontium isotopic signatures suggest two different sources of metals for Type I and Type II

571 mineralizations (Table 2 and Fig.12). The ^{87}Sr/^{86}Sr value of 0.70888 of barites of the Type I in

572 the Roche Percée paleo-pothole (RP2 Facies) is compatible with the direct participation of Sr

573 and associated Ba derived from the underlying Middle Triassic playa lake aquifer as the

574 signature is very similar to Triassic evaporites (^{87}Sr/^{86}Sr between 0.70745 and 0.70795 after

575 Koepnick et al. (1990) and up to 0.7086 after Song et al. (2015)). This direct connection

576 between the karst and the overlying depositional environment is also supported by the

577 synsedimentary features of mineralizations. On the contrary, the strontium isotopic signatures

578 of barites at the Belbezet Mine and Montifort Road outcrops (BM: ^{87}Sr/^{86}Sr of 0.71139; MR1:

579 ^{87}Sr/^{86}Sr of 0.71142), constituting the Type II mineralizations, are much more radiogenic than

580 Triassic evaporites (Fig.12) which preclude a direct link with the sulfate-rich lake waters and

581 rather suggest an external source of metals.

582 In the MR1 Facies, the high Th of fluid inclusions in barites, between 42 and 102°C,

583 and an elevated salinity (Fig.10), do not correspond to an early diagenetic stage close to the

584 SWI and necessarily involved the migration of deep basinal brines. The involvement of

585 basinal brines is supported by the systematical association of barites of the Type II and

586 hydrocarbon markers indicating that the petroleum system was still active during the Middle

587 Triassic. However, if the barite crystal initiated during deep basinal fluid migration, the

588 presence of single-phase liquid inclusion in the late stage of barite growing suggests that the

589 crystal development finalized within a low-temperature water (Goldstein and Reynolds, 1994).

590 Even if, the presence of oil in the Type II mineralization could indicate that the Middle

591 Triassic metallogenesis may be a simple continuation of the previous Late Permian fluid

592 migration (Laurent et al., 2017), we suggest that both episodes are decoupled. The cessation

593 of fluid migration linked to the 1500m post-rift exhumation of the basin margin during the

594 Middle Triassic (Lopez, 1992; Lopez et al., 1998; Laurent, 2015) is supported by the different

595 strontium isotopic signature between Middle Triassic barites and the latest generation of the

596 Late Permian Barites (Fig.12) (Laurent et al., 2017). The $^{87}Sr/^{86}Sr$ of the Type II barites are

597 very close to the barites associated with the first and second Late Permian fluid events

598 occurring in the Lodève Basin (Laurent et al., 2017) suggesting that metals for Type II

599 mineralizations were derived from the remobilization of previous barite-sulfide mineralization.

600 In addition the drastic decrease in the Sr concentration in the Middle Triassic barite (Fig.12) is

601 typical of the leaching of anterior barites by undersaturated water (Gordon et al., 1954; Cohen

602 and Gordon, 1961; Renault and Brower, 1971).

603

5.2 Ore trapping redox conditions

As demonstrated previously, strontium isotopic signatures of Type I barites confirm that the most valuable source of sulfur is the playa lake environment linked to semi-arid climate conditions. The high sulfur isotopes fractionation between Type I barite-sulfide deposits and the Triassic evaporites may indicate a process of BSR (Machel et al., 1995). In this case, we assumed that dark organic-rich facies infilling karstic cavities at the Roche Percée paleo-pothole (RP1 Facies) and local abundance of plants and wood debris in the basal debris-flow deposits at the Belbezet Mine could represent the source methane, necessary to bacteria metabolism. The presence of only primary single-phase liquid fluid inclusions indicates low-temperature precipitation, below 50°C (Goldstein and Reynolds, 1994) (Table 2), compatible with the BSR reaction which is stopped around 80°C (Postgate and Schwartz, 1985). The high values of the $\varepsilon^{34}S$, between 17.1 and 23.4‰ V-CDT (Fig.13 and 14), is consistent with the process of BSR development in a closed-system for sulfate supply (Harrison and Thode, 1958; Ohmoto, 1990; Canfield, 2001; Wortmann et al., 2001; Lerouge et al., 2011).

In the case of the Type II mineralization (MR1 and BM Facies), the $\delta^{34}S$ of sulfides show an important ^{34}S enrichment with $\delta^{34}S$ reaching the value of Triassic evaporites and synchronous barites (Fig.13 and 14). High values of $\delta^{34}S$ in sulfides in a low temperature sulfate-rich environment are generally attributed to the development of a SMTZ associated with a process of anaerobic oxidation of methane coupled with bacterial mediated sulfate reduction (AOM-SR). As explained in the introduction, the SMTZ is a redox boundary resulting from the coeval activities of sulfate-reducing bacteria and anaerobic methanotropic Archaea (Reeburgh, 1976; Alperin et al., 1988; Hoehler et al., 1994; Borowski et al., 1997; Borowski et al., 1999; Aloisi et al., 2000; Dickens, 2001; Niemann et al., 2006; Knittel and Boetius, 2009). At

628   the depth of SMTZ, AOM is responsible for the production of a significant amount of dis-

629   solved HS⁻ and because the interstitial sulfate is really enriched in ^{34}S at this depth, the reac-

630   tion between dissolved sulfur and metals results in the precipitation of ^{34}S-rich sulfides com-

631   pared to sulfides in the overlying sulfate reduction zone which is submitted to BSR, as it is the

632   case for the Type I mineralization. A crucial element in our study area is the migration of hy-

633   drocarbon contemporaneous to the Type II mineralizations. Consequently, we assume that, at

634   the time of a permanent shallow lake environment, a downward diffusion of sulfates toward

635   the karst network and the rise of deep hydrocarbons in the Cambrian basement were condu-

636   cive to the formation of a SMTZ (Fig.14). The undersaturation in SO_4^{2-} below the SMTZ

637   caused the dissolution the Late Permian barite-sulfide deposits thus constituting the main

638   source of sulfate and barium for the Type II mineralizations, as also demonstrated by the simi-

639   lar strontium isotopic signature between Type II and Late Permian barites. When hydrocar-

640   bons reached the SMTZ, the increase of alkalinity in the solution caused the formation of au-

641   thigenic carbonates (Moore et al., 2004; Raiswell and Fisher, 2004; Meister et al., 2007) as

642   evidenced by the hydrocarbon-rich ankerite minerals systematically surrounding the minerali-

643   zations in the endokartic cavities. Neo-formed barite forming at SMTZ is not so ^{34}S-enriched

644   compared to Triassic evaporites and the ε^{34}S is consequently very low (Fig.13 and 14). The

645   weak sulfur isotopes fractionation between sulfides and sulfates at SMTZ have been already

646   demonstrated for diagenetic fronts developed close to the seafloor and is the consequence of

647   an open system for sulfate supply (Jørgensen et al., 2004; Borowski et al., 2013; Magnall et

648   al., 2016).

