1 **Temperature micro-mapping in oscillatory zoned chlorite: Application to**

2 **study of a green-schist facies fault zone in the Pyrenean Axial Zone (Spain)**

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28   **Abstract**

29   Oscillatory compositional zoning in minerals has been observed in hydrothermal,

30   magmatic and metamorphic environments and is commonly attributed to chemical or physical

31   cyclical changes during crystal growth. Chemical zoning is a common feature of solid

32   solutions, which has been rarely reported in phyllosilicates. In this study, oscillatory zoning in

33   chlorite is described in samples from the Pic-de-Port-Vieux thrust, a minor thrust fault

34   associated to the major Gavarnie thrust fault zone (Central Pyrenees, Spain). The Pic-de-Port-

35   Vieux thrust sheet comprises a 1-20 meter thick layer of Triassic red pelite and sandstone

36   thrust over mylonitized Cretaceous dolomitic limestone. The thrust fault zone deformation

37   comprises secondary faults and cleavage affecting the Triassic pelite and sandstone. An

38   important feature responsible to this deformation is a set of veins filled by quartz and chlorite.

39   Chlorite is present in crack-seal extension veins and in shear veins, both structures opened

40   under the same stress conditions. In some shear veins, chlorite occurs as pseudo-uniaxial

41   plates arranged in rosette-shaped aggregates. These aggregates appear to have developed as a

42   result of radial growth of the chlorite platelets. Oscillatory zoning has been imaged by

43   backscattered scanning electron microscopy and by X-ray quantitative micro-mapping. These

44   oscillations correspond to chemical zoning with alternating iron-rich and magnesium-rich

45   bands. The chlorite composition ranges from a Fe-rich pole to a Mg-rich pole. $Fe^{3+}/\sum Fe$

46   values were measured in chlorite using μ-XANES spot analyses and vary from 0.23 to 0.44.

47   The highest values are in the Fe-rich area. Temperature maps, built from standardized

48   microprobe X-ray images and redox state using the program XMAPTOOLS, indicate oscillatory

49   variations from about 310 to 400±50°C during chlorite crystallization. These temperature

50   variations are correlated with a $Fe^{3+}/\sum Fe$ variation by $Al^{3+}Fe^{3+}_{-1}$ and di-trioctahedral

51   substitutions highlighted by Mg and Fe_{Tot} contents (Fe-Mg zoning). Chemical variations

52   could be then explained by alternation of cooling times and cyclical pulses of a fluid hotter

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53   than the host rock. It is however not excluded that kinetic effects influence the incorporation

54   of Mg or Fe during chlorite crystallization.

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56   **Introduction**

57   In sedimentary basins petrophysical characterization of a fault zone and reconstruction

58   of the pressure-temperature evolution during faulting activity are of major interest for both

59   fundamental research and oil industry. Indeed, faults can serve as drains or barriers for crustal

60   fluid flow, including hydrocarbons. They may also record fluid-rock interactions in

61   syntectonic veins (e.g., Lacroix et al. 2014). The fault cores are often mineralized with,

62   among other, clay rich zones (e.g., Buatier et al. 2012; Lacroix et al. 2012; Leclère et al. 2012;

63   Cantarero et al. 2014; Trincal et al. 2014a). The role of authigenic clay growth in clay-bearing

64   fault zones is increasingly recognized as a key to understand the mechanics of brittle faulting

65   and thrusting processes (e.g. Wintsch et al. 1995). This provides new insights into the ongoing

66   debate about the frictional strength of brittle faults (e.g., Chester et al. 1993; Bos and Spiers

67   2001; Holdsworth 2004; Haines and Van Der Pluijm 2012; Leclère et al. 2014). In rare cases,

68   oscillatory zoned minerals can be observed. These minerals witness fluid-rock interaction

69   processes such as mineralogical reactions and mass transfer assisted by fluids (e.g. Beaufort et

70   al., 2005). Their study allows a better understanding of processes such as pressure-solution,

71   fluid-rock interaction and recrystallization occurring during thrust faulting.

72   With the development of electron imaging techniques, chemical zoning patterns in

73   metamorphic, magmatic and hydrothermal minerals have been increasingly investigated (e.g.,

74   Jamtveit et al. 1993; de Andrade et al. 2006; Friel and Lyman 2006; Vidal et al. 2006; Dziggel

75   et al. 2009; Robyr et al. 2009, 2014; Pearce and Wheeler 2010; Blanco-Quintero et al. 2011;

76   Dare et al. 2011; Lanari et al. 2012, 2013, 2014b; Manzotti and Ballèvre 2013; Martin et al.

77   2013; Zhai et al. 2014). Depending on the geological environments and the minerals involved,

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78   chemical zoning reflects time series of equilibrium conditions experienced by the rock.

79   Several parameters such as pressure (P), temperature (T), oxygen fugacity (f_{O2}), water activity

80   (a_{H2O}), redox conditions (XFe^{3+}) and bulk-rock (solid) or fluid chemical compositions can be

81   involved. For example, the study of zoned minerals is critical to reconstruct detailed P-T paths

82   of individual samples. In low-grade metamorphic rocks, the diffusion processes are slow

83   enough to preserve successive stages of growth and continuous P-T conditions may be

84   derived by analyzing preserved local equilibria (Lanari et al. 2013 and references therein).

85   According to Kohn (2003) all minerals could show zoning for a particular element or isotope

86   at a given scale, and it is simply a matter of time or analytical precision increase before that

87   zonation is described. Chemical zoning patterns such as concentric zoning may result from

88   successive stages of crystallization. From a macroscopic point of view, the variations in

89   chemical composition from core to rim of minerals result of the variations in the relative

90   proportions in a solid solution between two or more end-member minerals. The final rim may

91   show a reversal trend due to late consumption or resorption during retrograde reactions

92   (Schumacher et al. 1999; Kohn and Spear 2000) and/or weathering, generating pellicular

93   patterns (Delvigne 1998).

94   Sector or hourglass zoning (Dowty 1976; Kwak 1981) and oscillatory zoning (see

95   Shore and Fowler 1996 for a review) are more complex patterns. Minerals showing

96   oscillatory zoning patterns exhibit repetitious concentric compositional zones, i.e. quasi-cyclic

97   alternation in the chemical compositions. Oscillatory mineral zoning has been reported from

98   open-system environments (e.g., Jamtveit 1991; Jamtveit and Andersen 1992; Jamtveit et al.

99   1993; Holten et al. 2000) in magmatic, metamorphic and hydrothermal rocks. Occurrences

100   have been found in at least 75 rock-forming and accessory minerals comprising most major

101   chemical groups: silicates (hydrous and anhydrous), sulfides, oxides, halides, carbonates,

102   phosphates and sulfates (Shore and Fowler 1996). The study of magmatic minerals showing

103   oscillatory zoning allows to deepen the understanding of magma evolution during the

104   crystallization of the rock (Putirka and Tepley 2008 and references therein). The best

105   candidate is plagioclase because its composition is sensitive to T, P, and H_2O content of the

106   melt (Shcherbakov et al. 2011). Recent studies interpreted the oscillatory zoning patterns in

107   plagioclase as convection of crystals across distinct zones of the magmatic chamber before

108   eruption (Nicotra and Viccaro 2012), or by frequent replenishments of the magma chamber

109   causing thermal and chemical interactions between melts and the growing crystals

110   (Shcherbakov et al. 2011). Oscillatory zoning patterns in garnet have been extensively studied

111   in order to track the metamorphic P-T-t path (e.g., Jamtveit and Andersen 1992; Garcia-Gasco

112   et al. 2002; Gaidies et al. 2008) or the hydrothermal fluid conditions evolution of skarn

113   deposits (Gaspar et al. 2008). In faults located in low-grade metamorphic environment,

114   minerals showing oscillatory zoning are common (Shore and Fowler 1996). This zoning is

115   due to the effect of large-scale processes (external dynamics) and/or to pattern formation

116   caused by self-organization of the local growth processes (internal dynamic) (Meth and

117   Carlson 2005; Shore and Fowler 1996; Carlson 2005; Gaspar et al. 2008; Zhai et al. 2014).

118   The previous studies on minerals showing oscillatory zoning allow a better

119   understanding of their crystallization mechanisms in magmatic and metamorphic rocks, but

120   are still insufficient to interpret those in phyllosilicates in hydrothermal environments. In most

121   cases, external changes of the fluid compositions are invoked to explain oscillatory zoning

122   patterns (e.g., Holten et al. 1997). In fluid-rich systems, complex zonings are commonly

123   interpreted to reflect changes in fluid composition or varied degrees of fluid buffering (e.g.,

124   Yardley et al. 1991; Beaufort et al. 2005; Jourdan et al. 2009). However, recent experimental

125   studies showed that rapid fluid-flow reactions and ultra-local kinetic effects could lead to

126   fluids with locally extreme non-equilibrium compositions (Borg et al. 2014).

127   Phyllosilicate are highly sensitive to P-T-X conditions making them good candidates

128   to geothermobarometry purposes (Vidal et al. 2001, 2005, 2006; Inoue et al. 2009; Bourdelle

129   et al. 2013; Lanari et al. 2014a). For example, chlorite polytypes may crystallize at different

130   temperature conditions (Hayes 1970; De Caritat et al. 1993; Walker 1993) ranging from 40°C

131   in diagenetic sandstones (Hiller and Velde 1991) to 600°C in high-grade metapelites (Vidal et

132   al. 2001). The chemical variations of chlorite are governed by three main none pressure

133   dependent substitutions (e.g., Shata et Hesse 1998; Zane et al. 1998; Vidal et al. 2001; Lanari

134   et al. 2014b): (i) The Tschermak substitution (TS), which consists in the combined

135   substitution of one divalent cation (Fe^{2+} or Mg^{2+}) and one Si^{4+} for two aluminum cations

136   ($Al^{IV}Al^{VI}Si_{-1}(Mg,Fe)_{-1}$), (ii) The Fe^{2+}-Mg^{2+}_{-1} substitution (FM), (iii) The di-trioctahedral

137   substitution which consists in the substitution of three Mg^{2+} and/or Fe^{2+} cations for two Al^{VI}

138   cations leading to the formation of a vacant site (($Mg^{2+},Fe^{2+})_3 \tilde{}_{-1}Al_{-2}$). In addition, chlorite

139   can incorporate ferric iron in its brucite-like layer by aluminum-iron substitution (De Grave et

140   al. 1987; Vidal et al. 2005, 2006; Muñoz et al. 2006, 2013; Lanari et al. 2014a). A challenging

141   issue is therefore to measure the XFe^{3+} ($Fe^{3+}/\Sigma Fe)_{chl}$ of chlorite to calculate the correct

142   structural formula.

143   In chlorite minerals, an important and unanswered question is to determine which

144   mechanisms and parameters control the formation of oscillatory zoning. To address this

145   question, we performed detailed X-ray EPMA (Electron Probe Micro-Analysis) mapping

146   coupled with XFe^{3+} Fe K-edge XANES (X-ray Absorption Near Edge Structure)

147   measurements on zoned chlorite crystals from the Pic-de-Port-Vieux thrust, in the Axial Zone

148   of the Pyrenees (Spain).

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150   **Geological background and description of the samples**

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151   The Pyrenean belt is a double-vergence orogenic wedge formed during the collision of

152   the Iberian and European plates between the Late Cretaceous and the early Miocene (e.g.,

153   Muñoz 1992; Roure et al. 1989; Teixell 1998). The south-vergent thrust system comprises

154   imbricated basement thrusts which form the anticlinal stack of the Axial Zone and pass

155   southwards to detachment levels within the sedimentary cover thrust units of the South-

156   Pyrenean Zone (Fig. 1a). The studied area is located in the Pyrenean Axial Zone, in the

157   eastern slope of the Pic-de-Port-Vieux (Fig. 1b). The major structure in this area is the

158   Gavarnie thrust (GT), involving a minimum southward displacement of 11.5 km (Grant 1989)

159   of Upper Paleozoic strata on Hercynian to Lower Paleozoic basement covered with Permo-

160   Triassic and Upper Cretaceous strata (Fig. 1c). The Gavarnie thrust activity is dated from the

161   Priabonian to Rupelian by stratigraphy in the South-Pyrenean foreland basin (Teixell 1996)

162   and to the Priabonian (36.5 ± 1.4 Ma) by ^{40}Ar-^{39}Ar isotopic dating on authigenic illite from

163   the thrust fault zone (Rahl et al. 2011). The latter authors also report a Maastrichtian (circa 70

164   Ma) age but the Jaca basin stratigraphic organization make it difficult to relate this age to an

165   early thrusting activity (i.e. the future Gavarnie thrust sheet area was tilting northward down

166   to basinal depths at that time, e.g., Teixell 1996). In the Pic-de-Port-Vieux culmination, a

167   secondary thrust occurs in the footwall of the Gavarnie thrust: the Pic-de-Port-Vieux (PPV)

168   thrust (Fig. 2). With a minimum southward displacement of 0.85 km (Grant 1990), the PPV

169   thrusting deformed, and is thus younger than, the Gavarnie thrust and emplaced Triassic

170   pelites/sandstones above Upper Cretaceous dolomitic limestone (Figs. 2 and 3a).

171   Structures and microstructures related to the PPV thrust emplacement have been

172   extensively studied by Grant (1990, 1992). In the hanging-wall of the major thrust surface, a

173   damage zone about 10 m-thick comprises four generations of extensional normal faults (Fig.

174   3c; see Grant 1992 for details). The last generation corresponds to low-angle synthetic normal

175   faults (Fig. 3c) related to the reactivation of the PPV thrust by spreading/gliding inducing

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176   shear and extension strain (Grant 1992). During this tectonic episode, previously formed (pre-

177   thrusting and syn-thrusting) high-angle faults were reactivated as conjugated normal faults.

178   The formation of these normal faults records syn-kinematic fluid-rock interactions in chlorite

179   ± quartz ± calcite extension veins and shear veins (Fig. 3b, Grant, 1992). Forty samples were

180   collected, for most of them, in faults and veins in the hanging-wall of the PPV thrust. The

181   stars in Figure 3c indicate the positions of zoned chlorite crystals, systematically localized in

182   the largest synthetic faults (labeled A and B in Fig. 3c).

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184   **Methodological procedures**

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186   **1. Analytical techniques**

187   Detailed investigation of textures, microstructures and related variations of chemistry

188   in chlorite was conducted using optical microscopy and scanning electron microscope (SEM)

189   coupled with energy dispersive spectrometer (EDS) analyses. Quantitative chemical analyses

190   were performed by electron probe micro-analysis (EPMA).

191   SEM observations were performed with a JEOL JSM5600 scanning electron

192   microscope coupled with a FONDIS energy dispersive analyzer (EDS) at the Renatech

193   network Femto laboratory (University of Franche-Comté). More detailed observations were

194   made with a JEOL JSM 6400F at the Institut Carnot de Bourgogne (University of

195   Bourgogne).

196   Quantitative chemical analyses of zoned chlorite minerals were performed using two

197   JEOL 8200 EPMA at ISTE (University of Lausanne) and at the Institute of Geological

198   Sciences (University of Bern). X-ray compositional maps were measured using wavelength

199   dispersive spectrometers (WDS) and analytical conditions of 15 keV accelerating voltage, 100

200   nA specimen current, 300-450 ms dwell time and 1 μm spot size. Punctual analyses were

201   acquired at the Institute of Geological Sciences (University of Bern), using common

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202   standards: albite (Si), phlogopite (K), ilmenite (Fe, Ti), orthoclase (Ca, Al), spinel (Mg),

203   tephroite (Mn) and enstatite (Cr) with 15 keV accelerating voltage, 10 nA specimen current

204   and 40 s dwell time.

205   Chemical analyses of unzoned chlorite crystals were performed using a CAMECA

206   model SX100 electron microprobe equipped with five WDS at the University of Montpellier.

207   The microprobe was operated at 20 keV accelerating voltage, with a specimen current of 10

208   nA and a beam diameter of 3 μm. The standards used were albite (Na), Al_2O_3 (Al), Fe_2O_3

209   (Fe), forsterite (Mg), orthoclase (K), TiO_2 (Ti) and wollastonite (Si, Ca) (for the choice of the

210   standards see Merlet and Bodinier 1990).

211   In order to determine the speciation of iron in chlorite crystals, Fe K-edge XANES (X-

212   ray Absorption Near Edge Structure) and XRF (X-ray Fluorescence) data were collected at

213   the BM23 beam-line of the European Synchrotron Radiation Facility (ESRF; Grenoble,

214   France) using the micro-focused experimental setup. The storage ring was operating in the 16-

215   bunch mode with an average current of 75 mA. X-rays were generated using a bending

216   magnet, and monochromatized with a double crystal fixed exit Si(111) monochromator.

