

# The tungsten-gold veins of Bonnac (French Massif central): new constraints for a Variscan granite-related genesis

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1	The tungsten-gold veins of Bonnac (French Massif central): new
2	constraints for a Variscan granite-related genesis
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4	Les filons à tungstène-or de Bonnac (Massif central français) :
5	nouvelles contraintes pour une genèse reliée aux granites
6	varisques
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#### 24 Abstract

25 In the Brioude-Massiac district (French Massif Central: FMC), a network of W-As-Bi-Au quartz veins constitutes the Bonnac deposit, where tungsten is the major economic element, 26 together with high-grade gold (up to 15 g/t Au). The evolution of this mineralization has been 27 divided into 3 stages: i) an early deep-seated wolframite-löllingite stage formed between 12 to 28 9 km, at up to 400°C, ii) a ductile/brittle deformation stage associated with scheelite and 29 arsenopyrite deposition, with an estimated temperature of 480-300 °C; iii) a late stage controlled 30 31 by fluid-overpressure potentially triggered by fault-valve mechanism, at a depth of 7 to 5 Km, and a temperature estimated between 266 to 240 °C, is marked by micro-fracturing infilled by 32 native bismuth, bismuthinite, hedleyite, electrum, pyrite and base-metals. Structural analysis, 33 and apatite LA-ICP-MS U/Pb dating, demonstrate a spatial and temporal link between the 34 emplacement of the peraluminous leucogranitic dykes and the Bonnac mineralization. In more 35 details, the mineralization was deposited between 321-316 Ma, during, or just after, the 36 emplacement of the peraluminous dykes estimated around 329-315 Ma, suggesting a magmatic-37 hydrothermal transition for the ore-forming process. In the proposed model, the cooling of a 38 39 hidden two-mica granitic pluton could have generated a magmatic fluid, and acted as the heat 40 source responsible for fluid flow towards inherited permeability zones. The magmatic fluid could have then re-equilibrated at high temperature by fluid-rocks interaction. The sharp 41 changes in pressure, associated with the decrease of the temperature, and sulfide-fugacity 42 43 generated by a late input of meteoric fluid were responsible for the deposition of the late goldstage. At the regional scale, the tungsten-gold event is ascribed to an early hydrothermal stage, 44 dissociated from the formation of the antimony event in the district. The leucogranitic dykes 45 and Bonnac quartz veins are controlled by a NW-SE stretching direction, interpreted as an 46 expression of the Serpukhovian-Bashkirian syn-orogenic extension (D4 event of the FMC). 47 These new data provide evidence for an early tungsten and gold metallogenic event in the FMC, 48

prior the "Or300" event. The genetic classification of the Bonnac mineralization is equivocal. 49 50 The W-As-Bi-Au-quartz veins exhibit the features of both an "orogenic gold" deposit at a relatively deep emplacement level (mesozonal), and an Intrusion-Related-Gold-Deposit 51 (IRGD) type with a spatial-temporal link with the peraluminous intrusion emplacement. We 52 propose that the Bonnac deposits represent an intermediate type between a typical orogenic-53 gold deposit and an IRGD. We argue that the presence of economic high-grade gold content in 54 tungsten vein-type, and more generally the IRGD deposits, have been underestimated in the 55 Variscan French Massif Central. 56

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58 Keywords. Tungsten-Gold ore deposit, French Massif Central, IRGD, Variscan metallogeny,
59 Brioude-Massiac district, Apatite U-Pb dating.

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### 62 **Résumé**

63 Dans le district de Brioude-Massiac (Massif Central Français ; FMC), les gîtes de Bonnac correspondent à un réseau de veines de quartz à W-As-Bi-Au. Le tungstène y est le principal 64 métal économique, et est associé à de fortes teneurs en or (entre 1 et 15 g / t Au). L'évolution 65 de cette minéralisation peut être divisée en 3 étapes: i) un stade précoce à wolframite et 66 löllingite, formé en profondeur, entre 12 et 9 km, et à des températures supérieures à 400 °C, 67 ii) un stade de déformation ductile / cassant qui contrôle le dépôt de scheelite et d'arsénopyrite, 68 estimé entre 480-300 °C; iii) un stade tardif, contrôlé par des surpressions de fluide marquées 69 par une micro-fracturation colmatée par une paragenèse à bismuth natif, bismuthinite, hedleyite, 70 électrum, pyrite associée à des métaux de base. Les surpressions de fluide seraient possiblement 71

provoquées par un mécanisme de valve-sismique, à des températures comprises entre 266 et 72 73 240 ° C, à une profondeur estimée entre 7 et < 5 km. L'analyse structurale, et les datations U/Pb sur apatite par la méthode LA-ICP-MS démontrent un lien spatial et temporel entre les dykes 74 leucogranitiques peralumineux et les gîtes de la région de Bonnac. La formation de la 75 minéralisation entre 321-316 Ma est contemporaine à légèrement plus jeune que celle des dykes 76 peralumineux mis en place autour de 329-315 Ma, ce qui suggère une genèse lors d'une 77 78 transition magmatique-hydrothermal. Dans ce modèle, le refroidissement d'un pluton granitique à deux micas sous-jacent, pourrait générer des fluides magmatiques et servir de source de 79 chaleur activant une circulation du fluide vers des zones à haute perméabilité comme des 80 81 fractures préexistantes. Le fluide magmatique aurait ensuite été rééquilibré à haute température 82 par des processus d'interaction fluide-roches. Les changements brusques de pression, la baisse des températures, et de fugacité du soufre générés par un apport tardif de fluides météoriques 83 84 semblent responsables du dépôt du stade aurifère tardif. À l'échelle régionale, l'événement ortungstène est attribué à un stade hydrothermal précoce, et dissocié de la formation de 85 l'événement à antimoine du district. La mise en place des dykes leucogranitiques et des veines 86 de quartz de Bonnac est contrôlée par une direction d'étirement NW-SE, interprétée comme une 87 expression de l'extension syn-orogénique d'âge Serpukhovien-Bashkirien (événement D4 du 88 89 Massif Central français). Ces nouvelles données fournissent des preuves d'une première période métallogénique à tungstène et or dans le FMC avant l'événement «Or 300». La classification 90 génétique des minéralisations de Bonnac est équivoque. Les veines de quartz à W-As-Bi-Au 91 92 présentent à la fois les caractéristiques du modèle de "l'or orogénique", avec un niveau relativement profond de mise en place (mésozonal), et celles du modèle Intrusion-Related-93 Gold-Deposit (IRGD) avec un lien spatio-temporel entre la minéralisation et une intrusion 94 peralumineuse. Nous proposons que Bonnac soit un type intermédiaire entre un modèle typique 95 de l'or orogénique, et un IRGD. Nous soutenons que la présence de teneurs économiques en or 96

97 dans les gisements de tungstène de type filonien, et plus généralement ceux de type IRGD, ont
98 été sous-estimés dans la partie varisque du Massif Central Français.

99 Mot clés : Minéralisation à Tungstène-Or, Massif-Central-Français, IRGD, métallogénie
100 Varisque, district de Brioude-Massiac, Age U-Pb sur apatite.

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### 103 **1. Introduction**

The French Massif Central (FMC) represents a prominent metallogenic province for gold (Bouchot *et al.*, 2005) but only a few tungsten deposits have been found, although resources of at least 45,000t of WO<sub>3</sub> have been estimated, (Audion and Labbé, 2012), this is probably the consequence of an under-exploration for this metal in the FMC. The ubiquity of the quartzwolframite hydrothermal veins makes it the main source of tungsten in the FMC. Some deposits with still a strong economic potential were formerly mined, such as Leucamp, Enguialès and Echassières (Marignac and Cuney, 1999; Fig. 1).

Among the wolframite-bearing veins of the FMC, some display a polymetallic content with 111 bismuth and gold in sub-economic grade (W-As-Bi-Au). They are ascribed either to the 112 113 perigranitic wolframite vein-type (Marignac and Cuney, 1999) or to orogenic gold deposit (Bouchot et al., 2005). In the FMC, occurrences of W-As-Bi-Au are known in gold mining 114 districts such as the Limousin (Marcoux and Bonnemaison, 1988), Pontgibaud (Marcoux and 115 116 Picot, 1985), Brioude-Massiac (Périchaud, 1970; Bril, 1982; Marcoux and Bril, 1986; Sandras, 1988; Bril and Beaufort, 1989; Bril et al., 1991), Montredon (Béziat et al., 1980), St-Mélany 117 (Charonnat, 2000; Chauvet et al., 2012), and Leucamp districts (Derré, 1983; Bogdanoff et al., 118 1987; Demange et al., 1988; Bouchot et al., 2005; Lerouge and Bouchot, 2009). The spatial 119 association of the wolframite-quartz veins with Carboniferous peraluminous two-mica granites 120

121 argues for an important role of this crustal magmatism in the genesis of the tungsten 122 mineralization (Marignac and Cuney, 1999, Cuney *et al.*, 2002; Bouchot *et al.*, 2005; Harlaux 123 *et al.*, 2018). However, the formation of these peri-granitic deposits is still debated. In particular, 124 the temporal and genetic links between the episodes of magmatism, deformation, and 125 hydrothermal mineralization are not fully clarified.

U-Pb TIMS dating on wolframite from the Limousin, Echassières, Montredon, and S<sup>t</sup>-Mélany 126 127 districts (Fig. 1) has been recently performed (Harlaux et al. 2018). The obtained U-Pb ages define the existence of three tungsten mineralizing events closely related to magmatic activity: 128 i) Visean to Serpukhovian mineralization (333 – 327 Ma) coeval with the emplacement ages of 129 130 large peraluminous two-mica plutons (ca. 335 – 325 Ma) during the syn-orogenic extension, ii) 131 Serpukhovian to Bashkirian mineralization (317 – 315 Ma) synchronous with the emplacement of syn-tectonic granites (ca. 315 – 310 Ma) during the late-orogenic extension, iii) Gzhelian to 132 Asselian mineralization (around 300 – 298 Ma), formed during the post-orogenic extension, 133 coeval with the metallogenic peak of the Or300 event during which the main orogenic gold 134 deposits were emplaced in the FMC (Bouchot et al., 2005). 135

In the central part of the FMC, i.e. in the Pontgibaud, Brioude-Massiac, and Leucamp 136 137 districts, the timing for the emplacement of the wolframite bearing veins remains poorly 138 constrained. Furthermore, the genetic relationships between the ore deposits and the granitic emplacement is not yet demonstrated. The Bonnac area, in the central part of the Brioude-139 Massiac district is a good target to address these questions (Fig. 1). Indeed, in this area, a dozen 140 141 of W-As-Bi-Au bearing quartz veins from the South of the Bonnac village to the Scoufour hamlet (Fig. 3) further north (Périchaud, 1970; Sandras, 1988) are spatially associated with a 142 143 leucogranitic dyke swarm dated at  $322 \pm 7$  Ma (K/Ar on muscovite, Bril *et al.*, 1991), while the W-As-Bi-Au mineralization yields late Permian age of about 250 Ma (K/Ar on muscovite from 144 Bonnac; Bril et al., 1991). Variable gold grades ranging from 1 to 15 g/t have been reported in 145

ore samples from the region (Périchaud, 1970; Sandras, 1988), but the relationship between goldand tungsten ore is not clearly documented.

