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# The Puy-les-Vignes breccia pipe (Massif Central, France): a unique occurrence of polymetallic W-Nb±Ta-HREE-Bi-Cu-As±Au-Ag mineralization in the Variscan belt

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**Abstract.** The Puy-les-Vignes deposit (Limousin, French Massif Central) represents an uncommon occurrence in the West European Variscan belt of a hydrothermal tungsten mineralization associated with a breccia pipe structure. A new study of this atypical quartz-wolframite-tourmaline deposit has been possible, allowing to revisit the mineral paragenesis and to identify four main successive stages of mineralization: (i) W-As-Nb±Ta stage corresponding to the historically economic mineralization hosted in quartz-wolframite-arsenopyrite veins; (ii) Fe-Cu-Zn±Mo stage represented by the deposition of base metal sulphides; (iii) Nb-Y-HREE stage associated with a late hydrothermal paragenesis in a tourmaline, adularia and chlorite matrix; (iv) Bi±Au-Ag stage, related to the late-Variscan regional metallogenic event in the Limousin.

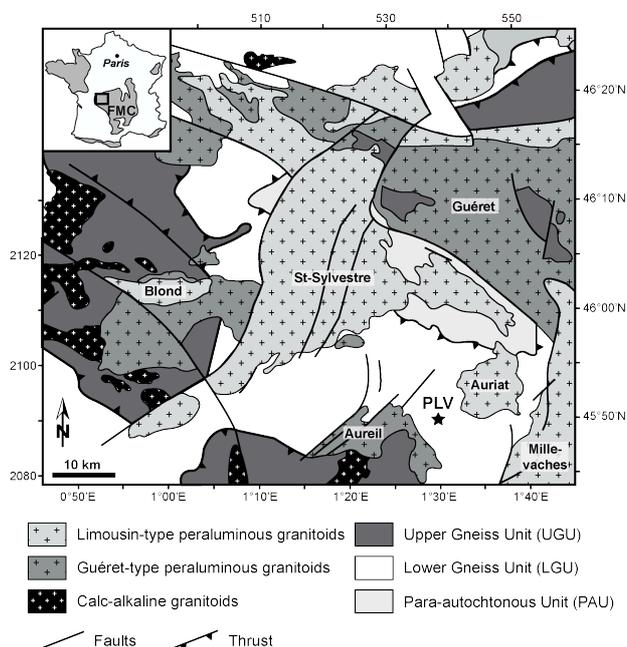
## Keywords.

Puy-les-Vignes; tungsten mineralization; breccia pipe; rare-metal; French Massif Central; Variscan belt.

## 1 Geological setting

The Puy-les-Vignes deposit is located in the northwestern part of the French Massif Central (FMC) in the Limousin area (Figure 1), which consists of a stack of metamorphic nappes emplaced during the continental collision between Gondwana and Laurussia through the Upper Paleozoic (Faure et al. 2009 and references therein). In France, the FMC is the largest area where Variscan terranes are exposed and has an important economic potential for the W-Sn and rare-metal deposits (Marignac & Cuney 1999, Cuney et al. 2002, Bouchot et al. 2005). The Puy-les-Vignes deposit was mined underground until 1957, producing around 4 kt WO<sub>3</sub>, and was the second ranking tungsten mine in France during the XX<sup>th</sup> century. The mineralization is contained in a breccia pipe with dimensions 80 x 340 m at surface and at least 300 m in depth, possibly located at the apex of a hidden granite, as already described for other breccia pipes by Sillitoe (1985). The pipe is hosted in the biotite-sillimanite gneisses of the Lower Gneiss Unit (LGU), the intermediate nappe in the three nappes pile of the FMC, and cuts two dykes of leucogranites and lamprophyres (Weppe, 1951). The deposit is in the close vicinity of the Auriat granite (324±1 Ma, Gebauer et al. 1981) and the Aureil granite (346±14 Ma, Duthou 1978), which are peraluminous “S-type” granites, respectively of the Limousin- and Guéret-types of Stussi (1989) (Figure 1). The tungsten mineralization has been dated at 323±0.9 Ma by <sup>40</sup>Ar/<sup>39</sup>Ar on muscovite associated with

the wolframite (Cuney et al. 2002) and would therefore be coeval with the emplacement of the regional Limousin-type peraluminous leucogranitic complexes, such as St-Sylvestre and Millevaches. According to Weppe (1951, 1958), the Puy-les-Vignes pipe resulted from: (i) a first stage of collapsing leading to a quartz-matrix supported breccia, with metric to centimetric angular clasts of the country rocks (mainly gneisses and granites), which are systematically rimmed by an aureole of tourmalinite, of which the thickness varies from a few millimeters to ten centimeters, until up to the complete tourmalinization of the fragments; (ii) a “mass collapsing” underlined by planar-curved quartz veins (“plateures”) within the breccia and quartz-filled decollements at the breccia to country rocks boundaries (“gaine”), which were the host for the economic mineralization, although the first breccia stage contains a potential low-grade tungsten mineralization.



