Mineralizing events in the Vosges massif: insights from the Mn-W Haut-Poirot deposit (NE France)

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Abstract. Vosges (NE France) and Schwarzwald (SW Germany) massifs are well known for their numerous structure-related base-metal deposits. Mineralization events are linked to activation and reactivation of crustal faults as well as hydrothermal episodes in relation with the Variscan orogenic cycle, Jurassic hydrothermalism and Cenozoic rifting. Some manganese veins have been studied in Schwarzwald (i.e. Eisenbach deposit) and provide K/Ar cryptomelane ages correlated to the aforementioned hydrothermal events but also to intense weathering during the Miocene. In the Vosges, the manganiferous Haut-Poirot deposit is hosted in biotite granite and took place at the end of the Variscan orogeny, based on geochemistry and the relatively high temperature assemblage of the primary ore. Despite the lack of datable manganese oxides, this deposit shows a multistage character that could be related to important mineralizing events as reported in the Eisenbach deposit located in Schwarzwald.

1 Introduction

In Western Europe, the Variscan belt outcrops in several massifs that represent some portions of the collision between three continents: Larussia, Baltica and Gondwana (e.g. Friedl et al. 2011). Within this belt, the massifs of Vosges and Schwarzwald (or Black Forest) take a linking position between the Massif Central and Bohemian massif (Fig. 1a, e.g. Echtler and Alther 1993). The Baden-Baden (Schwarzwald) and Lalaye-Lubine (Vosges) shear zones define the Saxotheruringian (North) and Moldanubian (South) parts of the orogenic belt (Fig. 1a, b, Wickert et al. 1990). Numerous mineral deposits are related to this major geodynamic event, well-documented in Central and Western Europe (e.g. Chantraine et al. 1994; Dallmeyer et al. 1995).

The meso-cenozoic evolution of Vosges and Schwarzwald massifs and their respective break-up on the flanks of the Rhine Valley is attributed to intensive Cenozoic rifting, in relation with the Alpine orogeny (Fig. 1b, Prodehl et al. 2006). The evolution of the Cenozoic Upper Rhine Graben was controlled by a repeatedly changing stress field and reactivation of a complex set of crustal discontinuities originated from the Variscan orogeny (e.g. Hinsken et al. 2007), leading to deposition of mineral vein-type deposits (Fluck and Stein 1992).

The occurrence of numerous veins of base-metal (Ag-Co-Cu-Fe-Mn-Mo-Au-Pb-Zn-Ba-F) in Vosges and Schwarzwald has led to a long duration mining activity during the past centuries. The Haut-Poirot deposit has been mined intermittently from 1890 and the end of the Second World War for its manganese and tungsten content (Fig. 1b, Lougnon 1981). Here, we refine the mineralogy and petrography of this deposit to correlate observations with the general chronologic framework and mineralizing events occurring in Vosges and Schwarzwald.

2 Metallogeny of Vosges and Schwarzwald

The common evolution of Vosges and Schwarzwald has has led to consider their metallogenic features together (Fluck and Weil 1976; Fluck 1977).

2.1 Classification of mineral deposits

Sedimentary deposits are missing in Paleozoic series and occur only in the Mesozoic cover: Triassic uranium and coal deposits (Southern Vosges), Jurassic evaporites (Vosges and Schwarzwald) and Fe-oolithe (Schwarzwald), and K-rich basins (Rhine Valley). Structure and/or magmatic-related are the most common deposits, but their complexity is somewhat difficult to provide clear classification between the two regions. Based on structural interactions, Fluck and Weil (1976) proposed...
these deposits to be associated directly to plutonic rocks or post-Triassic faults that clearly cross-cut the Triassic cover or follow the flanks of the Upper Rhine Graben (Ba, Ba-Fe, F and Q veins). However most of the tectonic-related veins are randomly distributed. Actually their source could be related to three periods: Variscan, post-Variscan or post-Triassic (Fig. 1b).

2.2 Mineralizing events

The timing of the numerous ore veins has long been unclear, mainly because of the lack of datable materials. However, several hydrothermal events are mentioned to explain the formation of structure-related deposits:

1) The Carboniferous is associated to a magmatic-metallogenetic period (+330-280 Ma) corresponding to a high temperature hydrothermal activity. This phase is recognized in other Variscan massifs and is connected to intensive, short-duration endogenic processes. It is responsible for late granitoid rocks and related Sn-W associations (Thomas and Tischendorf 1987). Sn, W, Mo, Cu, Fe, Mn, Au occurring in late two-mica granite are directly related to magmatic bodies (Fluck and Weil 1976).