The aim of this study is to better understand the W-As-Bi-Au quartz vein deposits in the FMC, and more particularly in the Bonnac area. It focuses on the structural control and the timing of these ore deposits, and their relationships with the Carboniferous tectonics and magmatism, and will be integrated within the hydrothermal framework of the Variscan FMC. Detailed field structural studies, and in-situ apatite LA-ICP-MS U/Pb dating were carried out. Mineralogical and geochemical studies were also performed to decipher the tungsten-gold relationships and propose an updated metallogenic model.

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### 156 2. Geological and metallogenic background

157 2.1 The Haut-Allier area in the FMC Variscan framework

Located in the central part of the FMC, the 1000 km<sup>2</sup> Brioude-Massiac polymetallic district 158 is covered by Cenozoic basaltic flows, and bounded to the northeast by the Oligocene Limagne 159 graben. The district that belongs to the Variscan orogen, is a N120-130°E trending antiform 160 that refolds the stack of metamorphic nappes recognized in the entire Massif Central (e.g. Burg 161 162 and Matte, 1978; Ledru et al., 1989; Faure et al., 2005, 2009; Fig. 1, 2). The core of the area is occupied by the Lower Gneiss Unit (LGU) represented by biotite-sillimanite paragneiss, 163 164 intruded by the Céroux orthogneiss derived from a Cambro-Ordovician alkaline granite (Burg 165 and Matte, 1978; Lasnier et al., 1982; Mathonnat, 1983; Thonat et al., 2014). The LGU is tectonically overlain by the Upper Gneiss Unit (UGU), which is formed by migmatitic 166 paragneiss with rare orthogneiss, and a felsic-mafic association called the "leptynite-167 168 amphibolite complex". The mafic rocks experienced an eclogite-facies or granulite-facies metamorphism during the eo-Variscan evolution (Marchand, 1974; Lasnier, 1977; Bernard-169 Griffiths et al., 1980). 170

The nappe stacking in the Haut-Allier area was probably acquired during the early 171 172 Carboniferous, around 350-340 Ma (monazite U/Pb dating on syntectonic granulite; Pin and Peucat, 1986). Then two extensional events, coeval with granitic intrusions accommodated the 173 crustal thinning widely observed in the FMC (e.g. Malavieille et al., 1990; Faure and Pons, 174 1991; Faure, 1995). i) The syn-orogenic extension at ca 330-310 Ma, called D4 event (Faure et 175 al. 2009), is characterized by a NW-SE maximum stretching recorded by the syn-tectonic 176 177 biotite monzogranite and the two-mica granite plutons and their country rocks. In the Brioude-Massiac area, and alusite-leucogranitic dykes and their related two-mica granites (Sandras, 178 1988; Bril et al., 1991) belong to this D4 event. ii) The late-orogenic extension (D5 event, 179 180 between 310 to 299 Ma; Faure et al., 2009), with a NNE-SSW maximum stretching direction, was contemporaneous with the emplacement of highly differentiated peraluminous intrusions 181 and pegmatites, and rare-metal granites (Cuney et al., 2002). The opening of the Late 182 183 Carboniferous coal basins belongs to the D5 event (Faure, 1995).

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### 185 2.2 The Bonnac W-As-Bi-Au deposits

The study area is located in the central part of the Brioude-Massiac polymetallic district which contains more than 200 veins-type deposits and occurrences with variable ore content: W, Sn or W-As-Bi-Au (Bonnac, Vèze-Bosberty veins), Sb (Au), Pb-Zn or F and Ba (Fig. 2). Antimony veins have been the main economic substance mined between 1850 and 1978 with an historical production of 43 000 t Sb metal (Périchaud, 1970; De Gramont *et al.*, 1990). The Bonnac area was only mined for gold between 1880 and 1911 with a production of only 2 kg of gold, and never for tungsten (Périchaud, 1970; De Gramont *et al.*, 1990).

193 The Bonnac W-As-Bi-Au quartz-veins are spatially associated with Sb (Au) quartz veins 194 (Fig. 2) and are located in the southwestern limb of a regional N120-130°E antiform. All veins 195 seem to crosscut the foliation of the LGU paragneiss (Fig. 2 and 3). Some quartz veins develop

immediately at the contact with andalusite leucogranitic dykes (Périchaud, 1970; Sandras, 196 197 1988). The ore mineralogy, is mainly represented by arsenopyrite-löllingite with wolframite, minor scheelite, associated with bismuthinite, native bismuth, tetradymite and visible gold in a 198 quartz gangue with muscovite clusters (Périchaud, 1970; Bril, 1982; Bril and Beaufort, 1989). 199 Detailed studies on fluid inclusions (Bril, 1982), hydrothermal alteration (Bril and Beaufort, 200 1989), and lead isotopic signature (Marcoux and Bril, 1986) allow to constrain the P-T 201 202 conditions of vein deposition. The Bonnac veins display two successive hydrothermal stages with an early high temperature (homogenization temperatures between 350-400 °C) CO<sub>2</sub>-CH<sub>4</sub>-203 rich ± N<sub>2</sub> aqueous fluid with low-salinity (about 5 equiv wt % NaCl), interpreted as of 204 205 metamorphic origin, and a late low temperature (homogenization temperatures between 200 -300 °C) aqueous fluid, with low-salinity, of meteoric origin, similar to the ore forming fluid 206 from the Sb (Au) deposits. According to the same authors, the formation of the W-As-Bi-Au 207 208 and Sb (Au) veins could be contemporaneous, the result of a single hydrothermal system coeval with the emplacement of an underlying, albeit hidden, Permian pluton. The ore veins were 209 considered to show a zonal distribution, with W-As-Bi-Au occurring in a limited area, near the 210 intrusion, the Sb (Au) veins being more distal. 211

212 2.3 The intrusive rocks

Leucogranitic dykes, striking N30°E, N60°E and sometimes N100°E, with a variable 213 thickness (between 50 cm to 20 m), and small extension (less than 3 km), are cropping out in a 214 215 few clusters in the district, the Bonnac area being one of the most important (Fig. 2 and 3). 216 These dykes display a homogeneous mineralogical and chemical composition in the overall district (Sandras, 1988). Quartz is the most abundant mineral, associated with plagioclase, and 217 218 sub-euhedral K-feldspar (< 5 mm) with biotite aggregates and muscovite. Andalusite is observed as small sized grains (0.6 to 0.8 mm), associated with the K-feldspar and quartz. A 219 temperature emplacement of ca 600-650 °C, and a pressure of 0.4 GPa, was estimated from the 220

andalusite-quartz assemblage (Sandras, 1988). An emplacement age of 322 ± 7 Ma was
documented by K/Ar radiometric dating on muscovite (Bril *et al.*, 1991).

223 The dykes chemical compositions correspond to a peraluminous two-mica granite with 74 to 76 % SiO<sub>2</sub> and a Al2O3/CaO+Na2O+K2O ratio up to 1.6 (see EDM. 1 for analytical details). 224 225 This bulk chemistry is similar to those found in the Chatelet gold district, and other Visean to Serpukhovian leucogranites from the Limousin district (e.g. S<sup>t</sup>-Sylvestre massif; Scaillet *et al.*, 226 1996). A local partial melting of the LGU paragneiss could be responsible for the genesis of 227 those intrusive rocks (Sandras, 1988). A spatial and potentially genetic link with the W-As-Bi-228 229 Au deposits of the Brioude-Massiac district is assumed. At Bonnac, the dykes are interpreted as the shallow expression of an underlying pluton (Sandras, 1988; Bril and Beaufort, 1989). 230

### 231 **3. Materials and methods**

232 The accessory mineral phases were identified using a Merlin compact Zeiss Scanning Electron Microscopy (SEM), co-operated by BRGM-CNRS-Orléans University, and equipped 233 with Energy Dispersive System (EDS) for qualitative analyses. In addition, SEM-234 235 cathodoluminescence images have been made using MEB-CL MIRA-3 Tescan (BRGM-CNRS-Orléans University). Chemical analyses of arsenopyrite were obtained with the Cameca 236 SX-Five Electron Probe Micro-Analyzer (EPMA) at the Institut des Sciences de la Terre 237 238 d'Orléans (ISTO). Analyses were performed using an accelerating voltage of 20 kv, a beam current at 40 nA, a beam diameter of 3 µm, and a counting time of 30 s for Fe, Ni, Co, Sb, Pb, 239 240 Cu, As, Zn, Ag, Bi, and 60 s for gold. Details on the method, parameters and analytical data are given in ESM2. 241

U/Pb dating on hydrothermal apatite from the mineralization was conducted in-situ by laser
ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the GeOHeLiS
analytical platform (Géosciences Rennes/OSUR, Univ. Rennes) using an ESI NWR193UC

Excimer laser coupled to an Agilent 7700x quadrupole ICP-MS equipped with a dual pumping system to enhance sensitivity (Paquette *et al.*, 2014). The analytical procedure followed the method described in Pochon *et al.* (2016). Details, standards analyses and analytical data are provided in ESM3. All errors are listed at  $2\sigma$  level. Concordia diagrams and calculated ages have been produced using IsoplotR (Vermeesch, 2018).

