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1 **Multistage development of a hydrothermal tungsten deposit during the**
2 **Variscan late-orogenic evolution: the Puy-les-Vignes W breccia pipe (Massif**
3 **Central, France)**

4
5 Développement multiphasé d'un gîte hydrothermal à tungstène au cours de
6 l'évolution tardi-orogénique varisque : le conduit bréchique à W de Puy-les-
7 Vignes (Massif Central, France)

8
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27 **Keywords:** Puy-les-Vignes deposit, breccia pipe, wolframite mineralization, peraluminous
28 granite, French Massif Central, Variscan belt.

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30 **Mots-clés:** gîte de Puy-les-Vignes, conduit bréchique, minéralisation à wolframite, granite
31 peralumineux, Massif Central Français, chaîne Varisque.

32 **Abstract [2000-3000 characters, spaces included]**

33 The Puy-les-Vignes W deposit, located in the northwestern French Massif Central (FMC),
34 is a rare occurrence of a wolframite-mineralized hydrothermal breccia pipe hosted in high-grade
35 metamorphic gneisses. We present an integrated study of this deposit aiming to characterize the
36 ore-forming hydrothermal system in link with the Variscan late-orogenic evolution of the FMC.
37 Based on a set of representative samples from the host rocks and mineralization, we describe a
38 detailed paragenetic sequence and we provide the major and trace element geochemistry of the
39 host rocks and W-Nb-Ta-Sn-Ti oxide minerals, *in situ* U/Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, and
40 a fluid inclusion study in quartz and wolframite. We demonstrate that the formation of this W-
41 mineralized breccia pipe results from a multistage development during ca. 25 My related to
42 four major episodes during the late Carboniferous. The first episode corresponds to the
43 emplacement of an unexposed peraluminous granite at ca. 324 Ma, which generated
44 microgranite dykes exposed at the present-day surface. The second episode is the formation of
45 the quartz-supported breccia pipe and wolframite mineralization at ca. 318 Ma at a paleodepth
46 of 7 km. The mineralizing fluids have a $\text{H}_2\text{O-NaCl-CO}_2\text{-CH}_4\text{-N}_2$ composition, a moderate-
47 salinity (<9 wt.% NaCl eq) and were trapped at high-temperatures (>400°C) during lithostatic
48 to hydrostatic pressure variations caused by hydrofracturing of the host rocks. Wolframite
49 deposition is interpreted to result from the mixing between a W-rich intermediate-density
50 magmatic fluid exsolved from an evolved leucogranite and low-salinity volatile-rich
51 metamorphic fluids of distal origin. The third episode corresponds to a magmatic-hydrothermal
52 Nb-Ta mineralization overprinting the W-mineralized system and interpreted to be related to
53 the intrusion at ca. 311 Ma of a rare-metal granite, which is part of a regional peraluminous
54 rare-metal magmatism during the 315-310 Ma period. Finally, the last episode corresponds to
55 a disseminated Bi±Au-Ag mineralization emplaced at ca. 300 Ma, which shares similar
56 mineralogical features with orogenic gold deposits in the FMC. The Puy-les-Vignes W deposit
57 records, therefore, a multistage and long-lived development that extends over a timespan of 25
58 million years in a regional setting dominated by protracted peraluminous magmatism and HT-
59 LP metamorphism. Although the local environment of ore deposition is atypical, our results
60 show that the mineral assemblages, alteration styles, and fluid characteristics of the Puy-les-
61 Vignes breccia pipe are similar to those of other peri-granitic W deposits in the FMC.

62 **Résumé [2000-3000 caractères, espaces inclus]**

63 Le gîte à W de Puy-les-Vignes, situé dans le nord-ouest du Massif Central Français (MCF),
64 est une occurrence rare de conduit bréchiqye hydrothermal minéralisé en wolframite et encaissé
65 dans des gneiss de haut-degré métamorphique. Nous présentons une étude intégrée de ce gîte
66 dans l'objectif de caractériser le système hydrothermal minéralisé en lien avec l'évolution tardi-
67 orogénique varisque du MCF. Sur la base d'un ensemble d'échantillons représentatifs des
68 roches encaissantes et de la minéralisation, nous décrivons une séquence paragénétique
69 détaillée et nous présentons la géochimie des éléments majeurs et traces des roches encaissantes
70 et des oxydes de W-Nb-Ta-Sn-Ti, la géochronologie U/Pb et $^{40}\text{Ar}/^{39}\text{Ar}$ *in situ*, et une étude des
71 inclusions fluides dans le quartz et la wolframite. Nous démontrons que la formation du conduit
72 bréchiqye minéralisé en W résulte d'une mise en place multiphasée durant environ 25 millions
73 d'années liée à quatre épisodes majeurs au cours du Carbonifère supérieur. Le premier épisode
74 correspond à la mise en place d'un granite peralumineux non-affleurant à environ 324 Ma, qui
75 a produit des dykes de microgranites affleurant à la surface actuelle. Le second épisode est la
76 formation du conduit bréchiqye quartzeux et de la minéralisation à wolframite à environ 318
77 Ma à une paléo-profondeur de 7 km. Les fluides minéralisateurs ont une composition à H₂O-
78 NaCl-CO₂-CH₄-N₂, une salinité modérée (<9 wt.% NaCl eq) et ont été piégé à hautes
79 températures (>400) pendant des variations de pressions lithostatiques à hydrostatiques causées
80 par la fracturation hydraulique des roches encaissantes. Le dépôt de la wolframite est interprété
81 comme le résultat du mélange entre un fluide magmatique riche en W de densité intermédiaire
82 issu d'un leucogranite évolué et de fluides métamorphiques riches en volatiles et de faible
83 salinité d'origine profonde. Le troisième épisode correspond à la formation d'une
84 minéralisation magmatique-hydrothermale à Nb-Ta se superposant au système minéralisé à W
85 et lié à une intrusion de granite à métaux rares mise en place à environ 311 Ma, qui fait partie
86 d'un magmatisme peralumineux à métaux rares d'échelle régionale pendant la période 315-310
87 Ma. Enfin, le dernier épisode correspond à une minéralisation disséminée à Bi±Au-Ag mise en
88 place à environ 300 Ma qui partage des similarités minéralogiques avec les gîtes d'or
89 orogéniques du MCF. Le gîte à W de Puy-les-Vignes enregistre donc un développement
90 multiphasé et de longue durée s'étalant sur 25 millions d'années dans un contexte régional
91 dominé par du magmatisme peralumineux prolongé et du métamorphisme de HT-BP. Bien que
92 l'environnement de formation du gîte soit atypique, nos résultats montrent que les assemblages
93 minéraux, les styles d'altérations et les caractéristiques des fluides du conduit bréchiqye de
94 Puy-les-Vignes sont similaires à ceux d'autres gîtes péri-granitiques à W du MCF.

95 1. Introduction

96

97 Tungsten and tin mineralization worldwide is spatially associated with granitoid intrusions
98 forming a large variety of magmatic-hydrothermal ore deposits including greisens, veins,
99 stockworks, skarns, pegmatites, porphyries, and breccia pipes (Černý et al., 2005; Romer and
100 Kroner, 2016). Peri-granitic vein systems represent an economically important class of W-Sn
101 deposits that are mostly spatially associated with metaluminous to peraluminous granites
102 (Wood and Samson, 2000; Černý et al., 2005). The European Variscan belt is a large
103 metallogenic province for W-Sn and rare-metal (Nb, Ta, Li, Be) deposits that are mainly located
104 in Cornwall, the Erzgebirge, and the Iberian Massif (Romer and Kroner, 2016). In France, most
105 W-Sn deposits are known in the French Massif Central (FMC; Marignac and Cuney, 1999), the
106 Armorican Massif (Chauris and Marcoux, 1994), and the French Pyrenees (Poitrenaud et al.,
107 2019). These deposits consist of wolframite-cassiterite-bearing quartz veins, greisen cupolas,
108 and scheelite skarns spatially associated with Carboniferous peraluminous biotite-cordierite or
109 two-mica granites (Stussi, 1989; Marignac and Cuney, 1999; Bouchot et al., 2005). Mining
110 production for W in France was about 26 kt WO₃ until 1986 and remaining resources are
111 estimated at about 83 kt WO₃ (Audion and Labbé, 2012).

112 The Puy-les-Vignes W deposit, located in the northwestern FMC, represents the only
113 known wolframite-mineralized hydrothermal breccia pipe in France. Another occurrence of
114 wolframite-bearing breccia pipe is known at Borralha, Portugal (Gonçalves et al., 2017; Bobos
115 et al., 2018). Tourmaline breccia pipes are commonly associated with porphyry Cu deposits
116 (Sillitoe, 1985; Skewes et al., 2003; Anderson et al., 2009), reduced intrusion-related Au
117 deposits (Baker and Andrew, 1991; Thompson et al., 1999; Chen et al., 2009), but more rarely
118 with granite-related W-Sn deposits (Ren et al., 1995; Somarin and Ashley, 2004; Yang and
119 Bodnar, 2004; Solomovich et al., 2012). Magmatic-hydrothermal breccia pipes generally form
120 cylindrical subvertical bodies in the upper part of shallow intrusions. They are generally
121 interpreted as the result of hydraulic brecciation and collapse caused by ascending
122 overpressured magmatic fluids (Sillitoe, 1985; Skewes et al., 2003; Yang and Bodnar, 2004;
123 Demirel et al., 2009). Release of magmatic fluids from crystallizing intrusions under specific
124 pressure-temperature conditions produces greater mechanical energy and volumetric expansion
125 of the host rocks resulting in the formation of collapse breccia pipes associated with
126 silicification and tourmalinization (Burnham, 1985; Pollard et al., 1987; Halls, 1994).

127 In this work, we present an integrated study of the Puy-les-Vignes W deposit aiming to
128 characterize the formation of this atypical breccia pipe in link with the Variscan late-orogenic

129 evolution of the FMC. Based on a set of representative samples from the host rocks and
130 mineralization, we present a detailed paragenetic sequence of the deposit. Building on this
131 sequence, we used a multi-method approach with the following objectives: (i) characterizing
132 the major and trace element geochemistry of granitic rocks and W-Nb-Ta-Sn-Ti oxides, (ii)
133 dating magmatic and hydrothermal events by *in situ* U/Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology, and
134 (iii) determining the origin and the conditions of the mineralizing fluids based on fluid inclusion
135 study in quartz and wolframite. We demonstrate that the formation of the Puy-les-Vignes
136 breccia pipe results from a multistage development between ca. 325 and ca. 300 Ma in a
137 regional setting dominated by protracted peraluminous granitic magmatism and HT-LP
138 metamorphism.

139

140 **2. Geological setting of the Puy-les-Vignes W deposit**

141

142 The Puy-les-Vignes W deposit (Lat. 45°49'34"N, Long. 1°31'51"E) is located in the
143 Limousin area in the northwestern part of the FMC (Fig. 1A), which belongs to the internal
144 zone of the European Variscan belt formed during the continental collision between Gondwana
145 and Laurussia through the Upper Paleozoic (Faure et al., 2009a; Lardeaux et al., 2014). The
146 geologic structure of the FMC consists of a stack of three major metamorphic nappes that are
147 from top to bottom (Faure et al., 2009a and references therein): (i) the Upper Gneiss Unit (UGU)
148 composed of ortho- and paragneisses derived from Cambrian to Early Ordovician protoliths
149 (530-470 Ma; Alexandrov et al., 2001; Berger et al., 2010; Chelle-Michou et al., 2017; Lotout
150 et al., 2017) having experienced MP-MT amphibolite- to granulite-facies metamorphism at
151 360-340 Ma (Chelle-Michou et al., 2017); (ii) the Lower Gneiss Unit (LGU) consisting of
152 ortho- and paragneisses similar to those of the UGU that were inherited from late Ediacarian
153 protoliths (620-540 Ma; Alexandre, 2007; Melleton et al., 2010; Chelle-Michou et al., 2017;
154 Couzinié et al., 2017, 2019); and (iii) the Para-Autochthonous Unit (PAU) that consists of low-
155 grade metasedimentary rocks (micaschists, metagreywackes, and quartzites) that were derived
156 from Neoproterozoic to Early Cambrian protoliths (650-530 Ma; Melleton et al., 2010). These
157 metamorphic units were intruded by numerous granitoids during the Carboniferous between
158 360 and 300 Ma (Faure et al., 2009a; Lardeaux et al., 2014; Couzinié et al., 2017; Laurent et
159 al., 2017; Moyen et al., 2017; Villaros et al., 2018).

160 The Puy-les-Vignes breccia pipe is hosted in migmatitic biotite-sillimanite paragneisses of
161 the Saint-Léonard-de-Noblat gneiss unit, which is structurally correlated with the LGU and is
162 located on the southern flank of the Thaurion anticline (Fig. 1B). The deposit is situated 20 km

163 south of the Saint-Sylvestre leucogranite complex dated at 324 ± 4 Ma (Holliger et al., 1986;
164 Cuney et al., 1990) and 15 km west of the Millevaches leucogranite complex emplaced between
165 335 Ma and 325 Ma (Rolin et al., 2014). The breccia pipe is close to two peraluminous granites
166 (Fig. 2A): the Auriat two-mica granite in the northeast dated at 324 ± 1 Ma (Gebauer et al.,
167 1981), and the Aureil biotite-cordierite granite in the southwest dated at 346 ± 14 Ma (Duthou,
168 1978). The breccia pipe has dimensions of 80 x 340 m at surface and is cut in two parts (west
169 and east) by a N30°E-trending sinistral strike-slip fault (“Faille Limite”) with a 120-m
170 horizontal displacement (Figs. 2B-C; Weppe, 1951, 1958). Only the eastern part of the breccia
171 pipe was mined down to a depth of 300 m whereas the western part was barely explored. The
172 vertical extent of the deposit is not known, and an unexposed granite may exist at depth as
173 described for other mineralized breccia pipes elsewhere (Sillitoe, 1985; Ren et al., 1995;
174 Somarin and Ashley, 2004; Yang and Bodnar, 2004; Solomovich et al., 2012). Regional
175 geophysical data reveal a low gravity anomaly with a NE-SW elongation around Puy-les-
176 Vignes, suggesting a possible extension of the Auriat granite beneath the breccia pipe (Melleton
177 et al., 2017). Microgranite and lamprophyre dykes, of 1-4 m thickness and NE-trending, are
178 located at the intersection with the breccia pipe and are fragmented within the breccia (Fig. 2B;
179 Weppe, 1951, 1958). Field relationships indicate that the microgranite postdate the
180 lamprophyre. At depth, another NE-trending lamprophyre dyke crosscuts the breccia pipe
181 possibly implying the existence of several generations of lamprophyre (Weppe, 1958). Similar
182 lamprophyre dykes crosscutting the Saint-Sylvestre and Millevaches leucogranitic complexes
183 yielded Rb-Sr whole rock ages of 285 ± 10 Ma (Leroy and Sonet, 1976) and 290 ± 5 Ma (Chalier
184 et al., 1994), respectively.