649   We saw that the precipitation of Type I and Type II can happened in distinct condi-

650   tions in terms of sulfate availability (open versus closed systems) that led to a different evolu-

651   tion of sulfur isotopic composition for the respective barite-sulfide deposits. Type I minerali-

652 zation was clearly associated to a shallow BSR during periodical sulfate-rich water percola-

653 tion from ephemeral playa lake occurring during the first step of the onlap of Middle Triassic

654 sediments (Fig.14). This configuration thus provided a limited quantity of sulfate. On the con-

655 trary, Type II mineralization reveals early burial conditions with an ore trapping in the karst

656 controlled by the convergence of a permanent downward sulfate flux from the overlying

657 evaporitic lake and the upward migration of deep hydrocarbon forming the SMTZ (Fig.14).

658 Perennial supply of sulfates for the Type II mineralization, defining the "open system", is

659 probably governed by the seal capacity for downward fluids at the unconformity surface. In

660 the case of Belbezet Mine and Montifort Road, the paleokarst surface is covered by thick

661 conglomerate and sandstones respectively, both lithologies favoring the continuous percola-

662 tion of the sulfate-rich water during the burial of the series. On the contrary, in the case of the

663 Olmet Road, the direct sealing of the paleokarst system by a thick marly cover could explain

664 the isolation during burial and the lack of Type II mineralization.

665

666

667 **5.3   Genetic model for synsedimentary to early diagenetic ore deposits**

668   The two distinct ore trapping mechanisms evidenced in this work during the Middle

669 Triassic period of the Lodève Basin allow us to propose a conceptual model of synsedimen-

670 tary to early diagenetic ore deposits. This model presents the interconnection of sedimentary

671 basin geodynamics, meteoric karst evolution and migration of deep basinal hydrocarbon-rich

672 fluids in the development of very shallow barite-sulfides deposits. Three main stages can be

673 distinguished (Fig. 15):

28

674   *(i) Stage 1: Intense weathering and epigenetic karstification after the post-rift exhumation of*

675   *the basin*

676   After the Permian rifting of the Lodève basin, a significant base level drop of about

677   1500m, resulting from a general uplift of the margins during the initiation of the Tethys-

678   Ligure basin opening (Lopez, 1992), caused the widespread erosion of the Late Permian

679   sedimentary deposits and the differential exhumation of the Hercynian basement (Fig.15 –

680   Stage 1). All the studied outcrops show precisely the base of the Middle Triassic pile

681   onlapping a well define paleokarstic surface characterized by paleolapiaz, potholes and exo-

682   and endokarstic cavity networks. At the Roche Percée ore dyke, relevant withdrawal

683   structures and collapse fabric indicate a mechanism of karstification associated to *per*

684   *descensum* sedimentary infilling of a major deep paleo-pothole developed along a vertical

685   permeability barrier between the calcschists and the dolomites. Exokarstic processes prior to

686   the deposition of Middle Triassic basal formation is also well-observed along the Olmet Road

687   with the development of paleo-potholes and weathering markers along the Middle Triassic

688   paleosurface. In addition, the Montifort Road outcrop reveals the strings of interconnected

689   planar cavities which indicate endokarstic dissolution processes at the front of a fluctuating

690   water table, prior to or just at the beginning of the deposition of the first Middle Triassic

691   sediments. During the dissolution of the surrounding calcschists, the insoluble fraction

692   including silt-sized quartz and iron oxides was accumulated in the cavities and conduits

693   forming typical vadose silt deposits with granules. Such micro-nodular pedogenic granules

694   were also described in the Late Cretaceous-Early Tertiary of the southern France by Plaziat

695   and Freytet (1978) with possible reverse grading reported to the development of pseudo-

696   microkarst (Freytet and Plaziat, 1978, 1982; Hay and Wiggins, 1980; Alonso-Zarza, 2003). In

697   this case overlapping of pedogenic, vadose and shallow phreatic processes led to the

698   granification of sediments (Mazzullo and Birdwell, 1989) controlled by periodical changes in

699   the position of the water table (Alonso-Zarza, 2003). This stage corresponds to the formation

700   of the karst trap for later mineralizations.

701

702   *(ii) Stage 2: Alkaline stage during the playa lake initiation*

703   The silicification strengthening the walls of the Roche Percée ore dyke occurred

704   before the main karstic infilling, partially plugging the karstic paleosurface of Montifort Road

705   and Belbezet Mine (Fig.15 – Stage 2). Silica came from the partial leaching of the quartz silt-

706   fraction dispersed in the basement from the exokarst to the drowned endokarst network. In the

707   surficial domain, the abundance of chalcedony filling the fracture network is compatible with

708   Group III silcrete pedogenesis of arid-alkaline environments as defined by Summerfield

709   (1983a, 1983b) and Wopfner (1983). In the endokarst, the alkaline tendency probably favored

710   silt-size quartz partial leaching. Periodical mixing with low acid rainwaters led to the growth

711   of drusy quartz in the residual intergranular space and to partial silicification of the

712   intrakarstic sediments (Nash and Ullyott, 2007; Ullyott and Nash, 2016).

713

714   *(iii) Stage 3: Early diagenetic ore deposition during the permanent evaporitic lake deposi-*

715   *tional system*

716   The karst reservoir was then subjected to two ore trapping stages during the

717   progressive emplacement by the permanent sulfate-rich lake system: a synsedimentary event

718   (Stage 3A) and an early burial process (Stage 3B) (Fig.15 – Stage 3).

719   *Stage 3A – Type I mineralization:* the karst sedimentary infilling was composed of

720   detrital-chemical depositional cycles compatible with humid-arid climate alternations and

721   emplacement of shallow sulfate-rich lake (Lopez and Mader, 1985). During humid periods,

722   part of the fine grained fraction derived from the weathering processes on the flanks of the

723   paleo-highs was mobilized by the running waters and transported from exokarst systems

724   toward the endokarstic cavities to form vadose silts and sands deposition. During the dry

725   season, the lake depositional system was submitted to intense evaporation and evaporite

726   precipitation. Part of the sulfate-rich waters and evaporite crystals were dragged toward the

727   exokarst systems to give cyclic chemical laminae. At the same time, the presence of organic

728   matter-rich material within karstic cavities favored the bacterial reduction of the downward

729   percolating sulfates in the karst network. The source of metals probably derived from the

730   meteoric leaching of outcropping previous MVT ore deposits from the paleoreliefs upstream

731   the karst trap. Therefore, Type I mineralization clearly conjugated a synsedimentary gravity-

732   driven mineralized brine with a BSR process that interacted in the meteoric karst network.

733   *Stage 3B – Type II mineralization:* during the early burial of the karst systems, the seal

734   capacity of the Middle Triassic marls led to the trapping of the ascending hydrocarbon-rich

735   fluids below this permeability barrier. Permanent downward sulfate-rich water still continued

736   to percolate into the buried karst where permeable coarse material locally onlapped the

737   paleosurface. The interaction between ascending hydrocarbon and the BSR zone formed a

738   SMTZ which represented the upper chemical boundary for an underlying zone undersaturated

739   in sulfates that led to the dissolution of previous buried Permian barite-rich ore deposits.