**Figure 1.** Location and geological setting of the Puy-les-Vignes (PLV) deposit in the Limousin area, French Massif Central (FMC).

## 2 Paragenetic sequence of the deposit

According to the descriptions of Alikouss (1993) and to new petrographic observations, the paragenetic sequence of the Puy-les-Vignes deposit can be divided into six main stages (Figure 2).

	Stage I		Stage II				Stage III	Stage IV	Stage V	Stage VI
	(a)	(b)	W-(Sn)-Nb-Ta				Fe-Cu-Zn±Mo	Nb-Y-HREE	Bi±Au-Ag	Late alterations
Quartz	I	II	III				IV			
Tourmaline	I	II	III					IV		
Muscovite	I		III							
Chlorite		I	III							
Rutile		I	II	III	IV			V		
Monazite										
Xenotime										
Zircon										
Wolframite										
Columbite										
Wolframo-ixiolite										
Ferberite					I				II	
Scheelite										
Arsenopyrite									II	
Ferroskutterudite										
Cassiterite										
Sphalerite										
Pyrrhotite										
Molybdenite										
Siderite										
Pyrite										
Chalcopyrite										
Enargite										
Stannite										
NTox										
Adularia										
Bismuth										
Russellite										
Electrum										
Sulfosalts										
Bismuthinite										
Illite										
Scorodite										
Rooseveltite										
Tungstite										
Fe-oxides										

Figure 2. Paragenetic sequence of the Puy-les-Vignes deposit.

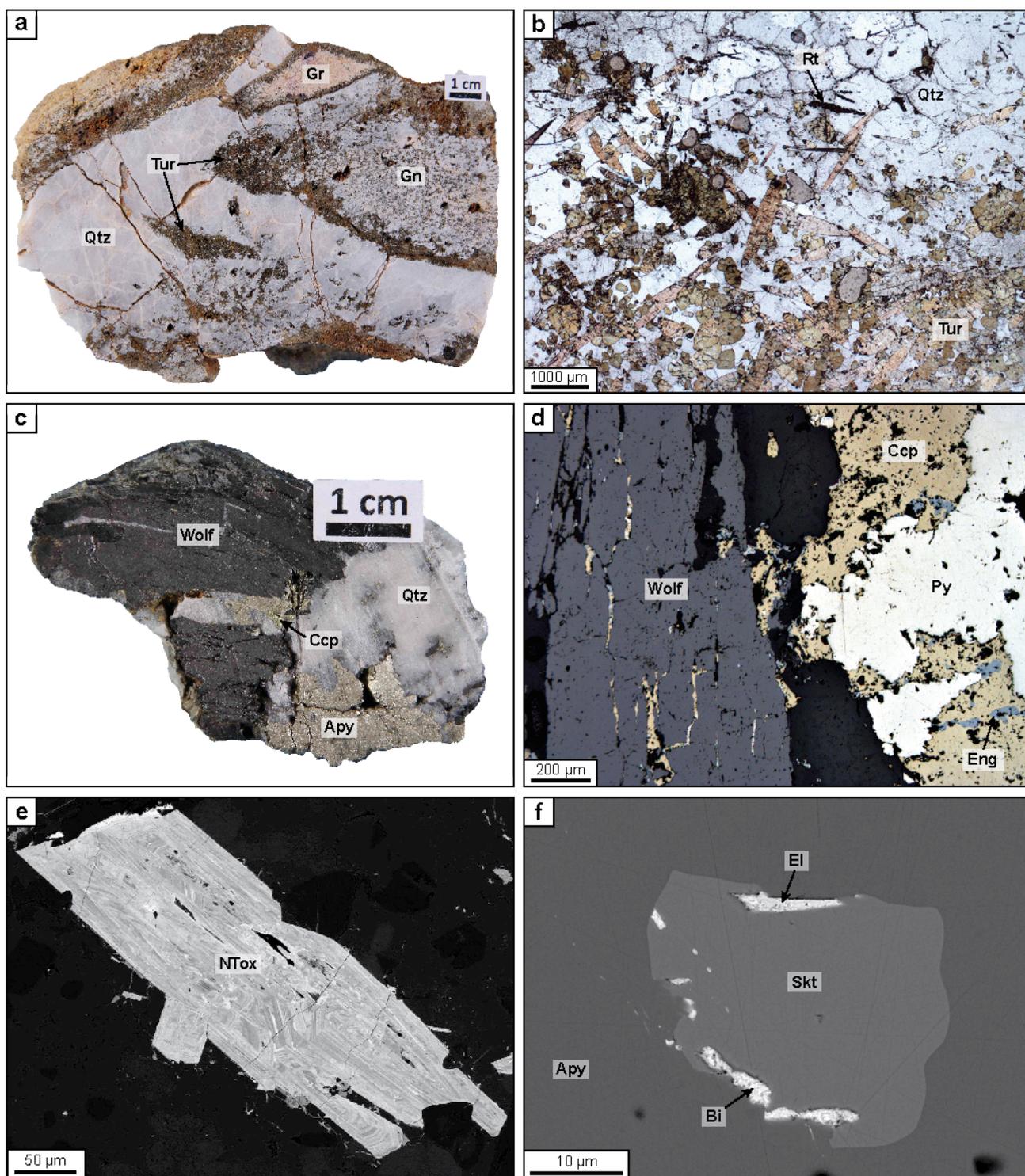
## 2.1 Stage I: Early hydrothermal alteration and brecciation