185 From a regional perspective, the Puy-les-Vignes deposit is centered on an extended W-As
186 geochemical stream-sediments anomaly (>60 ppm W; Bertrand et al., 2015). Peri-granitic
187 W \pm Sn deposits occur regionally such as Mandelasse (Guyonnaud et al., 1977), Saint-Goussaud
188 (Alikouss, 1993), and Vaulry (Vallance et al., 2001). Several W occurrences exist within a
189 distance of <2 km around the Puy-les-Vignes deposit, including quartz-wolframite veins and
190 stockworks at the localities Lifarnet, Le Moulard, Les Clauds, Etivaud, Chassagnat, and Beynat,
191 as well as a second possible wolframite-bearing breccia pipe at Les Caillaudoux (Weppe, 1951,
192 1958; Fig. 2A). Additional quartz-wolframite veins are known in an area between Cheissoux
193 and Villetelle, as well as a greisen-like cupola at Moissannes, respectively located at 15 km east
194 and 10 km north of Puy-les-Vignes (Dudek, 1978). The Puy-les-Vignes deposit was mined
195 underground between the mid 19th and 20th centuries (1855-1957) with a cumulated production
196 of 3,733 t WO₃ at an average grade of 0.5% WO₃ (Mouthier, 2005) and was the second-ranked

197 tungsten mine in France during the 20th century. Proved reserves are estimated at about 1,158 t
198 WO₃ based on mining archives (Melleton et al., 2017), but 3D numerical geologic modelling
199 re-estimated reserves of 2,500 t WO₃ for the eastern part of the breccia pipe by considering a
200 vertical extent of 235 m and an average grade of 0.2% WO₃ (J.J Royer, personal
201 communication). Peñarroya, after a diamond drilling campaign in the 1970's on the unexploited
202 western part of the Puy-les-Vignes breccia pipe, reported the discovery of a 4-m length intercept
203 at 3% WO₃ (Melleton et al., 2017). The potential for discovering new W resources is significant
204 at Puy-les-Vignes considering the number of wolframite occurrences in the district, that only
205 half of the breccia pipe was mined, that the vertical extent of the deposit remains unknown, and
206 that the whole breccia body represents a potential low-grade ore.

207 According to Weppe (1951, 1958), the formation of the Puy-les-Vignes breccia pipe would
208 result from three successive stages: (i) A first stage of hydraulic fracturing and mass collapse
209 produced a matrix-supported breccia composed of polygenic and heterometric clasts of the
210 country rocks (mainly gneisses) cemented by quartz constituting about 10% of the total volume
211 of the breccia. Metric-size clasts have undergone syn-collapse rotation as suggested by the
212 progressive tipping of gneissic blocks within the breccia where fragments adjacent to the pipe
213 margins are subvertical and those towards the center are subhorizontal (Fig. 2D); (ii) A second
214 collapse stage led to the formation of subvertical quartz-filled decollements (“gaine” and
215 “croiseurs”), delimiting the borders of the breccia pipe with the country rocks, and quartz-filled
216 planar-curved veins and dome structures (“plateures”) dipping at low-angle (<30°) within the
217 breccia. The contact between the breccia and the enclosing gneisses is sharp consisting of a 0.5-
218 to-3-m thick quartz vein delimiting the southern and northern boundaries of the pipe; (iii) A
219 third stage yielded the formation of a NE-trending network of subparallel quartz-wolframite-
220 sulfide veins (“filons”) dipping at high-angle (>50°) and crosscutting the entire breccia pipe
221 and the enclosing gneisses. These veins are about 400 m long with variable thickness of 0.2–1
222 m and contain most of the W mineralization with grades ranging from 0.2 to 2% WO₃
223 (Mouthier, 2005). The quartz-filled decollements at the breccia-country rock boundary and the
224 quartz cementing the breccia also contain wolframite but at lower grades (Fig. 3D). The W
225 mineralization is dated at 317.7 ± 0.7 Ma based on U/Pb dating of wolframite from a
226 mineralized vein (Harlaux et al., 2018a).

227

228 **3. Materials and analytical methods**

229

230 3.1. *Sampling*

231 The Puy-les-Vignes mine is closed since 1957 and the underground workings are no more
232 accessible. Previous work from Alikouss (1993) was based on a few samples taken from the
233 historical collection of M. Weppe coming from the underground workings and from samples
234 collected in mining dumps, which are less accessible today due to revegetalization. The present
235 work relies on access to private collections of old mine workers (P. Medda, G. Pradeau) and to
236 museum collections (Musée Minéralogique de l'Ecole des Mines d'Alès, France, Collection P.
237 Fitte) corresponding to samples coming directly from the underground mine when it was still
238 operating. Information on the precise depth location and underground adit was available for
239 some samples. Mining archives indicate that only ores from the Puy-les-Vignes mine were
240 processed on site (Mouthier, 2005), thus excluding any risks of mixing with ores coming from
241 other mines. Complementary samples for this study come from surface sampling of stripped
242 terrains and trenches during recent site reworking and from a small outcrop of the breccia (Fig.
243 3). The latter is located at the margin of the eastern part of the breccia pipe close to a formerly
244 mined quartz-wolframite vein ("filon 1") in proximity to the old mining headframe ("Puits
245 Girod"). An old underground adit of about 150 m in length cutting through the Saint-Léonard-
246 de-Noblat gneisses and intersecting quartz-wolframite-sulfide-tourmaline veins was also
247 studied at Lifarnet (<2 km north of Puy-les-Vignes). This diversified sampling offers a set of
248 representative samples from the host rocks and the mineralization of the Puy-les-Vignes deposit
249 (Fig. 4).

250

251 3.2. *Petrography and geochemistry*

252 Mineralogical analyses were performed at GeoRessources, Université de Lorraine (Nancy,
253 France), using an Olympus BX51 optical microscope and a JEOL J7600F scanning electron
254 microscope (SEM) equipped with a SDD-type energy dispersive X-ray spectrometer (EDS)
255 coupled to an Oxford Wave wavelength dispersive X-ray spectrometer (WDS). Backscattered
256 electron (BSE) images were acquired on carbon-coated polished thin sections with an
257 acceleration voltage of 15 kV. Chemical compositions of Nb-Ta-W-Ti-Sn oxides were measured
258 at GeoRessources using a CAMECA SX100 electron microprobe analyzer (EMPA) operated
259 with a 20 kV accelerating voltage, a 20 nA beam current, and a 1 μm beam diameter. The
260 following standards and elements were analyzed using WDS spectrometers: hematite (Fe $K\alpha$),
261 MnTiO_3 (Mn $K\alpha$, Ti $K\alpha$), olivine (Mg $K\alpha$), corundum (Al $K\alpha$), albite (Si $K\alpha$, Na $K\alpha$), Sc metal
262 (Sc $K\alpha$), chromite (Cr $K\alpha$), LiNbO_3 (Nb $L\alpha$), LiTaO_3 (Ta $L\alpha$), scheelite (W $L\alpha$), cassiterite (Sn
263 $L\alpha$), uraninite (U $M\alpha$), galena (Pb $M\alpha$). Counting times were 10 s on element peaks and 5 s on

264 background. Minor and trace elements in rutile were measured by laser ablation – inductively
265 coupled plasma – mass spectrometry (LA-ICP-MS) at GeoRessources using an Agilent 7500c
266 quadrupole ICP-MS coupled with a 193 nm GeoLas ArF Excimer laser (MicroLas, Göttingen,
267 Germany). Laser ablation was performed on polished thin sections with a constant 5 Hz pulse
268 frequency and a fluence of 7 J cm⁻² using variable laser spot diameters between 32 and 60 μm.
269 Helium was used as carrier gas to transport the laser-generated particles from the ablation cell
270 to the ICP-MS and argon was added as an auxiliary gas via a flow adapter before the ICP torch.
271 Typical flow rates of 0.5 L min⁻¹ for He and 0.9 L min⁻¹ for Ar were used. The certified reference
272 material NIST SRM 610 (Jochum et al., 2011) was used as an external standard for calibration
273 of all analyses and was analyzed twice at the beginning and at the end of each set of samples,
274 following a bracketing standardization procedure. The reference material NIST SRM 612 was
275 used as a control standard for the standardization. Calibration of the ICP-MS was optimized for
276 highest sensitivity on an intermediate m/Q range, while maintaining Th/U ~1 and ThO⁺/Th⁺
277 <0.5%, as determined on NIST SRM 610. The following isotopes were measured with a dwell
278 time of 20 ms for each: ²⁹Si, ⁴⁵Sc, ⁴⁷Ti, ⁵¹V, ⁵³Cr, ⁵⁷Fe, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁹⁰Zr, ⁹³Nb, ⁹⁵Mo, ¹¹⁸Sn,
279 ¹⁸¹Ta, and ¹⁸²W. The total cycle time was of 332 ms. Data reduction and absolute quantification
280 of signals were performed using the software StalQuant (Fricker, 2012) developed at ETH
281 Zürich (Switzerland) and the Ti content determined by EMPA. Limits of detection (LOD) were
282 calculated using the 3σ criterion of Longerich et al. (1996). Whole-rock geochemistry of
283 selected samples was determined at the SARM-CNRS (Vandoeuvre-lès-Nancy, France)
284 following the procedure described by Carignan et al. (2001).

285

286 3.3. U/Pb geochronology

287 U/Pb dating of rutile was performed at the GeOHeLiS analytical platform (Géosciences
288 Rennes/OSUR, University of Rennes, France) using an ESI NWR193UC Excimer laser system
289 coupled to an Agilent 7700x quadrupole ICP-MS. The rutile grains were previously
290 investigated by SEM and EMPA in order to select chemically homogeneous zones that lack
291 microinclusions and alteration features. Laser ablation was performed on polished thin sections
292 at repetition rate of 5 Hz, a fluence of 8.6 J cm⁻², and using spot diameters of 40 or 50 μm
293 depending on grain size. The ablated material was carried by He and then mixed with N₂ and
294 Ar (Paquette et al., 2014) before injection into the ICP torch equipped with a dual pumping
295 system to enhance sensitivity. Typical gas flows of 0.75 L min⁻¹ for He, 3 mL min⁻¹ for N₂ and
296 0.85 L min⁻¹ for Ar were used. Tuning of the instrument and mass calibration were performed
297 before the analytical session using the NIST SRM 612 reference material (Jochum et al., 2011)

298 by monitoring the ^{238}U signal and minimizing the ThO^+/Th^+ ratio $<0.5\%$. The signals of ^{204}Pb ,
299 ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , and ^{238}U were measured with a dwell time of 10 ms (30 ms for ^{207}Pb).
300 For each analysis, 20 s of background was integrated, followed by 60 s of laser-generated signal
301 acquisition. Each analysis was separated by a 15 s delay of wash-out. Data were corrected for
302 U/Pb fractionation and for the mass bias by standard bracketing with repeated measurements
303 of the R10 rutile (1090 Ma; Luvizotto et al., 2009) reference standard. The R19 rutile reference
304 material (489.5 ± 0.9 Ma; Zack et al., 2011) was analyzed as a secondary standard to control
305 the reproducibility and accuracy of the corrections and yielded an age of 492.9 ± 4.4 Ma
306 (MSWD = 0.89, $n = 13$). The U/Pb isotopic analyses of the rutile standards are reported in
307 Supplementary Table 1. Data reduction and age calculations were carried out with the
308 GLITTER software package (van Achterbergh et al., 2001). Analyses yielding non-radiogenic
309 isotopic ratios were rejected. Data were plotted using ISOPLOT v.3.75 (Ludwig, 2008). Error
310 propagation is by quadratic addition according to Horstwood et al. (2016). For more
311 information on the analytical procedure, see Boutin et al. (2016) and Supplementary Table 1.

312

313 *3.4. $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology*

314 $^{40}\text{Ar}/^{39}\text{Ar}$ analytical work was performed at the University of Manitoba (Canada) using a
315 multi-collector Thermo Fisher Scientific ARGUS VI mass spectrometer, linked to a stainless
316 steel Thermo Fisher Scientific extraction/purification line, Photon Machines (55 W) Fusions
317 10.6 CO_2 laser, and Photon Machines (Analyte Excite) 193 nm laser. Argon isotopes (from mass
318 40 to 37) were measured using Faraday detectors with low noise $10^{12} \Omega$ resistors and mass 36
319 was measured using a compact discrete dynode (CDD) detector. All specimens (samples and
320 standards) were irradiated for 17 hours in the Cadmium-lined, in-core CLICIT facility of the
321 TRIGA reactor at the Oregon State University, USA. Standards of Fish Canyon sanidine
322 (Kuiper et al., 2008) and GA1550 biotite (Spell and McDougall, 2003) were placed in a Cu
323 sample tray, with a KBr cover slip, in a stainless-steel chamber with a differentially pumped
324 ZnS viewport attached to a Thermo Fisher Scientific extraction/purification line and baked with
325 an infrared lamp for 24 hours. Unknowns consist of discs of 5 mm in diameter and $\sim 150 \mu\text{m}$
326 thick that were cut from thick polished section investigated by optical microscopy and SEM
327 prior to $^{40}\text{Ar}/^{39}\text{Ar}$ analyses. The discs were mounted using a ceramic adhesive (PELCO) on a
328 quartz slide placed in a stainless-steel chamber with a sapphire viewport attached to the same
329 stainless-steel high vacuum extraction system as the CO_2 laser, and baked with an infrared lamp
330 for 48 hours. For this study, a raster size of about $100 \mu\text{m} \times 100 \mu\text{m}$ was used and ablation pits
331 were excavated to an estimated depth of $50 \mu\text{m}$. Five argon isotopes were measured

332 simultaneously over a period of 6 minutes. Measured isotope abundances were corrected for
333 extraction-line blanks, which were determined before every sample analysis. Line blanks in
334 both the Excimer and CO₂ system averaged ~3 fA for mass 40 and ~0.013 fA for mass 36.
335 Detector intercalibration (IC) between the different faraday cups was monitored (in Qtegra)
336 every four days by peak hopping ⁴⁰Ar. Calculated values are ICH1: 1.0000, ICAX: 1.0745,
337 ICL1: 1.0637, and ICL2: 1.0534, with an error of ~0.2%. The intercalibration factor between
338 H1 and the CDD was measured using 70 air aliquots interspersed with the unknowns resulting
339 in ICCDD: 1.0081 ± 0.0002 per amu. A value of 295.5 was used for the atmospheric ⁴⁰Ar/³⁶Ar
340 ratio (Steiger and Jäger, 1977) for the purposes of routine measurement of mass spectrometer
341 discrimination using air aliquots, and correction for atmospheric argon in the ⁴⁰Ar/³⁹Ar age
342 calculation. Corrections are made for neutron-induced ⁴⁰Ar from potassium, ³⁹Ar and ³⁶Ar from
343 calcium, and ³⁶Ar from chlorine (Renne et al., 1998; Renne and Norman, 2001). Data collection,
344 reduction, error propagation and age calculation were performed using the MassSpec software
345 (v.8.091; Deino, 2013). The decay constants used were those recommended by Steiger and
346 Jäger (1977). Data were plotted using DensityPlotter (Vermeesch, 2012), and uncertainties in
347 tables and text are quoted at the 1σ and 2σ level, respectively.