740   Released barium, metals and sulfur were transported by the *per ascensum* reducing brine

741   containing the hydrocarbon. During the ascension through the sedimentary pile, this solution

742   reached the SMTZ window where dissolved sulfates were available. The increase of alkalinity

743   was first responsible for the precipitation of ankerite on the walls of the cavities, closely

744   associated with hydrocarbons markers. Barite and sulfides then precipitated, thus plugging the

745   cavities to form the Type II mineralizations.

746

747

6. Conclusions

749   The originality of this work lies in the multi-scale analysis of an exceptional field
750 example of continental diagenetic barite-sulfide deposits precipitated within meteoric karst
751 systems. Ore deposits have been the subject of sedimentological and texture analysis, sulfur
752 and strontium isotopes and fluid inclusions microthermometry. This methodology allows us to
753 propose a genetic model of synsedimentary to early diagenetic metallogenesis in which we
754 constrained all the factors whose interactions over time formed a favorable metallotect: karst
755 dynamics, chemistry of the water table linked to climate and depositional environment
756 changes, location of thermogenic hydrocarbons dysmigrations and the remobilization of
757 former polymetallic deposits.

758 Four keypoints can be retained from this study:

759   • The importance of the interaction between the evolution of meteoric karsts during
760   climate changes and the location of ore deposits. Epigene karstification plays both a
761   fundamental precursor role, guiding the path of mineralizing fluids and constituting
762   the main trap, and a passive role by undergoing the precipitation of the fluids which
763   will then stop the karst evolution at the origin of mineralized paleokarsts.

764   • The predominant control of climate fluctuations, depositional environment changes
765   and redox conditions at the water table on timing and texture of shallow continental
766   diagenetic ore deposits. We show that the progressive transition from ephemeral playa
767   lake to perennial evaporitic lake environments controls the supply of sulfates for min-
768   eralization and the position of the SMTZ by the interaction with ascending hydrocar-
769   bons.

770

- The significant impact of the thermogenic hydrocarbon migration in the metallogeny of sedimentary basins: passive role in the development of MVT ore deposits since the location of oil traps are constrained by the early mineralizations, and a foreground role in the supergene metallogeny by constituting a main vector in the redistribution of metals few meters below the SWI.

- The superimposition in a single trap of two very similar synsedimentary to early dia-genetic mineralizations but implying different origins of fluids (surficial versus deep basinal brines) during the first step of burial along a karstic surface (notion of *"sliding metallogenic window effect"*).

Figures captions

Figure 1: Geological setting of the Lodève Permian basin. A) Simplified geological map. The

black square indicates the location of the detailed geological map of the study area illustrated

in Fig.2A. B) North-south cross section of the Lodève half-graben. The location of the cross

section is indicated by the North-South bold line A-A' on Fig.1A.

Figure 2: A) Detailed geological map of the study area (see Fig.1A for the location). All the

studied outcrops are designated by a star and a letter, from a to j, that refers to the Appendix A.

B) SW-NE cross-section of the study area (the location is marked by a dashed line on Fig.2A).

C) Sedimentological log of the Triassic series above the post-rift unconformity of the Lodève

Basin.

Figure 3: The Roche Percée paleo-pothole. A) Geological map of the site. B) General

architecture of the paleokarst infill with the west side at left (View 1) and southern side at

right (View 2). C) Detailed views of the intrakarstic infilling with the section a (left) and

section b (right) located on the Fig.3A.

Figure 4: Close-up photos and photomicrographs of the Roche Percée paleo-pothole infill. A)

Successive breccia packages (c) bordered by the silicified calcschists (a) and including

collapsed silicified blocks (b) and gypsum-anhydrite boxworks (white arrows). B) Close-up

view of RP2 Facies showing millimetre-thick massive barite layers (white arrow) and nodules

(b) alternating with laminated dolomite-rich siltstone. C) Thin section of graded beds of the

RP2 Facies (plain-polarized light-PPL). D) Detailed view of a barite crystallite of the previous

thin section (C) showing clear corroded (yellow arrows) and broken surfaces (yellow circle)

(PPL). E. Photomicrograph of chalcopyrites crystallized within barite mineralization

(reflected light-RL).

Figure 5: General architecture of the Olmet Road paleo-lapiaz. A) Interpreted drawing of the

outcrop. B) Photo of the western part of the outcrop (see A for location) (tm: Triassic marls;

sd: sulfides-rich fine sandstones; ba: barite pockets; ib: sulfide impregnated bands and

fractures; cd: Cambrian dolomites. C) Photo of the central part of the outcrop (see A for

822 location) showing the main fault-damaged zone and barite-sulfide mineralizations in both

823 hanging wall and footwall of the fault (cd: Cambrian dolomites; ba: barite; fb: tectonic breccia;

824 ls: laminated sulfides-rich silty claystone; sd: sulfide-rich sandstone to siltstone; tm: Triassic

825 marls).

826

827 **Figure 6:** Architecture and mineralized facies of the Montifort Road planar cavities string. A)

828 General view and line-drawing of the outcrop showing the sub-planar endokarstic cavity

829 cluster crossing the Cambrian calcschists. B) Close-up drawing of the southern part of the

830 outcrop (see on A) with a detailed view of a planar cavity. C) Polished hand-sample section of

831 a karstic cavity infill (ba: barite; gr: reverse graded granules; sic: silicification; black arrows:

832 ankerite).

833

834 **Figure 7:** A) Photomicrographs of the base of figure 6C showing the intrakarstic sediments in

835 the mineralized cavities of Montifort Road (an/white arrows: ankerite; gr: iron-rich silty

836 dolomudstone grains; dq: drusy quartz; vs: geopetal silt infill) (Left PPL, Right cross-

837 polarized light-XPL). B) Drusy ankerites growing on the phreatic drusy megaquartz (PPL). C)

838 Contact zone between drusy ankerite and large barite slats (PPL). D) Photomicrograph in

839 fluorescence X showing organic matter patches at the contact between drusy ankerite and host

840 rock, and within barite mineralization. E) Scanning Electron Microscope (SEM) image

841 illustrating numerous euhedral pyrites close to the contact between barite and late sparitic

842 calcite.

843

844 **Figure 8:** General fabric of the Belbezet mine paleo-potholes and endokarst. A) Drawing of

845 the main gallery close to the entrance showing the architecture of the ore deposit. B) Detail

846 photo of the south-western face (see A for location) showing the Cambrian dolomites (cd)

847 grooved by decimetre to meter-deep potholes (white dotted line) and filled by sulfide/barite-

848 rich silty deposits (sb) reworked on top by bitumen-rich sulfide-barite deposits (rsb). C) Detail

849 photo of bitumen-rich barite mineralization cementing a block of Cambrian dolomite (circled

850 pencil is 15cm) (same legend than before). D) Close-up photo showing bitumen blebs (bi) and

851 partly weathered grey copper sulfides (cs) cementing the white barite breccia.

852

853 **Figure 9:** Photomicrographs of primary fluid inclusions trapped within barite (PPL). A)

854 Single-phase (1-phase FI) and two-phase (2-phase FI) inclusions in the barite (ba) sealing the

855 endokarstic network of the Montifort Road outcrop. B) Essentially single-phase liquid

856 inclusions (1-phase FI) entrapped within the barite of the Roche Percée paleo-pothole.