217   Micro-focusing KB mirrors were used to focus the beam down to 4 by 4 μm FWHM (Full

218   Width Half Maximum). Data were collected in fluorescence mode using a Vortex silicon-

219   drifted diode located at 85° of the incident X-ray beam. The samples were positioned

220   perpendicular to the X-ray beam to minimize self-absorption (Pfalzer et al. 1999). μ-XRF

221   maps were first recorded at 9 keV, with 10 μm spatial resolution and a dwell time of 0.5 s.

222   Then, μ-XANES spectra were collected at the Fe *K*-edge for different locations of the XRF

223   maps. Data normalization and pre-peak fits were performed with the XᴀsMᴀᴘ package,

224   originally dedicated to the dispersive micro-XANES mapping applications (Muñoz et al.

225   2006, 2008). The Fe *K*-edges were fitted between 7108 and 7118 eV using three pseudo-Voigt

226   functions, following the procedure of Muñoz et al. (2013). In order to derive the speciation of

227   iron, pre-edge calibration was based on the following powdered standards: staurolite

228   ($^{[IV]}Fe^{2+}$), siderite ($^{[VI]}Fe^{2+}$), andradite ($^{[VI]}Fe^{3+}$) and sanidine ($^{[IV]}Fe^{3+}$), according to Wilke et

229   al. (2001). Chlorite crystals were oriented in the magic angle geometry to prevent polarization

230   effects in the XANES and pre-edge regions (i.e. crystal orientation relative to the polarized X-

231   ray beam), in agreement with Muñoz et al. (2013).

232

233   **2. Data processing and thermometry calculation**

234   X-ray images data were processed using the program XMapTools 1.6.5 (Lanari et al.

235   2014b). The allocation of each pixel to one mineral phase (e.g., chlorite or quartz) was done

236   using all the elements analyzed by EPMA. Chlorite X-ray raw intensity of Si, Al, Ti, Fe, Mg,

237   Mn, Ca, Na, Cr and K were converted into oxide wt-% compositions SiO_2, Al_2O_3, TiO_2, FeO,

238   MgO, MnO, CaO, Na_2O, Cr_2O_3 and K_2O using internal standards, i.e. transects of point

239   analyses measured on the same area (de Andrade et al. 2006). Indeed, the reduction of

240   acquisition time at 200 ms per pixel allows significant time saving in the map creation, but

241   requires standardization with well localized spot analyses using a standard EPMA setup. The

242   'automatic median' approach available in XMapTools was used (Lanari et al. 2014b). The

243   quality of the standardization was tested by comparing the composition of the internal

244   standard and the composition of the corresponding pixel in the X-ray maps. Chlorite structural

245   formulas were then calculated for each pixel using the function available in XMapTools.

246   This function allows calculating a structural formula on a 14 oxygen-basis by distributing

247   elements on two tetrahedral (T1, T2) and three octahedral sites (M1, M2M3, M4) and

248   assuming equipartition between Fe^{2+} and Mg^{2+} (constant X_{Mg} = $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ on M1,

249   M2M3 and M4). The knowledge of the iron oxidation state (XFe^{3+} = $Fe^{3+}/(Fe^{3+}+Fe^{2+})$) of

250   chlorite is required to calculate the correct structural formula of chlorite without the

251   hypothesis of $\sum Fe$ = Fe^{2+}. It has been shown that incorporation of Fe^{3+} instead of Fe^{2+} may

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252 generate important changes of the calculated X_{Mg} and the amount of vacancy ($\square$) in M1 (Vidal

253 et al. 2005; Lacroix et al. 2012; Lanari et al. 2014a). End-member proportions of amesite,

254 clinochlore, daphnite and sudoite were estimated from the abundance of Al, Mg, Fe^{2+} and $\square$ in

255 the M1 site respectively.

256 Maps of formation temperature can be calculated from the oxide wt-% maps using the

257 different empirical and semi-empirical calibrations available in XMAPTOOLS (Lanari et al.

258 2014b). In this study, we used a calibration which allows the chlorite temperature calculation

259 knowing XFe^{3+}. Among the two recent calibrations using XFe^{3+} adapted to low grade

260 metamorphism context (Inoue et al., 2009 and Lanari et al., 2014a), we used the calibration

261 Chl(1) from Lanari et al. (2014a) that was better constrained, in particular with an adjustment

262 of the standard state thermodynamic properties of sudoite. The calibration of Inoue et al.

263 (2009) gives similar results. The Lanari et al. (2014a) calibration is based on the following

264 chlorite + quartz + water equilibrium:

265 2 clinochlore + 3 sudoite = 4 amesite + 4 H_2O + 7 quartz   (1)
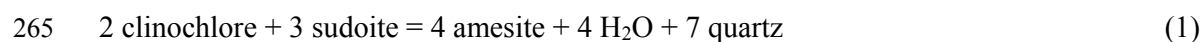
266 Ideal activities of amesite, clinochlore and sudoite are calculated using a site mixing model

267 for chlorite end-members and a_{H2O} = 1 (Lanari et al. 2014a), which allows the determination

268 of *ln(K)* using the following equation:

269 $\ln(K) = \ln(a^4_{ames} / a^2_{clin}a^3_{sud})$ (2)

270 Chlorite temperatures are then calculated using:

271 $T_{chlorite}$ (°C) = 172341 / (-Rln(K) + 315.149) - 273.15   (3)

272 An average temperature was calculated from quadrat samples of 20*20 μm (corresponding to

273 400 pixels) using a Monte Carlo technique (1,000 permutations for each pixel corresponding

274 to 400,000 calculations) to simulate the uncertainty of 5% on the XFe^{3+} determined by μ-

275 XANES measurements. The center of the quadrat location was superimposed to the XANES-

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276   related point. According to the number of data and the small heterogeneities of the sample, a 1

277   sigma standard deviation appears significant and was calculated for each quadrat.

278

Results

1 Host rock

281   The Pic-de-Port-Vieux thrust fault zone comprises pelites in the hanging-wall and

282   dolomitic limestone in the footwall (Fig. 4a). Pelite is constituted by phyllosilicates (mainly

283   illite-muscovite, but also chlorite), quartz, and dispersed grains of hematite, apatite, and rutile

284   (Fig. 4b); rare calcite is detected. Near the major thrust surface and along synthetic faults, the

285   red pelite turns to a greenish color. The green pelite is characterized by the absence of

286   hematite (Fig. 4c). Illite-muscovite is still abundant. Matrix quartz displays an elongated

287   morphology with long axis parallel to schistosity. Chlorite crystallized commonly along

288   extension veinlets and shear veinlets (Fig. 4c). In the footwall, the dolomitic limestone is

289   composed of euhedral dolomite crystals in a microcrystalline calcite matrix with rare iron

290   oxides (Figs. 4d). Approaching the thrust surface, dolomitic limestone is progressively

291   mylonitized (Fig. 4a). Dolomite is progressively dissolved (Figs. 4e and 4g) and secondary

292   calcite precipitated in dolomitic ghosts and cracks (Fig. 4f). Within the mylonite, dolomite

293   occurs only as anhedral remains in calcite.

294

2. Chlorite description

296   Two types of chlorite minerals crystallized in the Pic-de-Port-Vieux veins related to

297   synthetic fault activity. Figures 5a and 5b shows a syntaxial extension vein filled by quartz +

298   chlorite ± calcite. In these veins, chlorite crystals are preferentially developed along the vein-

299   host rock interface and quartz crystals occur as elongated crystal with axis perpendicular to

300   the vein boundaries. These textural observations suggest that chlorite nucleated first in contact

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301 to the host-pelite and grew toward the center of the vein with a growth direction parallel to the

302 schistosity planes. When a vein crosses pelite and silt alternating layers, chlorite is

303 preferentially present along the pelitic layers (Figs. 5a, 5b). In these extension veins, quartz

304 shows parallel inclusion bands (dust or secondary minerals inclusions parallel to the vein

305 wall) and serrated grain boundaries (called "radiator structure" within Bons et al. 2012)

306 indicating a crack-seal mechanisms of vein formation (Ramsay, 1980). The second type of

307 vein corresponds to shear vein filled by quartz, chlorite and locally calcite (Figs. 5c and 5d).

308 The quartz exhibits blocky crystals without any preferential orientation. Moreover, chlorite

309 occurs sometime in these shear veins as pseudo-uniaxial plates arranged in rosette-shaped

310 aggregates. These structures suggest that chlorite is followed by quartz during precipitation of

311 these minerals in open fractures. These two vein types are cogenetic and in accordance with

312 the orientation of the principal axes of the local field stress (Fig. 5e).

313   SEM images show that rosette chlorite from shear veins displays oscillatory zoning

314 pattern (Fig. 6a) while chlorite from extension veins is homogenous. The rosette-like

315 morphology of chlorite can be seen on Figures 6b and 6c. Both images show that the rosettes

316 correspond to the aggregation of individual platelet crystals composed of stacks of layers 20-

317 50 µm thick and 100-200 µm long. This morphology suggests that chlorite grew in an open

318 space and that quartz crystallization postdates chlorite growth as discussed above. However,

319 the contacts between quartz and chlorite grains are devoid of any corrosion texture (Figs. 6a,

320 6c).

321   Within a single vein, all chlorite aggregates exhibit similar zoning patterns with the

322 same number of contrasted layers. However, the thickness of the layers can vary from one

323 rosette to another (Fig. 6a). At higher magnifications, the zonation appears complex with

324 heterogeneous contrasts at the micrometric scale (Fig. 6d). The contrast distribution appears

325 as stair steps in section, seeming to follow the growth development of the chlorite crystals

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326   (layer by layer or by spiral growth) but with preferential growth directions perpendicular to c*

327   (F face is (001)) (Fig. 6e).

328

329   **3. Chlorite chemistry**

330   Two X-ray images were performed on aggregates of oscillatory zoned chlorite from a

331   shear vein using EPMA (maps A and B, Fig. 7). Five zones are distinguishable in the two

332   aggregates. Zone 1 is located in the core of the aggregate and zone 5 in the external rim (Figs.

333   7b). Backscattering oscillatory contrasts are caused by FeO and MgO content variation (Figs.

334   7c; 7d). FeO and MgO contents display strong opposite behaviors with absolute variations up

335   to 7 wt-%. FeO ranges from 16 to 23 wt-% and MgO from 21 to 13 wt-%. SiO_2 and Al_2O_3

336   contents show smaller variations (less than 2 wt-%). SiO_2 ranges from 25 to 27 wt-% and

337   Al_2O_3 from 22 to 24 wt-% (Figs. 7e and 7f). There is a slight increase of Al_2O_3 from zone 1

338   (core) to zone 4, whereas the external rim (zone 5), like zone 1, displays lower Al_2O_3. SiO_2

339   content is almost constant in all zones, except in zone 2 where it is about 2 wt-% higher. X-

340   ray image from chlorite extension veins was not performed due to the chemical homogeneity

341   of these minerals.

342   Based on both μ-XRF and EPMA chemical maps, μ-XANES measurements were

343   performed in five spots along a radius of zoned chlorite mineral that vas previously analyzed

344   (Fig. 8a). Normalized spectra are displayed in Figure 8b. Spectral signatures are typical of

345   clinochlore (e.g., Muñoz et al. 2013). Their similar shape suggests that similar crystal

346   orientations are considered for these measurements. However the Xan1 spectrum shows a

347   slightly different shape suggesting a small change in orientation, mostly because it is located

348   in the center of the concentric crystal. According to the work of Muñoz et al. (2013), this

349   shape might lead to a slight over-estimation of the XFe^{3+} (i.e. $Fe^{3+}/\sum Fe$) from the pre-edge

14

350 data reduction. But according to the same authors, this over-estimation should not exceed

351 0.07, which is in the same range of the typical accuracy of the method ($\pm$ 0.05).

352 Figure 8c shows the baseline-subtracted pre-edge peaks (white circles), together with their

353 best fits (solid lines) and pseudo-voigt peaks used for deconvolution (dotted lines). Results in

354 terms of integrated area and centroid energy positions are displayed in the variogram of

355 Figure 8d. The accuracy of the centroid value is $\pm$ 0.05 eV (Muñoz et al., 2013). This

356 variogram also shows reference values obtained for the standard compounds (white circles)

357 used for the calibration of the data (see Wilke et al. 2001 for details). Results obtained for the

358 different locations along the radius of the crystal all plot in between the two octahedral Fe^{2+}–

359 Fe^{3+} end-members, in agreement with the structure of clinochlore crystals (i.e. Fe located in

360 octahedral sites). The conversion into XFe^{3+} show periodic variations ranging from 23 to 44%

361 ($\pm$ 5%). In addition to the integrated area and the centroid position values, Table 1 shows the

362 XFe^{3+} values obtained from XANES normalization.

363   Assuming that each zone has homogeneous iron state oxidation, μ-XANES

364 measurements (Table 1) coupling with quantitative oxide wt-% composition maps (Fig. 7)

365 were used to calculate structural formulas for each pixel of chlorite (from a shear vein) using

366 *Chl-StructForm.m* function of XMAPTOOLS (Lanari et al. 2014b). XFe^{3+} values from chlorite

367 Map A are assumed to be the same as for Map B. In each zone from chlorite maps A and B,

368 representative structural formulas were given in Table 2 and plotted in Figure 9. The average

369 composition in map A are:

370 $[Si_{2.54}Al_{1.46}O_{10}](Al_{1.30}Fe^{2+}_{1.12}Fe^{3+}_{0.81}Mg_{2.44}\square_{0.32})(OH)_8$ in zone 1,

371 $[Si_{2.61}Al_{1.39}O_{10}](Al_{1.33}Fe^{2+}_{1.14}Fe^{3+}_{0.42}Mg_{2.92}\square_{0.18})(OH)_8$ in zone 2,

372 $[Si_{2.58}Al_{1.42}O_{10}](Al_{1.35}Fe^{2+}_{1.15}Fe^{3+}_{0.59}Mg_{2.62}\square_{0.26})(OH)_8$ in zone 3,

373 $[Si_{2.60}Al_{1.40}O_{10}](Al_{1.43}Fe^{2+}_{1.12}Fe^{3+}_{0.33}Mg_{2.92}\square_{0.18})(OH)_8$ in zone 4,

374 $[Si_{2.56}Al_{1.44}O_{10}](Al_{1.34}Fe^{2+}_{1.08}Fe^{3+}_{0.85}Mg_{2.34}\square_{0.37})(OH)_8$ in zone 5.

375   Two groups can be distinguished from these results. The first group includes structural

376   formulas from zones 1, 3 and 5; they correspond to Fe-rich chlorite (Fig. 9a). Their

377   compositions are closed to the unzoned chlorite (homogenous, without chemical variation)

378   from synkinematic extension veins and correspond to 40% of clinochlore+daphnite, 40% of

379   amesite and 20% of sudoite (Fig. 9b). The second group is enriched in Mg and corresponds to

380   the analyses of the zones 2 and 4 (Fig. 9a). Their compositions are out of the field of unzoned

381   chlorite and correspond to 20-30% of clinochlore+daphnite, 40% of amesite and 30-40% of

382   sudoite (Fig. 9b). The differences between the two chlorite groups are the Mg-$\sum$Fe

383   substitution in octahedron (Fig. 9a) and also a di-trioctahedral substitution (Fig. 9b). No

384   Tschermak substitution has to be invoked to explain the chemical variations.

385   Chlorite structural formulas are calculated from each pixel of the analyzed area, allow

386   building of Fe^{2+}, Fe^{3+} maps (Figs. 10a and 10b). In zones 1 and 5, Fe^{2+} content is equal to 1

387   a.p.f.u. while it reaches 1.1 to 1.2 in zones 2, 3 and 4. Fe^{3+} is equal to 0.8 a.p.f.u. in zones 1

388   and 5; 0.7 a.p.f.u. in zone 3 and 0.6 a.p.f.u. in zones 2 and 4. Fe^{2+} content shows small

389   variations probably due to edge effect (the XFe^{3+} between two successive zones probably

390   gradually changing), it may be considered constant throughout the crystallization. In contrast,

391   Fe^{3+} content displays strong variations. These results highlight an iron redox change during

392   crystal growth, with a cyclic alternation between more ferrous and more ferric chlorite layers.