2) The Permian corresponds to the initiation peak of long duration hydrothermal activity (280-260 Ma) at lower temperatures responsible for Ba-F and associated base-metal mineralization (e.g. Segev et al. 1991).

3) Early Jurassic is probably the most prominent mineralizing event recorded along basement faults in Vosges and Schwarzwald massifs (Clauer et al. 1996). Four successive pulses characterize this activity around 200 Ma, 180 Ma, 170 Ma and 150 Ma. Hydrothermal activity is synchronous with episodes of enhanced subsidence. As large parts of Europe were affected by an extensional stress regime, it is suggested that hydrothermal activity and subsidence resulted from extension, and pre-existing faults became reactivated (e.g. Wetzel et al. 2003). The granitoid rocks register temperature of mineralizing fluids up to 230°C (e.g. Clauser et al. 1996).

4) The Cretaceous corresponds to a weaker but higher temperature hydrothermal episode (+100 Ma) relative to the former stage (Segev et al. 1991, Wetzel et al. 2003) linked to a large domal uplift (Illies 1977, Geyer et al. 2011).


6) Recent low temperature hydrothermalism is still present with temperatures of about 140-160°C (e.g. Clauser et al. 1996) that leads to geothermal activity in the Upper Rhine Graben (Bailleux et al. 2013).

2.3 Weathering

Emersion periods from the Cretaceous to Paleocene periods suggest weathering processes to be registered in Vosges and Schwarzwald area. However, the first clear signs of weathering are related to the recent uplift of Vosges and Schwarzwald simultaneously with the Upper Rhine Graben rifting by the early Eocene in the Vosges (Fluck and Weil 1976) and at least Miocene in Schwarzwald (Hautmann and Lippolt 2000), leading to the formation of Fe or Mn gossans (Fluck and Weil 1976).

Figure 2. Petrography and mineralogy of the Haut-Poirot deposit. a Underground picture of the main ore vein and the associated manganiferous breccia. b Replacement texture of pyrolusite by W-rich hollandite. c Replacement texture of K-feldspars by braunite. Successive crystallisation of scheelite and barite onto braunite crystals. d Secondary brecciation of the main ore. e Replacement texture of braunite by svabite. Fk=K-feldspar; Qtz=quartz; Ho=hollandite; Py=pyrolusite; Br=braunite; Sch=scheelite; Ba=barite; Ca=manganan calcite; Hs=hausmannite; Sv=svabite.

3 Mn-W Haut-Poirot deposit

Numerous manganese veins occur in Vosges and Schwarzwald in association with some structures and faults (Fig. 1b). Manganese minerals might be decoupled from iron minerals and the veins are hosted both in the Variscan bedrock and the post-Variscan cover (Fluck and Weil 1976). Some of them have been considered in Schwarzwald to provide useful K/Ar and 40Ar/39Ar ages obtained on cryptomelane crystals (Segev et al. 1991; Hautmann and Lippolt 2000) in order to determine the
timing and processes responsible for their formation.

3.1 Manganiferous veins

The veins are located in the Haut-Poirot and Lyris woods in the Central Vosges Mountain, 7 km westward of Gérardmer (Fig. 1b, France). The mineralized veins are mainly hosted in biotite and in two-mica granite, part of the Central Vosges Granites (CVG), formed between 330 to 320 Ma during the Variscan cycle (Tabaud et al. 2014). The orebodies form two subparallel veins oriented N90° to N120° in a well-fractured zone. The vein 1 is ~600 m long with a thickness ranges from 1 to 0.4 m and a dip angle of 80° N. The second vein is subdivided in two segments with a thickness of about 0.4 m (Bonhomme 1958, Lougnon 1981).

3.2 Mineralogy and petrography

The main ore forms a tectonic breccia (Fig. 2a) filled by pyrolusite, braunite in a barite and quartz gangue (Fig. 2b, c). Scheelite and hollandite s.s. are associated to the ore (Fig. 2b, c), as well as U-minerals (francevillite, chalcolite and autunite, Jurain 1956, Weil et al. 1959, Lougnon 1981), bornite and chalcocite (Lougnon 1981) that have been described in the ore and host rock granite. The ore is brecciated itself enabling the formation of hausmannite cemented in manganese calcite and quartz (Fig. 2d). Svabite (Cas[AsO₄]₂F) replaces locally braunite (Fig. 2e). Iron oxides are nearly absent in the main ore vein.