The country rocks are affected by a pervasive greisenization, destabilizing the primary feldspars and biotites and forming a secondary quartz-muscovite±tourmaline assemblage. The foliation is partially preserved within the gneissic clasts and relicts of biotites and feldspars remain in unaltered parts of the clasts, suggesting that the greisenization is diffuse within the country rocks and likely limited to early fissural discontinuities. Fluid overpressures lead to the hydraulic brecciation and collapse of the enclosing rocks, forming the breccia pipe. The clast rims are intensely tourmalinized, forming a recrystallization front (boron metasomatism), regardless of their lithology (greisenized gneisses or granites) (Figure 3a). There were two successive steps: (i) chloritization of the residual biotites, forming secondary anhedral crystals (50-100 µm) of Ti-W oxides (~3-5% W), coeval with the crystallization of minor monazite, xenotime and zircon, followed by tourmalinization of the greisen, resulting in a quartz-tourmaline assemblage (Figure 3b); (ii) massive tourmalinization of the clasts rims, forming a tourmalinite aggregate composed of elongated prisms of tourmalines with a palissadic structure (Figure 3b).

## 2.2 Stage II: W-As-Nb±Ta mineralization

Second stage brecciation leads to the infilling by milky quartz, forming the matrix of the breccia and

cutting the tourmalinite rims (Figure 3a). The quartz contains the wolframite and arsenopyrite (Figure 3c), together with disseminated crystals of acicular tourmalines and muscovites. The wolframite forms euhedral prismatic crystals, millimetric to centimetric in size, growing onto tourmalinite, and sometimes broken and disseminated within latter quartz generation. Two types of accessory rare-metal oxides are associated to the wolframite within the quartz: (i) euhedral to sub-euhedral crystals (100-500 µm) of Ti-W oxides (~3-5% W), characterized by Nb (~15%) and Ta (~5%) bearing overgrowths with a patchy texture; (ii) sub-euhedral crystals (200-500 µm) of wolframo-ixiolite and Fe-columbite in microcavities infillings or in overgrowths on the quartz-cemented wolframite. The latter is partially replaced by ferberite 1 with a complex internal texture, along cracks or crystal borders, and crystallizing in overgrowth on wolframo-ixiolite. The arsenopyrite forms sub-euhedral crystals, which cut the wolframite within veinlets. Its deposition is coeval with the crystallization of minor cassiterite. The arsenopyrite is rich in Co (~4.5%) and Ni (~1%) and contains many inclusions, such as ferroskutterudite, pyrrhotite, wolframite, xenotime, monazite and rutile, the latter being particularly rich in Nb (up to 12%), Ta (up to 2.5%), W (up to 10%) or Cr (up to 6%). The presence of Co, Ni, Fe and Cr suggests the local contribution of a mafic or ultramafic source (e.g. lamprophyre dyke) during the crystallization of arsenopyrite. Scheelite occurs lately by replacement of the wolframite and ferberite 1, cutting the arsenopyrite within veins, and is itself replaced by ferberite 2 (so-called “reinite”).