393   In order to test whether the FM substitution is at the origin of the zonation between Fe-

394   rich and Mg-rich layers, an $X_{Mg}=Mg^{2+}/(Mg^{2+}+Fe^{2+})$ map has been produced (Fig. 10c). In

395   agreement with structural formulas (Table 2), X_{Mg} map (Fig. 10c) does show significant

396   variation. X_{Mg} is constant around 0.72 ± 0.03.

397

398   **4. Temperature map**

16

399   Temperature map (Fig. 10d) is derived using the Eq. (3), which is the thermometer

400   Chl(1) from Lanari et al. (2014a) in XMAPTOOLS using the XFe^{3+} measurements for each

401   zone (Table 1). In both maps A and B, average temperatures with associated uncertainty were

402   estimated and are reported in Table 2. For both aggregates, temperatures were estimated at

403   307°C ± 19°C to 347°C ± 27°C in zone 1, followed by 370°C ± 36°C to 396°C ± 29°C in

404   zone 2, 338°C ± 24°C to 354°C ± 23°C in zone 3, 402°C ± 49°C to 405°C ± 41°C in zone 4

405   and 316°C ± 20°C to 320°C ± 22°C in zone 5. Chlorite crystals A and B display the same

406   temperature evolution: they show a series of warming and cooling cycles during

407   crystallization. The temperature oscillation (up to 100°C range) is correlated to the chemical

408   zonation: Mg-rich layers correspond to hot areas while Fe-rich layers correspond to cold ones.

409

410   **Discussion**

411   Chlorite chemical zoning described above is characterized by Fe-Mg chemical

412   variations and increase in Fe^{3+} in the Fe-rich layers. These chemical changes may reflect

413   changes of local equilibrium conditions experienced during PPV thrust activity. Several

414   parameters such as pressure (P), temperature (T), oxygen fugacity (f_{O2}), water activity (a_{H2O}),

415   redox conditions (XFe^{3+}) and bulk system composition (including bulk-rock and fluid

416   compositions) could be invoked to explain the zoning. In the section below, we discuss the

417   effect of those parameters on the chlorite compositions in order to discriminate which can

418   have played a critical role during the growth of these aggregates.

419

420   **1. Significance of chemical and temperature oscillations registered by PPV thrust**

421   **chlorite aggregates**

422   Chlorite chemistry can be a very good indicator of temperature of crystallization (e.g.,

423   Cathelineau and Nieva 1985; Cathelineau 1988; de Caritat et al. 1993; Vidal et al. 2001, 2005,

424   2006; Inoue et al. 2009; Bourdelle et al. 2013; Lanari et al. 2014a). In this study, the

425   calibration *Chl(1)* of Lanari et al. (2014a) is used to calculate the formation temperature of

426   chlorite for a known XFe^{3+} content (obtained by μ-XANES). Temperature oscillations

427   between ~310°C and ~400°C are found in correlation to chemical variations for the two

428   studied chlorite aggregates. The core of the chlorite aggregates (zone 1) and the last rim (zone

429   5) with low Mg and high Fe^{3+} chemical composition recorded the lowest temperatures

430   (~310°C). These two zones correspond to the first and last stages of crystallization,

431   respectively. Between these two zones (i.e., zones 2, 3 and 4) the crystallization temperature

432   oscillates between 350-400°C with the highest temperatures corresponding to the layers with

433   the highest Mg and lowest Fe^{3+} contents, respectively.

434   The 1σ standard deviation on the average temperature of each growing zone is

435   reported in Table 2 and Figure 11. Such large errors could indicate that all the zones

436   crystallized around 350 ± 50°C if this standard deviation is considered to be representative of

437   the analytical uncertainty. However, temperature differences are significant between the

438   different zones as supported by the temperature map in Fig. 10d. The large 1σ deviations

439   calculated in this study are caused by the ultra-local chemical variability occurring within

440   each zone. As the standard deviation on the temperature is calculated from a local area (see §

441   methods), outliers such as grain boundaries or heterogeneities may cause a large dispersion.

442   The temperature map in Fig. 10d supports that at the scale of each growth zone, the

443   temperature variation is smaller than around ± 25°C. Thus, temperature differences

444   highlighted in this study between the different growth zones 1-5, 3 and 2-4 are significant.

445   Although the averages temperatures give values from 310 ± 50°C to 400 ± 50°C, it is more

446   accurate to consider a difference of at least 50°C between the two populations because of the

447   absolute uncertainty of thermodynamic models and mineral compositions.

18

448   The lowest temperatures (310 ± 50°C) recorded during the first and the fifth stages of

449   chlorite growth are similar to those calculated for unzoned chlorite located in extension and

450   shear veins from the same area (Fig. 9a). These temperatures are consistent with temperature

451   estimation of 250-300°C based on fluid inclusion microthermometry on quartz from extension

452   vein in the PPV thrust (Grant et al. 1990; Banks et al., 1991; McCaig et al., 2000). They are

453   also consistent with stable isotopic data on quartz and chlorite from the same area which

454   indicate a temperature of 320°C ± 30°C (Lacroix and Vennemann, 2015) and with carbonate

455   footwall temperature obtained with Raman spectroscopy of carbonaceous material (work in

456   progress). In contrast, chlorite layers with higher Mg content are probably formed at higher

457   temperature: 400 ± 50°C. The thermometry results suggest that the minimum ΔT between two

458   successive layers is about 20-30°C while the likely ΔT in all the chlorite is about 50-80°C.

459   Such temperature variation is discussed in detail in the following section.

460

461   **2. External and internal factors for chemical zonation**

462   Recent studies based on experimental fluid mineral reactions demonstrate that zoning

463   of mineral compositions does not always reflect the evolution of fluid composition (Borg et

464   al. 2014). These authors showed that during rapid fluid-rock reactions, ultra-local fluid

465   composition variation can form complex mineral zoning patterns, even when the overall

466   system is highly fluid-buffered. Wang and Merino (1992) proposed a dynamic model,

467   autonomously able to produce oscillatory zoning of trace elements in calcite without changes

468   in bulk water chemistry. In this model, the growth-induced H^+ buildup at the growth surface

469   of calcite making the surface more positive, thus repelling inhibited cations (such as Mn^{2+})

470   and accelerating the growth rate. The increase in growth rate in turn further accelerates H^+

471   accumulation (positive feedback) until the Ca^{2+} concentration becomes depressed next to the

472   surface and slows down the crystallization. Then, H^+ diffusion in fluid makes the surface less

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473   positive (or even negative) and allows restarting calcite crystallization with incorporation of

474   inhibiting cations. Another growth cycle is triggered. Previous studies in the PPV thrust

475   reveal a circulation of oilfield brines, highly concentrated in ions (Banks et al. 1991). As the

476   growth of chlorite aggregate is probably very rapid, ultra-local fluid disequilibrium cannot be

477   excluded to explain a part of the observed zonation. However, the chemical oscillation display

478   similar patterns at the vein scale suggesting large crystallization volumes (e.g. Fig. 6a). The

479   scale of zoning is very large and shows significant chemical contrasts. This suggests that

480   oscillatory zoning patterns are not due to local kinetic effects in the PPV thrust faults but to an

481   external parameter such as the variation of the oxygen fugacity.

482   Beaufort et al. (2005) described zoned chlorite spherules of hydrothermal origin in

483   sandstones near the uranium deposits of the East Alligator Rivers field in Australia. They

484   interpreted the chemical oscillatory zoning in Fe and Mg as the result of periodic changes in

485   physico-chemical condition of the hydrothermal solution during the crystallization process.

486   These authors have performed microprobe measurements to know the chlorite chemistry; they

487   showed significant variations in Mg but were not able to estimate the XFe^{3+} which would

488   have allowed a comparison with our data. In the present study, microprobe mapping of

489   chlorite chemistry (atom per formula unit, Fig. 10b) shows significant variations in Fe^{3+} (from

490   0.6 to 0.75 a.p.f.u.) during the crystallization. Highest $Fe^{3+}/\sum Fe$ values correspond to lowest

491   temperatures of chlorite formation. Several authors (Vidal et al. 2006; Tarantola et al. 2009;

492   Grosch et al. 2012; Lanari et al. 2012; Cantarero et al. 2014) found similar correlation

493   between $(Fe^{3+}/\sum Fe)_{chlorite}$ and temperature. In all these studies $(Fe^{3+}/\sum Fe)_{chlorite}$ was indirectly

494   estimated using the Vidal et al. (2005, 2006) approach. In a review paper, Lanari et al.

495   (2014a) found similar trend using both measured $(Fe^{3+}/\sum Fe)_{chlorite}$ and estimated $(Fe^{3+}/\sum Fe)$

496    $_{chlorite}$ using the approach of Vidal et al. (2005, 2006). In a $Fe^{3+}/\sum Fe$ versus temperatures

497   diagram (Fig. 11), Lanari et al. (2014a) identified two main trends using chlorite data reported

20

498   in the literature and calculation from Vidal et al. (2005, 2006). Both trends correspond to

499   chlorite formed under different redox condition, i.e. various samples where chlorite

500   crystallized under less oxidized or more oxidized conditions (see continuous and dashed

501   curves in Fig. 11 respectively). According to these authors, for a given fO_2, chlorite formation

502   temperature may control the amount of Fe^{3+} input in the structure. In other words, the amount

503   of Fe^{3+} cannot be considered alone without a formation temperature as a proxy for the redox

504   conditions. Estimated T and measured $Fe^{3+}/\sum Fe$ from chlorite of PPV thrust have been

505   reported in this diagram, they are located just above the more oxidized trend (Fig. 11). This

506   result implies that the $Fe^{3+}/\sum Fe$ variations of chlorite during its crystallization are mainly

507   caused by temperature variations. The redox conditions (fO_2) are the same during the chlorite

508   crystallization history. Indeed, if the fO_2 in the fluid would have change during chlorite

509   growth, the point analyses would be more scattered on both redox trends (e.g., arrows in Fig.

510   11).

511

512   **3. Origin of oscillatory zoned chlorite aggregates in the PPV thrust veins**

513   *Previous data and model:*

514   Chemistry, source, behavior and P-T conditions of fluids have been previously

515   investigated from fluid inclusions performed in PPV thrust quartz veins (Grant et al. 1990;

516   Banks et al. 1991; McCaig et al. 1995). Synthetized in McCaig et al. (2000), these analyses

517   reveal at least two distinct fluids. Both of them are hypersaline brines (Banks et al. 1991) with

518   a high Br/Cl ratio indicating seawater evaporation with halite precipitation origin (Banks et al.

519   1994). These brines could have been derived from the upper Triassic evaporites and stored in

520   the lower Triassic redbeds (McCaig et al. 2000). Part of this formation water could have been

521   stored in another rock, such as the Devonian phyllites or the Silurian graphitic slates, inducing

522   a change in the isotopic signature of the fluid (Banks et al. 1991). However, the latter

21

523   interaction has not been certified because no sample carried from local rocks has sufficiently

524   elevated ratio of all the Pb isotopes to explain the fluid inclusions data (McCaig et al. 2000).

525   According to (Grant 1989), chemical zonation in chlorite could be due to a mixing of two

526   distinct fluids. Reducing fluid interactions with Triassic pelites would permit the release of

527   Fe^{3+} by hematite dissolution along the PPV thrust and synthetic faults (Fig. 3c) (Rumble

528   1976; Beaufort et al. 1992, 2005). Furthermore, the fluid interaction with limestone allows the

529   release of Mg by dolomite dissolution (e.g., Figs. 4f, 4g).

530   Fluid inclusion microthermometry indicates temperatures never exceeding 300°C

531   during quartz vein formation (Grant et al. 1990; Banks et al. 1991) and fluid pressure

532   comprised between 1.5 and 2 kbar (Grant 1990), corresponding to a burial depth of 5-7.5 km.

533   Furthermore, measured homogenization temperatures (Tm) define two fluid populations that

534   have been interpreted as a variation of the pressure of 600 bar due to fault valve mechanism

535   (Grant et al. 1990; Banks et al. 1991, McCaig et al. 2000). Indeed, fault-valve process may

536   cause abrupt fluid pressure fluctuations during the thrust activity (Sibson 1990) and have been

537   highlighted by crack-seal structures, open-space filling textures of the quartz + chlorite ±

538   calcite veins and distribution of inclusions in quartz.

539

540   *New data and model:*

541   According to the present study, oscillatory zoned chlorite from the PPV thrust records

542   cyclic changes in temperature without any change of the fluid redox condition or kinetic

543   disequilibrium. The composition map reported in Figure 10c indicates that X_{Mg}

544   ($Mg^{2+}/(Fe^{2+}+Mg^{2+})$) in chlorite does not vary significantly within analytical uncertainties (X_{Mg}

545   = 0.70 ± 0.3) during the aggregate growth. These results suggest that the X_{Mg} of the system

546   does not change during the crystallization of chlorite (Lanari et al. 2014a and references

547   therein), i.e. the chemical composition of the mineralizing fluid remains constant. Indeed,

22

548   chlorite is very sensitive to bulk composition changes and its X_{Mg} would be modified in case

549   of alternation of two fluids chemistries during crystallization.

550   Thus, each vein containing oscillatory chlorite recorded distinct fluid flow history

551   implying a variation of the number and intensity of pulses, but also a variation in the kinetics

552   of cooling and crystallization. On the other hand, fluid inclusions from PPV thrust quartz

553   veins reveal temperatures from 250 to 300°C, never higher than 325°C (Grant et al. 1990;

554   Banks et al. 1991, McCaig et al. 2000). Several hypotheses can be raised on these differences:

555   (i) Quartz and zoned chlorite may not be strictly cogenetic. Indeed, in shear veins where

556   zoned chlorites formed, chlorite rosettes are always located against the walls of the veins

557   while quartz is in the center of the veins and fills the open spaces between the chlorite

558   rosettes, suggesting that quartz precipitation postdated chlorite formation. In these conditions,

559   quartz fluid inclusions do not represent the chlorite formation conditions. (ii) The two fluid

560   populations recorded by the fluid inclusion study could be related to temperature variation

561   instead of pressure variation, as evocated in Grant et al., (1990). (iii) Fluid inclusion and

562   chlorite sampling was not performed in similar veins. Chlorite sampled in crack-seal

563   extension veins and small shear veins gives similar to those obtained by fluid inclusions. In a

564   crack-seal vein, the opening of the crack (before the seal) is very small (of the order of 50

565   microns or less), the opening mechanism is relatively slow and thus it is impossible to keep a

566   thermal imbalance at this scale. Therefore, crack-seals would likely form during interseismic

567   periods (build-up of stress in the seismic valve model). In contrast the large shear veins that

568   are characterized by blocky texture would form during more dynamic rupture likely being the

569   break seismic (as suggested by Boullier and Robert, 1992). Thus, crack-seal veins open

570   progressively and slowly (opening speed almost equal to the speed of healing, if we integrate

571   all the small increments "cracks" and "seal"). By contrast, large shear veins can be opened by

23

572   large jolts as suggested by the blocky quartz texture (Figs. 5c, 5d) allowing chlorite

573   crystallization in thermal disequilibrium with host rock.

574

575   *How to get hot fluid inputs?*

576   The results discussed above suggest that oscillatory zoned chlorite recorded the

577   temperature variation of one fluid, sometime hot (more than 350°C) probably episodic and

578   minor; sometime colder reflecting a cooling down to lithostatic equilibrium around 300°C.

579   The question is how to explain this fast input of hotter fluid? No igneous activity has been

580   reported in this area at this time, so the uniqueness way to introduce a much hotter fluid into

581   the vein would be to move fluid up from deeper fault portions. For a geothermal gradient

582   close to 30°C/km as estimated in the Jaca basin (Lacroix et al. 2011), at least 2 km of vertical

583   movement, representing 4 km of fluid transport along the Gavarnie thrust considering a dip

584   about 30°, must be invoked. Such fluid transport scale implicates that the fluid had to ascend

585   through a narrow channelway (1) with no loss of heat in contact to the surrounding rocks,

586   implicating quasi-instantaneous emplacement (a 1cm thick vein will lose most of its excess

587   heat by conduction in few minutes (e.g., Carslaw et al., 1959)); (2) with channelway heating

588   and in this case the whole chlorite rosette and surrounding rocks for at least several meters

589   will have experienced the peak temperatures estimated. Several investigations can be explored

590   to try to resolve this paradox. It is possible that the geothermal gradient changed at greater

591   depth, reducing the fluid migration distance. Fault-valve process increases the fracture

592   permeability for fluid draining and related shear vein formation. Such process permits a high

593   temperature fluid discharge in open veins followed by a cooling event in contact to host rock

594   (pelite). This mechanism has been observed by several authors. For example Cantarero et al.