348

349 *3.5. Fluid inclusion analysis*

350 Fluid inclusions were studied using double-polished 150-200 μm thick sections of quartz-
351 wolframite vein samples. Petrographic and microthermometric analyses of quartz-hosted fluid
352 inclusions were performed at GeoRessources on a THMS 600 Linkam heating-cooling stage
353 mounted on an Olympus BX-51 microscope. The stage was calibrated at -56.6°C, 0.0°C, and
354 374.1°C using pure H₂O and H₂O-CO₂ synthetic fluid inclusion standards. Petrography and
355 microthermometry of wolframite-hosted fluid inclusions were carried out at the University of
356 Geneva (Switzerland) using a Linkam FTIR 600 stage mounted on an Olympus BH-51
357 microscope equipped with an Olympus XM-10 near-infrared (NIR) camera (Ortelli et al.,
358 2018). Calibration of the heating-cooling stage was performed regularly using SynFlinC
359 standards at -56.6°C, 0.0°C, and 374.1°C (Sterner and Bodnar, 1984). The visible light absorbed
360 by opaque minerals is partially converted into heat in proportion to the opacity and this could
361 potentially preclude accurate microthermometric measurements (Moritz, 2006). To avoid this
362 problem, a voltmeter was connected directly to the lamp of the microscope to control the power
363 of the incident light following the procedure described by Ortelli et al. (2018). Sample heating
364 is not high enough to affect microthermometric measurements if a 90% closed diaphragm, a
365 condenser at 0.3, and a power of <4 V depending on the transparency of the different zones of

366 the crystals are used (Casanova et al., 2018). The salinities, densities, and bulk compositions of
367 CO₂-bearing fluid inclusions were calculated based on the clathrate melting temperature (T_m
368 clat) and homogenization temperature of the CO₂ phase (T_h CO₂) using the Q2 program
369 developed by Bakker (1997) and the equations of state from Thiéry et al. (1994) and Duan et
370 al. (1996). Isochores were calculated using the ISOC program (Bakker, 2003) based on the
371 equations of state from Bakker (1999). For H₂O-NaCl fluid inclusions, the salinities, densities,
372 and isochores were calculated based on the ice-melting temperature (T_m ice) and total
373 homogenization temperature (T_h) using the HokieFlincs_H2O-NaCl program (Steele-MacInnis
374 et al., 2012). Raman spectroscopy analyses of fluid inclusions were carried out at
375 GeoRessources using a Horiba Jobin-Yvon LabRAM HR spectrometer equipped with a 1800
376 gr mm⁻¹ grating and an Edge filter. The excitation beam is provided by a Stabilite 2017 Ar⁺
377 laser (Spectra Physics, Newport Corporation) at 514.532 nm and a power of 400 mW focused
378 on the sample using x50 and x100 objectives mounted on an Olympus BX-40 optical
379 microscope. The signal-to-noise ratio was optimized, ideally lower than 1%, by adjusting the
380 acquisition time and accumulation number. Gas compositions of fluid inclusions were measured
381 at room temperature using a 500 µm confocal hole aperture and a 100 µm slit aperture. The
382 relative proportions of the gas species (mol%) were calculated using the peak area, acquisition
383 time, and the specific Raman scattering cross-sections (Burke, 2001).

384

385 **4. Paragenetic sequence of the Puy-les-Vignes deposit**

386

387 Petrographic observations from the outcrop- to the micrometer-scale, completing previous
388 descriptions (Weppe, 1951, 1958; Alikouss, 1993; Harlaux et al., 2015a; Harlaux, 2016), allow
389 proposing a detailed paragenetic sequence of the Puy-les-Vignes deposit divided into six main
390 stages (Fig. 5).

391

392 *4.1. Stage I: Early hydrothermal alteration and brecciation*

393 Greisenization of the country rocks (mainly gneisses) is the earliest hydrothermal alteration
394 episode identified at Puy-les-Vignes. It corresponds to dissolution of primary feldspar and
395 biotite in the Saint-Léonard-de-Noblat paragneisses and precipitation of secondary quartz,
396 muscovite, and tourmaline (“Tur 1” of Harlaux et al., 2019; Fig. 6A). The foliation is partly
397 preserved within the gneissic clasts (Figs. 3B and 6A) and relics of biotite and feldspar remain
398 in unaltered parts of the clasts, suggesting that greisenization was diffuse and limited to
399 structural discontinuities. Greisenization (stage Ia) was followed by hydraulic brecciation and

400 collapse of the host rocks resulting in a clast-supported tourmaline crackle breccia (stage Ib).
401 The clasts of gneisses and granites are angular to subangular in shape, centimetric to plurimetric
402 in size, and lack granulometric classification (Fig. 3A). They are surrounded by an irregular rim
403 of tourmalinite (tourmaline \pm quartz) of variable thickness, ranging from a few millimeters to
404 several centimeters (Figs. 3B-C and 4A-B), and up to complete tourmalinization of the clasts.
405 Hydrothermal alteration of the clasts results from two successive steps: (i) chloritization of
406 residual biotite associated with formation of Fe-W-rich rutile (Fig. 7A), monazite, xenotime,
407 and zircon; (ii) tourmalinization of the clasts rims forming dense aggregates of prismatic
408 tourmaline (“Tur 2” of Harlaux et al., 2019) cemented by quartz (Fig. 6B).

409

410 *4.2. Stage II: W-(Sn)-As-Nb-Ta mineralization*

411 Hydraulic brecciation and fluid-assisted reopening of the tourmaline crackle breccia
412 produced the quartz-supported breccia pipe and wolframite-bearing quartz veins. The contact
413 between the tourmaline-bordered clasts and the quartz cement is sharp and crack-seal textures
414 are common (Figs. 4A-B). Syn-collapse rotation of the clasts occurred prior or concomitantly
415 to quartz deposition as indicated by variable orientation of the foliation within gneissic clasts.
416 Quartz crystals of up to 20 cm-length are locally found in geodic cavities within the breccia
417 matrix. At the microscopic scale, quartz is composed of millimetric polycrystalline aggregates
418 showing evidence of ductile deformation (undulose extinction, lamellar deformation) and
419 dynamic recrystallization (bulging and subgrain rotation; Fig. 6C). Besides quartz, wolframite
420 and arsenopyrite are the main minerals in the mineralized veins (Figs. 4C-D). Wolframite is
421 euhedral ranging from millimetric to pluri-centimetric in size, exceptionally up to decimetric,
422 and grew directly onto the clast rims. Most wolframite is Fe-dominated ($\text{Fe}/(\text{Fe}+\text{Mn}) = 0.80-$
423 0.86 ; Harlaux et al., 2018b) but is locally replaced by a variety of wolframite having almost
424 pure ferberitic composition (ferberite-1; $\text{Fe}/(\text{Fe}+\text{Mn}) > 0.95$) along microcracks and crystal
425 borders (Figs. 6D and 7B). Arsenopyrite is the main sulfide in the quartz veins and is associated
426 with minor pyrrhotite and crosscuts wolframite (Fig. 6E). Most arsenopyrite is characterized
427 by a weight ratio of $\text{As}/\text{S} = 2.5$ but an early variety of arsenopyrite containing about 4.5 wt.%
428 Co and 1 wt.% Ni with a weight ratio of $\text{As}/\text{S} = 3$ was identified by EDS analyses (Fig. 7C).
429 Minor cassiterite is intergrown with arsenopyrite (Fig. 7D) and rare Cr-rich phengites
430 (“mariposite”) are also found in association with arsenopyrite. Accessory minerals of
431 tourmaline, muscovite, and Nb-Ta-W oxides are also present in the quartz veins. Prismatic
432 acicular tourmaline (“Tur 3” of Harlaux et al., 2019) occurs perpendicularly on clast rims and
433 as disseminations in quartz, and is also locally intergrown with wolframite. Muscovite consists

434 of millimetric flakes disseminated in quartz or overgrown on wolframite, and occasionally
435 shows kink-band deformation (Fig. 6C). Accessory Nb-Ta-W oxide minerals associated with
436 the stage II include (i) Nb-Ta-rich rutile disseminated in quartz (Fig. 7E), (ii) Fe-Nb-rich rutile
437 disseminated within ferberite-1 (Fig. 7F), (iii) Ta-Nb-rich ferberite (1.6 wt.% Ta, 0.4 wt.% Nb,
438 and 0.8 wt.% P; EDS analyses) in dissolution microvugs within wolframite (Fig. 7G), (iv) a
439 variety of W-rich ixiolite (hereafter named wolframoixiolite) in quartz-filled veinlets cutting
440 wolframite (Fig. 7H) and as disseminations overgrown by ferberite-1 (Fig. 7I), and (v) Cr-Nb-
441 W-rich rutile disseminated within arsenopyrite (Fig. 7J) together with inclusions of Fe-
442 skutterudite ($[\text{Fe,Co,Ni}]\text{As}_3$), wolframite, xenotime, and monazite. Scheelite is late relative to
443 the Nb-Ta-W oxides and occurs as centimetric bipyramidal euhedral grains having orange-
444 brownish-colors (Fig. 4E). Scheelite partly replaces wolframite and ferberite-1 (Fig. 6F),
445 crosscuts arsenopyrite along veinlets, and shows undulose extinction similar to quartz. A third
446 generation of wolframite of ferberitic composition (ferberite-2; $\text{Fe}/(\text{Fe}+\text{Mn}) > 0.95$) occurs as
447 pseudomorphs after ferberite-1 and scheelite and forms aggregates of randomly oriented fibrous
448 crystals (Figs. 6G-H). Locally, ferberite-2 forms octahedral crystals of pluri-centimetric size in
449 quartz geodic cavities (Fig. 4F), corresponding to the “reinite” described by Weppe (1951,
450 1958).

451

452 *4.3. Stage III: Fe-Cu-Zn±Mo mineralization*

453 Base metal sulfide assemblages, including pyrite, chalcopyrite, and sphalerite overprint the
454 mineral paragenesis of stages I and II. Pyrite and chalcopyrite are volumetrically the most
455 important minerals of this stage. They crosscut wolframite and arsenopyrite (Figs. 6I-K) and
456 are coeval with the deposition of quartz and chlorite (Fig. 7K). Sphalerite is early relative to
457 pyrite and chalcopyrite (Fig. 6L) and contains up to 2 wt.% Cd, as determined by EDS analyses.
458 Minor tennantite (identified by EDS) is associated with chalcopyrite (Figs. 6I-J). Molybdenite
459 is thought to be coeval with chalcopyrite but its paragenetic position remains uncertain. Stannite
460 is late and occurs locally as exsolution trails within chalcopyrite (Fig. 7L), as revealed by EDS
461 analyses. Deposition of sulfides is associated with recrystallization of quartz along the crystal
462 borders of wolframite and arsenopyrite. The sulfide assemblage and associated quartz are not
463 deformed, thus suggesting that stage III postdates the main ductile deformation episode.

464

465 *4.4. Stage IV: Nb-Y-HREE mineralization*

466 This stage is recorded by a millimeter-scale hydrothermal crackle breccia composed of
467 clasts of tourmaline (“Tur 4” of Harlaux et al., 2019) and vermicular chlorite cemented by

468 adularia and overprinting a deformed quartz-wolframite-scheelite-sulfide vein (Fig. 6M).
469 Adularia is not deformed indicating that the brecciation episode occurred after the main ductile
470 deformation that affected the deposit. The crackle breccia contains a series of accessory
471 minerals disseminated within adularia, including monazite, xenotime, zircon, Nb-Fe-W-rich
472 rutile, and Nb-Ti-Y-HREE-W-U oxides referred to as NTox (Fig. 6N). The latter minerals were
473 studied in detail by Harlaux et al. (2015b) and consist of subeuhedral grains (10-400 μm in size)
474 having complex internal textures and elevated concentrations of Nb, Ti, Y, HREE, and W. This
475 mineral paragenesis is characterized by a P, Y, HREE, Nb>Ta, Ti, Zr, and U geochemical
476 signature, which has been interpreted by Harlaux et al. (2015b) to result from rare-metal-
477 bearing hydrothermal fluids derived from an unknown peralkaline magmatic body at depth.

478

479 *4.5. Stage V: Bi±Au-Ag mineralization*

480 A volumetrically minor assemblage of native bismuth, bismuthinite (Bi_2S_3), Bi-Ag-Se-Te
481 sulfosalts, and electrum (ca. 78 wt.% Au and 22 wt.% Ag) fills microcavities and microcracks
482 overprinting quartz, wolframite and arsenopyrite from stage II, base metal sulfides from stage
483 III, and adularia from stage IV (Figs. 7I-M). Accessory Bi-Ag-Se-Te sulfosalt minerals include
484 hedleyite (Bi_7Te_3) and sztrokayite (Bi_3TeS_2). Quartz, siderite, arsenopyrite, and colloform As-
485 rich pyrite (1-10 wt.% As) precede the deposition of the Bi minerals (Figs. 6O and 7N-P).
486 Russellite (Bi_2WO_6) locally occurs as pseudomorph after ferberite at the contact with native
487 bismuth.

488

489 *4.6. Stage VI: Late hydrothermal and supergene alterations*

490 Late hydrothermal fluid circulations are responsible for alteration of arsenopyrite to
491 scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and other arsenates such as pharmacosiderite, carminite, and
492 beudantite. Scorodite is usually greenish in color, has a skeletal porous texture, and occurs as
493 pseudomorph after arsenopyrite or as veinlets crosscutting wolframite and chalcopyrite (Fig.
494 6P). Minor illite and rooseveltite (BiAsO_4) are associated with scorodite, indicating the
495 remobilization of bismuth during alteration of arsenopyrite. Supergene weathering of the
496 orebody resulted in the partial destabilization of wolframite and residual sulfides in secondary
497 minerals such as tungstite ($\text{WO}_3 \cdot \text{H}_2\text{O}$), colloform goethite, and Fe-oxides-hydroxides.

498

499 **5. Petrography and geochemistry of granitic rocks**

500

501 *5.1. Microgranite dykes*

502 Microgranite dykes crosscut the host paragneisses and are fragmented within the breccia
503 and cut by tourmaline veins, indicating an emplacement prior to the early hydrothermal
504 alteration and brecciation stages. The least altered sample of microgranite (sample PV-92-7),
505 collected at surface, is a fine-grained rock composed of quartz, plagioclase and muscovite (Figs.
506 4G and Fig. 8A). Quartz shows undulose extinction while feldspars are partly sericitized. The
507 microgranite composition is strongly peraluminous ($A/CNK = 1.54$) and plots along the
508 fractionation trend of evolved leucogranites, rare-metal granites (RMG), and rare-metal
509 pegmatites (RMP) from the northwestern FMC (Fig. 9; Table 1). Its trace element composition
510 overlaps those of muscovite-bearing peraluminous granitoids from the northwest FMC and is
511 characterized by low contents of Sr (95 ppm), Th (0.5 ppm), Zr (22 ppm), Hf (0.9 ppm), and
512 Pb (5.8 ppm), and high contents of Rb (156 ppm), W (9.7 ppm) and Sn (41 ppm), compared to
513 the upper continental crust (Fig. 10A). The REE contents are low (11 ppm) and show a
514 relatively flat spectrum ($La/Yb = 1.38$) with a positive Eu anomaly ($Eu/Eu^* = 1.66$), which
515 differs from the regional leucogranites (Fig. 10C). A strongly altered sample of microgranite
516 (sample PV-92-5), also collected at surface, shows higher contents of Fe_2O_3 (2.9 vs 0.5 wt.%)
517 and K_2O (4.3 vs 2.5 wt.%) and lower contents of SiO_2 (75.2 vs 78 wt.%) and Na_2O (0.2 vs 3.6
518 wt.%) compared to the unaltered precursor. The trace element composition is similar to the least
519 altered microgranite (Figs. 10A-C), except for W (30 ppm), Sn (98 ppm), Bi (34 ppm), As
520 (3,540 ppm), and Cu (246 ppm) reflecting the effect of hydrothermal alteration.