### 250 4. Field characterization of the W-As-Bi-Au quartz veins

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4.1 Field and structural features from the Bonnac area

The strike of the mineralized quartz veins displays three different orientations similar to 253 those of the leucogranitic dykes. The N30°E trend is represented by the Riolet, Androl, Rode, 254 Borie veins), the N60°E by the Costillon one, while few veins strike N90°E and N160-170°E 255 (Fig. 3). The vein dip varies between  $30^{\circ}$  to  $45^{\circ}$  to the SE whatever their strike. Mineralized 256 quartz veins are located in the hangingwall or footwall of the leucogranitic dykes (Fig. 4, 5). 257 They display similar features all around the area, with a lenticular shape, and a narrow width of 258 1 to 20 cm. The host-rocks are weakly affected by the hydrothermal alteration. The geometric 259 relationships show that the leucogranitic dykes crosscut the paragneiss foliation, and are cut by 260 261 the mineralized veins (Fig. 4B, 5) with locally developed breccias (Fig. 4B).

Most of the vein wallrocks are fault planes with a down-dip striation, indicating a normal motion (Fig. 5). Some veins display also a striation with a NE 40-50° pitch, in which quartz steps indicate a normal component of displacement (Fig. 5C, D). The observed kinematics of the Costillon vein (Fig. 4A) also indicate a normal motion that complies with the drag folds asymmetry developed around the leucogranitic dykes (Fig. 5B). Late N60-65°E striking subvertical barren faults, with gouge, offset the quartz veins (Fig. 4A).

269 4.2 Field and structural features from the Scoufour-area

The Scoufour mineralized quartz veins exhibit some differences with the Bonnac ones. Three 270 N10-30°E striking low-angle veins with a dip between 10 and 20° to the SE are observed (Fig. 271 6). Their thickness is comprised between 30 and 50 cm, but may exceed 1m. Here, leucogranitic 272 dykes are absent, and the host-rock underwent a hydrothermal alteration related to the 273 274 mineralization. A greisen-type alteration is thus observed up to 1 or 2 m from the vein, resulting in the bleaching of the paragneiss by transformation of biotite into muscovite with associated 275 silicification. Drag folds observed near the Ferbert vein show a normal motion (Fig. 6B). A late 276 fracturing event, represented by N20-25°E steeply NW dipping barren faults with gouge, is also 277 recognized (Fig. 6A). 278

All the structural features observed in the Bonnac and Scoufour areas are summarized in Figure 7. In both cases, the emplacement of the mineralized quartz veins occurred during a single deformation phase coeval with a hydrothermal event. The magmatic event responsible for dyke emplacement post-dated the regional metamorphism but preceded the ore veins emplacement. Furthermore, normal faults rework the pre-existing faults that controlled the emplacement of the leucogranitic dykes. Lastly, both dykes and mineralized veins are cut by NE-SW subvertical faults with subhorizontal striation indicating a sinistral motion.

### 286 5. Mineralogy and geochemistry of the W-As-Bi-Au ore veins

287 5.1 The mineralized facies

All the mineralized veins of the study area have similar habitus, with a massive infill of coarse white-grey quartz gangue with parallel ribbons of a few centimeters, or aggregates of arsenopyrite and coarse wolframite (Fig.4A and 8). Secondary scheelite is common in cm-scale pseudomorphic aggregates of early wolframite that may appear as rare relicts and rarely observed as isolated, coarse grains or infilling fractures. (Fig. 8). On the basis of gangue and ore mineral textural observations, 3 stages have been recognized, namely: i) stage 1 with tungsten and arsenic, ii) stage 2 with arsenic, and tungsten, iii) stage 3 with bismuth, gold, and base metals.

296 5.2 Stage 1: early tungsten and arsenic

The first opening of the veins corresponds to the deposition of a wolframite and löllingite 297 assemblage in a macrocristalline Qz1 quartz (crystal size > 500 µm; Fig. 9A, B). Observed with 298 cathodoluminescence, Qz1 displays a blocky habitus with regular growth bands without 299 significant deformations (Fig. 9B), and numerous fluid inclusions. Coarse euhedral wolframite 300 301 crystals (up to 1 cm) are associated with cm-size aggregates of löllingite (Fig. 9A). SEM 302 analyses of wolframite exhibits a high iron grade (6-8 wt %) and a lower manganese one suggesting a ferberite. Large apatite crystals (>  $100 \mu m$ ) have been observed within Qz1 in 303 304 close association with wolframite (Fig. 9C). Their euhedral shape and straight grain boundaries suggest it is coeval with Qz1. 305

306 5.3 Stage 2: arsenic and late tungsten

The beginning of stage 2 is marked by an intense and heterogenous episode of deformation (Fig. 9A, B, C, D) which has affected the previous stage 1 assemblage. Qz1 grains experienced a dynamic recrystallization (Stipp *et al.*, 2002) shown by undulose extinction, subgrain rotation and recrystallization with golfed or jagged shape of the Qz1 boundary, bulging and quartz neograin (Qz2) formation at the expense of the early Qz1 (Fig. 9 B, D and Fig. 10 A and B). Qz2 displays undulose extinction and grain size reduction and is located along 10 to more than 500 µm shear bands that surround the edges of Qz1, or crosscut it.

The crystallization of arsenopyrite (Fig. 9 B) and scheelite are coeval with the deformation episode. Arsenopyrite forms small rhombic crystals (up to 100  $\mu$ m) and fills the fracture network of the stage 1 löllingite or wolframite and sometimes totally pseudomorphs after löllingite. Xenomorphic scheelite forms at this stage by partial or total pseudomorphosis of
previous wolframite (Fig. 9 A, C). The scheelites, show rare inclusions of niobium oxides rich
in niobium as on the Ferbert vein, (65 wt % Nb<sub>2</sub>0<sub>5</sub>), iron (25 wt % FeO), manganese (4.5 wt %
MnO), tungsten (2.4 wt % WO<sub>3</sub>), titanium (2.2 wt % TiO<sub>2</sub>) and scandium (0.9 wt % Sc<sub>2</sub>O<sub>3</sub>).
Those uncommon oxides have been observed in the Puy-Les-Vignes tungsten deposit (Harlaux *et al.*, 2015).

The 56 EPMA analyses of arsenopyrite (see Table 1 and ESM 2 for detail) have been 323 324 compared with previous study of Bril (1983) from the Bonnac area and from other W-As-Au regional veins (Vèze and Bosberty, see Fig. 2 for localization). Arsenopyrite has a very similar 325 composition in all deposits with As % average values of 33.4 %, 32.8%, and 33.0 % for Bonnac, 326 Vèze, and Bosberty veins, respectively. Minor elements, e.g. Co, Ni, Sb, Au are under the 327 detection limit of the method. According to Kretschmar and Scott (1976), and Sharp et al. 328 (1985), the use of the arsenopyrite chemical compositions to assess ore formation temperatures 329 may be considered with a good confidence level, because of the absence of minor element. 330 Assuming the arsenopyrite-pyrrhotite equilibrium, the calculated formation temperature was 331 332 around 480 °C. These values are in the same range than those deduced from the H<sub>2</sub>O-CO<sub>2</sub>L1type fluid-inclusions (homogenization temperature between 300 and 420 °C; Bril, 1982). 333

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335 5.4 Stage 3: Bi-Te-Au and base metals

This stage is marked by the deposition of a new discrete quartz generation (Qz3) in the fractures of arsenopyrite or löllingite (Fig. 10 C, D). The medium grain-size (around 100  $\mu$ m) Qz3 displays a subeuhedral shape or elongate-fibrous habitus. Its hyaline aspect is due to the scarcity of fluid and solid inclusions. This Qz3 never experienced dynamic recrystallization (Fig. 10 C, D) and is coeval with a bismuth-telluride-gold-base metals assemblage (Fig. 10 C, D, E). Rhombic arsenopyrite crystals are commonly crosscut by large mm-size, subeuhedral pyrite, associated with bismuth-telluride and base-metals minerals (Fig. 11 D, E). The EPMA
chemical analysis of the pyrite from Bonnac veins does not show minor element.

Bismuthinite and native bismuth are the dominant minerals species of this stage 3. They 344 occur as 2 to 80 µm inclusions aligned along the cleavage plane of löllingite (Fig. 11A), also 345 within arsenopyrite, or wolframite (Figs. 10 C, D; 11 A, B, C), and as small-size aggregates (< 346 500 µm) or in fractures crosscutting löllingite or arsenopyrite (Fig. 10E, F). Native bismuth is 347 frequently observed as ovoidal inclusions within bismuthinite (Figs. 10 F; 11 C). Xenomorphic 348 349 hedlevite (Bi7Te3) is the main tellurium mineral, always closely associated with the bismuthinite and native bismuth. Tetrahedrite [(Cu,Fe)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>] and a bismuth-antimony-350 sulfide, close to the chemical composition of the horobetsuite [(Bi,Sb)<sub>2</sub>S<sub>3</sub>, have been identified 351 as inclusions in a hedleyite aggregate (Fig. 10 F). In the Ferbert vein, a late deposition of Cu-352 Zn-Pb minerals overprints and brecciating all the previous minerals. Chalcopyrite is the main 353 mineral, with small tetrahedrite inclusions (50 µm). Sphalerite and minor galena complete this 354 assemblage. This late deposition stage is associated with a Qz4 quartz generation displaying 355 undeformed pyramidal grains (Fig. 11E). 356

Visible gold has been commonly observed in thin-sections from all veins of the Bonnac area. Most of the gold intergrowths with the Bi-Te minerals, (Fig. 10 B, 11 A, B, C), or more rarely appears within sulfides (mainly chalcopyrite, Fig. 11 D, E), or sometimes pyrite or isolated between Qz2 grains. Gold patches range between 1  $\mu$ m to 25  $\mu$ m in size but can reach 50  $\mu$ m within sulfides. All display a xenomorphous rounded shape (Fig. 11). Rare maldonite (Au<sub>2</sub>Bi) has been observed by SEM analysis as a few microns inclusions intergrowths with native bismuth.

Ten EPMA analyses of gold grains intergrowths with native bismuth and within chalcopyrite from the Ferbert vein are provided in Table 1 (see EDM 2 for detailed analyses). The small size of the gold grains explains why the analyses do not reach 100 %. Silver is the only element
present with gold (average of 16.7 wt % Ag). "Gold" of Bonnac area is thus an electrum with
a gold fineness of 830 (Morisson *et al.*, 1991).

369 The three economic-stages described above are summarized in figure 12, however, this 370 evolution represents increments of a single progressive crystallization-deformation event.

371

It should be noted that, a poorly developed and uneconomic post-ore stage, macroscopically highlighted by a dark-gray quartz facies, has been only observed in the Ferbert vein. All the previous stages are brecciated and cemented by a chalcedonic quartz gangue with minor carbonates. The associated metallic-minerals are pyrite-marcasite aggregates with pyrrhotite relics, with a new generation of chalcopyrite, and sphalerite. This does not greatly affect the previous assemblages.