595   (2014) describe high geothermal gradients (50°C/km minimum) along fractures. Temperature

596   measurements in a fault after an earthquake indicate a slight positive anomaly that can be

597   interpreted by viscous heating (e.g., Brodsky et al., 2009). Strain heating results from the

598   conversion of mechanical energy into heat during progressive deformation and, for some

599   models indicate that temperature rises of a few hundred degrees can be expected in major

600   thrust sheets (Brun and Cobbold 1980; Souche et al., 2013). There is not strain heating

601   evidence in the Pic-de-Port-Vieux thrust, so the ΔT (>20-30°C) recorded by the chlorite

602   rosettes is most likely related to an increase in the permeability of the fault rock for hot fluids

603   flowing from deeper areas. Fluid flows associated to earthquakes reveal variations of flow

604   rate and fluid sources (e.g., Toutain et al. 1997, 2006; Manga et Wang 2007). For example,

605   Mogi et al. (1988) show hot spring temperature variations related to earthquakes occurrences.

606   These temperature variations can be explained by a model of earthquake-enhanced

607   permeability due to the dislodging of obstacles from clogged fluid channels, such as pre-

608   existing fractures. Unclogged fractures act to breach hydrologic barriers (such as aquitards)

609   and connect otherwise isolated aquifers or other fluid sources, causing fluid source switching

610   and/or mixing (Wang et Manga 2010). It is thus possible that the ΔT measured in zoned

611   chlorite from the PPV thrust reflects the discharge of a deeper and hotter aquifer by stronger

612   fluid flow during large earthquakes.

613

614   **Implications**

615   (1) This study shows how important is the measure of XFe^{3+} in low-grade

616   metamorphism chlorite to study their chemistry, because the proportion of Fe^{3+} can locally

617   reach up to 45% of the total amount of iron. To measure $Fe^{3+}/\sum Fe$ ratio XANES and

618   Mössbauer techniques may be used, but microanalyses can only be performed using μ-

619   XANES spectroscopy.

620   (2) With the development of chlorite thermometry, several models have recently

621   emerged including XFe^{3+} estimation (e.g., Vidal et al. 2005, 2006) or requiring the knowledge

622   of the XFe^{3+} (Inoue et al. 2009; Lanari et al. 2014a). These two semi-empirical geo-

623   thermometers were calibrated with the idea that iron in chlorite must be expressed as $Fe_{tot} =$

624   $Fe^{2+} + Fe^{3+}$. As demonstrated by Figure 11 there is no general relation between Fe^{3+} and T

625   except for given redox conditions (in this case, XFe^{3+} increases with decreasing T). The

626   results of this study confirm the existence of a highly oxidized trend that was before only

627   predicted by modeling and prove that XFe^{3+} in chlorite can reach 45%. This result

628   demonstrates that chlorite may be used to investigate the redox conditions in low-grade

629   metamorphic rocks and hydrothermal environments. Fe^{3+} end-members must be defined and

630   should be used in the framework of thermodynamic modeling. This is an important domain

631   for further research in chlorite geo-thermometry and the results reported in this study provide

632   first importance data to adjust such models.

633   (3) The quantitative micro-mapping technique used in this study is fundamental to

634   highlight variations of chemistry in 2D at the thin section scale. This method allows to

635   measure the chemical heterogeneity of minerals and to calculate maps of formation

636   temperature which are critical to see the relations between T and the geometry of the crystals.

637   Here we demonstrate that this method may be coupled with single-spot μ-XANES analyses to

638   generate maps of structural formulas (Fig. 10) with variable XFe^{3+}. This offers new

639   opportunities to apply the same strategy using other high-precision instruments such as La-

640   ICP-MS or SIMS.

641   (4) This paper demonstrates that the temperature of the fluid within a vein is an

642   important parameter that controls the composition of the growing minerals. The zoned

643   chlorite crystals record changes that are caused by hot fluids pulses intercalated with cooling

644   periods. The process of fault-valve behavior is an important process to explain the

645   crystallization of this chlorite in the PPV thrust veins. The detailed study of phyllosilicates

646   can help to better understand fluid flows in a fault and to investigate the relations of such

647   flows with the seismic activity of the thrust. The future results obtained using the strategy

648   detailed in this study may have large implications in geosciences.

649

650   **Acknowledgements**

659

660   **References**

661   Banks, D., Davies, G., Yardley, B.W., McCaig, A., and Grant, N. (1991) The chemistry of brines

662   from an Alpine thrust system in the Central Pyrenees: An application of fluid inclusion

663   analysis to the study of fluid behaviour in orogenesis. Geochimica et Cosmochimica Acta, 55,

664   1021–1030.

665   Beaufort, D., Patrier, P., Laverret, E., Bruneton, P., and Mondy, J. (2005) Clay Alteration

666   Associated with Proterozoic Unconformity-Type Uranium Deposits in the East Alligator

667   Rivers Uranium Field, Northern Territory, Australia. Economic Geology, 100, 515–536.

668   Blanco-Quintero, I.F., García-Casco, A., and Gerya, T.V. (2011) Tectonic blocks in serpentinite

669   mélange (eastern Cuba) reveal large-scale convective flow of the subduction channel.

670   Geology, 39, 79–82.

671 Borg, S., Liu, W., Pearce, M., Cleverley, J., and MacRae, C. (2014) Complex mineral zoning

672   patterns caused by ultra-local equilibrium at reaction interfaces. Geology, G35287.1.

673 Bos, B., and Spiers, C.J. (2001) Experimental investigation into the microstructural and

674   mechanical evolution of phyllosilicate-bearing fault rock under conditions favouring pressure

675   solution. Journal of Structural Geology, 23, 1187–1202.

676 Boullier, A.-M., and Robert, F. (1992) Palaeoseismic events recorded in Archaean gold-quartz vein

677   networks, Val d'Or, Abitibi, Quebec, Canada. Journal of Structural Geology, 14, 161–179.

678 Bourdelle, F., Parra, T., Beyssac, O., Chopin, C., and Vidal, O. (2013) Clay minerals as geo-

679   thermometer: A comparative study based on high spatial resolution analyses of illite and

680   chlorite in Gulf Coast sandstones (Texas, U.S.A.). American Mineralogist, 98, 914–926.

681 Brodsky, E.E., Rowe, C.D., Meneghini, F., and Moore, J.C. (2009) A geological fingerprint of

682   low-viscosity fault fluids mobilized during an earthquake. Journal of Geophysical Research:

683   Solid Earth (1978–2012), 114.

684 Brun, J.P., and Cobbold, P.R. (1980) Strain heating and thermal softening in continental shear

685   zones: a review. Journal of Structural Geology, 2, 149–158.

686 Buatier, M.D., Lacroix, B., Labaume, P., Moutarlier, V., Charpentier, D., Sizun, J.P., and Travé, A.

687   (2012) Microtextural investigation (SEM and TEM study) of phyllosilicates in a major thrust

688   fault zone (Monte Perdido, southern Pyrenees): impact on fault reactivation. Swiss Journal of

689   Geosciences, 105, 313–324.

690 Cantarero, I., Lanari, P., Vidal, O., Alías, G., Travé, A., and Baqués, V. (2014) Long-term fluid

691   circulation in extensional faults in the central Catalan Coastal Ranges: P–T constraints from

692   neoformed chlorite and K-white mica. International Journal of Earth Sciences, 103, 165–188.

693 Carslaw, H.S., Jaeger, J.C., and others (1959) Conduction of heat in solids Vol. 2. Clarendon Press

694   Oxford.

695   Cathelineau, M. (1988) Cation site occupancy in chlorites and illites as a function of temperature.

696   Clay Minerals, 23, 471 –485.

697   Cathelineau, M., and Nieva, D. (1985) A chlorite solid solution geothermometer the Los Azufres

698   (Mexico) geothermal system. Contributions to Mineralogy and Petrology, 91, 235–244.

699   Chester, F.M., Evans, J.P., and Biegel, R.L. (1993) Internal structure and weakening mechanisms

700   of the San Andreas Fault. Journal of Geophysical Research: Solid Earth, 98, 771–786.

701   Dare, S.A.S., Barnes, S.-J., Prichard, H.M., and Fisher, P.C. (2011) Chalcophile and platinum-

702   group element (PGE) concentrations in the sulfide minerals from the McCreedy East deposit,

703   Sudbury, Canada, and the origin of PGE in pyrite. Mineralium Deposita, 46, 381–407.

704   De Andrade, V., Vidal, O., Lewin, E., O'Brien, P., and Agard, P. (2006) Quantification of electron

705   microprobe compositional maps of rock thin sections: an optimized method and examples

706   RID C-2856-2009. Journal of Metamorphic Geology, 24, 655–668.

707   De Caritat, P., Hutcheon, I., and Walshe, J.L. (1993) Chlorite geothermometry; a review. Clays

708   and Clay Minerals, 41, 219–239.

709   De Grave, E., Vandenbruwaene, J., and Bockstael, M.V. (1987) 57Fe Mössbauer spectroscopic

710   analysis of chlorite. Physics and Chemistry of Minerals, 15, 173–180.

711   Delvigne, J.E. (1998) Atlas of Micromorphology of Mineral Alteration and Weathering, 520 p.

712   Mineralogical Association of Canada.

713   Dowty, E. (1976) Crystal structure and crystal growth; II, Sector zoning in minerals. American

714   Mineralogist, 61, 460–469.

715   Dziggel, A., Wulff, K., Kolb, J., Meyer, F.M., and Lahaye, Y. (2009) Significance of oscillatory

716   and bell-shaped growth zoning in hydrothermal garnet: Evidence from the Navachab gold

717   deposit, Namibia. Chemical Geology, 262, 262–276.

718   Friel, J.J., and Lyman, C.E. (2006) Tutorial Review: X-ray Mapping in Electron-Beam

719   Instruments. Microscopy and Microanalysis, 12, 2–25.

720 Gaidies, F., Capitani, C. de, Abart, R., and Schuster, R. (2008) Prograde garnet growth along

721   complex P–T–t paths: results from numerical experiments on polyphase garnet from the Wölz

722   Complex (Austroalpine basement). Contributions to Mineralogy and Petrology, 155, 673–

723   688.

724 García-Casco, A., Torres-Roldán, R.L., Millán, G., Monié, P., and Schneider, J. (2002) Oscillatory

725   zoning in eclogitic garnet and amphibole, Northern Serpentinite Melange, Cuba: a record of

726   tectonic instability during subduction? Journal of Metamorphic Geology, 20, 581–598.

727 Gaspar, M., Knaack, C., Meinert, L.D., and Moretti, R. (2008) REE in skarn systems: A LA-ICP-

728   MS study of garnets from the Crown Jewel gold deposit. Geochimica et Cosmochimica Acta,

729   72, 185–205.

730 Grant, N.T. (1989) Deformation and fluid processes in thrust sheets from the central Pyrenees.

731   PhD. Thesis, University of Leeds.

732 ——— (1990) Episodic discrete and distributed deformation: consequences and controls in a

733   thrust culmination from the central Pyrenees. Journal of Structural Geology, 12, 835–850.

734 ——— (1992) Post-emplacement extension within a thrust sheet from the central Pyrenees.

735   Journal of the Geological Society, 149, 775–792.

736 Grant, N.T., Banks, D.A., McCaig, A.M., and Yardley, B.W.D. (1990) Chemistry, Source, and

737   Behavior of Fluids Involved in Alpine Thrusting of the Central Pyrenees. Journal of

738   Geophysical Research, 95, 9123–9131.

739 Grosch, E.G., Vidal, O., Abu-Alam, T., and McLoughlin, N. (2012) P-T Constraints on the

740   Metamorphic Evolution of the Paleoarchean Kromberg Type-Section, Barberton Greenstone

741   Belt, South Africa. Journal of Petrology, 53, 513–545.

742 Hayes, J.B. (1970) Polytypism of Chlorite in Sedimentary Rocks. Clays and Clay Minerals, 18,

743   285–306.

744 Hillier, S., and Velde, B. (1991) Octahedral occupancy and chemical composition of diagenetic

745   (low-temperature) chlorites. Clay Minerals, 26, 149–168.

746 Holdsworth, R.E. (2004) Weak Faults--Rotten Cores. Science, 303, 181–182.

747 Holten, T., Jamtveit, B., Meakin, P., Cortini, M., Blundy, J., and Austrheim, H. (1997) Statistical

748   characteristics and origin of oscillatory zoning in crystals. American Mineralogist, 82, 596–

749   606.

750 Holten, T., Jamtveit, B., and Meakin, P. (2000) Noise and oscillatory zoning of minerals.

751   Geochimica et Cosmochimica Acta, 64, 1893–1904.

752 Inoue, A., Meunier, A., Patrier-Mas, P., Rigault, C., Beaufort, D., and Vieillard, P. (2009)

753   Application of chemical geothermometry to low-temperature trioctahedral chlorites. Clays

754   and Clay Minerals, 57, 371–382.

755 Jamtveit, B. (1991) Oscillatory zonation patterns in hydrothermal grossular-andradite garnet;

756   nonlinear dynamics in regions of immiscibility. American Mineralogist, 76, 1319–1327.

757 Jamtveit, B., and Andersen, T.B. (1992) Morphological instabilities during rapid growth of

758   metamorphic garnets. Physics and Chemistry of Minerals, 19, 176–184.

759 Jamtveit, B., Wogelius, R.A., and Fraser, D.G. (1993) Zonation patterns of skarn garnets: Records

760   of hydrothermal system evolution. Geology, 21, 113–116.

761 Jolivet, M., Labaume, P., Monié, P., Brunel, M., Arnaud, N., and Campani, M. (2007)

762   Thermochronology constraints for the propagation sequence of the south Pyrenean basement

763   thrust system (France-Spain). Tectonics, 26, 17 PP.

764 Jourdan, A.-L., Vennemann, T.W., Mullis, J., Ramseyer, K., and Spiers, C.J. (2009) Evidence of

765   growth and sector zoning in hydrothermal quartz from Alpine veins. European Journal of

766   Mineralogy, 21, 219–231.

767 Kohn, M.J. (2003) Geochemical zoning in metamorphic minerals. The Crust, 3, 229–261.

31

768 Kohn, M.J., and Spear, F. (2000) Retrograde net transfer reaction insurance for pressure-

769   temperature estimates. Geology, 28, 1127–1130.

770 Kwak, T.A.P. (1981) Sector-zoned annite 85 phlogopite 15 micas from the Mt. Lindsay Sn-W-F(-

771   Be) deposit, Tasmania, Australia. The Canadian Mineralogist, 19, 643–650.

772 Lacroix, B., and Vennemann, T. (2015) Empirical calibration of the oxygen isotope fractionation

773   between quartz and Fe–Mg-chlorite. Geochimica et Cosmochimica Acta, 149, 21–31.

774 Lacroix, B., Charpentier, D., Buatier, M., Vennemann, T., Labaume, P., Adatte, T., Trave, A., and

775   Dubois, M. (2012) Formation of chlorite during thrust fault reactivation. Record of fluid

776   origin and P-T conditions in the Monte Perdido thrust fault (southern Pyrenees).

777   Contributions to Mineralogy and Petrology, 163, 1083–1102.

778 Lacroix, B., Travé, A., Buatier, M., Labaume, P., Vennemann, T., and Dubois, M. (2014)

779   Syntectonic fluid-flow along thrust faults: Example of the South-Pyrenean fold-and-thrust

780   belt. Marine and Petroleum Geology, 49, 84–98.

781 Lanari, P., Guillot, S., Schwartz, S., Vidal, O., Tricart, P., Riel, N., and Beyssac, O. (2012)

782   Diachronous evolution of the alpine continental subduction wedge: Evidence from P–T

783   estimates in the Briançonnais Zone houillère (France – Western Alps). Journal of

784   Geodynamics, 56–57, 39–54.

785 Lanari, P., Riel, N., Guillot, S., Vidal, O., Schwartz, S., Pêcher, A., and Hattori, K.H. (2013)

786   Deciphering high-pressure metamorphism in collisional context using microprobe mapping

787   methods: Application to the Stak eclogitic massif (northwest Himalaya). Geology, 41, 111–

788   114.

789 Lanari, P., Wagner, T., and Vidal, O. (2014a) A thermodynamic model for di-trioctahedral chlorite

790   from experimental and natural data in the system MgO–FeO–Al2O3–SiO2–H2O: applications

791   to P–T sections and geothermometry. Contributions to Mineralogy and Petrology, 167, 1–19.