857

858 **Figure 10:** Histograms showing microthermometric Te, TmIce and Th data obtained for

859 primary two-phase fluid inclusions entrapped within barite crystals of the Montifort Road

860 outcrop corresponding to the mineralized infill of the planar cavities string (MR1 Facies) and

861 barite precipitated within veins affected the Cambrian dolomites (MR2 Facies).

862

863 **Figure 11:** Synthetic paragenetic sequence and associated fabric for the post-rift Middle

864 Triassic intrakarstic ore deposits.

865

866 **Figure 12:** Graph of $^{87}Sr/^{86}Sr$ vs Sr concentration (in ppm) of Middle Triassic post-rift barites

867 belonging to the MR1, BM and RP2 Facies and the three distinct Late Permian syn-rift

868 mineralizing events (described in Laurent et al., 2017). The range of strontium isotopic

869 composition of the Triassic evaporites is reported from Koepnick et al. (1990) and Song et al.

870 (2015). Analytical errors is ±0.000010 for $^{87}Sr/^{86}Sr$ in barites.

871

872

873 **Figure 13:** $\delta^{34}S$ diagram illustrating the signatures of the Triassic evaporites (grey star for

874 gypsum and hexagon for anhydrite), barites (white circles) and chalcopyrites (black rectangle

875 with error bars) of the Middle Triassic mineralizations (Type I and Type II) and Late Permian

876 MVT ore deposits (Laurent et al., 2017). Analytical errors are ±0.2‰ for $\delta^{34}S$ in barites and

877 Triassic evaporites, and ±1‰ for $\delta^{34}S$ in chalcopyrites.

878

879 **Figure 14:** $\delta^{34}S$-depth diagram showing the partitioning of barites and chalcopyrites for the

880 Type I and Type II Middle Triassic ore deposits compared to the Triassic evaporites signature.

881 The calculated $\varepsilon^{34}S$ (= $\delta^{34}S_{barite}$ - $\delta^{34}S_{chalcopyrite}$) is also indicated for each fronts (left figure).

882 The mineralized front migrated upward during the progressive onlap and base level rise along

883 the karstified paleosurface as a sliding biochemical window (right figure).

884

885   **Figure 15:** Conceptual model of the synsedimentary to early diagenetic ore deposition

886   following the post-rift exhumation of the Lodève Basin's northern margin: Stage 1 –

887   Exhumation, intense weathering and epigene karstification with vadose sediment infill; Stage

888   2 – Initial alkaline playa lake development, quartz leaching and vadose-phreatic silicifications

889   during an increase of acidification; and Stage 3 – Perennial sulfate-rich lake development and

890   synsedimentary to early diagenetic barite-sulfide trapping (Type I and Type II

891   mineralizations).

892

893   **Table 1:** Fluid inclusion petrography and microthermomety data (Te, TmIce, Th and salinity)

894   for the barites of the Middle Triassic ore deposits.

895

896   **Table 2:** $^{87}Sr/^{86}Sr$ and strontium concentration for barites and $\delta^{34}S$ for barites and

897   synchronous chalcopyrites in the ore facies of the different studied area in this paper and for

898   the three Late Permian MVT ore events presented in Laurent et al. (2017). Analytical errors

899   are ±0.2‰ for $\delta^{34}S$ in barites and Triassic evaporites, ±1‰ for $\delta^{34}S$ in chalcopyrites and

900   ±0.000010 for $^{87}Sr/^{86}Sr$ in barites.

901

902   **Appendix A:** Location and ore characteristics (architecture, mineralogy and classification) of

903   the 10 sites studied in this entire wotk. Only 4 sites (in bold letters) have been chosen for a

904   detailed description in this paper: Montifort Road, Roche Percée, Belbezet Mine and Olmet

905   Road. The small letters refer to the map in Fig.2A.

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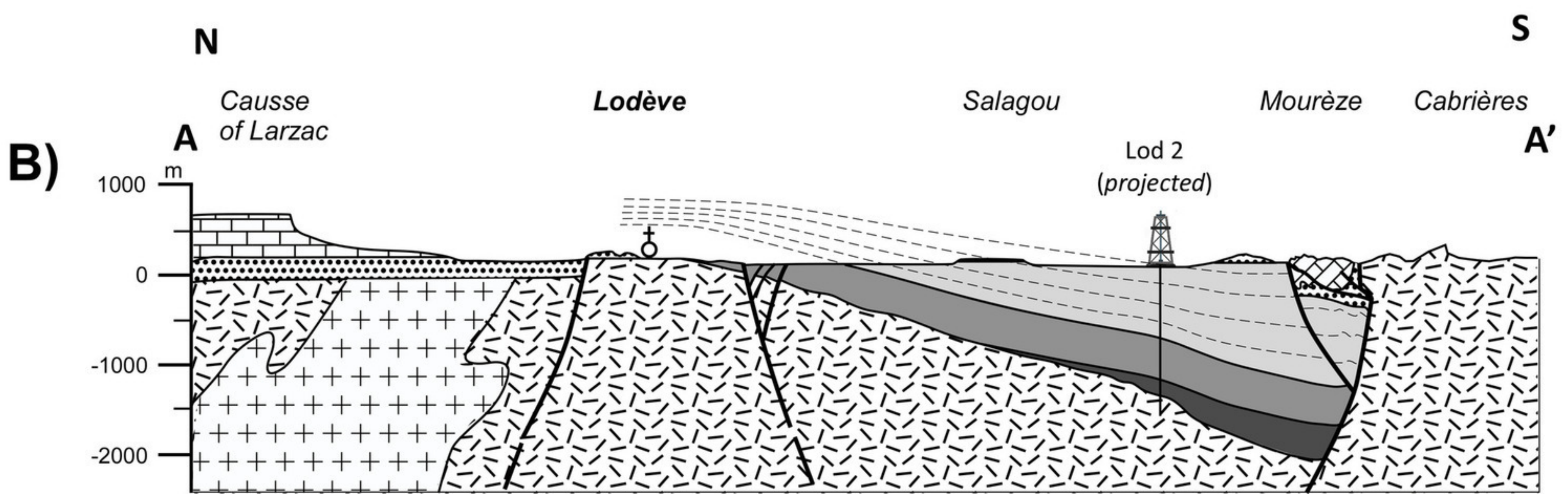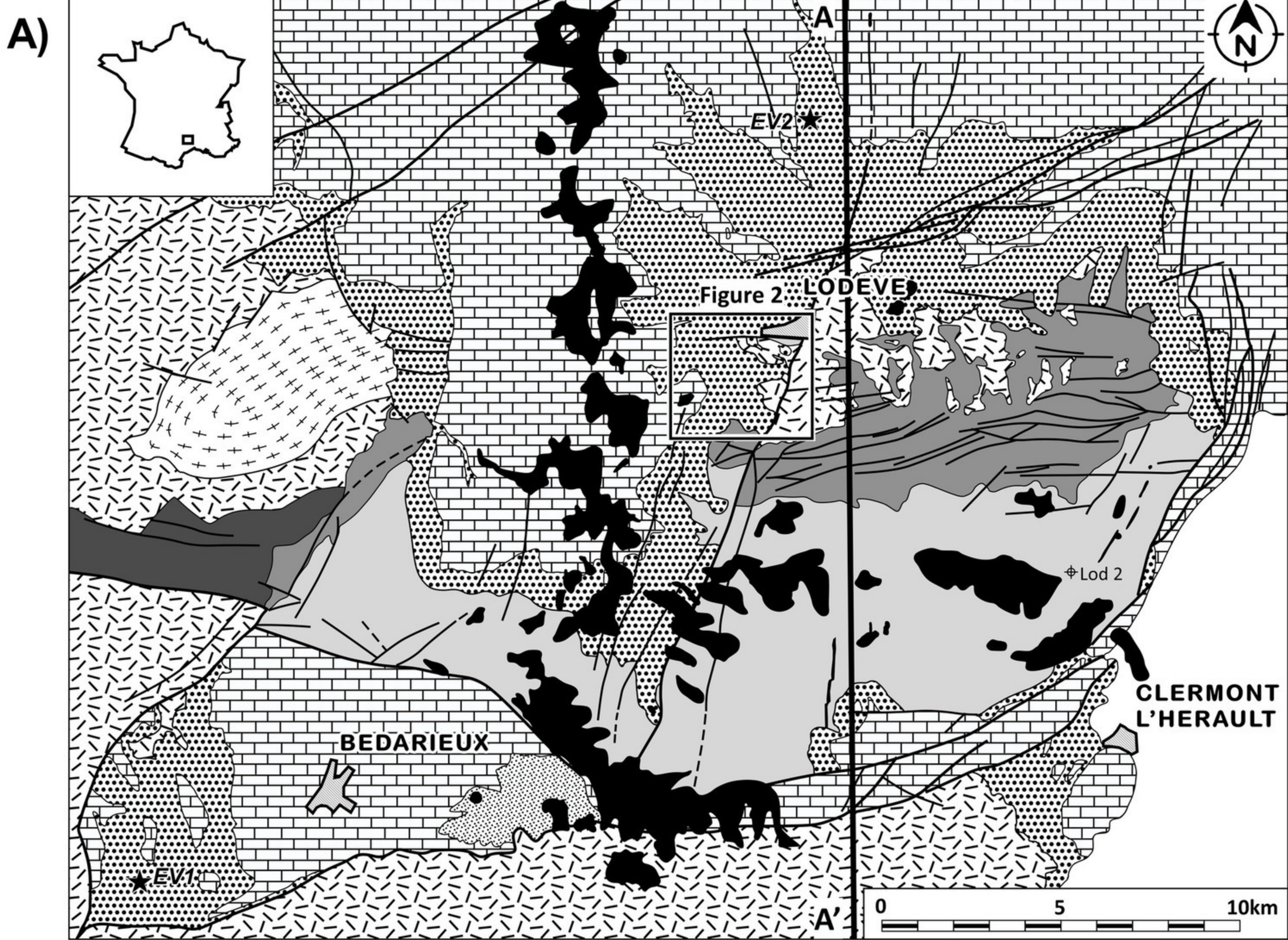1049   Verlag publisher.