521

522 *5.2. Granitic clasts*

523 The granitic clasts within the breccia are strongly greisenized and tourmalinized, indicating
524 that the granite emplacement preceded the sequence of hydrothermal events. Two samples of
525 strongly altered granitic clasts were collected at surface (samples PLV-02-10 and PLV-13-02).
526 These rocks are dominantly composed of secondary quartz and muscovite that replaced the
527 primary feldspars. The altered granitic clasts have strongly peraluminous compositions
528 ($A/CNK = 3.00-3.02$) that plot along greisenization trend in the geochemical diagrams together
529 with the strongly altered microgranite sample (Fig. 9; Table 1). Their trace element
530 compositions partly overlap those of muscovite-bearing peraluminous granitoids from the
531 northwestern FMC (Figs. 10A-C). The REE spectra of the altered granites show a fractionated
532 pattern ($La/Yb = 1.74-6.36$) with negative Eu anomalies ($Eu/Eu^* = 0.44-0.68$). Expectedly,
533 these altered granitic rocks have elevated concentrations of W (40-97 ppm), Sn (56-89 ppm),
534 As (2,235-2,275 ppm), Bi (26-28 ppm), and Cu (71-301 ppm) as a result of hydrothermal

535 alteration by mineralizing fluids.

536

537 *5.3. Rare-metal granite*

538 A unique sample of RMG coming from the Puy-les-Vignes mine has been studied (sample
539 PLV-02-02). The location of this granite as well as the relations with the breccia are unknown,
540 but it is certain that this sample was collected in the old underground workings. The RMG is a
541 fine-grained leucocratic rock showing a magmatic layering, which consists of a repetitive
542 sequence of quartz-albite-muscovite band (“B1” on Figs. 4H and 8B) progressively evolving to
543 albite-quartz band (“B2” on Figs. 4H and 8C). The transition between the two zones is marked
544 by a progressively decreasing grain size from 500-1,000 μm on average in the quartz-albite-
545 muscovite band to 100-200 μm in the albite-quartz band. Quartz consists of xenomorphic
546 globular phenocrysts containing poikilitic inclusions of albite laths in a typical “snowball”
547 helicitic texture (Fig. 8D) while the granitic groundmass is characteristic of fractionated albitic
548 cumulates. There is no evidence of post-magmatic deformation and hydrothermal alteration,
549 thus suggesting that the RMG emplaced after the main episode of ductile deformation
550 postdating the paragenetic stage II. Muscovites contain elevated Si/Al ratios (1.12-1.97, avg =
551 1.32) and high contents of F (2.3-8.5 wt.%, avg = 4.2 wt.%), as determined by EDS analyses.
552 Accessory minerals include apatite, cassiterite, and columbite-tantalite that are disseminated in
553 the albite-quartz bands. No magmatic zircons and monazite were found. The lower part of the
554 sample shows unidirectional solidification textures (UST) composed of perpendicularly
555 oriented K-feldspar phenocrysts relative to the magmatic layering. The albite-quartz band
556 (referred as PLV-02-02a) and the quartz-albite-muscovite band (referred as PLV-02-02b) have
557 been analyzed separately for whole-rock geochemistry. The RMG has a strongly peraluminous
558 composition ($A/CNK = 1.13-1.45$) that overlaps the fractionation trend of P-rich RMG-RMP
559 from the FMC (Fig. 9; Table 1). The trace element composition shares many similarities with
560 other RMG-RMP from the northwestern FMC, including depletion (<25 ppm) in Sr, Sc, V, Cr,
561 Co, Ba, Hf, Th, and Zr, and enrichment in P (1,833-2,357 ppm), Rb (329-1,151 ppm) and Cs
562 (58-170 ppm) compared to the upper continental crust (Fig. 10B). The rare-metal
563 concentrations are notably elevated for Nb (65-69 ppm), Ta (46-47 ppm), W (14-37 ppm), Sn
564 (853-3,044 ppm), and Be (74-113 ppm). The REE contents are low (4.0-6.5 ppm) with a flat
565 pattern ($La/Yb = 2.9-3.6$) and negative Ce and Eu anomalies ($Ce/Ce^* = 0.62-0.81$, $Eu/Eu^* =$
566 $0.55-0.64$), similar to other P-rich RMG-RMP from the FMC (Fig. 10D). Additionally, the
567 studied sample has low ratios of Zr/Hf (12.7-13.2) and Nb/Ta (1.41-1.45) typical of
568 peraluminous P-rich RMG (Ballouard et al., 2016).

569

570 6. Crystal chemistry of Nb-Ta-W-Ti-Sn oxides

571

572 6.1. Rutile

573 Chemical compositions of rutile were analyzed by EMPA and LA-ICP-MS and results are
574 reported in Supplementary Tables 2 and 3, respectively. The first type of rutile (Rt-1)
575 corresponds to subeuhedral Fe-W-rich rutile disseminated in the tourmalinite and in quartz
576 veins. It ranges from 250 to 1000 μm in size and shows sector zoning on BSE images (Fig. 7A).
577 Rt-1 is characterized by core having a homogeneous composition (96.5-99.6 wt.% TiO_2) and
578 sectors having high contents of Fe (up to 1.6 wt.% FeO), Sn (up to 0.5 wt.% SnO_2), and W (up
579 to 5.0 wt.% WO_3). The trace element composition shows low contents of Ta (41-250 ppm), Sc
580 (5-29 ppm), Zn (12-63 ppm), Zr (24-170 ppm), and moderate contents of Nb (576-2463 ppm),
581 Cu (3-369 ppm), and Cr (up to 1 wt.%). The second type of rutile (Rt-2) corresponds to Nb-Ta-
582 rich rutile disseminated in wolframite-bearing quartz veins as grains of 50-250 μm in size (Fig.
583 7E). Rt-2 shows similar compositions to Rt-1 but differs by rims having high contents of Nb
584 (up to 12 wt.% Nb_2O_5), Ta (up to 5.1 wt.% Ta_2O_5), and Fe (up to 4.8 wt.% FeO). The third type
585 of rutile (Rt-3) consists of subeuhedral (500 μm in size) Fe-Nb-rich rutile disseminated within
586 ferberite-1 (Fig. 7F). The chemical composition of Rt-3 is characterized by high contents of Nb
587 (up to 14.1 wt.% Nb_2O_5), Ta (up to 1.3 wt.% Ta_2O_5), and Fe (up to 4.5 wt.% FeO), with minor
588 amounts of W (up to 0.9 wt.% WO_3) and Sn (0.6 wt.% SnO_2). The last type of rutile (Rt-4) is
589 only found in arsenopyrite as euhedral grains (ca. 250 μm) of Cr-Nb-W-rich rutile showing
590 growth zoning (Fig. 7J). It has uncommon elevated major contents of Nb (up to 14.2 wt.%
591 Nb_2O_5), Ta (up to 2.3 wt.% Ta_2O_5), W (up to 12.1 wt.% WO_3), and Cr (up to 9.3 wt.% Cr_2O_3),
592 as well as trace element enrichment of V (314-1305 ppm), Sc (64-244 ppm), Zn (10-151 ppm),
593 Zr (100-234 ppm), and Sn (1940-2911 ppm). The different types of rutile plot along distinct
594 chemical trends in the ternary diagram (Nb+Ta)-(Sn+Ti+W)-(Fe+Mn), reflecting variable
595 contribution of the substitution mechanisms $\text{Ti}^{4+}_{-2}(\text{Fe},\text{Mn})^{2+}_{+1}\text{W}^{6+}_{+1}$, $\text{Ti}^{4+}_{-3}(\text{Fe},\text{Mn})^{2+}_{+1}(\text{Nb},\text{Ta})^{5+}_{+2}$,
596 $\text{Ti}^{4+}_{-2}(\text{Fe},\text{Mn})^{3+}_{+1}(\text{Nb},\text{Ta})^{5+}_{+1}$ (Fig. 11). Using the Zr-in-rutile
597 thermometer of Watson et al. (2006) based on the coexistence of zircon, rutile and quartz,
598 crystallization temperatures between 472 and 623°C (avg = $546 \pm 32^\circ\text{C}$; n = 75) were calculated
599 for all rutile grains (Supplementary Table 3).

600

601 6.2. Cassiterite

602 Cassiterite from the RMG and from a wolframite-bearing quartz vein were analyzed by

603 EMPA and the chemical compositions are reported in Supplementary Table 4. Magmatic
604 cassiterite disseminated in the RMG ranges from 100 to 500 μm in size and shows a discrete
605 zoning on BSE images (Fig. 12A). Its chemical composition is characterized by high contents
606 of Nb (up to 2.8 wt.% Nb_2O_5) and Ti (up to 1.6 wt.% TiO_2), and low contents of Fe (up to 0.7
607 wt.% FeO). Hydrothermal cassiterite hosted in a quartz-wolframite-sulfide vein consists of
608 subeuhedral grains of 200-400 μm in size with homogeneous texture (Fig. 12B). Its chemical
609 composition is close to the ideal formula of cassiterite with minor contents of W (up to 1.6 wt.%
610 WO_3), Fe (up to 1.5 wt.% FeO), and Nb (up to 0.2 wt.% Nb_2O_5). Magmatic and hydrothermal
611 cassiterite plot along distinct geochemical trends in the ternary diagram (Nb+Ta)-(Sn+Ti+W)-
612 (Fe+Mn), reflecting the two heterovalent substitution mechanisms Sn^{4+} -
613 $3(\text{Fe},\text{Mn})^{2+}_{+1}(\text{Nb},\text{Ta})^{5+}_{+2}$ and $\text{Sn}^{4+}_{-2}(\text{Fe},\text{Mn})^{2+}_{+1}\text{W}^{6+}_{+1}$ (Fig. 12C).

614

615 6.3. *Wolframoixiolite*

616 The W-rich variety of ixiolite (named wolframoixiolite) consists of subeuhedral grains of
617 200 to 500 μm in size that are found in quartz-filled veinlets cutting wolframite and as
618 disseminations in scheelite (Figs. 7H-I). At the grain scale, wolframoixiolite shows a complex
619 zoning composed of successive core, rim, and overgrowth. Chemical compositions of
620 wolframoixiolite were determined by EMPA and are reported in Supplementary Table 5. The
621 core and rim have overlapping compositions characterized by high contents of Nb (52.7-66.6
622 wt.% Nb_2O_5), Fe (13.6-17.1 wt.% FeO) and Mn (2.5-4.6 wt.% MnO), and low contents of W
623 (7.0-23.1 wt.% WO_3) and Ti (2.4-9.8 wt.% TiO_2). In contrast, the overgrowth is distinguished
624 by lower contents of Nb (40.4-49.7 wt.% Nb_2O_5) and higher contents of W (21.9-33.4 wt.%
625 WO_3). When plotted in the ternary diagram (Nb+Ta)-(Sn+Ti+W)-(Fe+Mn), the chemical
626 composition of wolframoixiolite reflects the coupled substitution mechanisms $(\text{Nb},\text{Ta})^{5+}$ -
627 $4(\text{Fe},\text{Mn})^{2+}_{+1}\text{W}^{6+}_{+3}$ and $(\text{Fe},\text{Mn})^{2+}_{-1}(\text{Nb},\text{Ta})^{5+}_{-2}(\text{Ti},\text{Sn})^{4+}_{+3}$ (Fig. 13).

628

629 6.4. *Columbite-tantalite*

630 Columbite-tantalite occurs as 100-200 μm -size subeuhedral grains disseminated in the
631 groundmass of the RMG or as microinclusions (5 to 20 μm) hosted in magmatic cassiterite. At
632 the microscopic scale, columbite-tantalite shows a zoning composed of five distinct zones (Fig.
633 14A): (i) ovoid dark core of 15-20 μm in size corresponding to the initial nucleus; (ii) an
634 irregular patchy zone close to the core; (iii) a rim-1 of medium grey color surrounding the core
635 and showing growth banding; (iv) a rim-2 having a light grey contrast in continuity to rim-1;
636 and (v) an overgrowth, rarely exceeding 10 μm in thickness, which shows dissolution texture

637 at the interface with the rim and represents a late stage of crystallization. Chemical
638 compositions of columbite-tantalite was determined by EMPA and results are shown in
639 Supplementary Table 6. The core has higher contents of Fe (up to 11.6 wt.% FeO) and Nb (up
640 to 65.6 wt.% Nb₂O₅) and lower contents of Mn (up to 9.2 wt.% MnO) and Ta (up to 19.6 wt.%
641 Ta₂O₅) relative to the rims. The overgrowth shows contrasting compositions with high contents
642 of Ta (up to 48.0 wt.% Ta₂O₅) and Mn (up to 10.2 wt.% MnO) and low contents of Fe (up to
643 7.7 wt.% FeO) and Nb (up to 36.7 wt.% Nb₂O₅). In the Ta/(Ta+Nb) vs Mn/(Fe+Mn) diagram
644 (Fig. 14B), the composition of columbite-tantalite shows a trend of increasing the Ta/(Ta+Nb)
645 ratio (from 0.07 to 0.51) at relatively constant Mn/(Mn+Fe) ratio (0.42-0.67) from core to
646 overgrowth. These chemical variations are related to the coupled heterovalent substitutions
647 (Nb,Ta)⁵⁺₋₂(Ti,Sn)⁴⁺₊₁W⁶⁺₊₁ and (Fe,Mn)²⁺₋₁(Nb,Ta)⁵⁺₋₂(Ti,Sn)⁴⁺₊₃, and the isovalent
648 substitutions Nb⁵⁺₋₁Ta⁵⁺₊₁ and Fe²⁺₋₁Mn²⁺₊₁.

649

650 7. U/Pb and ⁴⁰Ar/³⁹Ar geochronology

651

652 7.1. U/Pb dating of rutile

653 Two samples of quartz-wolframite-arsenopyrite veins (samples PLV-7574a and PLV-02-
654 28b) containing rutile were selected for *in situ* U/Pb LA-ICP-MS dating. Results are shown in
655 Figure 15 and data are reported in Table 2. The analyzed rutile grains have low U contents
656 ranging from 0.9 to 5.7 ppm and very low Pb contents ranging from 0.07 to 2.02 ppm. The Th
657 contents are below 1 ppm. The isotopic compositions of rutile are variable with ²³⁸U/²⁰⁶Pb ratios
658 ranging from 7.03 to 18.63 and ²⁰⁷Pb/²⁰⁶Pb ratios ranging from 0.09 to 0.54. All data are
659 discordant in the Tera-Wasserburg diagram, which is a common feature of hydrothermal rutile
660 (Boutin et al., 2016). Sample PLV-7574a contains hydrothermal rutile (Rt-2) disseminated in a
661 wolframite-bearing quartz vein and is thought to be formed prior or concomitantly to
662 wolframite deposition. The U and Pb contents of rutile range from 0.90 to 1.8 ppm and 0.07 to
663 0.22 ppm, respectively. The sample has relatively high radiogenic composition with ²³⁸U/²⁰⁶Pb
664 values ranging from 10.93 to 18.33 and ²⁰⁷Pb/²⁰⁶Pb values from 0.11 to 0.43. The data (n = 15)
665 define a discordia line with a lower intercept date of 322 ± 10 Ma (2σ, MSWD = 1.8; Fig. 15A).
666 Sample PLV-02-28b contains hydrothermal rutile (Rt-4) hosted in arsenopyrite from a quartz-
667 wolframite vein. Rutile grains from sample PLV-02-28b have low U and Pb contents ranging
668 from 3.5 to 5.7 ppm and 0.25 to 2.0 ppm, respectively. They have variable ratios of ²³⁸U/²⁰⁶Pb
669 (7.03-18.63) and ²⁰⁷Pb/²⁰⁶Pb (0.09-0.54). Linear regression of the data (n = 11) in the Tera-
670 Wasserburg diagram yields a lower intercept date of 323 ± 5 Ma (2σ, MSWD = 1.7; Fig. 15B).