792 Lanari, P., Vidal, O., De Andrade, V., Dubacq, B., Lewin, E., Grosch, E.G., and Schwartz, S.

793   (2014b) XMAPTOOLS: A MATLAB©-based program for electron microprobe X-ray image

794   processing and geothermobarometry. Computers & Geosciences, 62, 227–240.

795 Leclère, H., Buatier, M., Charpentier, D., Sizun, J.-P., Labaume, P., and Cavailhes, T. (2012)

796   Formation of phyllosilicates in a fault zone affecting deeply buried arkosic sandstones: their

797   influence on petrophysic properties (Annot sandstones, French external Alps). Swiss Journal

798   of Geosciences, 105, 299–312.

799 Leclère, H., Lacroix, B., and Fabbri, O. (2014) Fault mechanics at the base of the continental

800   seismogenic zone: Insights from geochemical and mechanical analyses of a crustal-scale

801   transpressional fault from the Argentera crystalline massif, French–Italian Alps. Journal of

802   Structural Geology, 66, 115–128.

803 Manga, M., and Wang, C.Y. (2007) Earthquake hydrology. Treatise on geophysics, 4, 29.

804 Manzotti, P., and Ballèvre, M. (2013) Multistage garnet in high-pressure metasediments: Alpine

805   overgrowths on Variscan detrital grains. Geology, 41, 1151–1154.

806 Martin, C., Debaille, V., Lanari, P., Goderis, S., Vandendael, I., Vanhaecke, F., Vidal, O., and

807   Claeys, P. (2013) REE and Hf distribution among mineral phases in the CV–CK clan: A way

808   to explain present-day Hf isotopic variations in chondrites. Geochimica et Cosmochimica

809   Acta, 120, 496–513.

810 McCaig, A.M., Wayne, D.M., Marshall, J.D., Banks, D., and Henderson, I. (1995) Isotopic and

811   fluid inclusion studies of fluid movement along the Gavarnie Thrust, central Pyrenees;

812   reaction fronts in carbonate mylonites. American Journal of Science, 295, 309–343.

813 McCaig, A.M., Wayne, D., and Rosenbaum, J. (2000) Fluid expulsion and dilatancy pumping

814   during thrusting in the Pyrenees: Pb and Sr isotope evidence. Geological Society of America

815   Bulletin, 112, 1199–1208.

816 Merlet, C., and Bodinier, J.-L. (1990) Electron microprobe determination of minor and trace

817   transition elements in silicate minerals: A method and its application to mineral zoning in the

818   peridotite nodule PHN 1611. Chemical Geology, 83, 55–69.

819 Meth, C.E., and Carlson, W.D. (2005) Diffusion-Controlled Synkinematic Growth of Garnet from

820   a Heterogeneous Precursor at Passo Del Sole, Switzerland. The Canadian Mineralogist, 43,

821   157–182.

822 Mogi, K., Mochizuki, H., and Kurokawa, Y. (1989) Temperature changes in an artesian spring at

823   Usami in the Izu Peninsula (Japan) and their relation to earthquakes. Tectonophysics, 159,

824   95–108.

825 Muñoz, J.A. (1992) Evolution of a continental collision belt: ECORS-Pyrenees crustal balanced

826   cross-section. In K.R. McClay, Ed., Thrust Tectonics pp. 235–246. Springer Netherlands,

827   Dordrecht.

828 Muñoz, M., De Andrade, V., Vidal, O., Lewin, E., Pascarelli, S., and Susini, J. (2006) Redox and

829   speciation micromapping using dispersive X-ray absorption spectroscopy: Application to iron

830   chlorite mineral of a metamorphic rock thin section. Geochemistry Geophysics Geosystems,

831   7, Q11020.

832 Muñoz , M., Pascarelli, S., Aquilanti, G., Narygina, O., Kurnosov, A., and Dubrovinsky, L. (2008)

833   Hyperspectral μ -XANES mapping in the diamond-anvil cell: analytical procedure applied to

834   the decomposition of (Mg,Fe)-ringwoodite at the upper/lower mantle boundary. High

835   Pressure Research, 28, 665–673.

836 Muñoz, M., Vidal, O., Marcaillou, C., Pascarelli, S., Mathon, O., and Farges, F. (2013) Iron

837   oxidation state in phyllosilicate single crystals using Fe-K pre-edge and XANES

838   spectroscopy: Effects of the linear polarization of the synchrotron X-ray beam. American

839   Mineralogist, 98, 1187–1197.

840 Nicotra, E., and Viccaro, M. (2012) Unusual magma storage conditions at Mt. Etna (Southern

841   Italy) as evidenced by plagioclase megacryst-bearing lavas: implications for the plumbing

842   system geometry and summit caldera collapse. Bulletin of Volcanology, 74, 795–815.

843 Pearce, M.A., and Wheeler, J. (2010) Modelling grain-recycling zoning during metamorphism.

844   Journal of Metamorphic Geology, 28, 423–437.

845 Putirka, K.D., and Tepley, F.J. (2008) Minerals, inclusions and volcanic processes. Mineralogical

846   Society of America, Chantilly, VA.

847 Rahl, J.M., Haines, S.H., and van der Pluijm, B.A. (2011) Links between orogenic wedge

848   deformation and erosional exhumation: Evidence from illite age analysis of fault rock and

849   detrital thermochronology of syn-tectonic conglomerates in the Spanish Pyrenees. Earth and

850   Planetary Science Letters, 307, 180–190.

851 Ramsay, J.G. (1980) The crack–seal mechanism of rock deformation. Nature, 284, 135–139.

852 Robyr, M., Carlson, W.D., Passchier, C., and Vonlanthen, P. (2009) Microstructural, chemical and

853   textural records during growth of snowball garnet. Journal of Metamorphic Geology, 27, 423–

854   437.

855 Robyr, M., Darbellay, B., and Baumgartner, L. p. (2014) Matrix-dependent garnet growth in

856   polymetamorphic rocks of the Sesia zone, Italian Alps. Journal of Metamorphic Geology, 32,

857   3–24.

858 Roure, F., Choukroune, P., Berastegui, X., Munoz, J.A., Villien, A., Matheron, P., Bareyt, M.,

859   Seguret, M., Camara, P., and Deramond, J. (1989) Ecors deep seismic data and balanced cross

860   sections: Geometric constraints on the evolution of the Pyrenees. Tectonics, 8, 41–50.

861 Schumacher, R., Roetzler, K., and Maresch, W.V. (1999) Subtle oscillatory zoning in garnet from

862   regional metamorphic phyllites and mica schists, western Erzgebirge, Germany. The

863   Canadian Mineralogist, 37, 381–403.

864 Shata, S., and Hesse, R. (1998) A refined XRD method for the determination of chlorite

865   composition and application to the McGerrigle Mountains anchizone in the Quebec

866   Appalachians. The Canadian Mineralogist, 36, 1525 –1546.

867 Shcherbakov, V.D., Plechov, P.Y., Izbekov, P.E., and Shipman, J.S. (2011) Plagioclase zoning as

868   an indicator of magma processes at Bezymianny Volcano, Kamchatka. Contributions to

869   Mineralogy and Petrology, 162, 83–99.

870 Shore, M., and Fowler, A.D. (1996) Oscillatory zoning in minerals; a common phenomenon. The

871   Canadian Mineralogist, 34, 1111–1126.

872 Sibson, R.H. (1990) Conditions for fault-valve behaviour. Geological Society, London, Special

873   Publications, 54, 15–28.

874 Souche, A., Medvedev, S., Andersen, T.B., and Dabrowski, M. (2013) Shear heating in extensional

875   detachments: Implications for the thermal history of the Devonian basins of W Norway.

876   Tectonophysics, 608, 1073–1085.

877 Tarantola, A., Mullis, J., Guillaume, D., Dubessy, J., de Capitani, C., and Abdelmoula, M. (2009)

878   Oxidation of CH4 to CO2 and H2O by chloritization of detrital biotite at 270 +/- 5 degrees C

879   in the external part of the Central Alps, Switzerland. Lithos, 112, 497–510.

880 Teixell, A. (1996) The Anso transect of the southern Pyrenees: basement and cover thrust

881   geometries. Journal of the Geological Society, 153, 301–310.

882 ——— (1998) Crustal structure and orogenic material budget in the west central Pyrenees.

883   Tectonics, 17, PP. 395–406.

884 Toutain, J.P., Munoz, M., Poitrasson, F., and Lienard, A.C. (1997) Springwater chloride ion

885   anomaly prior to a ML= 5.2 Pyrenean earthquake. Earth and planetary science letters, 149,

886   113–119.

36

887 Toutain, J.-P., Munoz, M., Pinaud, J.-L., Levet, S., Sylvander, M., Rigo, A., and Escalier, J. (2006)

888   Modelling the mixing function to constrain coseismic hydrochemical effects: An example

889   from the French Pyrénées. pure and applied geophysics, 163, 723–744.

890 Trincal, V., Lacroix, B., Buatier, M.D., Charpentier, D., Labaume, P., and Lahfid, A. (2014a) Low

891   grade metamorphism fluid circulation in a sedimentary environment thrust fault zone:

892   properties and modeling Vol. 16, p. 12078. Presented at the EGU General Assembly

893   Conference Abstracts.

894 Trincal, V., Charpentier, D., Buatier, M.D., Grobety, B., Lacroix, B., Labaume, P., and Sizun, J.-P.

895   (2014b) Quantification of mass transfers and mineralogical transformations in a thrust fault

896   (Monte Perdido thrust unit, southern Pyrenees, Spain). Marine and Petroleum Geology, 55,

897   160–175.

898 Vidal, O., Parra, T., and Trotet, F. (2001) A thermodynamic model for Fe-Mg aluminous chlorite

899   using data from phase equilibrium experiments and natural pelitic assemblages in the 100

900   degrees to 600 degrees C, 1 to 25 kb range. American Journal of Science, 301, 557–592.

901 Vidal, O., Parra, T., and Vieillard, P. (2005) Thermodynamic properties of the Tschermak solid

902   solution in Fe-chlorite: Application to natural examples and possible role of oxidation.

903   American Mineralogist, 90, 347–358.

904 Vidal, O., De Andrade, V., Lewin, E., Muñoz, M., Parra, T., and Pascarelli, S. (2006) P-T-

905   deformation-Fe3+/Fe2+ mapping at the thin section scale and comparison with XANES

906   mapping: application to a garnet-bearing metapelite from the Sambagawa metamorphic belt

907   (Japan). Journal of Metamorphic Geology, 24, 669–683.

908 Walker, J.R. (1993) Chlorite polytype geothermometry. Clays and Clay Minerals, 41, 260–260.

909 Wang, C., and Manga, M. (2010) Earthquakes and water Vol. 114. Springer Science & Business

910   Media.

911 Wilke, M., Farges, F., Petit, P.-E., Brown, G.E., and Martin, F. (2001) Oxidation state and
912   coordination of Fe in minerals: An Fe K-XANES spectroscopic study. American
913   Mineralogist, 86, 714–730.

914 Wintsch, R.P., Christoffersen, R., and Kronenberg, A.K. (1995) Fluid-rock reaction weakening of
915   fault zones. Journal of Geophysical Research, 100, 13021–13,032.

916 Yardley, B.W.D., Rochelle, C.A., Barnicoat, A.C., and Lloyd, G.E. (1991) Oscillatory zoning in
917   metamorphic minerals: an indicator of infiltration metasomatism. Mineralogical Magazine,
918   55, 357–365.

919 Zane, A., Sassi, R., and Guidotti, C.V. (1998) New data on metamorphic chlorite as a petrogenetic
920   indicator mineral, with special regard to greenschist-facies rocks. The Canadian Mineralogist,
921   36, 713–726.

922 Zhai, D.-G., Liu, J.-J., Zhang, H.-Y., Wang, J.-P., Su, L., Yang, X.-A., and Wu, S.-H. (2014)
923   Origin of oscillatory zoned garnets from the Xieertala Fe–Zn skarn deposit, northern China:
924   In situ LA–ICP-MS evidence. Lithos, 190–191, 279–291.

925

Figure captions

927 **Figure 1.** (a) Structural map of the Pyrenees with the location of study area (modified from
928   Teixell 2000). Geological map (b) and (c) cross section AB of the Gavarnie thrust sheet
929   showing the location of the study area (Pic de Port Vieux) modified from Grant (1992) and
930   Jolivet et al. (2007). MPT: Monte Perdido thrust; PT: Pineta thrust.

931

932 **Figure 2.** (a) View of the Pic de Port Vieux massif. (b) Pic de Port Vieux thrust culmination
933   showing the main study area, modified from Grant (1989). (c) Schematic stratigraphic log
934   through the Pic de Port Vieux culmination, modified from Grant (1990). GT: Gavarnie
935   Thrust; PPVT: Pic de Port Vieux Thrust.

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936

Figure 3. (a) Pic de Port Vieux outcrop showing hanging-wall Triassic pelites and footwall Cretaceous dolomitic limestone separated by the PPV thrust. (b) Outcrop view of shear and extension veins filled by quartz and chlorite in hanging wall Triassic pelite. (c) Detailed sketch of synthetic faults (faults A and B); others faults and veins are indicated in grey (modified from Grant 1989). Stars: samples with oscillatory zoned chlorite, from Grant (1989) (NF) and from this study (PPV). Red and green colors correspond to red pelite and altered green pelite, respectively.

944

Figure 4. (a) Schematic diagram of the structural organization of the studied fault zone outcrop. (b) SEM image of pelite showing quartz, muscovite, chlorite, hematite, rutile and apatite minerals; PPV12-06B sample. (c) SEM image of green pelite with almost the same mineralogy as B except for hematite; PPV12-05 sample. (d) Optical microscopic image from dolomitic limestone showing euhedral dolomite in micritic calcite matrix; PPV11-01 sample. (e) SEM image of euhedral dolomite and iron oxides in micritic calcite. (f) Zoom from (e) on a dolomite crystal partially dissolved in calcite matrix. Newly formed calcite precipitated inside dolomitic cracks and dissolution ghosts (in black). (g) SEM image of a fractured and microveined dolomitic limestone sampled closed to thrust in the footwall.

954

Figure 5. Microscopic observation of thin sections from the studied fault zone. (a-b) quartz + chlorite ± calcite extension crack-seal syntaxial vein showing chlorite nucleation in contact with host-pelite preferentially to silt; in PPL and XPL respectively from sample PPV11-11B. (c-d) shear vein showing blocky quartz ± calcite crystal textures and rosette shaped zoned chlorite; in PPL and XPL respectively from sample PPV11-25B. (e) Representative sketch of

39

960   veins cogenetic to synthetic fault. In extension veins, quartz crack-seal appears parallel to the

961   vein wall. Key: S: schistosity plane; PPL: plane polarized light; XPL: cross polarized light.

962

963   **Figure 6.** (a)vSEM images of oscillatory zoning pattern chlorite crystals from sample PPV11-

964   XX. The rosette like morphology of the chlorite aggregates is imaged (b) in 3D on PPV11-16

965   sample and (c) in thin section on sample PPV11-19. (d) Contrasted layers can have different

966   thickness from one rosette to another and zonation can be complex as imaged in sample

967   PPV11-25B. (e) At a higher magnification, the contrast distribution seems to follow the

968   growth development of the chlorite crystals but with preferential growth directions as

969   highlighted in sample PPV11-25B.

970

971   **Figure 7.** Microprobe X-Ray (WDS) images from sample PPV11-XX. Values of each box are

972   reported table 1. (a) SEM-BSE image of the analyzed area (b) Zone 1 to 5 defined from (a)

973   based on electronic contrast. (c) FeO in wt%. (d) MgO in wt%. (e) SiO_2 in wt%. (f) Al_2O_3 in

974   wt%.

975

976   **Figure 8.** (a) Scheme of the mapped area showing growth bands in clinochlore concentric

977   crystal (sample PPV11-XX MapA), and the locations of µ-XANES measurements; (b)

978   corresponding normalized XANES spectra; (c) baseline-subtracted pre-edge peaks (white

979   circles), best fits (solid lines) and peaks used for deconvolution (dashed lines); (d) integrated

980   area versus centroid position variogram showing the positions of standards together with the

981   data from clinochlore crystal. Values are reported Table 1 and converted in XFe^{3+} based on

982   the calibration curve of Wilke et al. (2001).