378

### 379 6. LA-ICP-MS U/Pb geochronology on apatite

Hydrothermal apatite from the early tungsten-arsenic stage 1 (Fig. 9C and Fig. 12) of the 380 Androl (Bonnac area) and Ferbert veins (Scoufour area) have been carefully characterized and 381 382 15 grains have been selected for dating. Namely, 9 from the Ferbert vein (mineralized quartz 383 vein sample BM46D) and 6 from Androl vein (mineralized quartz vein sample BM39A; ESM 384 3 for analytical details). The cathodoluminescence image shows growth zones without evidence 385 complex zoning (Fig. 13 A, B). Between 2 and 6 U/Pb analysis have been performed on each grain (Fig. 13C, D). Apatite grains from the Ferbert vein have variable <sup>207</sup>Pb/<sup>206</sup>Pb ratios, 386 ranging between 0.1849 and 0.7010. The discordant points plot along a discordia line that yields 387 388 a lower intercept date of  $315.6 \pm 2.8$  Ma (MSWD = 3.7; Fig. 13C). The data plot along a discordia line yielding a lower intercept date of  $323.4 \pm 3.2$  Ma (MSWD = 2.4, Fig. 13D). The 389 intersect point of the discordia give the isotopic composition of the initial lead of the dated 390

apatite (Fig. 13C, D). Their composition shows some difference between the Ferbert vein and 391 392 the Androl vein with respectively 0.823±0.005 and 0.853±0.013. Those results are consistent with initial <sup>207</sup>Pb/<sup>206</sup>Pb ratios measured in different nearby mineralized veins, and main 393 lithological formations of the Brioude-Massiac area (Marcoux and Bril, 1986). Thus, the 394 Fournial (Pb-Ag-Sn-As veins) have <sup>207</sup>Pb/<sup>206</sup>Pb ratios different 0.86234±0.00027 (n=14), but 395 that of the Sb-(Au) vein of the Céroux is closer 0.8598±0.0014 (n=1). On the other Sb-(Au) 396 397 veins, the isotopic compositions of the lead remain variable within de district. The aplitic dykes close to a leucogranitic composition from the la Margeride pluton, in the southern part of the 398 district, show the strongest correlation with the Androl vein with a <sup>207</sup>Pb/<sup>206</sup>Pb ratio of 0.8569 399 400 (n=1, composition recalculated at 320 Ma).

### 401 **7. Discussion**

402 7.1 Mechanisms of ore-vein formation and chemical-thermal evolution

403

During **stage 1**, the initial vein opening, coeval with the massive crystallization of the Qz1 under low-strain, was contemporaneous with a high temperature (up to 400 °C) paragenesis with wolframite and löllingite from an As and W enriched fluid with low-salinity (about 5 equiv wt % NaCl) CO<sub>2</sub>-CH<sub>4</sub>-rich  $\pm$  N<sub>2</sub> aqueous fluid (V-type fluid inclusions in the classification of Bril, 1982).

A ductile/brittle deformation episode marks the beginning of **stage 2** (Fig. 12). The first Qz1 experienced a dynamic recrystallization shown by undulose extinction, subgrain rotation recrystallization, bulging and quartz neograin (Qz2) formed at the expense of the early Qz1. Ductile/brittle deformation features argue for a deep-seated formation between 12 to 9 km (Scholz, 1988). This is supported by the range of temperature for this stage, estimated around 480 °C, based on the arsenopyrite thermometry and, in agreement with the estimated temperature range (400 to 500 °C) deduced from the quartz textural observations (e.g. Stipp *et* 

al., 2002). Those depth and temperature estimation are in good agreement with the estimated 416 417 emplacement conditions of the leucogranitic dykes of Bonnac (see part 2.3). The transformations of wolframite into scheelite, and löllingite into arsenopyrite suggest a change 418 in fluid chemistry, still rich in As and W, and marked by an increase in sulfur fugacity and in 419 the calcium activity. The pseudomorphic textures argue for a remobilization of the tungsten 420 from the previous ferberite. The increase of the Ca/Fe ratio in the fluid, associated with a 421 422 slightly decrease of the temperature, as predicted by Wood and Samson, (2000) could possibly correspond to higher fluid interaction with the surrounding metamorphic formations. This fluid 423 could correspond to the L1-type fluid inclusions defined by Bril, (1982), with low-salinity (3.5-424 425 0 equiv wt % NaCl), lower CO<sub>2</sub> aqueous fluid, and trapping temperature estimated around 300 to 400 °C (Fig. 14). 426

The onset of stage 3 (Fig. 12) was marked by brittle fracturing. The previous assemblage 427 was micro-brecciated, and invaded by a hyaline, low-strain Quartz (Qz3). This new quartz 428 429 generation was coeval with the deposition of native bismuth, bismuthinite, hedleyite, electrum, pyrite, and base-metals minerals (chalcopyrite, sphalerite, galena). The microcrack infill as well 430 as fluid and solid-inclusions bands (Fig. 10 A, B) suggest fluid-assisted fracturation under a 431 hydrostatic regime at a depth comprised between 7 and < 5 km (Scholz, 1988). This stage 3 432 might be interpreted as a consequence of a crack-and-seal trigged by a fluid overpressure 433 mechanism (Ramsay, 1980). The emplacement of the previous massive quartz generations 434 435 could have sealed the porosity in the fault zone and act like an impermeable barrier to fluid flow allowing an increase in the fluid pressure. The crack-and-seal process has triggered pressure 436 drop from lithostatic to hydrostatic regime, and might be interpreted as a consequence of a fault-437 valve mechanism (Sibson et al., 1988; Cox et al., 1991; Robert et al., 1995; Gaboury and 438 Daigneault, 2000). The textural evolution reflects the transition from a lithostatic pressure 439 440 context during stages 1 and 2 with a limited permeability to pervasive fluid circulation in 441 connected fractures, therefore implying a transition from, an aseismic to, a seismic environment
442 (Cox, 1987; Cox *et al.*, 1991).

The deposition temperature of gold during stage 3 can be deduced from the paragenetic 443 association of native bismuth and bismuthinite. According to Barton and Skinner (1979), a 444 range of temperature between 320 to 240 °C can be proposed. However, the association of 445 native bismuth and hedlevite can only be stable below a temperature of 266°C (Dimitrova and 446 Kerestedjian, 2006). Therefore, we propose a temperature range between 266 to 240 °C for the 447 deposition of stage 3, which is in good agreement with a ca 200 °C homogenization temperature 448 deduced from the L2-type secondary aqueous fluid inclusions (Bril, 1982). This relatively low 449 temperature accounts for the deposition of antimony-rich Bi-Te minerals like the horobetsuite 450 or the tetrahedrite. 451

452

### 453 7.2 Possible mechanisms for gold deposition

The common occurrence of electrum within Bi-Te minerals might emphasize the role of a 454 polymetallic melt/liquid for the concentration of precious metal, as already reported for similar 455 mineralization (Ciobanu et al., 2006; Cook et al., 2007; Ciobanu et al., 2010; Zacharias et al., 456 2014). The polyphase character of the ore-inclusions (electrum intergrowth in native bismuth, 457 or electrum, native bismuth intergrowths in hedleyite), the ovoidal shape of the electrum inside 458 459 native bismuth, and the presence of minerals such as maldonite or horobetsuite might support this mechanism (Ciobanu et al., 2006; Zacharias et al., 2014). But our deposition temperature 460 estimate, between 266 to 240 °C, is too close to, or even below, the bismuth solidus temperature, 461 and the eutectic temperature of the Au-Bi system (241 °C). This leads us to suggest that a large 462 part of the gold and Bi-Te phases probably precipitated directly form a hydrothermal fluid 463 enriched in Bi-Te-Au and were not scavenged by a bismuth-rich liquid/melt. 464

Between stages 1 and 3, a temperature decrease is observed (Fig. 14). In addition, the stage 3 underwent a significant pressure drop associated with a change in tectonic regime, which might have triggered the input of a meteoritic fluid (Bril, 1982; Fig. 14). Furthermore, the decrease in the sulfide activity in the ore-fluid could be responsible for the gold deposition by destabilization of gold-sulfide complexes associated with the ongoing sulfide precipitation (Williams-Jones *et al.* 2009).

471

472 7.3 Tectonic control and timing of ore deposits within the Variscan evolution framework for473 the French Massif Central

474

The vein geometry observed in the field is controlled by the inherited structures. The medium dip (30-50° SE) of the Bonnac veins reused the previous fault system coeval with dyke emplacement, whereas the low-angle dip Scoufour veins are controlled by the host-rock foliation. These anisotropy surfaces can be easily reactivated during faulting, and channeled the ore-bearing fluids.

Kinematic data on the striated fault planes coeval with W-As-Bi-Au veins allowed us to 480 derive the stress tensor by an optimized inversion method (Delvaux and Sperner, 2003). The 481 482 result indicates an extensional tectonic regime with the maximum ( $\sigma_1$ ), intermediate ( $\sigma_2$ ), and minimum ( $\sigma_3$ ) principal stress axes oriented 39°E/86°, 37°E/04° and 127°E/0°, respectively 483 (Fig. 15). The W-As-Bi-Au quartz veins deposition was controlled by a NW-SE horizontal 484 485 extension direction, consistent with the NW-SE stretching direction documented for the D4 tectono-magmatic event in the FMC (Faure, 1995). This widespread event, related to the syn-486 orogenic Variscan extension in the FMC, dated between 325 and 310 Ma, is contemporaneous 487 488 with the emplacement of the leucogranitic and monzogranitic syn-tectonic plutons (Figs. 1, 16;

489 Faure and Pons, 1991; Faure 1995; Faure *et al.*, 2009; Talbot *et al.*, 2005a, 2005b; Joly *et al.*,
490 2007, 2009).