671

672 7.2. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of micas and adularia

673 Five samples containing micas and one sample with adularia were selected for *in situ*
674 $^{40}\text{Ar}/^{39}\text{Ar}$ dating. Results of the $^{40}\text{Ar}/^{39}\text{Ar}$ analyses are shown in Figure 16 and the dataset is
675 reported in Table 3. Magmatic muscovite from a microgranite (sample PV-92-7) gives $^{40}\text{Ar}/^{39}\text{Ar}$
676 apparent ages ranging from ca. 306 to ca. 336 Ma ($n = 12$) and a weighted mean date of $323 \pm$
677 4 Ma (2σ , MSWD = 1.7; Fig. 16A). The $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages for magmatic biotite from a
678 lamprophyre (sample PV-92-17) overlap between ca. 325 and ca. 347 Ma ($n = 3$) and yield a
679 weighted mean date of 331 ± 14 Ma (2σ , MSWD = 0.8; Fig. 16B). Magmatic muscovite from
680 the RMG (sample PLV-02-02b) yields $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages comprised between ca. 293 and
681 ca. 323 Ma ($n = 7$) and a weighted mean date of 311 ± 5 Ma (2σ , MSWD = 2.6; Fig. 16C).
682 Hydrothermal muscovite from a greisenized gneiss clast (sample PLV-02-01a; stage I) yields
683 $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages ranging from ca. 308 to ca. 326 Ma ($n = 6$) and a weighted mean date
684 of 318 ± 5 Ma (2σ , MSWD = 1.2; Fig. 16D). The $^{40}\text{Ar}/^{39}\text{Ar}$ apparent ages for hydrothermal
685 muscovite from a quartz-wolframite vein (sample PV1; stage II) range between ca. 310 and ca.
686 338 Ma ($n = 8$) and yield a weighted mean date of 324 ± 5 Ma (2σ , MSWD = 1.7; Fig. 16E).
687 Adularia from a tourmaline microbreccia (sample PLV-02-13b; stage IV) gives $^{40}\text{Ar}/^{39}\text{Ar}$
688 apparent ages between ca. 296 and ca. 310 Ma ($n = 6$) and a weighted mean date of 302 ± 4 Ma
689 (2σ , MSWD = 1.7; Fig. 16F).

690

691 **8. Fluid inclusions**

692

693 8.1. Petrography and microthermometry of fluid inclusions hosted in quartz

694 Fluid inclusions (FIs) have been studied in representative quartz-wolframite vein samples
695 (“filon 2” and “filon T18”) from the Puy-les-Vignes deposit. The studied FIs were identified in
696 two distinct generations of quartz. Quartz Q1 forms the main gangue of the vein, similar to the
697 breccia cement, and is interpreted as coeval with wolframite deposition (stage II). Quartz Q1
698 consists of large crystals having a milky color with a high density of FIs and showing evidence
699 of ductile deformation and dynamic recrystallization. Primary zoning is locally preserved in Q1
700 but most FIs aligned along growth zones are decrepitated. Quartz Q2 is found in recrystallized
701 zones of Q1 and is coeval with the base metal sulfide assemblage (stage III). In contrast to Q1,
702 quartz Q2 corresponds to fully transparent undeformed quartz crystals containing less FIs.
703 Based on petrography and microthermometry, three main types of quartz-hosted FIs are
704 distinguished in both Q1 and Q2 (Table 4):

705 (i) *Aqueous-carbonic Lc-w*: They are mainly found in Q1 either as isolated or
706 clustered FIs, interpreted as primary, and as pseudo-secondary FI planes (FIP) sealing
707 microcracks. Many Lc-w show reequilibration features (e.g., stretching, leaking, neonate halo)
708 or are decrepitated (Figs. 17A-C). The Lc-w contain three phases at room temperature or upon
709 the beginning of cooling, i.e., a carbonic liquid phase (L_{car}), a carbonic vapor phase (V_{car}), and
710 an aqueous liquid phase (L_{aq}). They occasionally contain small ($<2 \mu\text{m}$) dark solids that could
711 not be analyzed by Raman spectroscopy but may be graphite. The Lc-w have variable
712 morphology, ranging from very irregular to regular (Figs. 17F-J). Their size varies between 5
713 and $70 \mu\text{m}$ (avg = $20 \mu\text{m}$), with the regular FIs being generally smaller ($5\text{-}20 \mu\text{m}$) than the
714 irregular ones ($30\text{-}70 \mu\text{m}$). The ratio between the volatile phase and the FI volume at room
715 temperature (R_v) is highly variable ($0.10\text{-}0.70$, avg = 0.40). The Lc-w have low CO_2 melting
716 temperatures ($T_m \text{CO}_2 = -64.3$ to -56.6°C) and variable clathrate melting temperatures ($T_m \text{clat}$
717 = 3.9 to 13.1°C), indicating the presence of other gases in the volatile phase in addition to CO_2
718 (Figs. 19A-B). Homogenization of the volatile phase occurs dominantly to the vapor phase (T_h
719 $\text{CO}_2 = -9.7$ to 23.3°C) but homogenization in the liquid or critical phase has been observed. The
720 eutectic temperatures ($T_e = -24.5$ to -21.1°C) indicate an $\text{H}_2\text{O-NaCl-(KCl)}$ composition. Total
721 homogenization of the Lc-w occurs dominantly to the liquid phase over a large range of
722 temperatures ($T_h = 249$ to 455°C). Decrepitation before total homogenization of Lc-w is
723 frequent upon heating ($T_d = 250$ to 400°C). Salinities calculated based on the $T_m \text{clat}$ and T_h
724 CO_2 range from 2.2 to $8.1 \text{ wt.\% NaCl eq}$ (avg = $5.3 \text{ wt.\% NaCl eq}$) and bulk densities are
725 comprised between 0.36 and 0.92 g cm^{-3} (avg = 0.67 g cm^{-3} ; Figs. 19A-C).

726 (ii) *Aqueous-carbonic Lw-c*: They correspond to primary and pseudo-secondary FIP
727 forming trails along grain boundaries and growth zones in Q1 and Q2 (Figs. 17C-E).
728 Crosscutting relations suggest that the Lw-c postdate the Lc-w. The Lw-c consist of two-phase
729 FIs at room temperature with a dominant aqueous liquid phase (L_{aq}) over the vapor phase (V)
730 with variable R_v ratios ($0.10\text{-}0.50$, avg = 0.20). Some Lw-c hosted in Q2 contain chalcopyrite
731 microinclusions resulting likely from heterogeneous trapping. The Lw-c have variable size (10-
732 $50 \mu\text{m}$, avg = $20 \mu\text{m}$) and morphology, ranging from very irregular to regular, the largest ones
733 commonly showing irregular shapes (Figs. 17K-N). Although the carbonic liquid phase is
734 absent, many Lw-c exhibit melting of a carbonic phase upon heating following freezing. The
735 measured $T_m \text{CO}_2$ varies from -103.3 to -57.4°C , indicating the presence of other components
736 than CO_2 in the volatile phase, which is confirmed by the range of $T_m \text{clat}$ ($2.9\text{-}15.2^\circ\text{C}$). The
737 Lw-c hosted in Q1 and Q2 differ by their $T_m \text{CO}_2$ and $T_m \text{clat}$ values (Figs. 19A-B). The
738 eutectic temperatures ($T_e = -38$ to -21.1°C) are consistent with a $\text{H}_2\text{O-NaCl-(KCl)}\pm(\text{MgCl}_2)$

739 composition. Total homogenization occurs dominantly to the liquid phase between 246 and
740 412°C. Decrepitation of irregular Lw-c before total homogenization is frequent upon heating at
741 temperatures similar to the Lc-w. Calculated salinities are comprised between 0.7 and 5.8 wt.%
742 NaCl eq (avg = 2.6 wt.% NaCl eq) and bulk densities range from 0.47 to 0.92 g cm⁻³ (avg =
743 0.67 g cm⁻³; Fig. 19C).

744 (iii) *Aqueous Lw*: They occur as secondary FIP cutting the Lc-w and Lw-c FIs (Fig.
745 18D). The Lw are two-phase at room temperature with a dominant aqueous liquid phase over
746 the vapor phase (Rv = 0.05-0.35, avg = 0.10). They are generally small (typically <10 μm) and
747 have regular shapes (Figs. 17O-P). The eutectic temperatures (Te = -23 to -21.6°C) indicate a
748 H₂O-NaCl composition of the aqueous phase. Ice melting temperatures show a limited range
749 of values (Tm ice = -5.5 to -0.2°C). No clathrate melting was observed. Total homogenization
750 always occurs to the liquid phase between 124 and 391°C. Salinities calculated based on the
751 Tm ice are comprised between 0.3 and 8.6 wt.% NaCl eq (avg = 4.9 wt.% NaCl eq) and bulk
752 densities range from 0.63 to 0.99 g cm⁻³ (avg = 0.85 g cm⁻³; Fig. 19D).

753

754 8.2. Petrography and microthermometry of fluid inclusions hosted in wolframite

755 Wolframite from a quartz vein sample (“filon 2”) has been studied by NIR microscopy for
756 complementing the study of FIs hosted in the coexisting quartz. Under NIR transmitted light,
757 wolframite shows evidence of deformation and is crosscut by numerous cracks that opacify the
758 crystal (Figs. 18A-B). Two main types of FIs were observed in transparent zones within
759 wolframite: aqueous-carbonic (Lw-c) and aqueous (Lw) FIs. Three-phase volatile-rich Lc-w
760 FIs have not been found in wolframite. The Lw correspond to secondary FIP of small (5-15
761 μm) two-phase (L_{aq} + V) FIs. They have a negative crystal shape making most of them
762 completely opaque under NIR microscopy (Fig. 18C). Only the Lw-c could be analyzed by
763 microthermometry (Table 4). They correspond to primary FIs aligned along the c-axis of
764 wolframite (Fig. 18D) and trails of pseudo-secondary FIs (Fig. 18E). The Lw-c have regular to
765 slightly irregular shapes and their size range from 20 to 50 μm (avg = 30 μm). They are two-
766 phase at room temperature with equal proportions of the vapor phase and the aqueous liquid
767 phase (Rv = 0.30-0.60, avg = 0.45; Figs. 18F-M). No CO₂ melting and eutectic melting
768 temperatures were observed. Ice-melting temperatures are comprised between -5.6 and -3.0°C
769 and clathrate melting temperatures range from 11.0 to 14.5°C (Fig. 19B). Total homogenization
770 occurs to the liquid phase between 344 and 365°C. Salinities calculated based on the Tm ice
771 are comprised between 5.0 and 8.7 wt.% NaCl eq (avg = 6.6 wt.% NaCl eq) and bulk densities
772 range from 0.66 to 0.73 g cm⁻³ (avg = 0.69 g cm⁻³; Fig. 19C).

773

774 *8.3. Raman spectroscopy and bulk compositions of fluid inclusions*

775 Raman spectroscopy data were acquired for quartz-hosted Lc-w and Lw-c only (Table 4,
776 Figs. 19E-F). Due to their small size, no Raman spectroscopy analysis of Lw was possible. The
777 Lc-w and Lw-c have a mixed volatile content composed of CO₂, CH₄ and N₂ (Fig. 19E). The
778 volatile phase of Lc-w is dominantly composed of CO₂ (69-98 mol%) and N₂ (0-26 mol%) with
779 minor amount of CH₄ (0-12 mol%) and traces of H₂S (up to 0.3 mol%). In contrast, the Lw-c
780 contain highly variable contents of CO₂ (0-100 mol%), CH₄ (0-86 mol%) and N₂ (0-41 mol%)
781 with traces of H₂S (up to 1.1 mol%). The Lc-w and Lw-c hosted in Q1 are characterized by
782 higher CO₂/CH₄ ratios relative to the ones hosted in Q2 (Fig. 19E). Compared to the Lw-c, the
783 calculated bulk compositions of Lc-w are lower for H₂O (71-88 mol%) and CH₄ (0.2-4.9 mol%)
784 but higher for CO₂ (9-26 mol%). The bulk NaCl content of FIs increases (from 0.1 to 2.1 mol%)
785 when the volatile content decreases (from 28 to 2.5 mol%; Fig. 19F). From Q1 to Q2, the Lc-
786 w and Lw-c have increasing CH₄ content in the volatile phase (from 0-20 mol% in Q1 to 20-60
787 mol% in Q2) while the N₂ content does not vary significantly. No Raman spectroscopy
788 measurements of FIs in wolframite could be performed due to the strong laser energy absorption
789 by the host mineral. However, the absence of observable CO₂ melting in wolframite-hosted Lw-
790 c indicates a low volatile content while the values of T_m clat >10°C suggest the presence of
791 CH₄ and N₂.

792

793 **9. Discussion**

794

795 *9.1. Timing of magmatic and hydrothermal episodes in the Puy-les-Vignes deposit*

796 The ⁴⁰Ar/³⁹Ar mica dates obtained in this work yield a weighted mean date of 321 ± 2 Ma
797 (2σ, MSWD = 1.7; n = 36), which falls in the same interval than the U/Pb rutile dates. Because
798 the closure temperature for Ar diffusion in mica (ca. 350-400°C; Harrison et al., 2009) is much
799 lower than Pb diffusion in rutile (>600°C; Vry and Baker, 2006), the obtained ⁴⁰Ar/³⁹Ar mica
800 dates correspond either to crystallization ages or to ages of isotope resetting during fluid-rock
801 interactions. The paleodepth of formation of the Puy-les-Vignes deposit is estimated at ca. 7 km
802 (see section 9.2), which corresponds to regional temperatures of about 280°C assuming a
803 geothermal gradient of 40°C km⁻¹ typical for continental collisional orogens (Huerta et al.,
804 1998). The estimated temperatures are lower than the temperature of Ar retention in micas
805 implying that magmas intruded into the regional host rocks or hydrothermal fluids circulating
806 through will cool down rapidly by thermal conduction. Therefore, we interpret the ⁴⁰Ar/³⁹Ar

807 mica and adularia dates obtained in this work as crystallization ages.

808 The earliest magmatic event at Puy-les-Vignes corresponds to the emplacement of
809 lamprophyre dykes into the Saint-Léonard-de-Noblat gneisses at the intersection with the
810 breccia pipe. The dated lamprophyre sample yielded a weighted mean $^{40}\text{Ar}/^{39}\text{Ar}$ biotite date of
811 331 ± 14 Ma. The lower limit of this date is intersected by the dated microgranite that is known
812 to crosscut the lamprophyre and yields a weighted mean $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite date of 323 ± 4
813 Ma. This indicates an episode of mantle melting between ca. 345 and ca. 327 Ma, similar to
814 vaugnerite dykes dated at 334 ± 1 Ma and 336 ± 2 Ma in the eastern FMC (Laurent et al., 2017).
815 The date of the microgranite falls into the age range of two-mica peraluminous granitoids from
816 the northwestern FMC (Fig. 20), such as the Saint-Sylvestre leucogranitic complex (324 ± 4
817 Ma; Holliger et al., 1986) or the nearby Auriat granite (324 ± 1 Ma; Gebauer et al., 1981).
818 Therefore, we interpret the $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite date for the microgranite to represent the
819 crystallization age. The last known magmatic event at Puy-les-Vignes corresponds to the
820 intrusion of a RMG that yielded a weighted mean $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite date of 311 ± 5 Ma. This
821 date falls in the same age interval of ca. 315-310 Ma than other RMG-RMP in the Limousin
822 (Fig. 20; Cheilletz et al., 1992; Alexandrov et al., 2000; Cuney et al., 2002; Melleton et al.,
823 2015). Because the studied RMG lacks hydrothermal alteration features, the $^{40}\text{Ar}/^{39}\text{Ar}$ date of
824 311 ± 5 Ma is interpreted as the crystallization age.