**Figure 3.** Photographs of samples from the Puy-les-Vignes deposit. (a) Clasts of greisenized gneisses (Gn) and granites (Gr) rimmed by an aureole of tourmalinite (Tur) and cemented within the milky quartz (Qtz) forming the matrix of the breccia pipe. (b) Microphotograph in transmitted light of the tourmalinite aureole formed by a quartz-tourmaline-rutile (Rt) assemblage, progressively passing to an aggregate of tourmaline crystals. (c) Sample of mineralized quartz vein containing an association of wolframite (Wolf) and arsenopyrite (Apy) with overgrowths of chalcopyrite (Ccp) and enargite (Eng) in overgrowths and infillings into the wolframite. (d) Microphotograph in reflected light showing an association of pyrite (Py), chalcopyrite (Ccp) and enargite (Eng) in overgrowths and infillings into the wolframite. (e) BSE image of a Nb-Ti-Y-HREE-W-U oxide (NTox), displaying complex internal textures, within a tourmaline-adularia-chlorite matrix. (f) BSE image of native bismuth (Bi) and electrum (El) infilling the ferroskutterudite (Skt) within arsenopyrite (Apy).

### 2.3 Stage III: Fe-Cu-Zn±Mo mineralization

An association of base metals (Fe-Cu-Zn±Mo) sulphides formed mainly by pyrite, chalcopyrite and sphalerite, with minor pyrrhotite, enargite, stannite and

molybdenite, fills the microcracks and microcavities within the tourmalinite from the stage I and ore minerals from the stage II (Figure 3d). Sulphide deposition is accompanied by the recrystallization of the milky quartz along the wolframite and arsenopyrite.

## 2.4 Stage IV: Nb-Y-HREE mineralization

A late hydrothermal stage is associated to the formation of a crackle-breccia with a tourmaline-adularia-chlorite matrix, coeval with the crystallization of a series of accessory minerals comprising monazite, xenotime, zircon, Nb-Fe-W-rich rutile and Nb-Ti-Y-HREE-W-U oxides, referred to as NTox (Figure 3e). The latter are particularly rich in Nb (up to 30%), Y (up to 13%), HREE (up to 5%), W (up to 5%), U (up to 3%) and Ta (up to 1%), with uncommon chemical composition and complex internal textures.

## 2.5 Stage V: Bi±Au-Ag mineralization

A discrete mineralization of native bismuth, Bi-Ag-Se-Te sulphosalts and electrum (Au-Ag) fills microcavities and microcracks within the quartz, wolframite and arsenopyrite from the stage II and the base metal sulphides from the stage III (Figure 3f). This mineral paragenesis cuts also the adularia-chlorite-tourmaline matrix from the stage IV. An association of siderite, arsenopyrite and As-rich pyrite precedes the deposition of the Bi-phases. A rim of bismuthinite (Bi<sub>2</sub>S<sub>3</sub>) surrounds occasionally the native bismuth, indicating a progressive sulphidation of the latter. Ferberite 2 is locally transformed in russellite (Bi<sub>2</sub>WO<sub>6</sub>) at contact with native bismuth.

## 2.6 Stage VI: Late hydrothermal and supergene alterations

Late hydrothermal circulations are responsible for alteration of arsenopyrite in scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O) and the crystallization of illite in residual microcavities within minerals of the previous stages. Scorodite veins contain in particular inclusions of rooseveltite (BiAsO<sub>4</sub>), indicating the remobilisation of bismuth during the alteration of arsenopyrite. Finally, supergene alteration affects the ore body forming secondary minerals, such as tungstite (WO<sub>3</sub>·H<sub>2</sub>O) and Fe-oxides.

## Conclusion

Four main successive stages of mineralization have been identified in the paragenetic sequence of the Puy-les-Vignes deposit: (i) a W-As-Nb±Ta stage associated with the deposition of quartz, wolframite, scheelite, arsenopyrite and rare-metal oxides in the hydrothermal veins through the breccia pipe; (ii) a Fe-Cu-Zn±Mo sulphide stage cutting the minerals of the previous stage; (iii) a Nb-Y-HREE stage, associated with a late hydrothermal paragenesis composed of zircon, xenotime, monazite, Nb-Fe-W-rich rutile and complex Nb-Ti-Y-HREE-W-U oxides (NTox), within an adularia-tourmaline-chlorite matrix; (iv) a Bi±Au-Ag stage, likely related to the late-Variscan regional hydrothermal circulations in the Limousin ca. 300 Ma (Bouchot et al. 2000, Boiron et al. 2003).

The peraluminous signature of the main W-As-Nb±Ta mineralization (stage II) contrasts with the late P, Y, HREE, Nb>Ta, Ti, Zr, U signature (stage IV), which

would be more typical of a rare-metal peralkaline signature and could likely represent the contribution of peralkaline hydrothermal fluids derived from an unknown source at depth. In this respect, the Puy-les-Vignes breccia pipe appears unique in the West European Variscan belt.

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