The hydrothermal apatite grains from two localities in the Bonnac area yield LA-ICP-MS 491 U/Pb dates of  $315.6 \pm 2.8$  for the Ferbert vein (Scoufour area) and  $323.4 \pm 3.2$  Ma for the Androl 492 493 vein (Bonnac area), respectively interpreted as the emplacement age of the W-As-Bi-Au veins. This age of ca. 320 Ma is consistent with the D4 tectonic, which is also coeval with the 494 Serpukhovian-Bashkirian generation of tungsten ore deposits with minor gold in the FMC as 495 496 the Puy-les-Vignes or S<sup>t</sup>-Mélany (Fig. 16; Harlaux et al., 2018). Closer to the Brioude-Massiac district, the Leucamp and Enguialès ore deposits in the Châtaigneraie district yielded the most 497 important tungsten resources of the FMC (Derré, 1983; Bogdanoff et al., 1987; Demange et al., 498 1988; Lerouge and Bouchot, 2009) are other examples of this tungsten ore deposition event. 499

All previous works (Périchaud, 1970; Bril et Beaufort, 1989) in the Brioude-Massiac district, 500 proposed a single hydrothermal event, responsible for the formation of both antimony and 501 tungsten-gold from a perigranitic metal zonation. This model seems to be challenged by our 502 results. Despite their spatial link with the antimony veins, the W-As-Bi-Au ones yield a distinct 503 504 age, since the antimony veins of the Brioude-Massiac district belong to a younger hydrothermal 505 event referred to as the "Or 300" event (Bouchot et al., 2005; Cheval-Garabédian, 2019). We have shown that the Bonnac W-As-Bi-Au mineralizations have a polyphased history in a 506 507 continuum of time (Fig. 12), which fits with a unique deformation event, decorrelated with the 508 Or300 event. The three mineralized stage are all trapped in quartz-veins with same and distinct 509 structural control (D4 tectonic event), same kinematics, a same infilling chronology with a continuity from a ductile/brittle to only-brittle regime, associated with a progressive cooling of 510 511 the ore-fluid (Fig. 12 and 14), and by the absence of late remobilization textures during the gold stage 3. This, is also attested by the obvious age difference. 512

Our results, together with the emplacement ages obtained on the gold-bearing quartz 513 514 veins from the Cévennes district (Chauvet et al., 2012) argue for an earlier Bashkirian-Moscovian gold-hydrothermal event, sometimes associated with tungsten, during the D4 event. 515 Our data allow us to propose a polyphase history in the FMC characterized by two distinct 516 hydrothermal events carrying gold, namely: i) a first Serpukhovian to Bashkirian, and, ii) a 517 second, Gzhelian-Asselian, as the Or300 event, that might have re-used the structural 518 519 discontinuities that controlled the early event. Recent new data obtain on the orogenic-gold deposit of the la Bellière district (Armorican Massif) argue also for a tectonic-hydrothermal 520 gold event earlier than the Or300 event around 340-325 Ma (Cheval-Garabédian et al., 2020). 521

522

523 7.4 Genetic link with the Serpukhovian leucogranites and ore deposit model for the Bonnac524 area

525

Based on our results, the genetic relationships between the mineralization and the 526 527 leucogranitic dykes can also be re-assessed. The leucogranitic dykes from Brioude-Massiac, 528 dated at  $322 \pm 7$  Ma (Bril *et al.*, 1991) were emplaced contemporaneously with the D4 event 529 and are spatially related to the W-As-Bi-Au deposits. The mineralizing event that followed the intrusive rocks emplacement could be interpreted as a magmatic-to-hydrothermal evolution 530 531 (Fig. 17; Linnen and Cuney. 2005; Gloaguen, 2006) with a relatively long-time duration, around 329-316 Ma (dating of the leucogranitic magmatic event). Several lines of evidence support 532 533 this interpretation as: i) the spatial and temporal link between dykes and mineralized veins; ii) their formation during the D4 tectonic event; iii) the high temperature paragenesis of stage 1 at 534 400-500 °C, close to the 600-650 °C emplacement temperature estimated for the andalusite-535 536 leucogranitic dykes, iv) their close emplacement depths estimated around 10 km (Sandras, 1988), v) the reworking of previous structural discontinuities. Throughout the Variscan Orogen, 537

there are examples of W-Au deposits that were emplaced within a time gap of ca. 10 Ma after
the intrusions of peraluminous magmas (Romer and Kroner, 2016). In France, the Puy les
Vignes deposit (Harlaux *et al.*, 2018), and the Salau deposit in the French Pyrenees (Poitrenaud *et al.*, 2019), or in the Bohemian Massif, the Mokrsko deposit (Zacharias *et al.*, 2014), are good
examples of this relation.

A two-stage evolutive model for the magmatic-hydrothermal system in the Bonnac area is proposed in a continuum of time (Fig. 17). Between 329 and 315 Ma, the emplacement of leucogranitic dykes, related to an underlying pluton, was controlled by normal faulting in the regional NW-SE extensional regime. Slightly younger from the dyke crystallizations, between 321 to 316 Ma, the deformation became more localized and contemporaneous with quartz veins emplacement that recorded a magmatic-to-hydrothermal transition (Fig. 17 stage 2). These hydrothermal fluids have reused the previous discontinuities as feeder channels.

The metamorphic or magmatic origin of the ore-forming fluid for peri-granitic ore deposits 550 is still a matter of debate (Lang and Backer, 2001; Boiron et al., 2001; Hart et al., 2002; Bouchot 551 et al., 2005; Hart, 2007; Zacharias et al., 2014; Marcoux et al., 2015). In the Bonnac area, the 552 magmatic origin of the fluid is not fully demonstrated by the existing fluid inclusion study (Bril, 553 554 1982) as they rather display a metamorphic origin (low salinity, complex chemistry enriched in CO<sub>2</sub>). However, a magmatic fluid affinity is pointed out by: i) the presence of magmatic affinity 555 556 element such as the W and the Bi-Te-Au association (Lang and Backer, 2001; Blevin, 2004) 557 and by ii) the spatial and temporal link with leucogranitic dykes. In addition, the lead isotopic compositions measured for different mineralized veins and main lithological formations of the 558 Brioude-Massiac area support such magmatic origin of the metals (Marcoux and Bril, 1986). 559 The <sup>207</sup>Pb/<sup>206</sup>Pb ratios estimated on our dating are close to those obtained on the aplitic dykes 560 of leucogranitic composition of the la Margeride granite (see part 6 for the data). 561

To take into account all those features, we propose a genetic link between those mineralized 562 563 veins and the leucogranitic dykes, where the initial magmatic fluids were derived from the crystallization of an underlying granitic pluton. The heat source supplied by the pluton was 564 responsible for fluid migration toward the high permeability zones. The high temperature (400-565 500 °C) interaction between the fluid and the host-rocks (greisen type alteration in the vein 566 hanging walls) could have re-equilibrated the fluid, overprinting its initial magmatic signature 567 568 Then fault-valve mechanisms channeled the ore-fluids into structural discontinuities (Sibson et al., 1988), and fluid overpressure associated with potential fault-valve mechanism could be 569 responsible for vein opening and the gold-stage 3 deposition, in a shallow crustal environment. 570

571

The chemical composition of the Brioude-Massiac andalusite-leucogranitic S-type magma dykes (EDM 1) is characterized by an oxidizing redox state (Fig. 18), although a reduce redox state is more commonly observed. These characteristics are considered as more favorable than a reduce redox state to form a tungsten ore deposit. Indeed the early magnetite precipitation allows the preservation of Au in the melt fraction of granitic magmas (Blevin, 2004).

577

578 7.5 A new ore deposit model for the Bonnac deposits?

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Because of the metamorphic origin of fluids, the Bonnac deposits was previously classified as an orogenic gold deposit (Bouchot *et al.*, 2005), although they do not fulfil all the necessary criteria (Groves *et al.*, 1998).

The Bonnac deposits share some of the characteristics of the IRGD type (Thompson *et al.*, 1999; Lang and Baker, 2001; Hart *et al.*, 2002; Gloaguen, 2006; Hart, 2007; Zacharias *et al.*, 2014; Marcoux *et al.*, 2015) such as: i) the spatial and temporal relationships between oredeposition and peraluminous granite emplacement, ii) the peculiar relation between magmaticsource-related ore phases such as bismuth, tellurides, wolframite, löllingite or molybdenite, iii)
the contemporaneous bismuth-telluride-gold deposition, iv) the vein deposition during the synorogenic extensional period. The redox state of the leucogranitic dykes that spans the boundary
of the ilmenite series (Fig. 18) is also a favorable context for IRGD deposits (Lang and Backer,
2001; Blevin, 2004).

592 On the other hand, the structural evolution from a ductile/brittle deformation to a brittle one, 593 fault-valve mechanism features, and the presence of a late meteoric fluid input, are classical 594 features found for the orogenic gold type deposits (Boiron *et al.*, 1990, 2003; Groves *et al.*, 595 1998; Bouchot *et al.*, 2005).

Therefore, the Bonnac ore-zone represents a mineralization type intermediate between the orogenic-gold and IRGD models as already demonstrated for the Mokrsko gold deposit in the Bohemian-Massif for example (Zacharias et al., 2014).

### 599 8. Conclusions

The Bonnac veins show a W-As-Bi-Au paragenesis that results from polyphase 600 hydrothermal and magmatic events. Three stages of ore deposition have been identified starting 601 with wolframite and löllingite in a deep-seated setting, between 12 to 9 km and up to 400 °C. 602 603 The second ductile/brittle deformation stage was responsible for scheelite and arsenopyrite 604 deposition at 480-300 °C. The late stage was marked by brittle micro-fracturing infilled with native bismuth, bismuthinite, hedleyite, electrum, pyrite and Cu-Zn-Pb minerals at 266 to 240 605 °C and 7 to <5 km depth. This could be the result of fault-valve mechanism. The decrease of 606 607 the temperature-pressure and the sulfide activity caused by ongoing sulfide precipitation seems to be the major factors responsible for the gold deposition during the late stage of deposition. 608

The mineralized veins are spatially and temporally linked to the emplacement of the 609 610 andalusite-leucogranitic dykes of the Brioude-Massiac district around 329-315 Ma. Our new LA-ICP-MS U/Pb dating on hydrothermal apatite from the deposit documents an emplacement 611 age around 320 Ma. This genetic link suggests a magmatic-to-hydrothermal transition for the 612 Bonnac ore-forming process. In the newly proposed model, the cooling of a peraluminous 613 pluton might have supplied magmatic fluids, and heat source for mineralized fluid flows toward 614 615 high permeability zones such as previous discontinuities. The magmatic origin of the fluid has been partly overprinted by fluid-rocks interaction. 616

The emplacement of both the andalusite-leucogranitic dykes and quartz veins was controlled at the regional scale by a NW-SE extensional direction, consistent with the tectono-magmatic D4 event corresponding to the syn-orogenic extension in the FMC Variscan orogen. This geodynamic event is older than the "Or 300" one, suggesting therefore an earlier fertile metallogenic period at ca. 320 Ma for tungsten and gold deposition in the FMC.