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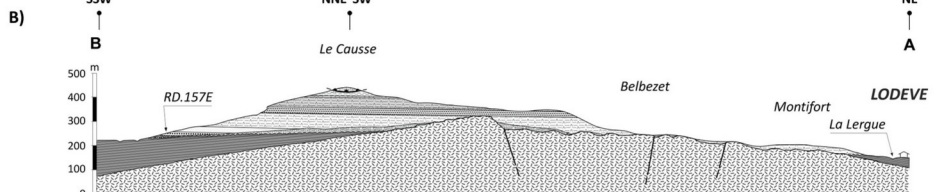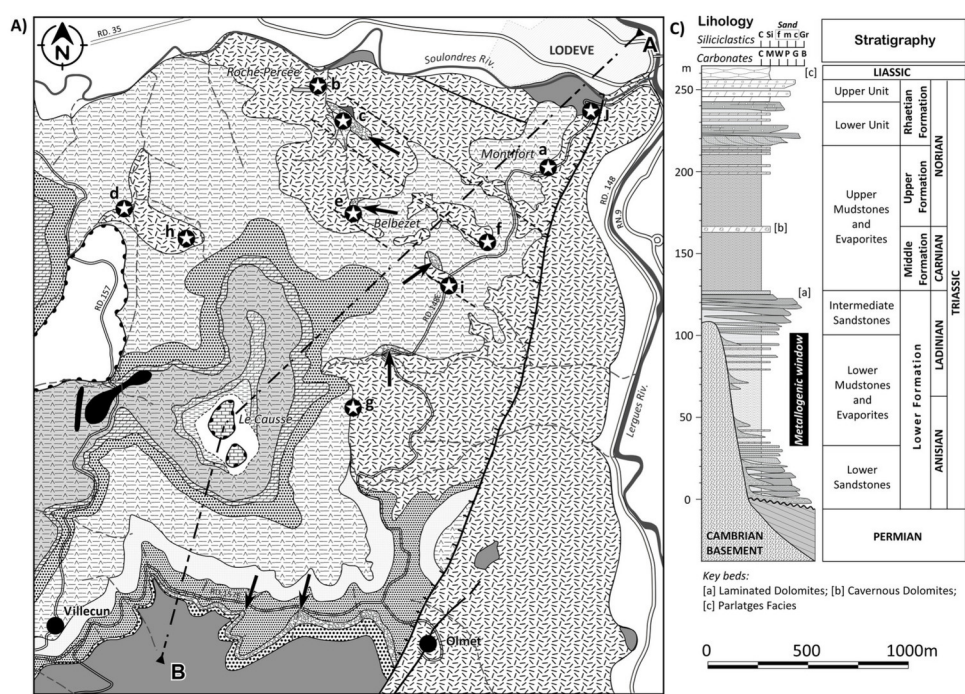1133   and formation of heavy barites in diagenetic fronts. Chem. Geol. 127, 125–139.

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1154

1155

A)

Figure 2

EV2 ★

LODÈVE

Lod 2

CLERMONT L'HERAULT

BEDARIEUX

EV1 ★

N

0   5   10km

A'

B)

N   S

Causse   **Lodève**   Salagou   Mourèze   Cabrières
of Larzac

A   A'

Lod 2
(*projected*)

■	Plio-Quaternary basaltic volcanism		Lower Permian
☐	Neogene to Quaternary		Upper Carboniferous
	Paleogene		Hercynian basement
	Jurassic		Mendic Granite
	Triassic		Main faults
	Middle to Upper Permian	★	Location of the Triassic evaporite samples

A) Geological map showing Soulondres Riv., LODEVE, Roche-Percée, Montfort, Belbezet, Le Causse, Villecun, Olmet, La Lergue Riv., Lergues Riv., and roads RD. 35, RD. 148, RD. 9, RD. 157, RD. 157E, RD. 15. Studied outcrops: a, b, c, d, e, f, g, h, i, j. Cross-section line A–B.