983

40

984   **Figure 9.** Plot of the chlorite compositions from boxes samples in (a) chemical elements of

985   the octahedron; (b) Amesite-(clinochlore + daphnite)-sudoite end-member ternary diagram

986   including iron state oxidation data. FM = Fe-Mg substitution; TK = Tschermak substitution;

987   DT = Ditrioctahedral substitution.

988

989   **Figure 10.** Microprobe X-Ray images from sample PPV11-XX with Fe^{3+}/Fe_{Tot} specific for

990   each chlorite band. Representative values of each zone are reported table 1. (a) Fe^{2+} in a.p.f.u..

991   (b) Fe^{3+} in a.p.f.u.. (c) $X_{MG} = Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ratio. (d) Temperature map from Lanari et al.

992   (2014a) model calculation.

993

994   **Figure 11.** Relationships between the $(Fe^{3+}/\sum Fe)_{chl}$ value in chlorite and the temperatures

995   estimate from the Lanari et al. (2014a) geo-thermometer. Two main trends were reported from

996   Lanari et al. (2014a) corresponding on two redox conditions of fluid, which are less oxidized

997   (continuous line) and more oxidized (dashed line). Each sample number refers to its zone in

998   MapA (in blue) or in MapB (in red); for example the red star corresponds to the zone 5 in

999   MapB.

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1001

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1003   **Tables**

Spot	Integrated area	Centroid energy (eV)	XFe^{3+}
Xan1	0.1021	7113.55 ± 0.05	42 (7)
Xan2	0.0969	7113.33 ± 0.05	27 (5)
Xan3	0.1029	7113.45 ± 0.05	34 (5)
Xan4	0.0940	7113.27 ± 0.05	23 (5)

41

| Xan5 | 0.1281 | 7113.59 ± 0.05 | 44 (5) |

1004 **Table 1.** Results from XANES and pre-edge spot analyses, showing the integrated area and

1005 centroid position of pre-edge peaks and XFe^{3+} values obtained from XANES normalization.
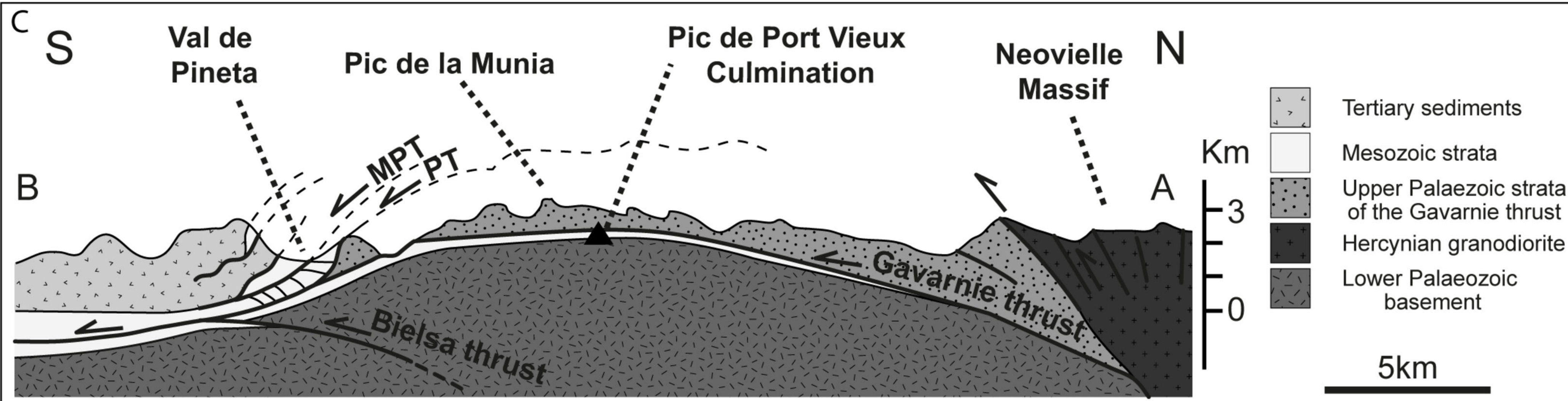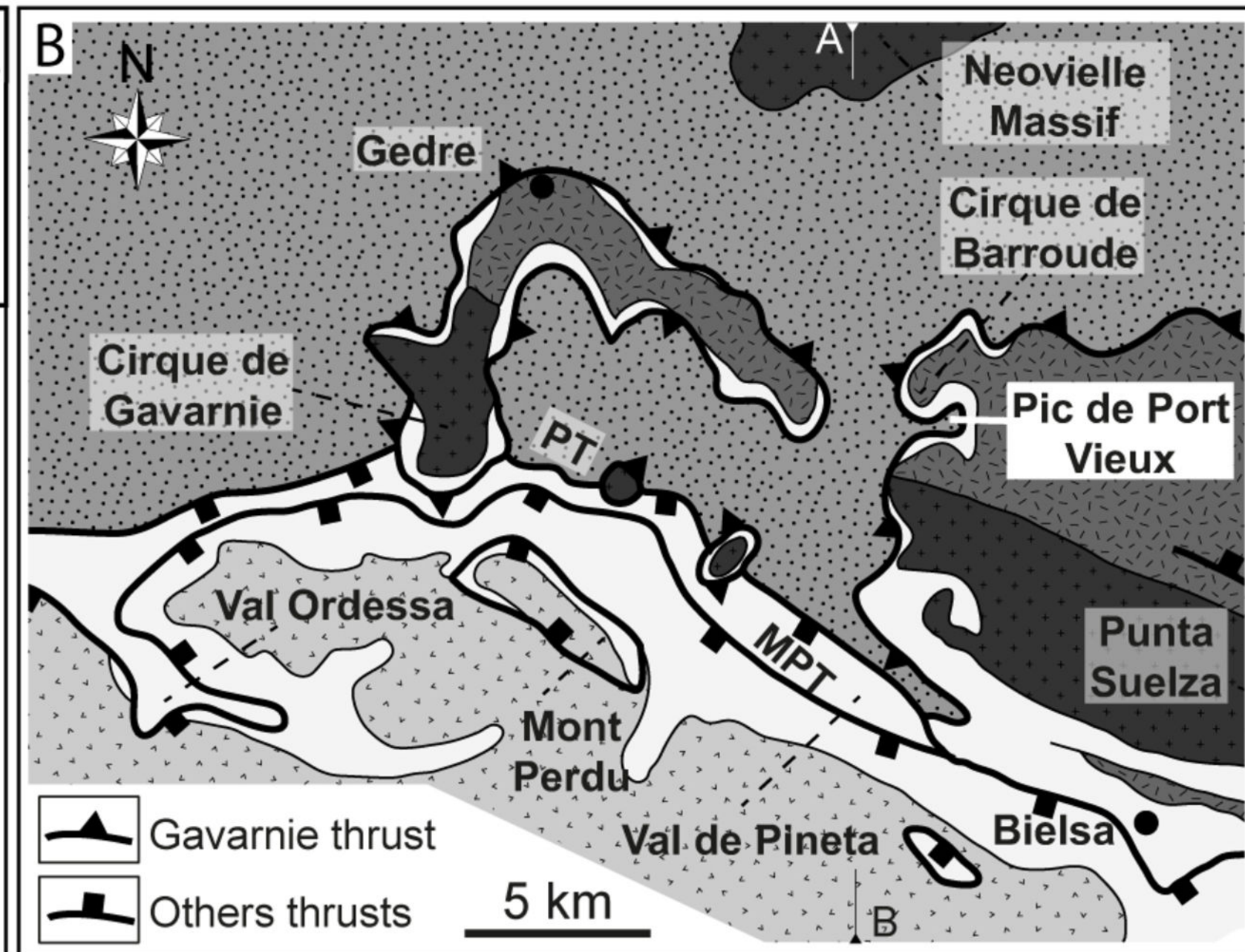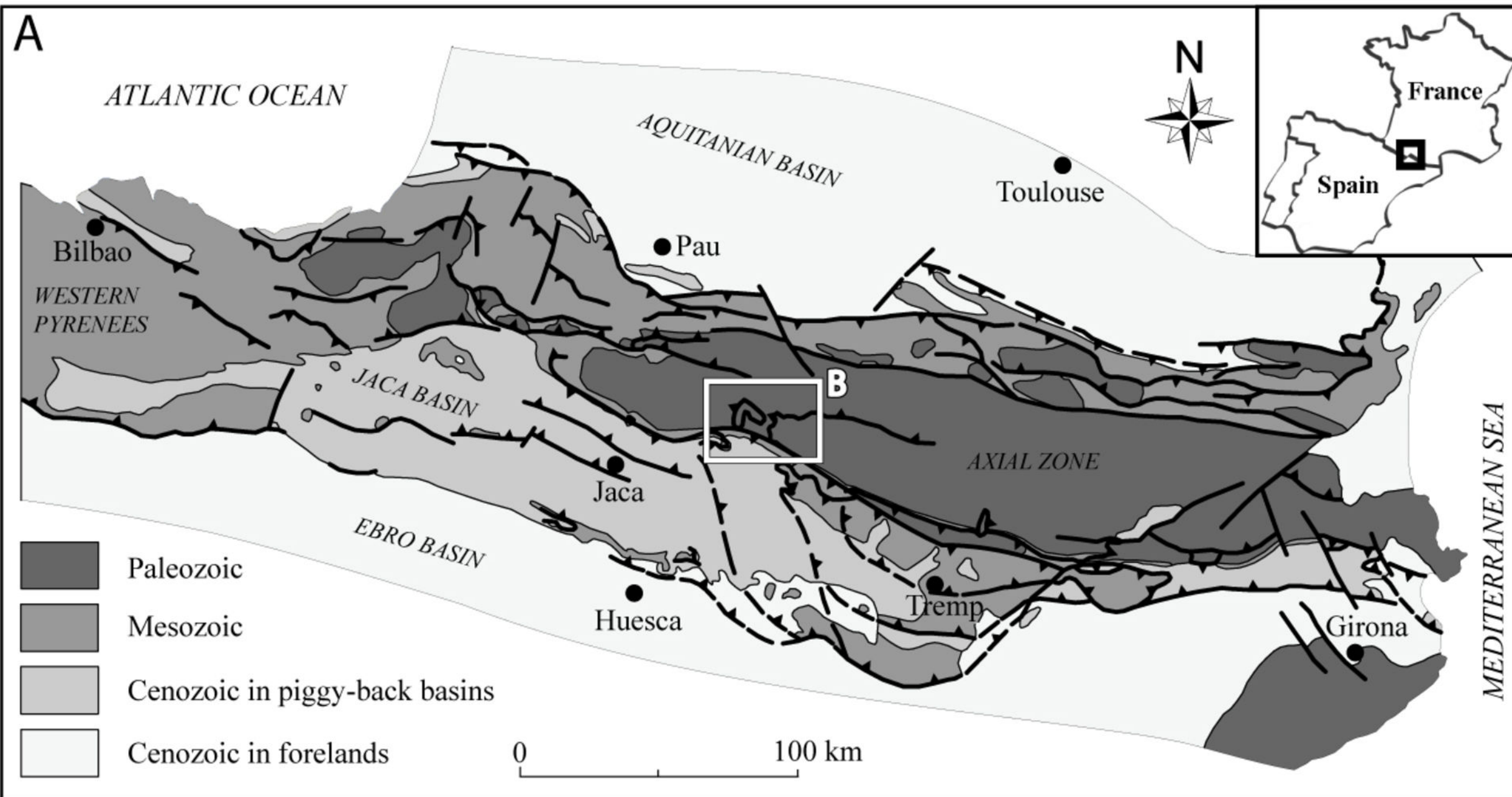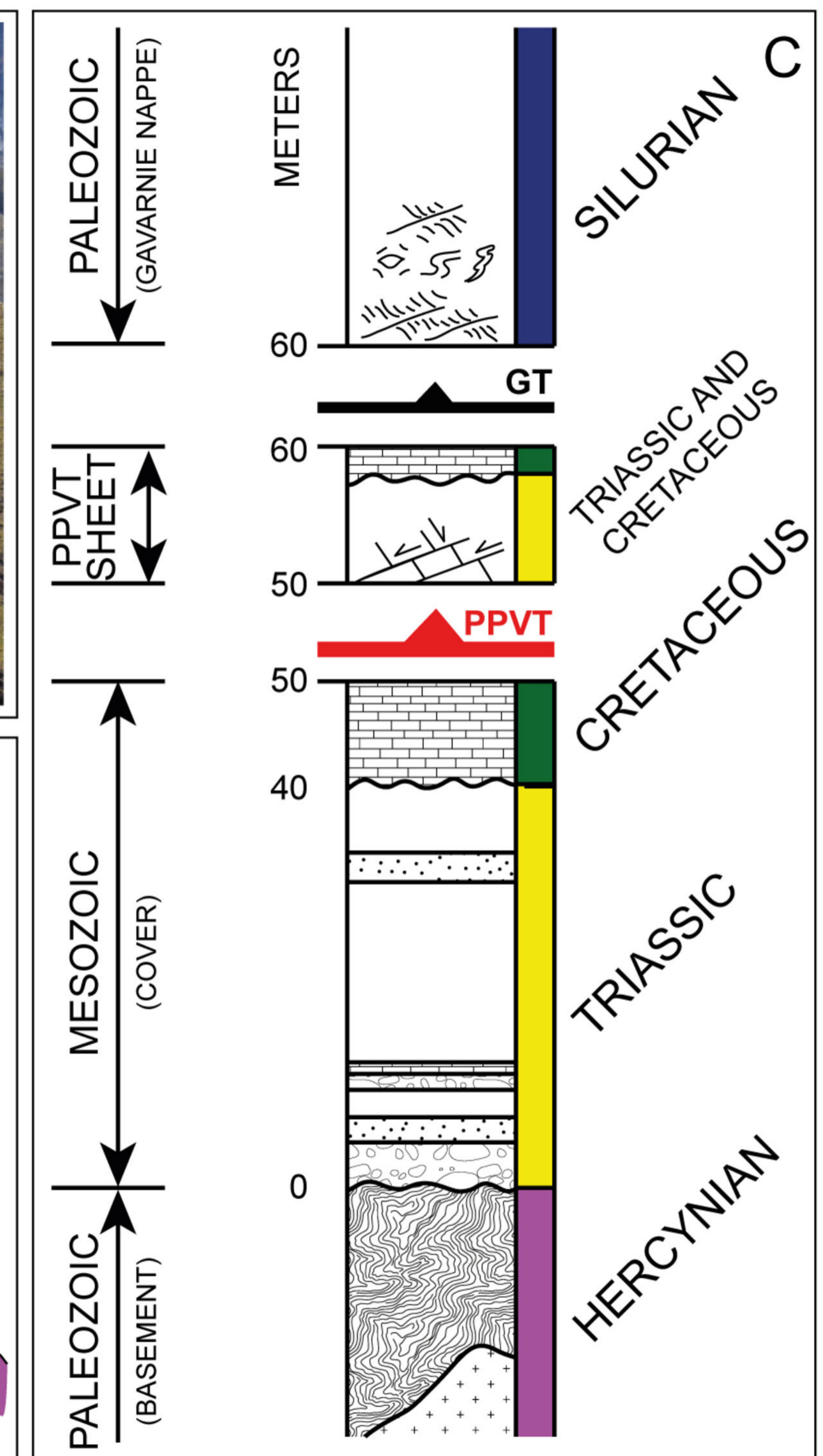
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Zones	MapA						MapB					Unzoned
	1A	2A	3A	4A	5A		1B	2B	3B	4B	5B	
SiO$_2$	25.17 (49)	26.11 (36)	25.74 (33)	25.98 (43)	25.53 (44)		25.76 (33)	26.39 (37)	25.75 (34)	25.85 (39)	25.55 (33)	26.57 (71)
TiO$_2$	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)		0.02 (0)	0.01 (0)	0.02 (0)	0.01 (1)	0.02 (0)	0.03 (8)
Al$_2$O$_3$	22.76 (52)	22.93 (29)	23.25 (32)	23.65 (56)	23.16 (46)		22.91 (42)	23.00 (41)	23.17 (39)	23.55 (43)	23.05 (41)	22.91 (66)
FeO	20.98 (88)	18.43 (76)	20.43 (62)	18.39 (91)	21.94 (81)		21.92 (42)	17.59 (48)	20.47 (45)	18.70 (77)	21.48 (42)	24.27 (176)
MgO	17.27 (76)	19.64 (63)	17.86 (54)	19.09 (75)	16.41 (65)		16.36 (43)	19.83 (54)	17.44 (45)	18.83 (70)	16.58 (42)	14.54 (136)
MnO	0.09 (3)	0.09 (3)	0.09 (3)	0.09 (3)	0.08 (3)		0.10 (2)	0.11 (2)	0.11 (2)	0.11 (2)	0.11 (2)	0.05 (5)
CaO	0.02 (1)	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)		0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)	0.03 (4)
Na$_2$O	0.02 (0)	0.02 (0)	0.02 (0)	0.02 (0)	0.02 (0)		0.03 (1)	0.03 (1)	0.03 (1)	0.03 (1)	0.03 (1)	0.00 (2)
Cr$_2$O$_3$	0.05 (2)	0.05 (2)	0.05 (2)	0.05 (2)	0.04 (2)		0.05 (1)	0.05 (1)	0.05 (1)	0.05 (1)	0.05 (1)	
K$_2$O	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)		0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)	0.01 (0)	0.03 (14)
Σ	86.37 (116)	87.29 (54)	87.47 (53)	87.30 (131)	87.23 (96)		87.17 (76)	87.02 (74)	87.04 (73)	87.15 (72)	86.87 (70)	88.20 (112)
Si	2.58 (3)	2.63 (2)	2.60 (3)	2.62 (3)	2.59 (3)		2.62 (3)	2.65 (3)	2.62 (3)	2.61 (3)	2.60 (3)	
Al^{IV}	1.42 (3)	1.37 (2)	1.40 (3)	1.38 (4)	1.41 (3)		1.38 (3)	1.35 (3)	1.38 (3)	1.39 (3)	1.40 (3)	
Al^{VI}	1.33 (4)	1.35 (3)	1.37 (3)	1.42 (5)	1.37 (4)		1.37 (3)	1.38 (4)	1.39 (3)	1.42 (4)	1.37 (3)	
Fe^{2+}	1.04 (5)	1.13 (5)	1.14 (4)	1.19 (6)	1.04 (4)		1.08 (2)	1.08 (3)	1.15 (3)	1.22 (5)	1.02 (2)	
Fe^{3+}	0.68 (3)	0.38 (2)	0.53 (2)	0.32 (2)	0.74 (3)		0.70 (1)	0.36 (1)	0.53 (1)	0.33 (1)	0.72 (2)	
Mg	2.64 (10)	2.95 (8)	2.69 (8)	2.87 (10)	2.48 (10)		2.48 (6)	2.97 (7)	2.64 (6)	2.84 (9)	2.52 (6)	
Fe^{3+}/Fe$_{Tot}$	**0.42**	**0.27**	**0.34**	**0.23**	**0.44**		**0.42**	**0.27**	**0.34**	**0.23**	**0.44**	