The genetic classification of the Bonnac mineralization is equivocal. The W-As-Bi-Auquartz veins exhibit the features of both orogenic gold (relatively deep level of emplacement) and IRGD model (spatial-temporal link between the mineralization and the peraluminous intrusion). We propose that it represents an intermediate type between the typical orogenic-gold and IRGD model.

The Serpukhovian to Bashkirian peraluminous and alusite-leucogranitic dyke swarms appear as a favorable metallotect for future mining exploration in the FMC. The widespread occurrences related to this type of magmatism in the FMC suggest that other Bonnac-like, or IRGD-like, deposits probably exist. IRGD deposits, and the economic high-grade gold content in tungsten vein-type, might have been underestimated in the FMC.

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### 905 Figures captions

Fig. 1. Geological map of the French Massif Central (modified from Faure *et al.*, 2009), with
the location of, the tungsten deposits and occurrences (from Audion and Labbé, 2012), and the
study area. Tungsten district name abbreviations: ECH: Echassières; ENG: Enguialès; FUM:
Fumade; GOU: St-Goussaud; LCP: Leucamp; MAN: Mandelesse; ML: MontredonLabessonniè; NF: Neuf-Jours; PLV: Puy-les-Vignes; SM: St-Mélany; VAU: Vaulry.

Fig. 2. Location of the study area within the geological and metallogenic framework of the
Brioude-Massiac district. The simplified geology modified from Lasnier *et al.* (1982) and
Thonat *et al.* (2014). Location and extension of mineralized veins are from Périchaud, (1970).

- Fig. 3. Geological and structural map of the Bonnac area with the location of most interestingoutcrops.
- 916 **Fig. 4.** A) Representative arsenopyrite (Asp) and wolframite (Wolf) bearing quartz vein from
- 917 the Costillon vein (outcrop A in Fig.3) showing the structural features and the relationships

918 with the paragneiss host-rock and the leucogranitic dykes. B) Detail of drag folds developed in

- the country-rock paragneiss along the contact between the arsenopyrite (Asp) and wolframite
- 920 (Wolf) bearing quartz veins and leucogranitic dyke. La Borie vein (outcrops B in Fig.3).
- **Fig. 5.** A) Detail picture of the Fig.4B W-As-Bi-Au bearing quartz vein crosscutting leucogranitic dykes, (La Borie vein, outcrops B in Fig.3). B) Fault plane seen on Fig. 5A with high angle pitch striation. C) Cm-sized mineralized quartz veins network crosscutting the leucogranitic dyke (the Rode vein, outcrops C on Fig.3). D) Focus on the fault plane in the mineralized vein of the figure 5C showing a normal kinematics.
- Fig. 6. Mine gallery opened in the Ferbert vein. A) Low angle wolframite (Wolf) and
  arsenopyrite (Asp)-bearing quartz vein (outcrops D in Fig.3). The vein is cut by late sub-vertical
  barren fault. B) Detail of the quartz vein showing normal kinematics.
- Fig. 7. A) 3D block showing the main structural observations made on the mineralized quartz
  veins from Bonnac area. They allow us to propose a relative chronology of the structures
  developed in the paragneissic host-rock, the leucogranitic dykes and the quartz veins. B)
  Stereogram (lower hemisphere projection) of the poles of the fault planes coeval with the
  emplacement of the mineralized veins, leucogranitic dykes, and late faults measured in the field.
- Fig. 8. Representative W-As-Bi-Au-bearing quartz hand sample from the Androl vein (see
  Fig.3 for localization), with arsenopyrite, wolframite, scheelite, and muscovite. Sample is
  observed in natural light (left) and UV light (254 nm, right).
- **Fig. 9.** Microphotographs showing the mineralogy of the stages 1 and 2 at Bonnac. A) Coarse wolframite (Wolf) with lollingite (Lo) fractured and cemented by rhombic arsenopyrite (Asp). Secondary scheelite (Sch) pseudomorphs after wolframite. Arsenopyrite is fractured and cemented by bismuthinite (Bit), (Androl vein). B) Cathodoluminescence view showing the relationships between lollingite (Lo), weakly deformed macrocristalline quartz (Qz1), and arsenopyrite (Asp) rhombic crystals cutting Qz1, (Costillon vein). C) Wolframite (Wolf) and

943 coarse hydrothermal apatite (Ap) assemblage fractured and cemented by secondary scheelite
944 (Sch) and minor pyrite (Py), (Ferbert vein). D) Highly sheared macrocristalline quartz (Qz1)
945 crosscut by a second quartz generation (Qz2), (see text for further explanation). Relics of Qz1
946 clasts are present in the upper right part of the photograph, (Ferbert vein).

Fig. 10. Microphotographs showing the mineralogy of stage 3. A) Macrocristalline quartz 947 (Qz1) and highly sheared quartz (Qz2) crosscut by microcracks with fluid inclusions and 948 bismuth minerals (Bi minerals), (Ferbert vein). B) Relationships of sheared quartz (Qz1) with 949 neoformed quartz (Qz2), crosscut by microcracks with bismuthinite (Bit) and electrum (El), 950 (Ferbert vein. C) Lollingite aggregates (Lo) highly fractured and cemented by hyaline quartz 951 (Qz3) with bismuthinite (Bit), (La-Rode vein. D) Same picture as C) in transmitted, polarized 952 light. E) Lollingite (Lo) crosscut by an assemblage of native bismuth (Bi) and bismuthinite 953 954 (Bit), (Androl vein). F) back scattered electron image of the complex Bi-Te assemblage formed in stage 3. Native rounded shape bismuth (Bi) with bismuthinite (Bit) and tetrahedrite (Ttr), 955 horobetsuite (Hor) in a hedlevite (Hed) crystal. Ox: unknown oxydes, (Ferbert vein). 956

957 Fig. 11. Microphotographs showing gold habits of stage 3 at Bonnac. A) Lollingite (Lo) with inclusions of electrum (El) within a native bismuth (Bi) - bismuthinite (Bit) patch, (Androl 958 vein). B) Fractured wolframite (Wolf) cemented by bismuthinite (Bit), electrum (El), hedleyite 959 960 (Hed) and native bismuth (Bi), (Ferbert vein). C) Residual lollingite (Lo) fractured and cemented by arsenopyrite (Asp) at its turn fractured and cemented by bismuthinite (Bit), 961 electrum (El), hedlevite (Hed) and native bismuth (Bi), (Ferbert vein). D) Fractured 962 arsenopyrite (Asp) cemented by chalcopyrite (Ccp) with bismuthinite (Bit) inclusions, 963 964 sphalerite (Sp), electrum (El), (Ferbert vein). E) Fractured arsenopyrite (Asp) cemented by chalcopyrite (Ccp) with bismuthinite (Bit) inclusions, sphalerite (Sp), tetrahedrite (Trt), 965 euhedral pyrite (Py) contemporaneous with euhedral quartz (Qz4), (Ferbert vein). 966

967 **Fig. 12.** Paragenetic succession of the Bonnac W-As-Bi-Au mineralization. See text for details.

**Fig. 13.** A) and B) cathodoluminescence images of some of the dated apatite grains from Bonnac (A, Androl vein, B, Ferbert vein). C) and D) Tera-Wasserburg concordia diagrams for the hydrothermal apatite from Bonnac. n corresponds to the number of apatite grains analyzed. Ellipses and errors are reported at  $2\sigma$ .

Fig. 14. Summary of the evolution of the estimated mineral deposition temperatures for the 3
stages of mineralization of the Bonnac veins, based on all available data. Fluids inclusions data
are from Bril (1982), estimated temperature for quartz textural deformation are from Stipp *et al.* (2002).

- **Fig. 15.** Stereographic projection of faults planes contemporaneous of mineralized quartz veins with their kinematics and associated striae.  $\sigma 1$ ,  $\sigma 2$ ,  $\sigma 3$ : orientation of principal stress axe calculated from fault-slip data inversion using WinTensor software in Schmidt's lower hemisphere equal-area projection (Delvaux and Sperner, 2003).
- Fig. 16. A) Synthesis of the structural control and radiometric age compilation of orogenic gold
   ± antimony district, W-Sn and W-Bi-Au vein-type districts (Beziat *et al.*, 1980; Bouchot *et al.*,

2005; Harlaux et al., 2018). White boxes correspond to U-Pb dating on wolframite by TIMS method, from Harlaux et al. (2018). Black boxes correspond to Ar/Ar dating on muscovite from Monier *et al.* (1999, 2000). For the orogenic-gold deposits, le Châtelet dating (K/Ar on illites) is from Bouchot et al. (2005); from Nicaud, (2001) for Saint-Yrieix district (K/Ar on illite); from Chauvet et al. (2012) for the Cévennes district (Ar/Ar on muscovite). District name abbreviations are the same as in figure 1. Geological map modified after Chantraine et al. (1996). B) The Bonnac hydrothermal event is replaced in the different geodynamic events of the Variscan orogen in the French Massif Central (Faure et al., 2009). 

990 Fig. 17. Metallogenic model of the Bonnac W-Bi-Au quartz veins system (not to scale).

**Fig. 18.**  $Fe_2O_3/FeO$  vs SiO<sub>2</sub> diagram for granitoid rocks associated with various mineral deposits, compiled from Harlaux *et al.* (2018). Data from the leucogranitics dykes of the Brioude-Massiac district are from Sandras, (1988).

Table 1 Summary of the EPMA assays obtained on arsenopyrite from the Brioude-Massiac W As-Bi-Au veins and gold from Bonnac. Estimated temperatures of crystallization with the
 arsenopyrite geothermometer are compared with the fluid-inclusions data (Bril, 1982).