C) Lithology / Stratigraphy

Siliciclastics: Sand (C Si f m cGr), Carbonates (CMWPGB)

m		Stratigraphy			
250	[c]	LIASSIC			
		Upper Unit	Rhaetian Formation		
		Lower Unit		NORIAN	
200	[b]	Upper Mudstones and Evaporites	Upper Formation		TRIASSIC
150	[a]		Middle Formation	CARNIAN	
		Intermediate Sandstones		LADINIAN	Lower Formation
100	Metallogenic window	Lower Mudstones and Evaporites		ANISIAN	
50					
0		Lower Sandstones			
	CAMBRIAN BASEMENT	PERMIAN			

Key beds:
[a] Laminated Dolomites; [b] Cavernous Dolomites;
[c] Parlatges Facies

Scale: 0 – 500 – 1000m

B) Cross-section B (SSW) to A (NE), showing RD.157E, Le Causse, Belbezet, Montfort, LODEVE, La Lergue. Elevations 0–500 m.

LEGEND

Basement
- Cambrian dolomites and calcschists

Permian deposits
- Lower Permian sandstones and pelites

Triassic deposits
- Lower Sandstones: Basal sandstone body
- Lower Sandstones: Debris-flow breccia
- Lower Sandstones: Upper sandstone body
- Lower Mudstone and Evaporites: Basal sandstone-marl alternations
- Lower Mudstone and Evaporites: Marls, gypsum and anhydrite alternations
- Intermediate Sandstones
- Laminated Dolomites
- Upper Mudstones and Evaporites: Marls, gypsum and anhydrite alternations
- Upper Mudstones and Evaporites: Cavernous Dolomites
- Upper Mudstones and Evaporites: Marls and accessory gypsum and sandstones

Jurassic deposits
- Hettangian dolomudstones

Plio-Quaternary deposits
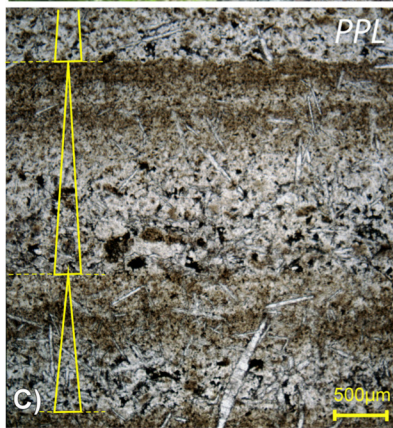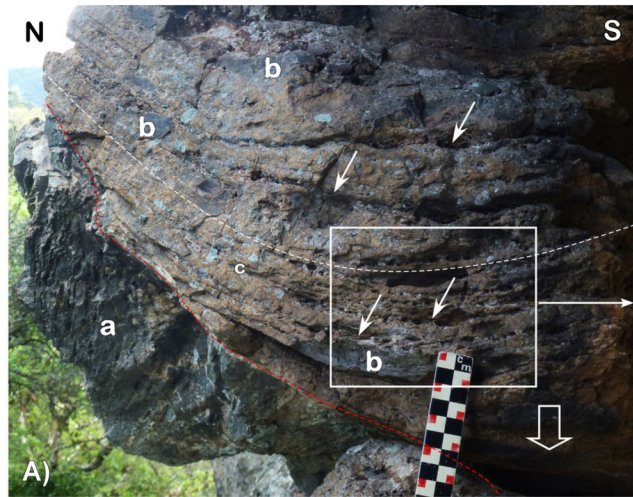- Alluviums

Structures
- Main fault
- Partly covered fault
- Landslide sole
- Main transport direction
- ☆ Studied outcrops

A)

View-1

35

a

b

N

5m

View 2

N   S   W   E

View 1   View 2

2m

1

2m

B)

N   Fig. 4A   S   N   S

C)

Section a   Section b

10 cm   10 cm

① Tepee antiform structures

Dolomite

Calcschists

Barite-silica rich intrakarstic breccia (Facies RP3)

Barite-silica rich intrakarstic arenite (Facies RP2)

Fine organic-rich intrakastic sandstone (Facies RP1)

Silicified facies

Karstic withdrawal

strike-slip fault

A) N ... S; a, b, b, b, c, b

B) b

C) PPL, 500μm

D) PPL, 250μm

E) RL, Barite, Chalcopyrite, 30μm

W **E**

A)

Anisian (Lower Mudstone Fm.):
- Fine to very fine sandstones
- Bluish evaporitc marls and thin sandstone interbedded
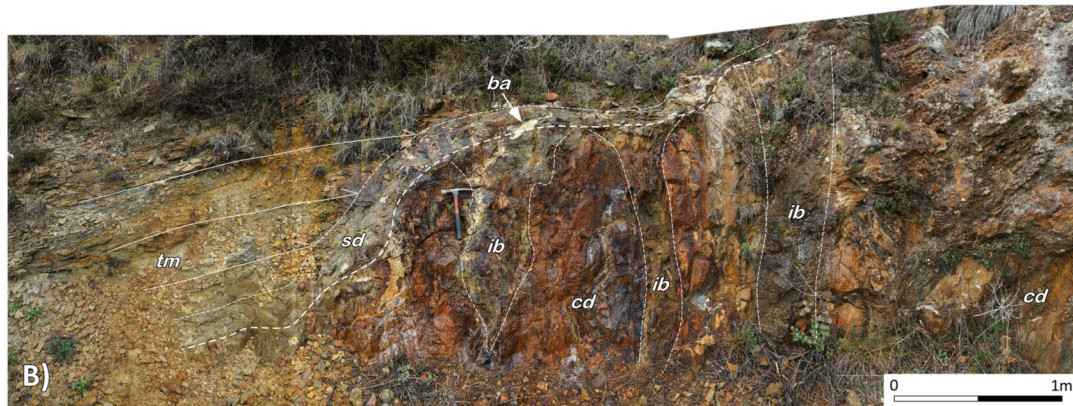
Cambrian basement:
- Secondary dolomites
- Karstified paleosurface

Mineralizations:
- Partly oxidized carbonate and sulfides-rich massive to locally bedded very fine sandstone to silstone
- Partly laminated sulfides-rich bluish vadose silty-claystone (**OR**)
- Partly oxidized sulfide-impregnated fracture-controlled bands in the Cambrian dolomites
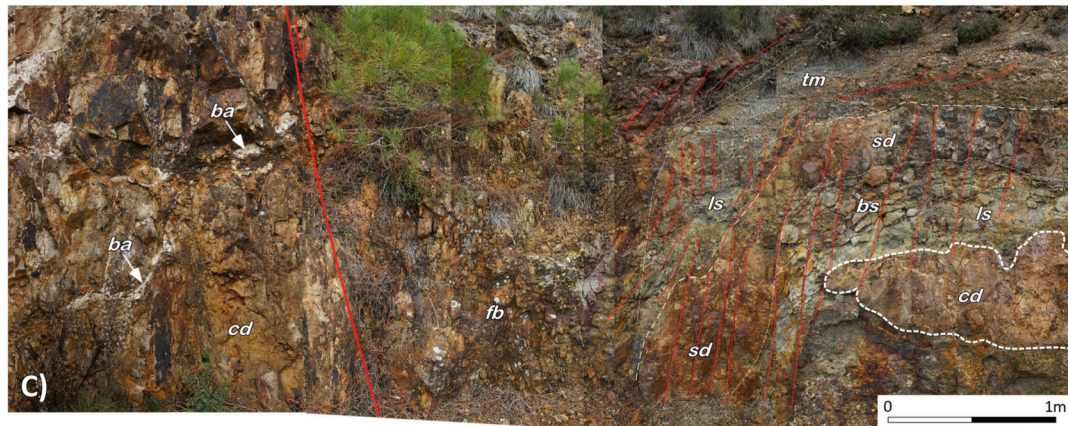- Barite veins and filled cavities in the Cambrian basement