![Figure 3. REE pattern of the host rock and manganese ores of the Haut-Poirot deposit normalized to chondrite.](image)

3.3 Geochemistry

The peraluminous host granite shows typical concentration in manganese compared to mean value of granitoid rocks (Li 2000), as well as REE patterns characterized by Eu negative anomaly and enrichment in LREE compared to HREE (Fig. 3).

Mn ores of the Haut-Poirot deposit are characterized by high grade manganese (69.57-72.02 wt. % MnO), silica (3.87-12.39 wt. % SiO₂), tungsten (0.48-0.89 wt. % W) and copper (0.05-0.25 wt. %) and very low phosphor (0.03-0.08 wt. % P₂O₅) and iron (0.08-0.14 wt. % Fe₂O₃). Arsenic, antimony and REE are substantially enriched to thousands of ppm in some samples. The geochemical signature of the ore is typical for hydrothermal deposits (Nicholson 1992) and REE patterns follow the granite trend for HREE and MREE, while LREE are depleted compared to the host granite (Fig. 3).

3.4 Timing and origin of the ore

The most striking feature of the manganiferous vein in the Haut-Poirot deposit is the occurrence of, at least, two distinct mineral assemblages (Fig. 4): 1) the main ore stage is marked by the formation of relatively high temperature paragenesis (braunite and scheelite, Fig. 2c) followed by a O₂-rich mineral assemblage with pyrolusite and then barite (Fig. 2b), after the brecciation of the granite; 2) the brecciation of the ore itself, characterizes a second minor mineralizing event marked by carbonates, hausmannite and probably arsenate (svalbite, Fig. 2d, e) corresponding to reduced conditions of the mineralizing fluid. A pre-ore stage is identified by Weil et al. (1959) and corresponds to the formation of quartz-hematite breccia. Weathering processes are poorly recorded such as typical Mn-rich gossan that could be found in other hydrothermal deposits worldwide. However, we could expect some of the observed textures and minerals to be attributed to such processes. For example, it is complex to assign hollandite s.s. to hydrothermal alteration, or weathering processes (Fig. 2b). Coronadite and Pb-rich hollandite occur in the Haut-Poirot deposit as replacement material for biotite in the wall-granite. Biotite is sensitive to oxidation at surface conditions, and can then be easily weathered into oxide minerals, such as Mn-oxides. Lead enrichment in hollandite might be assigned to weathering processes, while pure and tungsten-rich hollandite could be formed by hypogene and/or supergene processes (Fig. 2b). Some of the pyrolusite could form during supergene processes by replacing coronadite crystals.

Despite the occurrence of hollandite group minerals, their sizes are too small in the Haut-Poirot deposits to be dated by K/Ar or ⁴⁰Ar/⁹⁰Ar methods. However, considering the close genetic relationship between Vosges and Schwarzwald massifs and especially the similarities with the Eisenbach deposit in Schwarzwald (Segev et al. 1991), we could expect manganiferous veins to be affected by the relatively same processes. Although the geochemistry together with the high temperature mineral assemblage observed in the main ore of the Haut-Poirot veins could only be related to variscan magmatic bodies, the multistage/polyphased character (Fig. 4) allows the ore to be (re)activated several times, probably during faulting and hydrothermal periods registered in the whole area. As an example, Segev et al. (1991) show that the main manganese mineralizing event in the Eisenbach deposit are associated to post-Variscan mineralization periods at relatively low temperature. Intensive tectonic movements related to riftogenic regime of the Upper Rhine Graben lead to Cretaceous ages, corresponding to the initiation of rift activity. Hautmann and Lippolt (2000) show intense weathering of manganese deposits during the Miocene, in
relation with the uplift of Schwarzwald and Vosges. Weathering periods could also be extended to Cretaceous considering that most of the ancient massifs in Western Europe are exposed during that time (e.g. Quesnel 2003), explaining the Early Cretaceous ages obtained by Segev et al. (1991) as well as the lack of Cretaceous sediments.

Figure 4. Refined paragenetic sequence for the Mn-W deposit of the Haut-Poirot. Triangles=main brecciation events; HT=High Temperature.

4 Conclusion

In conclusion, the petrology and mineral assemblages observed in the manganiferous Haut-Poirot deposit corroborate the multistage/polyphased character of manganese veins in the Vosges, which could be correlated to the mineralizing events reported in several deposits in Schwarzwald.

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