50 Km

2 E

W skarn-type deposit

4 E

0 E



















# **Figure 8**





1061			
1062			
1063			
1064			
1065			
1066			
1067			





	Stage 1	$\backslash$	Stage 2	$\mathbb{N}$	S	Stage	3
Mineral	W + As		As + W		As + Fe + Bi + Au	$\left \right\rangle$	Cu + Zn + Au
Macrocrystalline Qz1				$\mathbb{N}$		$\mathbf{X}$	
Sheared Qz2				$\bigcirc$		$\left( \right)$	
Hyaline Qz3				$\bigcirc$			
Euhedral Qz4				$\left \right\rangle$		$\bigcirc$	
Muscovite				X		$\wedge$	
Apatite				$\mathbb{N}$		$\mathbb{N}$	
Wolframite (ferberite)				$\bigcirc$		$\left\{ \right\}$	
Scheelite				X			
NbTiFe oxydes		] \		КX		КŻ	
Electrum		1 /		1X			
Lollingite			77 77	КХ		КŻ	
Arsenopyrite		1 /					
Pyrrhotite				КX		КŻ	
Marcasite		]′_		]X		စို	
Bismuthinite		io l		КХ			
Native bismuth		nat		]X		t t	
Hedleyite		OL		(D)		Ļ	
Maldonite		def		Lin		8	
Horobetsuite		le		5		i i i	
Chalcopyrite		Ē		La(		E	
Tetrahedrite		<b>  </b>		e i		\ <b>E</b> \	
Pyrite		tile		Ē		e p	
Galena		D D				di.	
Sphalerite				$\mathbb{N}$		Tal	
Molybdenite (Périchaud, 1970)				$\langle \rangle$		KN	
Cubanite (Périchaud, 1970)		]/		$ \rangle$		$\left  \right\rangle $	
Native arsenic (Périchaud, 1970)		<u> </u>		$\square$		$\angle \downarrow$	
Ferbert vein	Costi	illon	vein, Andr	ol vei	in, la Rodd	e vei	n

# 1085 Figure 13





1093

1094 Figure 15



1096 Figure 16



1098 Figure 17





Arsenopyrite composition	Number of analysis	S (Wt. %	) Std	Fe	Std	As	Std	Sb	Std	Au S	itd Tota	I As (at%	) Std	T (°C) Kretschmar and Scott, 1976	Trapping temperature (°C) estimated by fluid inclusions (Bril, 1982)
Asp from Bonnac W-As-Bi- Au veins (data from this study and Bril, 1983)	60	19.30	0.50	34.40	0.32	45.70	0.68	0.01	0.03	bdl	99.4	33.4	0.66	485°C	> 350°C
Asp from Vèze W-As-Bi-Au veins (data from Bril, 1983)	3	19.74	0.63	34.87	0.26	45.39	0.89	bdl		bdl	100	32.8	0.87	470°C	> 350°C
Asp from Bosberty W-As- Bi-Au veins (data from Bril, 1983)	4	19.10	0.46	35.43	0.19	45.47	0.63	bdl		bdl	100	33.0	0.61	480°C	> 350°C

	Gold composition	Number of analysis	Ag (Wt. %)	Std	Au	Std	Total
-	Gold from W-As-Bi-Au veins	10	16.7	5.70	82.60	6.92	99.30
11			Std = stand	ard dev	bdl = bel	ow dete	ection limi

# 1123 Supplementary data

## **ESM 1**



## 1127 ESM 2

Arsénop	oyrites	Weight%					Det.Lim ppm					Atomic%					
Localisation	Commentaires	S	Sb	Fe As	Au	Total	s	Sb	Fe	As	Au	S	Sb	Fe	As A	u 1	Гotal
Bonnac	BM29A_Asp1_coeur2	18.85	bdl	34.45 45.92	bdl	99.22	336	592	317	881	953	32.34	0.00	33.93	33.72 0.	00	100
Bonnac	BM29A_Asp2_coeur	18.92	0.09	34.23 46.14	bdl	99.38	367	606	316	876	-	32.43	0.04	33.68	33.84 0.	00	100
Bonnac	BM29A_Asp2_bord	18.65	bdl	34.19 46.79	bdl	99.63	364	596	311	885	-	31.99	0.00	33.67	34.34 0.	00	100
Bonnac	BM29A_Asp3_C	19.00	0.09	34.58 46.44	bdl	100.11	390	605	323	882	-	32.34	0.04	33.79	33.83 0.	00	100
Bonnac	BM29A_Asp3_B	19.38	bdl	34.62 45.88	bdl	99.87	363	-	311	876	-	32.91	0.00	33.75	33.34 0.	00	100
Bonnac	BM29A_Asp4_C	19.19	bdi	34.13 45.96	bdl	99.27	389	599	318	880	-	32.83	0.00	33.52	33.65 0.	00	100
Bonnac	BM29A_Asp5_B	19.17	bdi	34.27 46.36	bdi	99.79	3/4	602 E06	317	882	-	32.67	0.00	33.52	33.81 0.	00	100
Bonnac	BIVIZ9A_ASP5_C	10.90	bdi	34.23 40.38	bdl	99.39	380	590	212	001 997	-	22.45	0.00	22.05	33.94 0.	00	100
Bonnac	BM29A_Aspo_C BM29A_Asp6_C2	19.14	bdl	34.00 40.10	bdl	100 22	367	596	315	868	-	32.55	0.00	33.85	33.00 0.	00	100
Bonnac	BM29A Asp7 C	19.27	bdl	34.61 45.69	bdl	99.56	351	591	321	891	959	32.83	0.00	33.85	33.31 0.	00	100
Bonnac	BM29A Asp8 C	18.85	0.11	34.31 45.94	bdl	99.22	362	593	319	880	-	32.37	0.05	33.82	33.76 0.	00	100
Bonnac	BM29A Asp9 C	19.30	bdl	34.49 45.70	bdl	99.49	363	-	323	872	-	32.91	0.00	33.75	33.34 0.	00	100
Bonnac	BM29A_Asp10_C	19.05	bdl	34.44 45.65	bdl	99.14	344	595	319	885	-	32.65	0.00	33.88	33.47 0.	00	100
Bonnac	BM29A_Asp11_C	19.22	bdl	34.32 45.96	bdl	99.50	359	588	320	879	964	32.81	0.00	33.62	33.57 0.	00	100
Bonnac	BM29A_Asp12_C	19.30	bdl	34.54 45.78	bdl	99.62	338	577	317	886	959	32.87	0.00	33.77	33.36 0.	00	100
Bonnac	BM29A_Asp13_C	19.48	bdl	34.61 45.63	bdl	99.72	317	598	321	884	-	33.09	0.00	33.74	33.17 0.	00	100
Bonnac	BM29A_Asp13_B	18.86	bdl	34.04 46.29	bdl	99.19	388	583	321	874	-	32.40	0.00	33.57	34.03 0.	00	100
Bonnac	BM29A_Asp13_B2	20.10	bdl	34.49 44.91	bdl	99.49	396	597	317	867	-	34.00	0.00	33.49	32.51 0.	00	100
Bonnac	BM29A_Asp14_C	19.41	bdl	34.42 45.69	bdl	99.52	372	597	314	872	-	33.06	0.00	33.64	33.30 0.	00	100
Bonnac	BM29A_Asp15_B	19.16	bdi	34.34 46.29	bdi	99.79	389	602	317	8/4	-	32.64	0.00	33.60	33.76 0.	00	100
Bonnac	BM29A_Asp16_C	18.88	bal	34.26 46.28	bal	99.42	359	584	320	8/5	-	32.35	0.00	33./1	33.94 0.	00	100
Bonnac	BM29A_ASP16_B	19.00	bdi	33.37 45.21	bdi	97.59	347	200	314 217	000 000	-	33.05	0.00	33.60	33.04 0.	00	100
Bonnac	$BM29A_Asp17_C$ BM29A_Asp18_C	19.02	hdl	34 56 45 91	hdl	99.52	366	594	322	875	956	32.57	0.00	33.05	33.43 0	00	100
Bonnac	BM29A Asp18 B	19.99	bdl	34.37 44.25	bdl	98.61	379	586	314	868	-	34.08	0.00	33.64	32.28 0.	00	100
Bonnac	BM29A Asp19 C	19.57	bdl	34.55 45.19	0.13	99.44	364	585	319	876	959	33.30	0.00	33.75	32.91 0.	04	100
Bonnac	BM29A_Asp20_C	19.24	bdl	34.19 45.78	bdl	99.21	379	585	318	869	-	32.92	0.00	33.57	33.51 0.	00	100
Bonnac	BM29A_Asp21_C	19.21	bdl	34.37 45.94	bdl	99.51	380	-	311	881	-	32.79	0.00	33.67	33.55 0.	00	100
Bonnac	BM29A_Asp22_C	19.84	bdl	34.47 44.46	bdl	98.76	376	584	316	861	-	33.83	0.00	33.74	32.44 0.	00	100
Bonnac	BM29A_Asp23_C	19.24	bdl	34.36 45.80	bdl	99.40	388	597	314	870	-	32.85	0.00	33.68	33.47 0.	00	100
Bonnac	BM29A_Asp23_B	19.89	bdl	34.32 45.19	bdl	99.40	397	-	311	875	957	33.76	0.00	33.43	32.81 0.	00	100
Bonnac	BM29A_Asp24_B	19.11	bdl	34.34 46.04	bdl	99.48	388	-	322	879	958	32.65	0.00	33.68	33.67 0.	00	100
Bonnac	BM29A_Asp25_C	19.28	0.15	34.39 45.88	bdl	99.69	367	600	316	870	-	32.84	0.07	33.63	33.45 0.	00	100
Bonnac	BM29A_Asp25_C2	19.43	וממ	34.58 45.80	וסמ	99.80	389	579	317	8/0	-	33.00	0.00	33./1	33.29 0.	00	100
Bonnac	BM29A_Asp25_B	19.54	bdi	34.03 45.59	bai	99.75	309	570	318	875	-	33.10	0.00	33.74	33.11 0.	00	100
Bonnac	BM29A_ASp20_C	19.04	0 11	34.42 40.08	hdl	99.54	365	592	310	880	555	32.55	0.00	33.67	33.70 0.	00	100
Bonnac	BM29A_Asp27_C	19.82	bdl	34.54 45.34	bdl	99.70	355	608	318	880	956	33.56	0.00	33.58	32.86 0.	00	100
Bonnac	BM29A Asp28 B	19.17	bdl	34.59 46.09	bdl	99.84	393	-	315	873	_	32.63	0.00	33.80	33.57 0.	00	100
Bonnac	BM29A_Asp29_C	18.71	bdl	34.09 46.69	bdl	99.50	367	579	314	876	-	32.12	0.00	33.59	34.29 0.	00	100
Bonnac	BM29A_Asp_30C	19.21	bdl	34.34 45.66	bdl	99.21	352	-	322	858	-	32.86	0.00	33.72	33.42 0.	00	100
Bonnac	BM29A_Asp_30B	19.88	bdl	34.57 44.95	bdl	99.40	359	-	316	868	-	33.71	0.00	33.66	32.63 0.	00	100
Bonnac	BM29A_Asp_31C	19.28	bdl	34.23 45.54	0.15	99.19	361	594	314	867	952	32.99	0.00	33.63	33.34 0.	04	100
Bonnac	BM29A_Asp_31B	19.16	bdl	34.19 45.48	bdl	98.83	364	583	322	871	963	32.89	0.00	33.70	33.41 0.	00	100
Bonnac	BM29A_Asp_32C	19.12	bdl	34.48 46.36	bdl	99.96	363	592	316	873	-	32.55	0.00	33.69	33.76 0.	00	100
Bonnac	BM29A_Asp_32B	19.88	bdl	34.45 45.10	bdl	99.43	373	579	316	875	-	33.72	0.00	33.55	32.74 0.	00	100
Bonnac	BM29A_Asp_33C	19.23	bdi	34.27 45.47	bdl	98.98	361	-	321	887	970	32.95	0.00	33./1	33.34 0.	00	100
Bonnac	BIVIZ9A_ASP_34C	19.02	Dai bd	34.10 40.20	bdi	99.44	407	-	319	880 870	950	32.56	0.00	33.50 22.92	33.88 0.	00	100
Bonnac	BIVIZ9A_ASP_35C	19.11	bdi	34.02 40.17	bdi	99.90	224	-	321	863	959	32.54	0.00	22.03	33.03 0.	00	100
Bonnac	BM29A Asn 37C	20 11	bdl	34.49 44 74	bdl	99.32 99.34	377	-	313	870	955	34.05	0.00	33.53	32.42 O	00	100
Bonnac	BM29A Asp 37B	18.84	bdl	34.01 46.40	bdl	99.24	378	595	322	877	-	32.36	0.00	33.53	34.11 0	00	100
Bonnac	BM29A Asp 38B	18.85	bdl	34.06 46.43	bdl	99.34	380	593	316	871	-	32.35	0.00	33.55	34.10 0.	00	100
Bonnac	BM29A_Asp_38C	19.43	bdl	34.40 45.52	bdl	99.34	367	597	304	883	-	33.12	0.00	33.67	33.21 0.	00	100
Bonnac	 BM29A_Asp_39C	18.52	bdl	34.04 46.76	bdl	99.32	363	593	316	883	-	31.89	0.00	33.65	34.45 0.	00	100