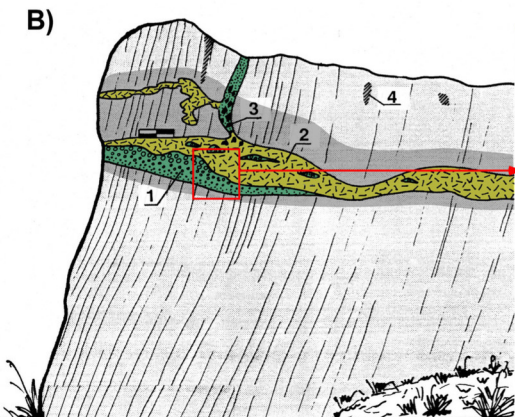- Fault breccia
- Fault
- Fracture
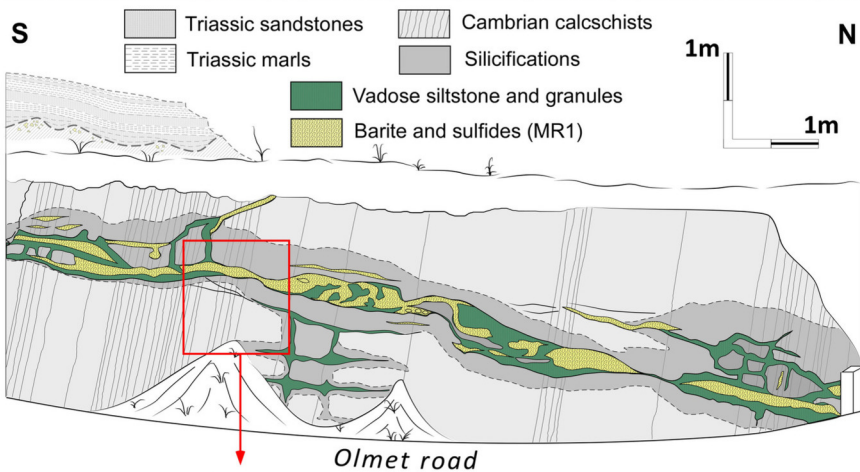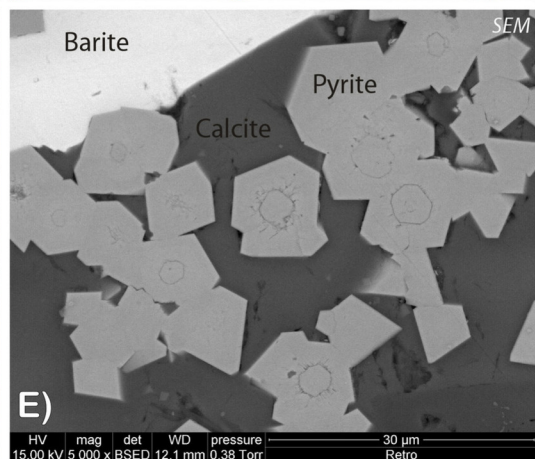- Bedding

0   m   10

B)

C)

A)

S | N

Triassic sandstones | Cambrian calcschists
Triassic marls | Silicifications
Vadose siltstone and granules
Barite and sulfides (MR1)

1m

1m

S | N

Olmet road

B)

3

4

2

1

C)

2 cm

ba

gr

sic

Matrix supported conglomerate (debris-flow deposit) Middle Triassic

Reworked bitumen-rich sulfide-barite deposit

Partly silicified Cambrian dolomites

Sulfide-barite-rich silty clayey intrakarstic deposit (**BM**)

A) *ba* — PPL. Labels: *2-phase FI*, *1-phase FI*. Scale bar: 30μm.
B) *1-phase FI*. Scale bar: 30μm.

Main Facies	Mineral phases	Fabric	Time — Syn-rift - Late Permian: MVT ore deposits	Post-rift - Middle Triassic: Karstification and weathering	Alkaline leaching	Mineralizing events
Late Permian MVT deposits Facies MR2	Barite-sulfides	Multiple (Laurent et al., 2017)	▬▬▬▬			
	Intrakarstic sediments	Granulation		▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬		
	Silicification	Anhedral		▬▬▬		
	Vadose silts	Geotropic		▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬▬		
	Phreatic quartz	Drusic		▬		
	Ankerite	Anhedral / Drusic		▬▬▬▬▬▬▬		▬▬▬
(Type I mineralization)						
Facies RP2	Pyrite/chalcopyrite/galena	Anhedral		▬▬▬▬▬		
	Barite	Massive laminae Sheaf-like				▬▬▬
Facies OR	Siltstone rich in pyrite/chalcopyrite/galena/sphalerite/tetraedrite	Anhedral and very oxidized				▬▬▬
	Barite	Sheaf-like within pockets				▬▬▬▬
(Type II mineralization)						
Facies MR1	Pyrite/chalcopyrite/galena	Euhedral				▬▬
	Barite	Cockade clusters				▬▬▬
Facies BM	Sulfide-barite-rich silty-clayey matrix	Disseminated				▬▬▬
	Barite	Massive layer				▬▬
Facies MR1 & BM	Calcite and chalcopyrite	Euhedral				▬
	Hydrocarbon	Bitumen and oil				▪▪▪▬▬

Vertical gray band: *Major gap (15Myr) - 1500m regional uplift*

δ³⁴S (‰ V-CDT)

Samples

Late Permian MVT ore deposits

Triassic evaporites — *EV1*, *EV2*

Middle Triassic ore deposits — Type I: *RP2*, *OR*; Type II: *BM*, *MR1*

☆ *Gypsum*   ⬡ *Anhydrite*   ◯ *Barite*   ■ *Chalcopyrite*

Stage 1:
Intense weathering and epigenic karstification

Exokarst: lapiaz, sinkhole

Ore leaching
Runoff
M+ dispersion

Deep endokarst - Pothole (Roche Percée type)

Phreatic karst (Montifort Road type)

Shallow endokarst (Belbezet Mine type)

Intense weathering - ankerite crust

Local debris-flow emplacement

Exokarst - Lapiaz (Olmet Road type)

Endokarst; Potholes, caves, phreatic cavities

Previous Permian ore (MVT-Type)

Cambrian basement

Vadoze zone

Phreatic zone

Water table oscillation

Base level

Withdrawing

Vadose to phreatic karst infilling by the residual insoluble fraction

Organic-rich vadose silt deposition

Reverse graded granules

Stage 2:
Initial fringing alkaline playa-lake
Silica partial leaching and silicifications