825 Based on field relationships and petrographic observations, the Puy-les-Vignes breccia
826 pipe results from multistage hydrothermal fluid episodes. The $^{40}\text{Ar}/^{39}\text{Ar}$ dates of 324 ± 5 Ma
827 and 318 ± 5 Ma on hydrothermal muscovite and the U/Pb dates on rutile of 322 ± 10 Ma and
828 323 ± 5 Ma from stages I and II overlap between ca. 323 and ca. 318 Ma (Fig. 20). These ages
829 are consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ plateau age of 323 ± 2 Ma obtained on a muscovite interpreted
830 to be prior or coeval to wolframite deposition (Cuney et al., 2002). U/Pb dating of wolframite
831 yielded a concordia age of 317.7 ± 0.7 Ma (Harlaux et al., 2018a), which is compatible with the
832 previous ages and points toward a W mineralization episode at ca. 318 Ma. The period of ca.
833 325 to ca. 315 Ma is synchronous to the emplacement of two-mica peraluminous leucogranites
834 in the Limousin such as the La Porcherie granite (317 ± 3 Ma; Lafon and Respaut, 1988), the
835 Courcelles granite (318 ± 3 Ma; Cartannaz et al., 2007), the Glény granite (318 ± 3 Ma; Faure
836 et al., 2009b), the Pradines granite (313 ± 4 Ma; Gébelin et al., 2009), and the Livradois granite
837 (315 ± 4 Ma; Gardien et al., 2011). Crustal melting was coeval with HT-LP metamorphism as
838 evidenced by cordierite-sillimanite migmatites that formed at 315 ± 5 Ma and 316 ± 2 Ma along
839 the western border of the Millevaches leucogranitic complex (Gébelin et al., 2009). The
840 $^{40}\text{Ar}/^{39}\text{Ar}$ adularia date of 302 ± 4 Ma (stage IV) records a late hydrothermal episode that is

841 temporally disconnected from previous stages. This age is synchronous with the cooling and
842 exhumation of the Limousin metamorphic basement at ca. 305-300 Ma (Scaillet et al., 1996a;
843 Le Carlier de Veslud et al., 2013) related to the late- to post-orogenic uplift and generalized
844 extension of the FMC (Faure et al., 2009a). The Bi±Au-Ag assemblage (stage V) was therefore
845 formed during or after the 305-300 Ma period coevally with orogenic Au deposits in the FMC
846 that share mineralogical features and result from the mixing of metamorphic and meteoric fluids
847 (Boiron et al., 2003; Bouchot et al., 2005).

848

849 *9.2. Nature and pressure-temperature conditions of the mineralizing fluids*

850 The W-mineralizing fluids in the Puy-les-Vignes deposit are characterized by a low to
851 moderate salinity (0.7-8.7 wt.% NaCl eq), elevated homogenization temperatures (250-455°C),
852 and high contents of CO₂ (avg = 10 mol%), CH₄ (avg = 1.6 mol%), and N₂ (avg = 1.1 mol%).
853 These fluid compositions belong to the C-O-H-N system and are similar to other peri-granitic
854 W-Sn deposits in the FMC (Ramboz et al., 1985; Bril and Beaufort, 1989; Cuney et al., 1992;
855 Lerouge et al., 2000; Vallance et al., 2001). Similar C-O-H-N fluids have been described in
856 other Variscan W-Sn deposits (Noronha et al., 1992; Vindel et al., 1995; Chicharro et al., 2016),
857 in evolved pegmatites and leucogranites (Charoy and Noronha, 1996; Fuertes-Fuente et al.,
858 2000; Bakker and Schilli, 2016), and in metamorphic environments (Van der Kerkhof et al.,
859 1991; Guedes et al., 2002; Boiron et al., 2007). The presence of CO₂ and CH₄ in FIs can result
860 from different mechanisms including high-temperature graphite-water interactions in
861 metasediments (Ramboz et al., 1985; Dubessy et al., 1989), degassing or flushing of CO₂ from
862 silicate melts (Lowenstern, 2001; Blundy et al., 2010), CO₂ reduction by hydrogen (Hall and
863 Bodnar, 1990), or boron complexing in aqueous-carbonic fluid (Huff and Nabelek, 2007). The
864 release of N₂ can originate from the breakdown of NH₄⁺-bearing mica and feldspar during
865 dehydration-melting of metasediments (Moine et al., 1994; Bebout et al., 1999; Pitcairn et al.,
866 2005) or from strongly reduced silicate melts (Boulliung et al., 2020).

867 Raman spectroscopy data of FIs from Puy-les-Vignes show an evolutionary trend between
868 a CO₂(>CH₄)-rich fluid endmember and a CH₄(>CO₂)-rich fluid endmember from Q1 to Q2
869 (Fig. 19E), which is compatible with decreasing temperatures of the graphite-water equilibrium
870 from >550°C to 400°C (Huizenga, 2001). While the relatively high N₂ content of FIs could
871 indicate a metamorphic component in the hydrothermal system, the variable CH₄ to N₂ ratios
872 suggest a two-component origin. Therefore, we interpret the C-O-H-N fluid compositions as
873 resulting from a moderate-salinity (>9 wt.% NaCl eq) and high-temperature (>450°C)
874 hydrothermal fluid that interacted with volatile-rich metasedimentary rocks and/or that mixed

875 with low-salinity metamorphic fluids equilibrated with such rocks. The Lw show a trend of
876 decreasing salinity (from >8.0 to <0.5 wt.% NaCl eq) with decreasing temperature (from >350
877 to <150°C), which is interpreted as a cooling-dilution trend (Fig. 19D). The Th variations for a
878 given composition are interpreted as recording anisothermal mixing under fluctuating pressure
879 conditions from lithostatic to hydrostatic (Dubessy et al., 2003) and partially disturbed by post-
880 entrapment reequilibration (e.g., necking-down). Two fluid endmembers are involved in the
881 mixing, i.e. a high-temperature (>350°C) and moderate-salinity (>9 wt.% NaCl eq) fluid L1,
882 similar to the mineralizing fluids from the stages II and III, and a low-temperature (<150°C)
883 and low-salinity (<0.5 wt.% NaCl eq) fluid L2, possibly of meteoric origin.

884 Pressure-temperature conditions of the Puy-les-Vignes deposit were reconstructed based
885 on representative isochores (Fig. 21). No boiling assemblages were observed in the FI
886 inventory, which precludes determining directly entrapment pressures based on
887 homogenization temperatures. In Q1, two families of isochores are distinguished for the Lc-w
888 and Lw-c (Fig. 21A): (i) high-angle isochores corresponding mostly to the regular and small
889 FIs; and (ii) low-angle isochores corresponding to the majority of irregular and large FIs
890 showing reequilibration features and to large and regular FIs. The two sets of isochores intersect
891 geothermal gradients at 60-70°C km⁻¹ for trapping temperatures of ca. 400-450°C and pressure
892 variations from ca. 190 MPa (lithostatic) to ca. 70 MPa (hydrostatic). These pressure estimates
893 indicate that the Puy-les-Vignes deposit formed at a paleodepth of ca. 7 km. Similar trapping
894 conditions are estimated for the Lw-c hosted in wolframite. The pressure variations, from
895 lithostatic to hydrostatic, are interpreted to result from the hydraulic fracturing of the host rocks
896 during the breccia pipe formation. The differential pressure of 120 MPa between the lithostatic
897 and hydrostatic gradients is equal to the minimum ΔP required to reequilibrate a 20 μm diameter
898 FI hosted in quartz (Bodnar et al., 1989). Trapping temperatures are more than 100°C lower
899 than those calculated by the Zr-in-rutile thermometer of $546 \pm 32^\circ\text{C}$, suggesting that
900 hydrothermal rutile yields overestimated temperatures, as also documented by Cabral et al.
901 (2015). Representative isochores for the Lc-w and Lw-c hosted in Q2 yield similar trapping
902 conditions of ca. 400-420°C and pressure fluctuations from ca. 190 MPa (lithostatic) to ca. 70
903 MPa (hydrostatic) for high geothermal gradients of 60-70°C km⁻¹ (Fig. 21B). Pressure
904 variations from ca. 135 MPa (lithostatic) to ca. 50 MPa (hydrostatic) are estimated for trapping
905 of the Lw, when the same ΔP is encountered for the L1 (380°C with a 70°C km⁻¹ gradient) and
906 L2 (210°C with a 40°C km⁻¹ gradient) fluid endmembers (Fig. 21C). This would correspond to
907 a paleodepth of ca. 5 km for trapping of Lw. Compared to previous stages, the Lw records a
908 decrease of the reservoir depth (from 7 to 5 km) likely related to an increased exhumation.

909 Assuming an erosion rate of 0.5-1.0 mm yr⁻¹, representative for the exhumation of the Variscan
910 basement during the late Carboniferous (Scaillet et al., 1996b; Schulmann et al., 2002), the
911 erosion of 2 km of rock thickness between the stage II and the Lw stage would require between
912 2 and 4 My. Considering that the W mineralization formed at ca. 318 Ma, the Lw would have
913 been trapped between 314 and 316 Ma. The Lw represent, therefore, a late stage in the Puy-les-
914 Vignes hydrothermal system, which possibly records the infiltration of meteoric waters during
915 the late Carboniferous uplift of the FMC, as also evidenced in other W-Sn deposits (Vallance et
916 al., 2001) and orogenic Au deposits (Boiron et al., 2003) from the Limousin area.

917

918 *9.3. Hydrothermal fluid origin and wolframite precipitation*

919 The Puy-les-Vignes breccia pipe resulted from intense hydrofracturing of the Saint-
920 Léonard-de-Noblat gneiss unit by overpressured hydrothermal fluids, as evidenced by
921 characteristic textures of hydraulic brecciation and fluid-assisted rotation of metric-size clasts
922 (Jébrak, 1997). Wolframite from Puy-les-Vignes shows similar trace element composition than
923 evolved peraluminous granites from the FMC (Harlaux et al., 2018b), suggesting that W and
924 related metals were sourced from an unexposed leucogranite located beneath the breccia pipe.
925 Tungsten could be released either by magmatic fluids due to elevated fluid-melt-crystal
926 partitioning coefficients (Hulsbosch et al., 2016; Schmidt et al., 2020) or by metamorphic fluids
927 during high-temperature interactions with two-mica leucogranite (Vallance et al., 2001; El Korh
928 et al., 2020; Carocci et al., 2020). The importance of fluid-rock interactions is also supported
929 by the chemical and boron isotope compositions of tourmaline that are compatible with both a
930 magmatic and a metamorphic fluid source (Harlaux et al., 2019) as well as by the Fe-dominated
931 composition of wolframite (Michaud and Pichavant, 2019). The origin of the hydrothermal
932 fluids (magmatic vs metamorphic) can be further discussed based on estimation of the volume
933 of fluids required for precipitation of quartz and wolframite (Supplementary Table 7).
934 Considering an elliptic surface of dimensions 340 x 80 m and a vertical extension of 600 m
935 (i.e., twice the known height) for the breccia pipe, the total volume of rock would be of $5.1 \times$
936 10^7 m³. Assuming that quartz represents about 10% of the total volume of the breccia (Weppe,
937 1951, 1958), a mass of 1.3×10^{10} kg of quartz can be estimated. Taking into account a quartz
938 solubility of 55 mmol kg⁻¹ for a hydrothermal fluid at 10 wt.% NaCl eq, 500°C and 100 MPa
939 (Monecke et al., 2018) and an average fluid density of 0.67 g cm⁻³, we estimate a volume of
940 fluids of 6.1×10^9 m³ (6.1 km³). Following the same reasoning for wolframite, we can estimate
941 a volume of fluids of 1.6×10^8 m³ (0.16 km³) by assuming an average grade of 0.5% WO₃ and
942 considering a W solubility of 500 ppm for a fluid at 10 wt.% NaCl eq, 500°C, and 100 MPa

943 (Wood and Samson, 2000). Therefore, the minimum volume of hydrothermal fluids required
944 for the formation of the wolframite-bearing breccia pipe would be of about 6.2 km³. It is
945 noteworthy that these calculations assume 100% efficiency of mineral precipitation and no fluid
946 loss in the host rocks, implying that the volume of fluids involved should be larger than this
947 estimation.

948 (i) *Magmatic fluid origin:* Assuming that the volume of fluids of 6.2 km³ was
949 entirely produced by a water-saturated intrusion containing an initial water content of 5 wt.%,
950 this would require a minimum volume of melt of ca. 36 km³ for an average melt density of 2.3
951 g cm⁻³ (Supplementary Table 7). Considering a volume contraction of 10% from liquidus to
952 solidus (Bea, 2010), this would correspond to a volume of granite of 33 km³, i.e. a pluton of
953 dimensions 1.5 x 4.7 x 4.7 km. Fluids that exsolve from an intrusion at a depth >6 km
954 (corresponding to a lithostatic pressure >150 MPa) are in the single-phase domain at magmatic
955 conditions and remain in this state during cooling to 500°C (Driesner and Heinrich, 2007).
956 Consequently, fluids trapped at these pressure-temperature conditions have a moderate salinity
957 (ca. 10 wt.% NaCl eq), an intermediate density (ca. 0.6 g cm⁻³) and do not undergo boiling. This
958 model explains the absence of coexisting vapor and hypersaline fluid inclusions (boiling
959 assemblage), the moderate fluid salinity (<9 wt.% NaCl eq), as well as the high geothermal
960 gradients of 60-70°C km⁻¹ determined from the P-T reconstruction. The overpressures
961 generated by the exsolved magmatic fluids could be a mechanism for the hydraulic brecciation,
962 as generally proposed for the formation of breccia pipes (Burnham, 1985; Sillitoe, 1985; Jébrak,
963 1997). The high CO₂ content (avg = 10 mol%) determined in FIs fall in the same range than
964 magmatic fluids from porphyry systems (Kouzmanov and Pokrovski, 2012). In this scenario,
965 magmatic fluids exsolved from an evolved leucogranite would have interacted with volatile-
966 rich metamorphic rocks resulting in the cooling, dilution, and enrichment in metamorphic-
967 derived volatiles (mainly CH₄ and N₂). The main limitation of this model is the volume of fluids
968 required since numerical modelling shows that magmatic fluids are released by successive
969 pulses from crystallizing intrusions (Weis et al., 2012; Lamy-Chappuis et al., 2020). This would
970 imply a much larger volume of granitic melt than the one estimated in order to supply in a single
971 time the volume of fluids required to generate the breccia pipe.