Grains o	l'or	Weight%		Det.Lim ppm									
Localisation	Commentaires	Ag	Au	Hg	Sb	Total	Ag	Au	Hg	Sb			
Bonnac	Or dans Py/Ccp	16.07	84.57	bdl	bdl	100.64	696	2284	-	-			
Bonnac	Or dans Py/Ccp	11.05	89.77	bdl	bdl	100.82	692	2307	-	-			
Bonnac	Or dans Py/Ccp	8.81	92.37	bdl	bdl	101.18	584	1975	-	1190			
Bonnac	Or dans Py/Ccp	7.85	91.86	bdl	bdl	99.71	552	1936	-	-			
Bonnac	Or dans Py/Ccp	17.18	83.07	bdl	bdl	100.26	609	1971	-	1216			
Bonnac	Or dans Py/Ccp	19.63	77.84	0.29	bdl	97.77	594	1985	1136	-			
Bonnac	Or dans Py/Ccp	20.05	78.97	bdl	bdl	99.02	598	1967	1131	-			
Bonnac	Or inclus dans Ccp+Bi	19.68	79.53	bdl	bdl	99.21	589	1977	-	1174			
Bonnac	Or inclus dans Ccp+Bi	22.14	76.34	bdl	bdl	98.48	594	1968	-	1213			
Bonnac	Or inclus dans Asp	24.51	72.12	0.42	bdl	97.04	613	1964	1121	1175			

# 1129 ESM 3

	ESM 3 Table 1: Operating conditions for the LA-ICP-MS equipment
Laboratory & Sample Preparation	
Laboratory name	Géosciences Rennes, UMR CNRS 6118, Rennes, France
Sample type/mineral	apatite
Sample preparation	Thin and polished sections
Imaging	MEB Merlin Compact Zeiss with EDS detector EDS (Bruker, Quantax – Xflash6– 129 eV)
Laser ablation system	
Make, Model & type	ESI NWR193UC, Excimer
Ablation cell	ESI NWR TwoVol2
Laser wavelength	193 nm
Pulse width	< 5 ns
Fluence	6.5 J/cm <sup>2</sup>
Repetition rate	5 Hz
Spot sizes	40 μm (round spot)
Sampling mode / pattern	Single spot
Carrier gas	100% He, Ar make-up gas and N2 (3 ml/mn) combined using in-house smoothing device
Background collection	20 seconds
Ablation duration	60 seconds
Wash-out delay	15 seconds
Cell carrier gas flow (He)	0.75 l/min
ICP-MS Instrument	
Make, Model & type	Agilent 7700x, Q-ICP-MS
Sample introduction	Via conventional tubing
RF power	1350W
Sampler, skimmer cones	Ni
Extraction lenses	Х туре
Make-up gas flow (Ar)	0.87 l/min
Detection system	Single collector secondary electron multiplier
Data acquisition protocol	Time-resolved analysis
Scanning mode	Peak hopping, one point per peak
Detector mode	Pulse counting, dead time correction applied, and analog mode when signal intensity > $^{\sim}10^{6}$ cps
Masses measured	<sup>43</sup> Ca, <sup>204</sup> (Hg + Pb), <sup>206</sup> Pb, <sup>207</sup> Pb, <sup>208</sup> Pb, <sup>232</sup> Th, <sup>238</sup> U
Integration time per peak	10-30 ms
Sensitivity / Efficiency	28 000 cps/ppm Pb (50µm, 10Hz)
Dwell time per isotope	5-70 ms depending on the masses
Data Processing	
Gas blank	20 s on-peak
Calibration strategy	Madagascar apatite used as primary reference material, Durango and McClure apatite standards
	used as secondary reference material (quality control)
Reference Material info	Madagascar (Thomson et al., 2012) Durango (McDowell et al., 2005) McClure (Schoene and Bowring, 2006)
Data processing package used	Iolite (Paton et al., 2010), VizualAge_UcomPbine (Chew et al., 2014)
Quality control / Validation	Durango: Weighted average $^{207}$ Pb corrected age = 31.89 ± 0.70 Ma (MSWD = 0.62)
	McClure: Weighted average $^{207}$ Pb corrected age = 526 ± 14 Ma (MSWD = 1.7)

	ESM 3 Table 2: LA-ICP-MS U/Pb analyses for apatites for studied samples										
		U (ppm)	Pb (ppm)	238U/206Pb	Error (2o)	207Pb/206Pb	Error (2o)	Final 207 Age	Error (2σ)		
	BM46d_1	111.90	7.82	15.830	0.250	0.2212	0.0054	317	16		
	BM46d_2	122.60	7.77	16.130	0.220	0.2083	0.0030	316	14		
	BM46d_3	115.90	8.24	15.530	0.220	0.2283	0.0053	317	13		
	BM46d_4	88.40	8.02	14.510	0.130	0.2680	0.0031	318	17		
	BM46d_5	127.60	10.31	15.700	0.130	0.2254	0.0024	316	17		
	BM46d_7	66.10	7.61	13.350	0.130	0.3069	0.0044	324	19		
	BM46d_8	73.70	7.89	13.620	0.180	0.2896	0.0054	327	16		
	BM46d_9	176.80	10.11	16.340	0.230	0.1849	0.0039	324	17		
	BM46d_10	64.44	7.24	13.640	0.120	0.2992	0.0037	322	18		
	BM46d_11	148.70	10.11	15.750	0.190	0.2071	0.0027	324	16		
	BM46d_13	66.79	10.16	11.660	0.140	0.3781	0.0048	323	22		
	BM46d_14	158.30	13.75	14.540	0.120	0.2616	0.0031	322	16		
	BM46d_15	90.33	14.57	11.950	0.130	0.3472	0.0039	336	21		
	BM46d_16	97.10	10.38	13.500	0.200	0.3023	0.0110	322	21		
	BM46d_17	41.64	21.18	5.768	0.096	0.6060	0.0063	344	43		
	BM46d_18	39.08	40.03	3.384	0.055	0.7010	0.0070	369	63		
	BM46d_19	51.83	12.96	9.000	0.160	0.4660	0.0077	343	30		
	BM46d_20	51.96	39.50	4.255	0.091	0.6550	0.0077	377	44		
	BM46d_21	38.60	33.40	3.870	0.130	0.6810	0.0066	362	40		
	BM46d_22	207.80	17.13	14.780	0.200	0.2421	0.0078	327	16		
	BM46d_23	204.30	22.95	13.660	0.160	0.3051	0.0062	317	11		
Ferbert vein	BM46d_24	68.00	32.18	6.160	0.100	0.5915	0.0075	341	20		
Bonnac	BM39a_2	29.06	3.39	12.930	0.150	0.3233	0.0063	324	14		
	BM39a_3	30.09	3.58	12.970	0.180	0.3140	0.0110	333	13		
	BM39a_4	26.70	2.79	13.030	0.170	0.2997	0.0074	336	16		
	BM39a_5	24.32	2.65	13.500	0.280	0.3000	0.0120	325	22		
	BM39a_6	11.66	2.86	9.440	0.160	0.4710	0.0085	323	28		
	BM39a_7	13.39	3.39	9.730	0.150	0.4550	0.0083	326	23		
	BM39a_8	13.13	3.52	9.510	0.140	0.4573	0.0075	333	25		
	BM39a_9	13.53	2.97	10.730	0.340	0.4260	0.0090	321	29		
	BM39a_10	11.25	3.02	9.240	0.130	0.4747	0.0140	326	24		
	BM39a_11	23.39	3.31	12.420	0.180	0.3438	0.0077	324	16		
	BM39a_13	138.10	5.24	16.830	0.150	0.1567	0.0027	325	11		
	BM39a_14	76.90	5.10	15.340	0.240	0.2360	0.0047	319	12		
	BM39a_15	315.50	6.81	17.830	7.830 0.220 0.1208 0.0026		324	12			
	BM39a_16	79.80	5.17	15.220	0.260 0.2271 0.0045 3		325	13			
	BM39a_17	76.51	4.93	15.650	0.150	0.2160	0.0027	320	12		
	BM39a_19	243.20	5.29	17.940	0.160	0.1138	0.0027	324	11		
	BM39a_21	34.74	3.53	13.280	0.160	0.2944	0.0052	332	16		
	BM39a_24	48.50	4.04	14.260	0.200	0.2660	0.0052	326	15		