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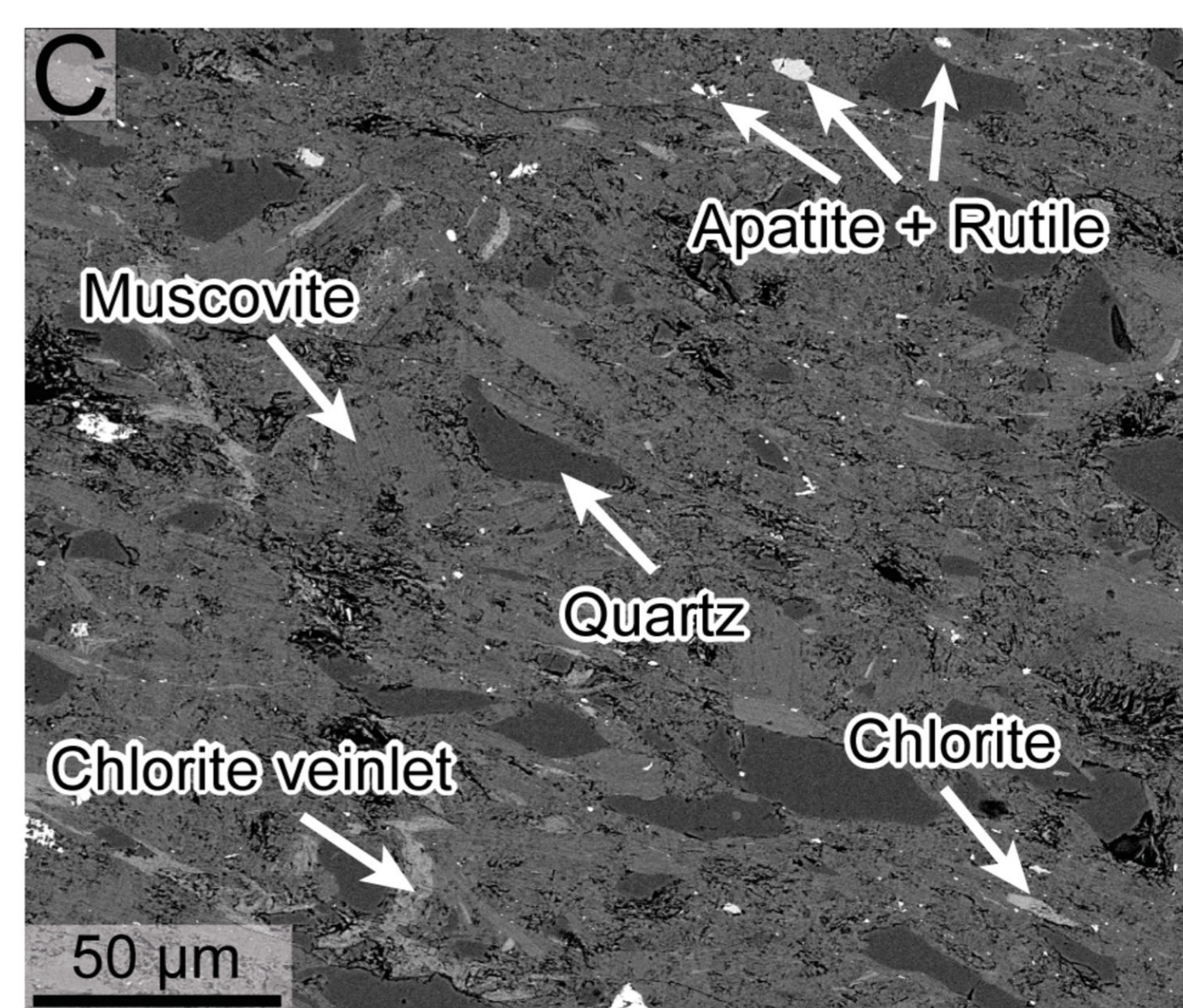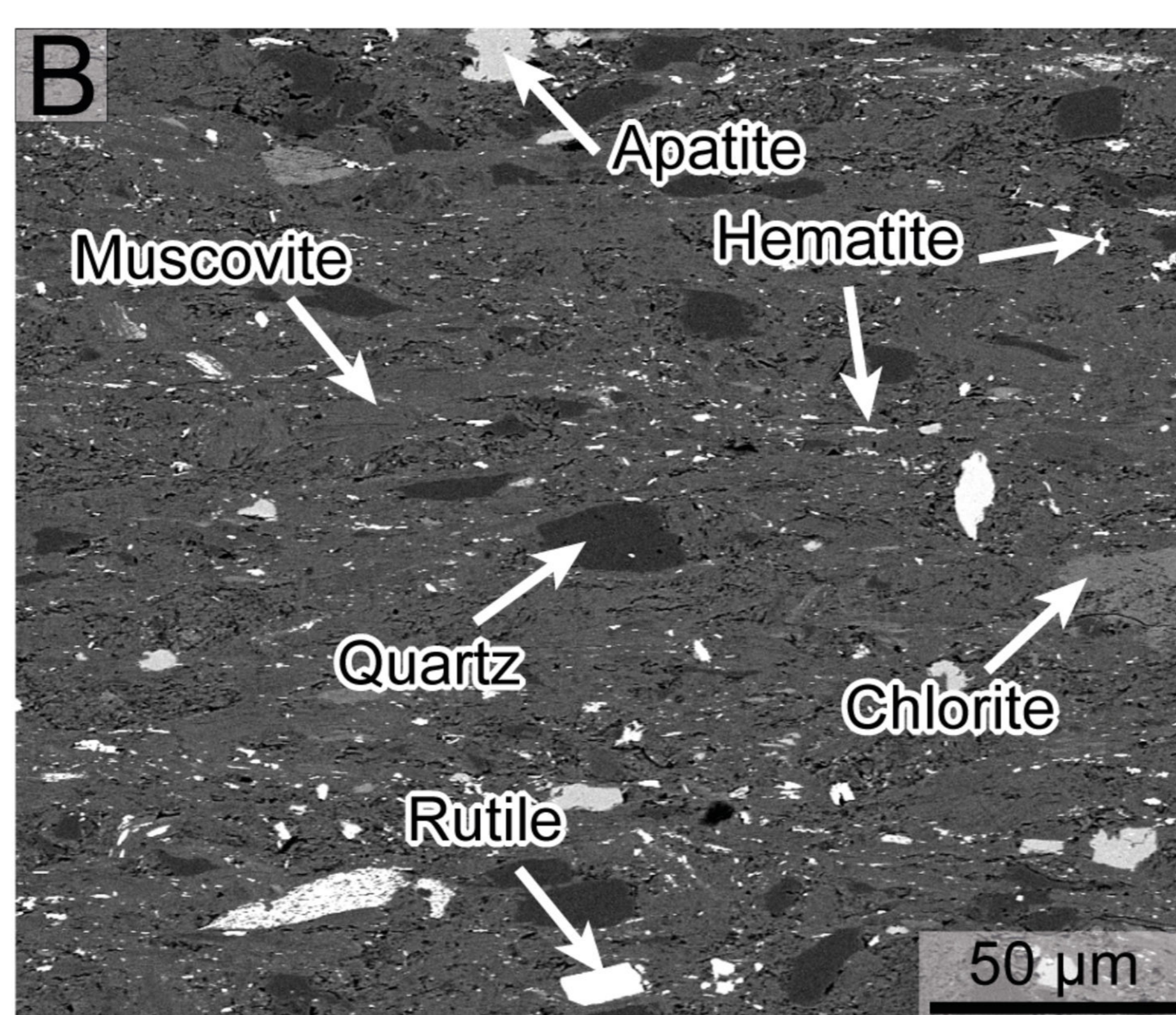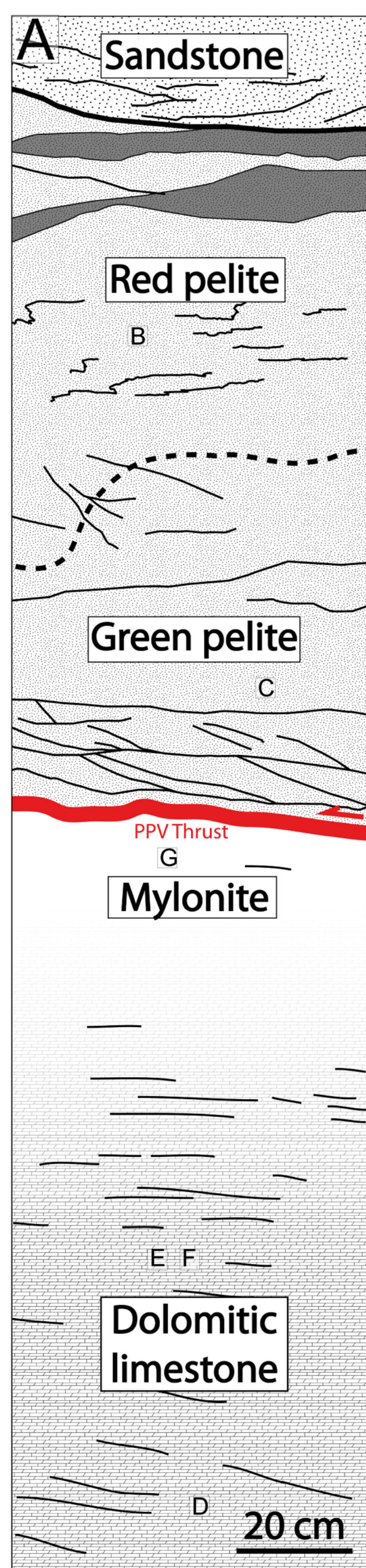| Al M1 = Xame	0.43 (3)	0.38 (2)	0.40 (3)	0.39 (3)	0.41 (3)	0.39 (3)	0.35 (3)	0.39 (3)	0.39 (3)	0.40 (3)	
Mg M1 = Xclin	0.20 (2)	0.32 (2)	0.24 (2)	0.31 (2)	0.17 (2)	0.19 (1)	0.33 (2)	0.24 (2)	0.30 (2)	0.18 (1)	
Fe M1 = Xdap	0.08 (1)	0.12 (0)	0.10 (0)	0.13 (1)	0.07 (1)	0.08 (1)	0.12 (1)	0.10 (1)	0.13 (1)	0.07 (1)	
Vac = Xsud	0.29 (3)	0.18 (2)	0.25 (2)	0.18 (3)	0.35 (3)	0.34 (2)	0.19 (3)	0.27 (2)	0.18 (3)	0.34 (2)	
X_{Mg}	0.72 (2)	0.72 (1)	0.70 (1)	0.71 (2)	0.70 (2)	0.70 (1)	0.73 (1)	0.70 (1)	0.70 (2)	0.71 (1)	
T (°C)	341 (26)	396 (29)	351 (22)	405 (56)	312 (21)	302 (18)	370 (36)	336 (24)	406 (41)	310 (19)	

1007 **Table 2.** Chlorite structural formulas from sample PPV11-XX maps A and B. Unzoned

1008 medians and standard deviation oxides %wt were added for comparison. X_{MG} =

1009 $Mg^{2+}/(Fe^{2+}+Mg^{2+})$. Oxides in wt%, atoms in a.p.f.u.. Each data represent the average and

1010 standard deviation of 400 points corresponding to 20*20 μm^2 in the map. XFe^{3+} standard

1011 deviation induce small variations in the structural formulas; they have not been reported in