972 (ii) *Metamorphic fluid origin:* Considering that the fluids were produced by
973 devolatilization reactions of volatile-rich metasedimentary rocks, the question arises about the
974 source reservoir. The LGU hosting the Puy-les-Vignes deposit experienced migmatization
975 during the Middle Devonian (385-375 Ma) at metamorphic conditions of 650-750°C and 700
976 MPa (“D1 event” of Faure et al., 2009a) implying the muscovite- and biotite-breakdown

977 reactions. Consequently, the LGU paragneisses cannot be a local source of metamorphic fluids
978 at 318 Ma. In contrast, the PAU, structurally located below the LGU, never experienced the D1
979 metamorphism nor migmatization and records maximum metamorphic conditions of 500-
980 600°C and 700-800 MPa (Do Couto et al., 2016) during the early Carboniferous (360-350 Ma)
981 (“D2 event” of Faure et al., 2009a). Thus, the PAU micaschists underlying the LGU gneisses
982 may represent a distal source of metamorphic fluids produced by the HT-LP metamorphism
983 during the late Carboniferous (320-315 Ma). Deep metamorphic fluids could be gathered into
984 a collection zone, then focused and channelized in a mid-crustal fault zone, ascending at high
985 rates up to a dispersion region in cooler rocks (Thompson and Connolly, 1992; Connolly, 1997;
986 Carocci et al., 2020). The half-width of both collection and dispersion zones is typically in the
987 3-5 km range, and the height of the system is on the order of 10 to 15 km. This model accounts
988 for the high volume of fluids required, the upward heat advection, and the high CO₂-CH₄-N₂
989 contents of the fluids. The rapid and adiabatic ascending of pressurized volatile-rich fluids
990 along a crustal fault zone under the LGU carapace may represent a mechanism for generating
991 hydraulic fracturing of the host rocks. The main limitation of this model is that devolatilization
992 of graphite-rich pelitic metasediments only produce low-salinity (typically <5 wt.% NaCl eq)
993 metamorphic fluids (Guedes et al., 2002; Yardley and Graham, 2002).

994 Based on available data, we favor an intermediate model involving a W-bearing magmatic
995 fluid exsolved from an evolved leucogranite that interacted and possibly mixed with low-
996 salinity volatile-rich metamorphic fluids of distal origin (Fig. 22). Experimental works and
997 thermodynamic modelling show that the solubility of wolframite in hydrothermal fluids
998 increases with increasing temperature and salinity and with decreasing pH and Fe contents of
999 the fluid (Wood and Samson, 2000; Wang et al., 2019). Addition of non-polar molecules such
1000 as N₂, CO₂, and CH₄ yields a decrease of W concentration in solution (Dubessy et al., 1989;
1001 Gibert et al., 1992). Precipitation of wolframite at Puy-les-Vignes could have been triggered by
1002 several processes including cooling, depressurization, fluid mixing, and fluid-rock interaction
1003 (Heinrich et al., 1990; Wei et al., 2012; Dewaele et al., 2016; Chicharro et al., 2016;
1004 Lecumberri-Sanchez et al., 2017; Legros et al., 2019, 2020; Monnier et al., 2020). In particular,
1005 fluid pressure drop induced by hydrofracturing of the host rocks results in significant decrease
1006 of CO₂ solubility and pH increase, which can cause in turn wolframite precipitation (Liu et al.,
1007 2017).

1008

1009 *9.4. Overprint of the W-mineralized system by a rare-metal granite*

1010 Wolframite deposition in the Puy-les-Vignes deposit occurred during the main ore stage II

1011 at 318 Ma and was followed by precipitation of accessory W-Nb-Ta oxide minerals
1012 (wolframoixiolite, Ta-Nb-ferberite, and W-Nb-Ta-rutile). Wolframoixiolite is found as infill of
1013 dissolution microvugs in wolframite, in quartz-filled veinlets cutting wolframite, and as
1014 disseminations overgrown by ferberite-1 within scheelite; all together suggesting that the fluid
1015 having precipitated wolframoixiolite was out of equilibrium with wolframite. Ferberite-1 cuts
1016 and replaces wolframite along crystal borders and in dissolution microvugs and locally shows
1017 Ta-Nb-rich primary zoning. Such primary textures are similar to those described for Nb-rich
1018 ferberite from the Echassières W deposit in the northern FMC (Aïssa et al., 1987; Harlaux et
1019 al., 2018a,b). Nb-Ta-rich rutile is found as disseminations within ferberite-1 and forms
1020 corrosive overgrowths on Fe-W-rutile, the latter being interpreted as coeval with wolframite
1021 deposition similarly to the findings of Carocci et al. (2019) in the Panasqueira W deposit
1022 (Portugal). Several studies showed that the association of Ta-Nb-ferberite, W-Nb-Ta-rutile,
1023 wolframoixiolite, and columbite-tantalite minerals is a marker of the magmatic-hydrothermal
1024 transition in RMG-RMP (Breiter et al., 2007, 2017; Alekseev et al., 2011; René and Škoda,
1025 2011; Zhu et al., 2015, 2019; Michaud et al., 2020). The studied sample of RMG exhibits all
1026 the mineralogical and geochemical features of a highly fractionated P-rich peraluminous RMG
1027 cupola (Cuney et al., 1992; Raimbault et al., 1995; Zhu et al., 2001; Breiter et al., 2005; Linnen
1028 and Cuney, 2005) and shows similarities with other P-rich peraluminous RMG-RMP from the
1029 northern FMC (Aubert, 1969; Mourey, 1985; Cuney et al., 1992; Raimbault et al., 1995;
1030 Raimbault, 1998). Additionally, columbite-tantalite disseminated in the RMG exhibits an
1031 increasing Ta/(Ta+Nb) ratio at relatively constant Mn/(Mn+Fe) ratio from core to rim, as also
1032 documented in other RMG-RMP from the northern FMC (Wang et al., 1992; Belkasmı and
1033 Cuney, 1998; Belkasmı et al., 2000). The progressive increase in the Ta/(Ta+Nb) ratio may
1034 reflect either a magmatic fractionation trend due to the higher solubility of tantalite relative to
1035 columbite in peraluminous melts, or the effect of fluid-mineral interaction during a late
1036 hydrothermal remobilization (Linnen and Cuney, 2005; Van Lichtenvelde et al., 2007; Breiter
1037 et al., 2007; Zhu et al., 2015; Wu et al., 2018).

1038 Experimental works and fluid-melt-crystal partitioning calculations show that W partitions
1039 readily into magmatic fluid relative to the silicate melt in peraluminous granites (Zajacz et al.,
1040 2008; Hulsbosch et al., 2016; Schmidt et al., 2020). In contrast, Nb and Ta preferentially
1041 partition into the silicate melt (Linnen and Cuney, 2005; Borodulin et al., 2009). However, the
1042 solubility of Nb and Ta is strongly enhanced in F-rich hydrothermal fluids as shown by
1043 experimental studies (Zaraisky et al., 2010; Timofeev et al., 2015, 2017). As a consequence, F-
1044 rich magmatic fluids released during crystallization and water saturation of a RMG melt can

1045 transport significant amounts of W, Nb, and Ta. This is confirmed by elevated concentrations
1046 of W (>100s ppm) and Nb-Ta (>1,000s ppm) measured in individual primary fluid inclusions
1047 (400 to >600°C, 18 to 48 wt.% NaCl eq) from the Beauvoir RMG, for which a F content of
1048 about 1.6-2.0 wt.% was estimated in the magmatic fluid (Harlaux et al., 2017). The nearby La
1049 Bosse quartz-ferberite stockwork was strongly overprinted by the magmatic fluids issued from
1050 the Beauvoir granite, resulting in crystallization of topaz, partial dissolution of quartz, and
1051 precipitation of accessory Li-micas and W-Nb-Ta oxides (Aïssa et al., 1987; Cuney et al., 1992).
1052 Specifically, Ta-rich ferberite, wolframoixiolite, and columbite-tantalite minerals were
1053 described in dissolution microvugs within ferberite and were interpreted to be precipitated by
1054 the magmatic fluids released from the Beauvoir granitic melt (Cuney et al., 1992; Harlaux et
1055 al., 2017). Consequently, we propose that the W-Nb-Ta oxide assemblages observed in the
1056 quartz-wolframite veins from the Puy-les-Vignes deposit were precipitated from a magmatic-
1057 hydrothermal fluid issued from a concealed P-rich peraluminous RMG that overprinted the W-
1058 mineralized system (Fig. 22).

1059

1060 **10. Conclusions**

1061

1062 We showed that the formation of the Puy-les-Vignes W breccia pipe results from a
1063 multistage development between ca. 25 My related to four major episodes during the late
1064 Carboniferous. The first episode corresponds to the emplacement of an unexposed
1065 peraluminous granite at ca. 324 Ma, which generated microgranite dykes exposed at the
1066 present-day surface. The second episode consists of the formation of the quartz-supported
1067 breccia pipe and wolframite mineralization at ca. 318 Ma at a paleodepth of ca. 7 km. The
1068 mineralizing fluids have a H₂O-NaCl-CO₂-CH₄-N₂ composition, a moderate-salinity (<9 wt.%
1069 NaCl eq) and were trapped at high-temperatures (>400°C) during lithostatic to hydrostatic
1070 pressure variations caused by hydrofracturing of the host rocks. We interpret wolframite
1071 precipitation as the result of mixing between a W-rich magmatic fluid exsolved from an evolved
1072 leucogranite and low-salinity volatile-rich metamorphic fluids of distal origin. The third
1073 episode corresponds to a Nb-Ta mineralization interpreted to be related to the intrusion at ca.
1074 311 Ma of a P-rich peraluminous RMG overprinting the W-mineralized system. The last
1075 episode corresponds to a disseminated Bi±Au-Ag mineralization emplaced at ca. 300 Ma,
1076 which shares mineralogical features with orogenic Au deposits in the FMC.

1077

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1094

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1759 **Figure captions**

1760

1761 **Fig. 1.** (A) Geological setting and location of the Puy-les-Vignes (PLV) deposit in the
1762 northwestern French Massif Central (FMC). (B) Simplified geologic NE-SW cross-section
1763 through the northwestern FMC showing the stack of metamorphic nappes (modified from
1764 Lardeaux et al., 2014). The location of the cross-section is reported on Figure 1A (dashed red
1765 line).

1766

1767 **Fig. 2.** Regional geological setting of the Puy-les-Vignes (PLV) deposit. (A) Geological map
1768 of the Puy-les-Vignes area and location of the surroundings W occurrences (modified from
1769 Chenevoy et al., 1984). (B) Close-up sketch of the breccia pipe structure at surface intersected
1770 by wolframite-bearing veins (modified from Weppe, 1951). (C) Interpretative cross-section
1771 through the Puy-les-Vignes breccia pipe projected along the NW-SE major axis (modified from
1772 Weppe, 1951, 1958). (D) Simplified sketch showing the apparent rotational movement of the
1773 clasts within the breccia pipe according to Weppe (1951, 1958).

1774

1775 **Fig. 3.** Field relations of the Puy-les-Vignes breccia pipe. (A) Outcrop of the polygenic breccia
1776 composed of decimetric to metric clasts of altered gneisses (Gn) and granites (Gr) partially to
1777 completely tourmalinized. The clasts are angular to subangular in shape and are systematically
1778 rimmed by tourmaline (Tur) and cemented by quartz (Qtz). (B-C) Details of greisenized
1779 gneissic clasts showing relict foliation (white dashed lines) and an irregular tourmalinite aureole
1780 of variable thickness. (D) Wolframite (Wfm) disseminated within the quartz of the breccia and
1781 partially altered by goethite (Gt). (E) Wolframite-bearing quartz vein with tourmaline selvages
1782 crosscutting the St-Léonard-de-Noblat gneisses observed in an old underground adit at Lifarnet.

1783

1784 **Fig. 4.** Representative samples of host rocks and orebodies from the Puy-les-Vignes deposit.
1785 (A) Polygenic breccia constituting the main body of the pipe composed of angular to subangular
1786 clasts of greisenized gneisses (Gn) and granites (Gr) rimmed by an aureole of tourmalinite and
1787 cemented by milky quartz (sample PLV-02-04). (B) Typical clast of greisenized gneiss rimmed
1788 by a cm-thick aureole of tourmalinite and cemented by quartz (sample PLV-7571). (C)
1789 Wolframite-bearing quartz vein crosscutting gneiss (sample PLV-7574). (D) Typical vein
1790 assemblage composed of quartz, wolframite and arsenopyrite with minor chalcopyrite (sample
1791 PLV-02-29). (E) Wolframite partially replaced by orange-brownish-colored scheelite in a quartz
1792 vein (sample PLV-3071). (F) Spectacular sample of centimetric ferberite pseudomorph after

1793 scheelite (“reinite”). (G) Microgranite dyke (Mg) crosscutting the foliation of biotite-sillimanite
1794 gneiss (sample PV-92-7). (H) Rare-metal granite (RMG) showing a magmatic layering
1795 composed of a repetitive sequence of quartz-albite-muscovite bands (“B1”) evolving to albite-
1796 quartz bands (“B2”) (sample PLV-02-02). The last albite-quartz zone in the lower part of the
1797 sample shows unidirectional solidification texture (UST) preceding the transition to a granitic
1798 pegmatite (Pgm). Mineral abbreviations according to the IMA.

1799

1800 **Fig. 5.** Paragenetic sequence of the Puy-les-Vignes deposit showing the succession of six main
1801 hydrothermal stages. Dash lines represent minor episodes of hydraulic fracturing. See text for
1802 details.

1803

1804 **Fig. 6.** Photomicrographs of mineral assemblages for paragenetic stages I to VI of the Puy-les-
1805 Vignes deposit. (A) Greisenized gneiss composed of secondary quartz, muscovite and
1806 tourmaline with partially preserved foliation (stage Ia; crosspolarized transmitted light, sample
1807 PLV-02-01a). (B) Tourmalinite rim on a gneissic clast composed of prismatic tourmaline
1808 aggregates cemented by macrocrystalline quartz (stage Ib; plane-polarized transmitted light,
1809 sample PLV-02-01a). (C) Subeuhedral wolframite grain overgrown by muscovite showing
1810 kink-band deformation (stage II; crosspolarized transmitted light, sample PLV-02-03). (D)
1811 Wolframite partially replaced by ferberite-1 along crystal borders and crosscut by scheelite
1812 veinlets (stage II; reflected light, sample PLV-7597a). (E) Wolframite partially replaced by
1813 arsenopyrite showing dissolution features (stage II; reflected light, sample PLV-02-28b). (F)
1814 Scheelite replacing wolframite and showing dissolution textures (stage II; plane-polarized
1815 transmitted light, sample PLV-7597b). (G) Polycrystalline aggregates of randomly-oriented
1816 fibrous ferberite-2 crystals (“reinite”) within ferberite-1 (stage II; reflected light, sample PLV-
1817 02-11). (H) Ferberite-2 pseudomorph after scheelite (“reinite”) (stage II; plane-polarized
1818 transmitted light, sample PLV-02-26). (I) Base metal sulfide association (pyrite, chalcopyrite
1819 and tennantite) overprinting wolframite (stage III; reflected light, sample PLV-02-29). (J)
1820 Arsenopyrite crosscut by a chalcopyrite-tennantite veinlet (stage III; reflected light, sample
1821 PLV-7574a). (K) Pyrite-chalcopyrite veinlet crosscutting wolframite and scheelite (stage III;
1822 reflected light, sample PV-2a). (L) Sphalerite crosscut by chalcopyrite and pyrite association
1823 (stage III; reflected light, sample PV-3). (M) Scheelite containing relicts of wolframite and
1824 fragmented by a tourmaline-adularia crackle breccia (stage IV; plane-polarized transmitted
1825 light, sample PLV-02-13a). (N) Detail of the microbreccia composed of clasts of tourmaline,
1826 vermicular chlorite, and Nb-Ti-Y-HREE-W-U oxides (NTox) within an adularia matrix (stage

1827 IV; plane-polarized transmitted light, sample PLV-02-13a). (O) Adularia veinlet crosscutting
1828 quartz, siderite and chalcopyrite association (stage IV; reflected light, sample PV-2b). (P)
1829 Wolframite overprinted by scorodite and goethite resulting from complete dissolution of
1830 arsenopyrite (stage VI; plane-polarized transmitted light, sample PLV-02-17). Mineral
1831 abbreviations according to the IMA.