Exokarst: lapiaz, sinkhole

Ore leaching
Runoff
M+ dispersion

Silcrete pedogenesis

Early alkaline playa-lake

Partial silica leaching

Endokarst; Potholes, caves, phreatic cavities

Previous Permian ore (MVT-Type)

Cambrian basement

Vadoze zone

Phreatic zone

Water table rise

Base level

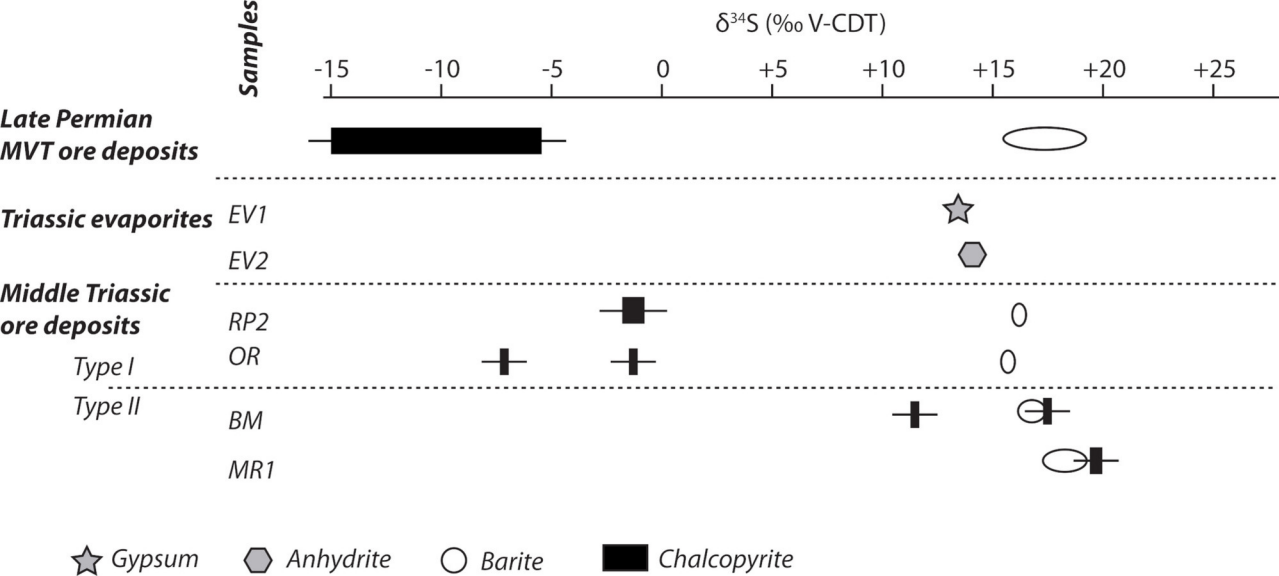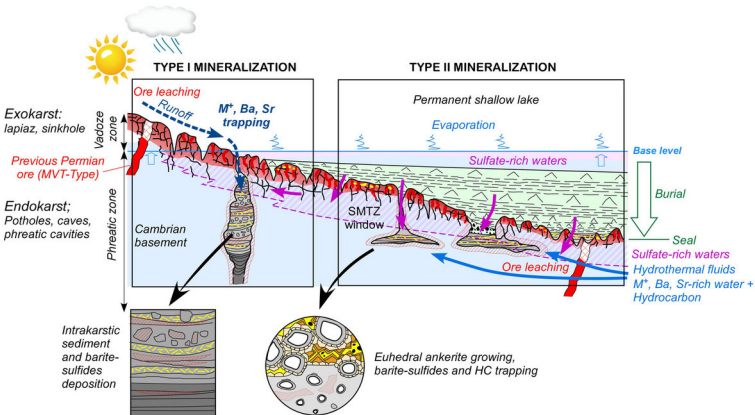Alcaline waters

Alkaline front

Withdrawing

Vadose/phreatic silicification

Intrakarstic sediment deposition

Geopetal pattern infilling, euhedral quartz growing and partial silicification

Stage 3:
Permanent sulfate-rich shallow-lake - Barite and sulfides trapping

Coeval gravity-driven synsedimentary ore trapping upstream (Type I mineralization) and early burial hydrothermal-driven trapping downstream (Type II mineralization).

TYPE I MINERALIZATION

TYPE II MINERALIZATION

Exokarst: lapiaz, sinkhole

Ore leaching
Runoff
M+, Ba, Sr trapping

Permanent shallow lake

Evaporation

Endokarst; Potholes, caves, phreatic cavities

Previous Permian ore (MVT-Type)

Cambrian basement

Sulfate-rich waters

SMTZ window

Vadoze zone

Phreatic zone

Base level

Burial

Seal

Ore leaching

Sulfate-rich waters Hydrothermal fluids M+, Ba, Sr-rich water + Hydrocarbon

Intrakarstic sediment and barite-sulfides deposition

Euhedral ankerite growing, barite-sulfides and HC trapping

Location	Textural facies	Host mineral	Primary fluid inclusion	Te (°C)	TmIce (°C)	Th (°C)	Mean salinity (wt.%eq.NaCl)
Montifort Road	MR1	Barite (N=23)	Two-phase	-28 to -21	-15 to -5	48 to 102	13.56
		Barite	Single-phase				
Montifort Road	MR2	Barite (N=13)	Two-phase	-28 to -21	-13 to -5	139 to 195	12.6
Roche Percée	RP2	Barite	Single-phase				
Olmet Road	OR						

Location	Textural facies	Host mineral	$^{87}Sr/^{86}Sr$	Sr (ppm)	$\delta^{34}S$ (‰ V-CDT)
Middle Triassic ore deposits					
Roche Percée	RP2	Barite	0.708880	11850.29	+16.2
		Chalcopyrite			-2.1 -1.4
Olmet Road	OR	Barite			+15.7
		Chalcopyrite			-7.2 -1.7
Belbezet Mine	BM	Barite	0.711419	4412.85	+16.2/+16.7
		Chalcopyrite			+11.9 +17.1
Montifort Road	MR1	Barite	0.711386	10739.52	+16.9/+18.5
		Chalcopyrite			+18.9

Triassic evaporites					
Quarry of Notre Dame de Capimont	EV1	Gypsum			+13.7 +14.7
Pégairolles de l'Escalette (drillcore)	EV2	Anhydrite			+14.6 +14.9

Late Permian ore deposits *(compilation from Laurent, 2015 and Laurent et al., 2017)*					
1st mineralizing phase		Barite	0.711913 0.711826	42192.21 27764.87	+17.2/+17.6 +15.6/+16.9
		Chalcopyrite			-15
2nd mineralizing phase		Barite	0.711014 0.710936 0.710471 0.710637 0.711222	37413.52 43803.11 21466.55 19500 42225.3	+17.3/+17.9 +16.6/+16.8 +16/+16.4 +17.5 +17.8/+18.4
		Chalcopyrite			-10 -13 -6/-5
3rd mineralizing phase		Barite	0.710000 0.710081 0.710294 0.710003	43855.8 32585.4 28491.79 28964.38	+16.4/+17.2 +16.1/+16.9 +16.2/+16.7 +17
		Chalcopyrite			-12/-11 -8