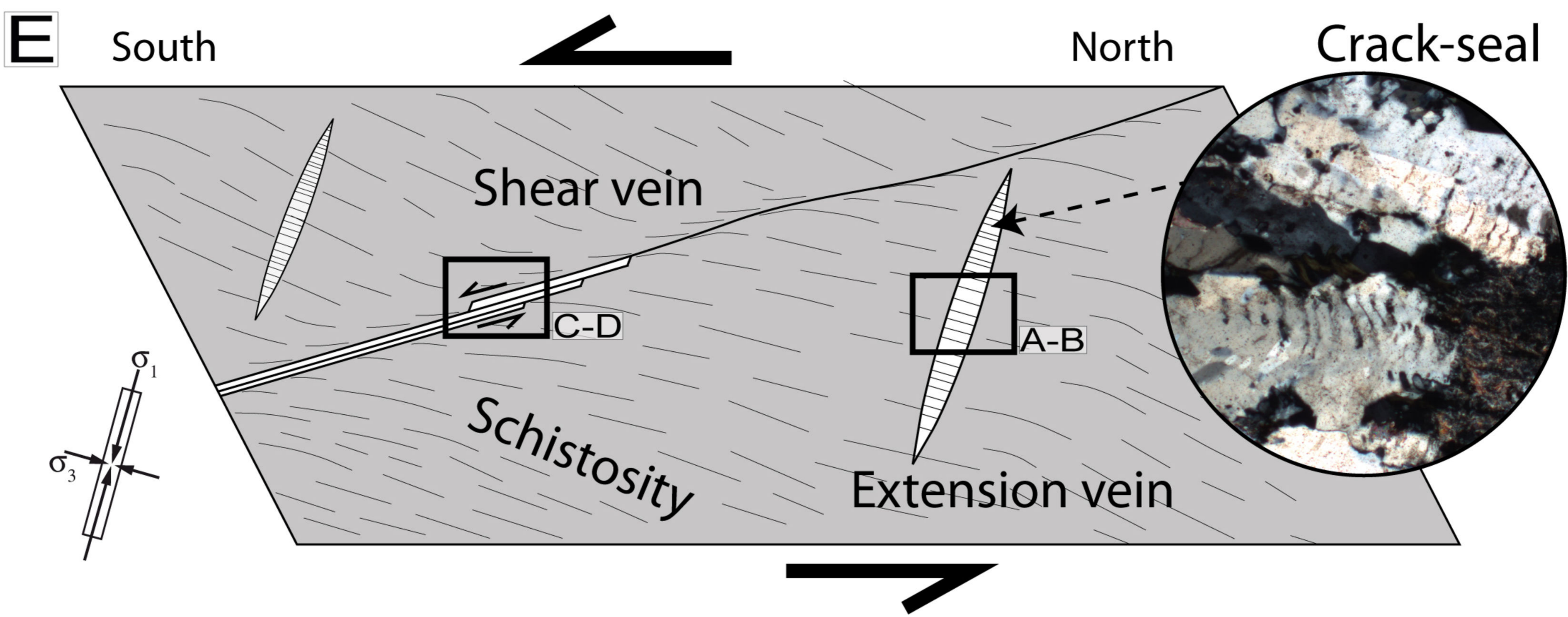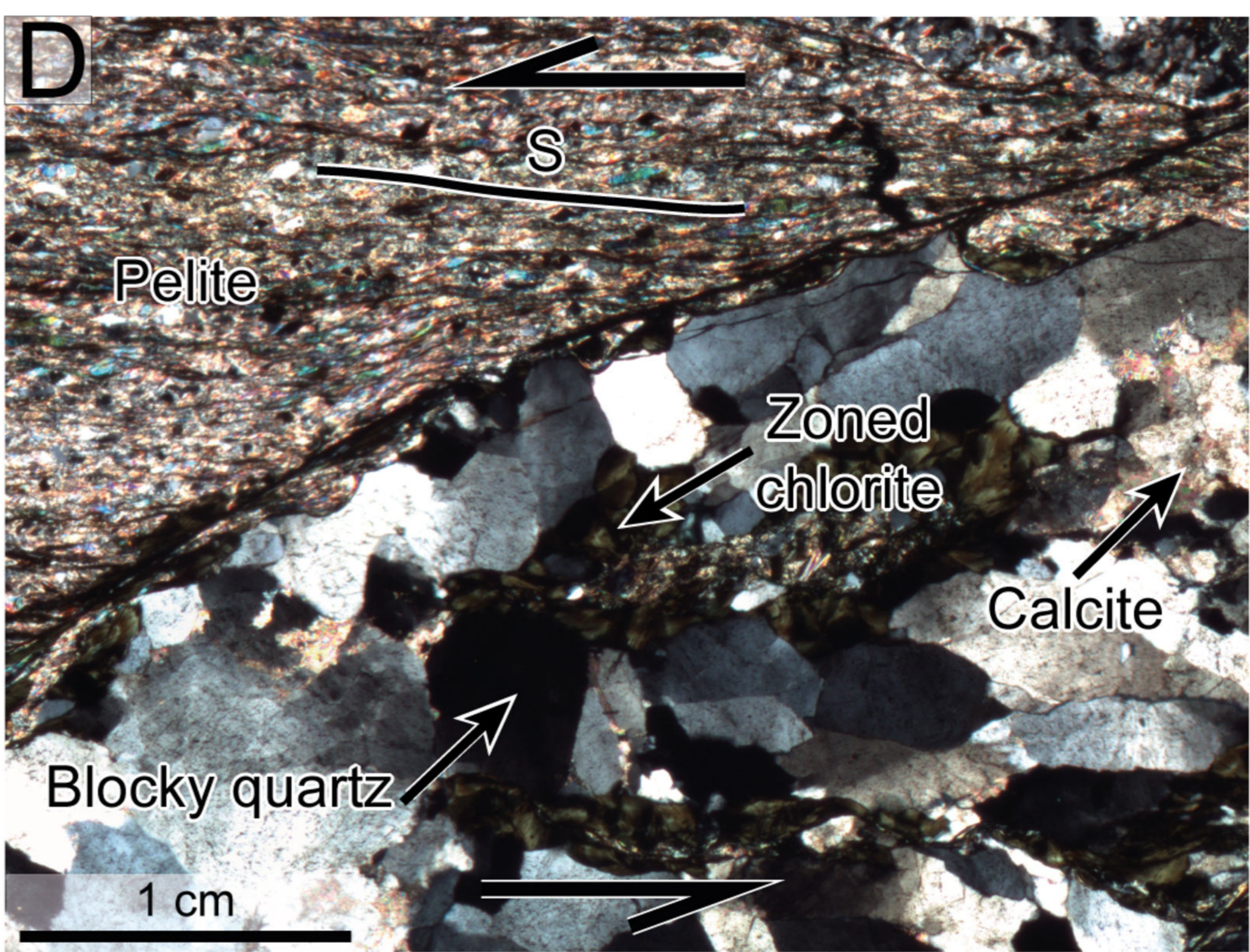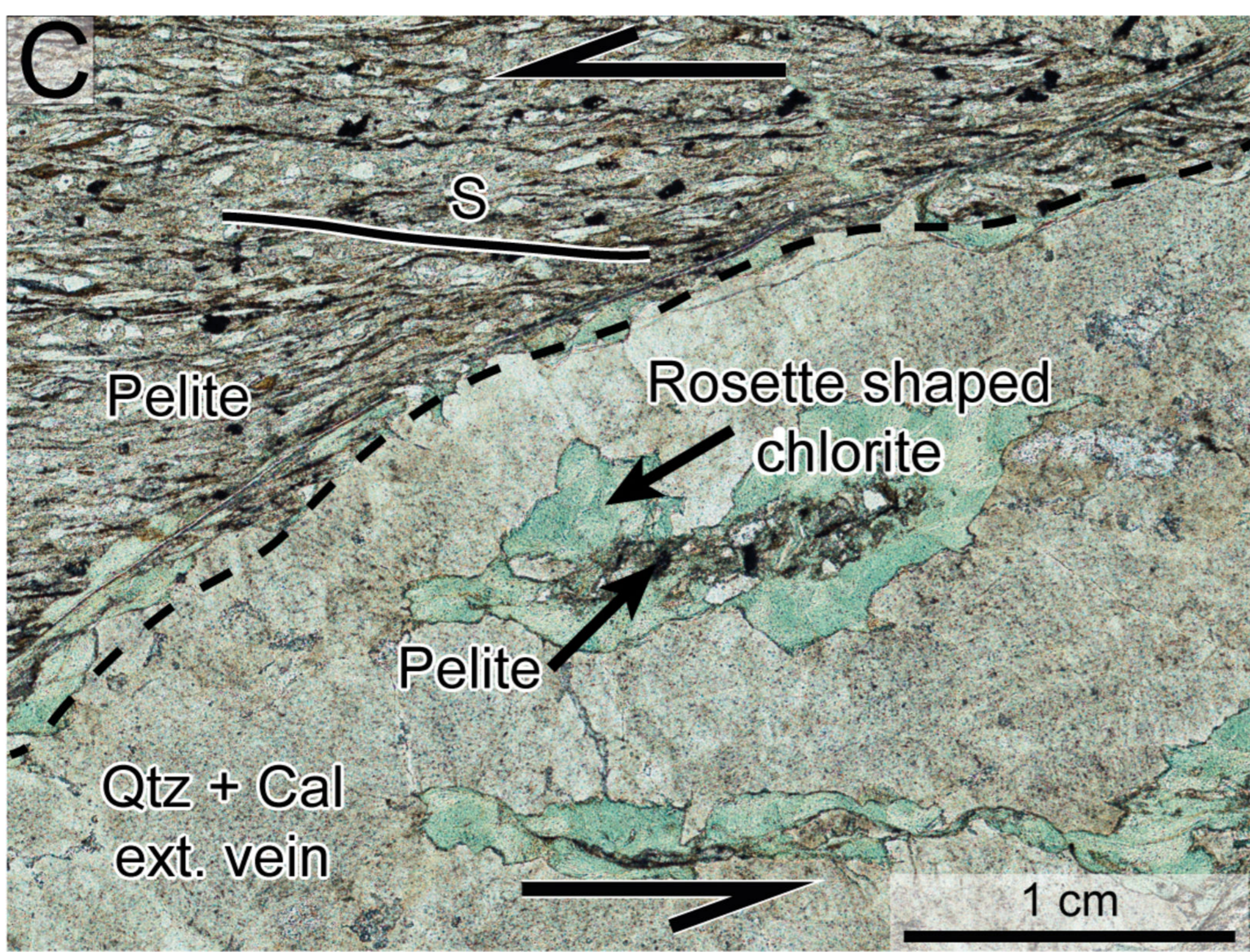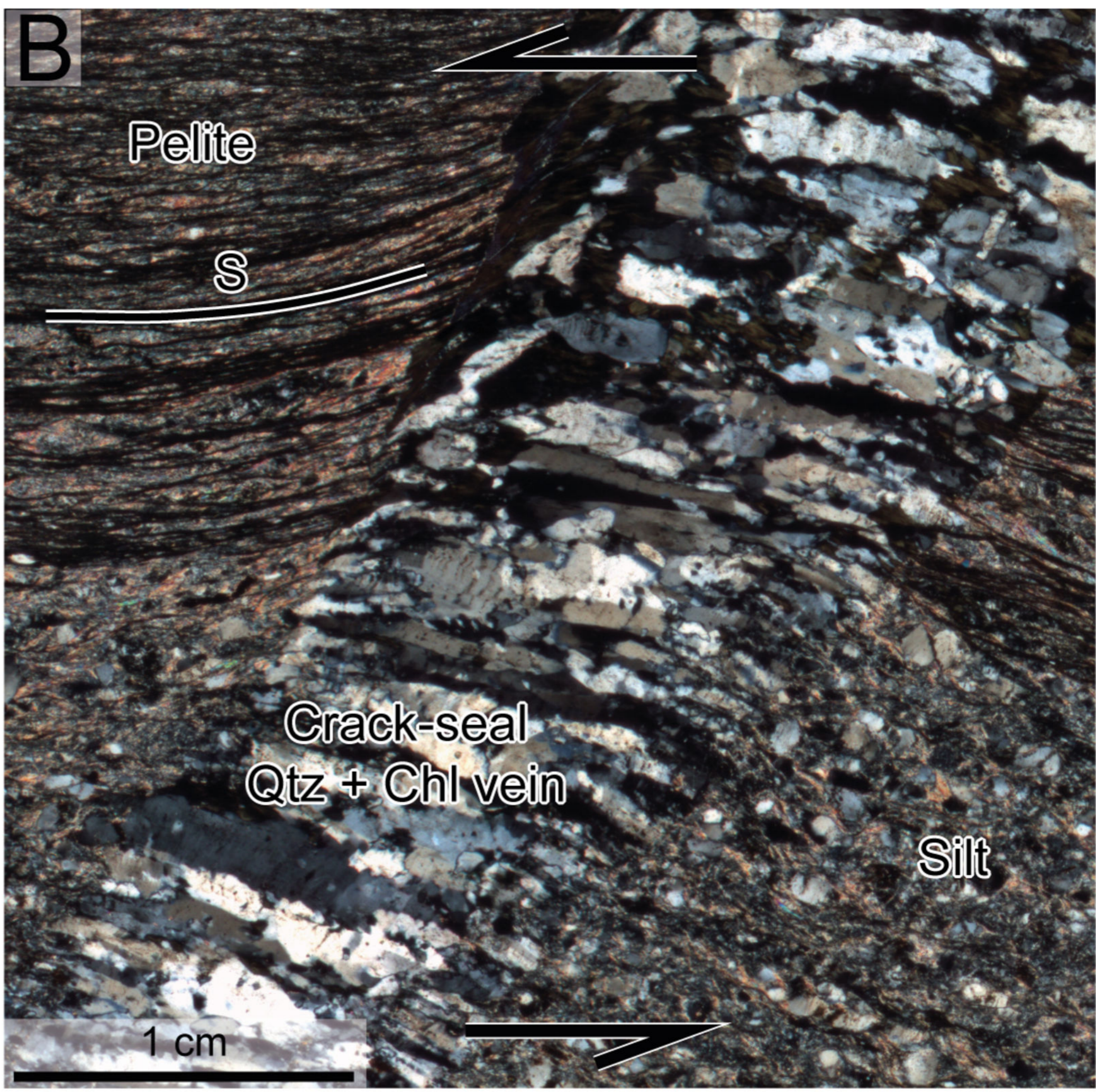1012 this table. Points are reported on Figure 10.

1013

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A — ATLANTIC OCEAN; AQUITANIAN BASIN; Toulouse; France; Spain; Bilbao; Pau; WESTERN PYRENEES; JACA BASIN; Jaca; AXIAL ZONE; MEDITERRANEAN SEA; EBRO BASIN; Huesca; Tremp; Girona; B

Legend:
- Paleozoic
- Mesozoic
- Cenozoic in piggy-back basins
- Cenozoic in forelands

0 — 100 km

B — N; Neovielle Massif; Gedre; Cirque de Barroude; Cirque de Gavarnie; PT; Pic de Port Vieux; Val Ordessa; MPT; Punta Suelza; Mont Perdu; Val de Pineta; Bielsa

- Gavarnie thrust
- Others thrusts

5 km

C — S; Val de Pineta; Pic de la Munia; Pic de Port Vieux Culmination; Neovielle Massif; N; B; MPT; PT; A; Gavarnie thrust; Bielsa thrust; Km; 3; 0

Legend:
- Tertiary sediments
- Mesozoic strata
- Upper Palaezoic strata of the Gavarnie thrust
- Hercynian granodiorite
- Lower Palaeozoic basement

5km

A

0   100   200m

B

Pic de Port Vieux

S   N   NE

- Silurian Phylites
- Hercynian Granites
- Triassic Pelites/Sandstones
- Crétaceous Limestones

Pic de Port Vieux thrust

P.P.V.T   G.T.

meters

2700

2650

2600

2550

0   100   200m

C

PALEOZOIC (GAVARNIE NAPPE)

METERS   SILURIAN

60

GT

PPVT SHEET   TRIASSIC AND CRETACEOUS

60

50

PPVT

50   CRETACEOUS

40

MESOZOIC (COVER)   TRIASSIC

0

PALEOZOIC (BASEMENT)   HERCYNIAN

A — S / N: Triassic Pelites; PPV Thrust; Cretaceous Dolomitic Limestones; 1 m

B — S / N: Pelites; Shear vein; Extensive vein; 1 cm

C — S / N: Triassic pelites; Fault A; Fault B; NFS4.1; NFS4.2; PPV11-26A; NFS2,S3; PPV11-25B; PPV11-23; PPV11-XX; PPV11-21B; PPV11-19; PPVT; Rock fall; Cretaceous Limestone; PPVT; 0 1 2 3 4 5 metres

A — Stratigraphic column:
- Sandstone
- Red pelite (B)
- Green pelite (C)
- PPV Thrust (G)
- Mylonite
- Dolomitic limestone (E, F, D)
- 20 cm

B — Muscovite, Apatite, Hematite, Quartz, Chlorite, Rutile — 50 µm

C — Muscovite, Apatite + Rutile, Quartz, Chlorite veinlet, Chlorite — 50 µm

D — Micritic calcite, Dolomite, Iron oxide — 250 µm

E — Dolomite, Micritic calcite, Oxide — 500 µm

F — Calcite, Dolomite, Calcite — 100 µm

G — Calcite vein, Oxide, Dolomite residues — 100 µm

A Pelite / S / Chlorite / Crack-seal quartz / Silt / 1 cm

B Pelite / S / Crack-seal Qtz + Chl vein / Silt / 1 cm

C S / Pelite / Rosette shaped chlorite / Pelite / Qtz + Cal ext. vein / 1 cm

D S / Pelite / Zoned chlorite / Calcite / Blocky quartz / 1 cm

E South / North / Crack-seal / Shear vein / Schistosity / σ_1 / σ_3 / C-D / A-B / Extension vein

(001)

c*

A — Map A and Map B (BSE images with red dashed zone boundaries), 200 μm scale bar

B — Map A and Map B with colored zones overlay, 200 μm scale bar
Zone 1 (orange)
Zone 2 (red)
Zone 3 (yellow)
Zone 4 (dark green)
Zone 5 (green)

C — FeO (wt.%), 200 μm scale bar; color scale 16, 18, 20, 22

D — MgO (wt.%), 200 μm scale bar; color scale 14, 16, 18, 20

E — SiO₂ (wt.%), 200 μm scale bar; color scale 25, 25.5, 26, 26.5, 27

F — Al₂O₃ (wt.%), 200 μm scale bar; color scale 22, 22.5, 23, 23.5, 24

A — 200 μm — Fe^{2+} (p.f.u.) — Map A — Map B — 1.0 1.1 1.2 1.3

B — 200 μm — Fe^{3+} (p.f.u.) — Map A — Map B — 0.65 0.7 0.75

C — 200 μm — $X_{Mg} = Mg/(Fe^{2+}+Mg)$ — Map A — Map B — 0.65 0.7 0.75

D — 200 μm — T (°C) — Map A — Map B — 300 350 400