1832

1833 **Fig. 7.** Backscattered electron images of mineral assemblages for paragenetic stages I to VI of
1834 the Puy-les-Vignes deposit. (A) Subeuhedral Fe-W-rutile (Rt-1) intergrown with tourmaline on
1835 a greisenized granitic clast (stage I; sample PLV-02-04a). (B) Wolframite partially altered to
1836 ferberite-1 and scheelite showing patchy texture at microscopic scale (stage II; sample PLV-
1837 7597a). (C) Arsenopyrite-1 (stage II) cut by arsenopyrite-2 veinlets and hosting numerous tiny
1838 inclusions of native bismuth (stage V; sample PLV-7597a). (D) Cassiterite intergrown with
1839 arsenopyrite (stage II) crosscut by chalcopyrite veinlets (stage III; sample PV-2a). (E)
1840 Subeuhedral Fe-W-rutile (Rt-1) overgrown by Nb-Ta-rich rutile (Rt-2) disseminated in a quartz-
1841 wolframite vein (stage II; sample PLV-7574a). Fe-W-rutile shows a homogeneous core (dark
1842 grey) with W-rich sectors (light grey) having growth zoning. (F) Fe-Nb-rich rutile (Rt-3) within
1843 ferberite-1 showing growth banding (stage II; sample PLV-02-17). (G) Ta-Nb-rich ferberite-1
1844 in a dissolution microvug within wolframite showing Ta-Nb-rich growth bands at the
1845 micrometer scale (stage II; sample PV-3). (H) Wolframoixiolite in a quartz-filled veinlet
1846 crosscutting wolframite (stage II; sample PV-5a). (I) Wolframoixiolite rimmed and partially
1847 replaced by ferberite-1 within scheelite (stage II; sample PLV-02-13b). (J) Subeuhedral grains
1848 of Cr-Nb-W-rich rutile (Rt-4) disseminated within arsenopyrite (stage III; sample PLV-02-28b).
1849 (K) Arsenopyrite crosscut by chalcopyrite-pyrite-chlorite veinlets (stage III) and overprinted by
1850 native Bi microinclusions (stage V; sample PV-3). (L) Exsolution trails of stannite within
1851 chalcopyrite (stage III; sample PV-2a). (M) Association of native Bi and electrum (Au-Ag) in
1852 microvugs infilling arsenopyrite and Fe-skutterudite (stage V; sample PLV-7597a). (N)
1853 Colloform As-rich pyrite overgrown on euhedral arsenopyrite-3 and chalcopyrite (stage V;
1854 sample PV-2b). (O) As-rich pyrite and siderite (stage V) overgrown on sphalerite and
1855 chalcopyrite from stage III (sample PV-2b). (P) As-rich pyrite and siderite crosscutting an
1856 adularia veinlet (stage V; sample PV-2b). Mineral abbreviations according to the IMA.

1857

1858 **Fig. 8.** Photomicrographs of granitic rocks from the Puy-les-Vignes deposit. (A) Microgranite
1859 dyke composed of quartz, plagioclase and muscovite showing sericitic alteration
1860 (crosspolarized transmitted light, sample PV-92-7). (B) Quartz-albite-muscovite zone within

1861 the RMG (crosspolarized transmitted light, sample PLV-02-02). (C) Albite-quartz zone within
1862 the RMG containing disseminated cassiterite (crosspolarized transmitted light, sample PLV-02-
1863 02). (D) Globular “snowball” quartz phenocryst containing poikilitic inclusions of rotated albite
1864 laths (white dashed lines) in the RMG (crosspolarized transmitted light, sample PLV-02-02).
1865 Mineral abbreviations according to the IMA.

1866

1867 **Fig. 9.** Major element compositions of granitic rocks from the Puy-les-Vignes deposit compared
1868 to the main peraluminous granitoids from the northwestern French Massif Central (FMC). (A)
1869 Alumina saturation diagram representing the molar ratio $A/NK = Al_2O_3/(Na_2O+K_2O)$ as
1870 function of the molar ratio $A/CNK = Al_2O_3/(CaO+Na_2O+K_2O)$. (B) B-A diagram representing
1871 the differentiation index $B = Fe+Mg+Ti$ as function of the peraluminous index $A = Al-$
1872 $(Na+K+2Ca)$ expressed in millications (after Debon and Lefort, 1983). The peraluminous
1873 granite fields of Villaseca et al. (1998) represent highly peraluminous granitoids (h-P),
1874 moderately peraluminous granitoids (m-P), low peraluminous granitoids (l-P), and highly felsic
1875 peraluminous granitoids (f-P). (C) P-Q diagram representing the relative proportion of feldspar
1876 $P = K-(Na+Ca)$ as function of the quartz content $Q = Si/3-(Na+K+2Ca/3)$ expressed in
1877 millications (after Debon and Lefort, 1983). (D) Total alkali-silica (TAS) diagram representing
1878 the Na_2O+K_2O vs SiO_2 content (after Le Bas et al., 1986). Whole-rock compositions of the
1879 granitic rocks are reported in Table 1. Data sources: *rare-metal granites and pegmatites*: Aubert
1880 (1969), Mourey (1985), Cuney et al. (1992), Raimbault et al. (1995), Raimbault (1998),
1881 Raimbault and Burnol (1998); *muscovite-bearing peraluminous granitoids*: Gauthier (1973),
1882 Burnol (1974), Arniaud et al. (1984), Soufi (1988), Leger et al. (1990), Downes et al. (1997),
1883 Solgadi et al. (2007), Moyen et al. (2017), Villaros and Pichavant (2019); *cordierite-bearing*
1884 *peraluminous granitoids*: Downes and Duthou (1988), Williamson et al. (1996), Downes et al.
1885 (1997), Cartannaz (2005), Solgadi et al. (2007), Couzinié (2017), Moyen et al. (2017).

1886

1887 **Fig. 10.** Trace element compositions of granitic rocks from the Puy-les-Vignes deposit
1888 compared to the main peraluminous granitoids from the northwestern French Massif Central
1889 (FMC). (A-B) Multi-element diagrams normalized by the upper continental crust (UCC) values
1890 from Rudnick and Gao (2003). (C-D) Rare earth element diagrams normalized by chondrite
1891 values from McDonough and Sun (1995). Whole-rock compositions of the granitic rocks are
1892 reported in Table 1. Data were compiled from the same sources as Figure 9.

1893

1894 **Fig. 11.** Chemical compositions of hydrothermal rutile from Puy-les-Vignes plotted in the

1895 ternary diagram (Nb+Ta)-(Ti+Sn+W)-(Fe+Mn+Cr+Sc).

1896

1897 **Fig. 12.** Backscattered electron images and chemical compositions of magmatic and
1898 hydrothermal cassiterite from Puy-les-Vignes plotted in the ternary diagram (Nb+Ta)-
1899 (Ti+Sn+W)-(Fe+Mn). Magmatic cassiterite differs texturally from hydrothermal cassiterite by
1900 a discrete zoning and microinclusions of columbite-tantalite minerals (Clb-Tnt).

1901

1902 **Fig. 13.** Chemical compositions of wolframoixiolite from Puy-les-Vignes plotted in the ternary
1903 diagram (Nb+Ta)-(Ti+Sn+W)-(Fe+Mn).

1904

1905 **Fig. 14.** (A) Backscattered electron images of columbite-tantalite disseminated in the Puy-les-
1906 Vignes RMG. (B) Chemical compositions of columbite-tantalite plotted in the Ta/(Ta+Nb) vs
1907 Mn/(Fe+Mn) diagram.

1908

1909 **Fig. 15.** Tera-Wasserburg diagrams for two samples of hydrothermal rutile hosted in quartz-
1910 wolframite-arsenopyrite veins from the Puy-les-Vignes deposit. Weighted mean ages are
1911 calculated from linear regression of the discordia line crossing the concordia curve at its lower-
1912 age intercept. Error ellipses are quoted at 2σ level of uncertainty. U/Pb isotopic data are reported
1913 in Table 2.

1914

1915 **Fig. 16.** $^{40}\text{Ar}/^{39}\text{Ar}$ weighted mean ages obtained for micas and adularia from the Puy-les-Vignes
1916 deposit. Blue lines represent apparent age calculated for each individual $^{40}\text{Ar}/^{39}\text{Ar}$ analysis.
1917 Black curves represent the probability density distribution of the data. Error bars are reported
1918 at 2σ level of uncertainty. $^{40}\text{Ar}/^{39}\text{Ar}$ isotopic data are reported in Table 3.

1919

1920 **Fig. 17.** Transmitted light photomicrographs of fluid inclusions (FIs) hosted in wolframite-
1921 bearing quartz veins from the Puy-les-Vignes deposit (sample PLV-7591, “filon 2”; sample PV-
1922 1, “filon T18”). (A) Isolated primary Lc-w surrounded by a halo of small neonate fluid
1923 inclusions (nFI) resulting from post-entrapment reequilibration. (B) Elongated cluster of
1924 decrepitated FIs possibly located at a growth zone boundary. (C) Cluster of decrepitated
1925 primary FIs cut by two pseudosecondary (ps) fluid inclusion planes (FIP) of regular Lw-c. (D)
1926 Clusters of partly decrepitated Lc-w cut by pseudosecondary FIP of partly decrepitated Lw-c
1927 and by secondary (s) FIP of regular Lw. (E) Pseudosecondary FIP of Lw-c, partly decrepitated,
1928 located at grain boundaries. (F) Isolated irregular three-phase Lc-w containing a carbonic liquid

1929 phase (L_{car}), a carbonic vapor phase (V_{car}), and an aqueous liquid phase (L_{aq}). (G) Very irregular
1930 two-phase FI showing an “atoll-like” stretching texture. (H) Isolated regular three-phase Lc-w.
1931 (I) Highly irregular three-phase Lc-w. (J) Isolated irregular three-phase Lc-w. (K) Two-phase
1932 Lw-c having variable vapor to liquid ratios. (L) Regular two-phase Lw-c along a
1933 pseudosecondary FIP. (M) Cluster of irregular two-phase Lw-c (sample PLV-02-12). (N)
1934 Isolated regular two-phase Lw-c. (O) Secondary FIP of regular two-phase Lw. (P) Regular two-
1935 phase Lw along a secondary FIP.

1936

1937 **Fig. 18.** Near-infrared (NIR) transmitted light photomicrographs of fluid inclusions (FIs) hosted
1938 in wolframite from the Puy-les-Vignes deposit (sample PLV-7591, “filon 2”). (A) Global view
1939 of the studied euhedral wolframite (Wfm) crystal hosted in quartz (Qtz). (B) Intracrystalline
1940 zone showing numerous primary (p) and secondary (s) FIs. (C) Secondary fluid inclusion planes
1941 (FIP) of Lw having negative crystal shapes crosscutting wolframite. (D) Primary Lw-c aligned
1942 along the c-axis of wolframite. (E) Pseudo-secondary (ps) FIP of Lw-c showing regular to
1943 slightly irregular shapes. (F-M) Representative two-phase Lw-c showing variable shapes and
1944 containing a vapor phase (V) and an aqueous liquid phase (L_{aq}).

1945

1946 **Fig. 19.** Compositions of fluid inclusions from the Puy-les-Vignes deposit determined by
1947 microthermometry and Raman spectroscopy. (A-C) Homogenization temperature for the Lc-w
1948 and Lw-c hosted in quartz and wolframite as function of the CO_2 melting temperature (T_m
1949 CO_2), the clathrate melting temperature (T_m clat), and salinity. (D) Homogenization
1950 temperature for the Lw hosted in quartz as function of salinity. (E) Volatile composition of the
1951 gas phase of Lc-w and Lw-c plotted in the CO_2 - CH_4 - N_2 ternary diagram. (F) Bulk composition
1952 of Lc-w and Lw-c plotted in the $H_2O/10-\Sigma$ volatile-NaCl ternary diagram.

1953

1954 **Fig. 20.** Summary of geochronological data for the Puy-les-Vignes deposit and comparison
1955 with published ages of peraluminous granitoids from the northwestern French Massif Central.
1956 Errors are reported at 2σ level of uncertainty. Black curves represent the probability density
1957 distribution of integrated ages. Data sources for the granitoids: Duthou (1978), Berthier et al.
1958 (1979), Gebauer et al. (1981), Duthou et al. (1984), Holliger et al. (1986), Lafon and Respaut
1959 (1988), Cheilietz et al. (1992), Cuney et al. (1993), Roig et al. (1996, 2002), Alexandrov et al.
1960 (2000), Bertrand et al. (2001), Alexandre et al. (2002), G ebelin (2004), Cartannaz (2005),
1961 Cartannaz et al. (2007), G ebelin et al. (2007, 2009), Joly et al. (2007), Rolin et al. (2009, 2014),
1962 Faure et al. (2009b), Gardien et al. (2011), Thi ery and Rolin (2012), Melleton et al. (2015).

1963 Data sources for Puy-les-Vignes: (1) Cuney et al. (2002), (2) Harlaux et al. (2018a).

1964

1965 **Fig. 21.** Pressure-temperature reconstruction of the fluid conditions in the Puy-les-Vignes
1966 deposit. (A) Representative isochores for the Lc-w and Lw-c fluid inclusions trapped in quartz
1967 Q1 and wolframite from the stage II. (B) Representative isochores for the Lc-w and Lw-c fluid
1968 inclusions trapped in quartz Q2 from the stage III. (C) Representative isochores for the Lw fluid
1969 inclusions trapped in quartz Q1 and Q2 during a late stage. Lithostatic and hydrostatic
1970 geothermal gradients between 40 and 70°C km⁻¹ are shown.

1971

1972 **Fig. 22.** Conceptual model of the Puy-les-Vignes ore-forming hydrothermal system. (A)
1973 Crustal-scale model showing the stack of metamorphic nappes (UGU = Upper Gneiss Unit,
1974 LGU = Lower Gneiss Unit, PAU = Para-Autochthonous Unit) in the Limousin area and the
1975 formation of the W breccia pipe as the result of mixing between W-rich magmatic fluid
1976 exsolved from an evolved leucogranite and low-salinity volatile-rich metamorphic fluids issued
1977 from devolatilization of deep-seated metasediments. The estimated temperatures correspond to
1978 a regional geothermal gradient of 40°C km⁻¹. (B) Schematic cross-section of the Puy-les-Vignes
1979 breccia pipe showing the superimposition of three concealed granitic intrusions: (i) a
1980 peraluminous granite emplaced at ca. 324 Ma generating microgranite dykes exposed at the
1981 present-day surface, (ii) an evolved leucogranite emplaced at ca. 318 Ma yielding the formation
1982 of the quartz-supported breccia pipe and wolframite-bearing quartz veins, and (iii) a rare-metal
1983 granite emplaced at ca. 311 Ma that produced a disseminated Nb-Ta mineralization overprinting
1984 the W-mineralized system.