Periodico di Mineralogia (2013), 82, 1, 129-140 DOI: 10.2451/2013PM0008

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on Environment, Archaeometry and Cultural Heritage

The Mérinchal antimoniferous district (French Massif Central)

Vincent Thiéry[1,*] and Charles Cartannaz[2]

[1]Mines Douai, LGCgE MPE-GCE, F-59508 Douai, France
[2]Bureau de Recherches Géologiques et Minières (BRGM), 1, avenue du Parc de Brabois, 54500 Vandœuvre-lès-Nancy
[*]Corresponding author: *vincent.thiery@mines-douai.fr*

Abstract

This article presents the Mérinchal antimoniferous district (French Massif Central) from the historical and metallogenic points of view. This small district has been mined in the early 20th century. Subsequent characterization of mineralized indexes occurred afterwards in the 1960's and 1980's. We briefly describe its history and the mining works carried out. Finally, we add to the previously known minerals of this deposit (mainly berthierite and stibnite) some species not mentioned yet (dyscrasite, pyrargyrite, tetrahedrite-freibergite). The goal of the present study is to present and illustrate the textural relationships between minerals.

Key words: Mérinchal; French Massif Central; antimony; sulfosalts; environmental impact of abandoned mining works.

Introduction

France, although having a long history of mining, is currently facing the challenges of post-mining (BRGM, 2007). The characterization of former mining sites in this context is of key importance to assess their related pollution. But in the same way, in an ever increasing need to find new mineral resources, the knowledge of almost forgotten mining areas may yield new data concerning future mining possibilities. The district that we present in this work is located within the Variscan French Massif Central (FMC) (Figure 1), which is a former mining area as a whole (Bitri et al., 1999; Bouchot et al., 2005; Marignac and Cuney, 1999).

Geological context

The Guéret batholith

The district is hosted in the eastern part of the Guéret batholith, where several cordierite-bearing and cordierite devoid granitoids are nested (Cartannaz et al., 2008; Sabourdy and Tempier, 1982). In the Mérinchal area, the Sb-bearing veins are closely spatially associated with microgranites (Figure 2), as previously outlined in several others Sb districts throughout the French Massif Central (Marignac and Cuney, 1999; Périchaud, 1980).

Metallogenesis in the FMC

The inner position of the FMC within the Variscan orogeny contributes to its overall richness and diversity in ore deposits (Bouchot et al., 2005). As a complete review of all deposits types and their corresponding period would be beyond the scope of the present article, we guide the reader toward the complete and seminal work of Marignac and Cuney (1999). According to those authors, the rich metallogenesis within the FMC is due to two main causes: the successions of three Wilson cycles and a large lithospheric delamination during Late Carboniferous -Early Permian.

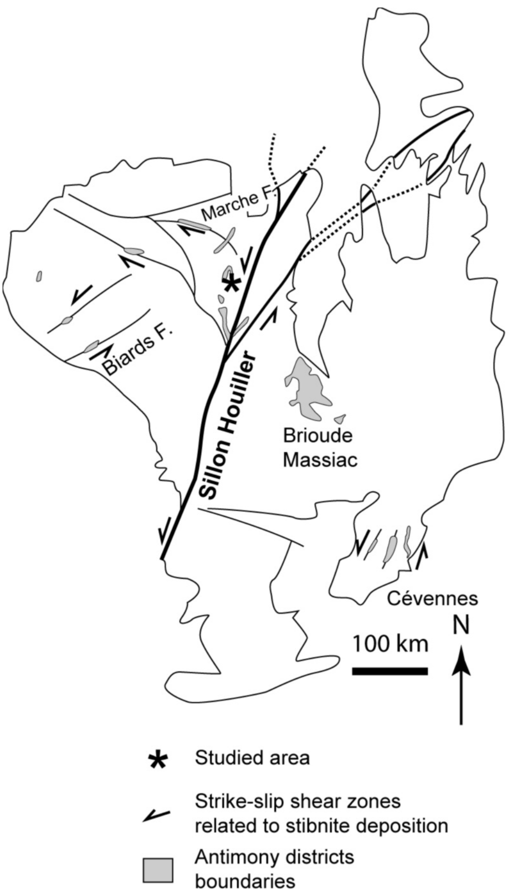

Figure 1. After Bellot et al. (2003): location of the Mérinchal Sb district within the French Massif Central.

Antimony is no longer mined in France, but it is worth noting that it has been a widely searched and extracted substance in the FMC. The main Sb repository in the FMC consists on quartz veins with arsenopyrite (FeAsS), pyrite, sphalerite (ZnS), berthierite ($FeSb_2S_4$) and stibnite (Sb_2S_3) (Marignac and Cuney, 1999). Several districts can be outlined, generally related to major strike-slip faults (Munoz et al., 1992) such as for example the Marche fault within which the Villeranges and Châtelet gold deposits have been widely documented (i.e. Boiron et al., 1989; Bouchot et al., 1994; Piantone et al., 1994) and the Biards Sb-Au shear zone (Bellot, 2004; Bellot et al., 2003) in the western part of the FMC or the Brioude-Massiac district (Courtin-Nomade et al., 2012; Périchaud, 1980; Roger, 1972) more to the south-east.

During the 330-300 Ma period, an abnormal heat gradient develops in the FMC, associated to Au, Sb and Pb mineralization (Bouchot et al., 1997; Marignac and Cuney, 1999; Roig et al., 2002): this event is known as the "Au-300 Ma mineralizing event" (Lescuyer et al., 1993). This gradient is known in coal basins (Berquer-Gaboreau, 1986; Copard et al., 2000; Robert et al., 1988) and in their enclosing basement rocks, as exemplified by Van Hinsberg et al. (2007) in the Haut-Allier area (Barlet unit near the Langeac coal basin) with garnet neoformation and prograde crossing of the biotite isograde.

Materials and methods

The samples have been collected in 2004 during the regular geological mapping at the 1/50,000 scale for the French geological survey (BRGM-Bureau de Recherches Géologiques et Minières) on the Aubusson geological map (Cartannaz et al.,

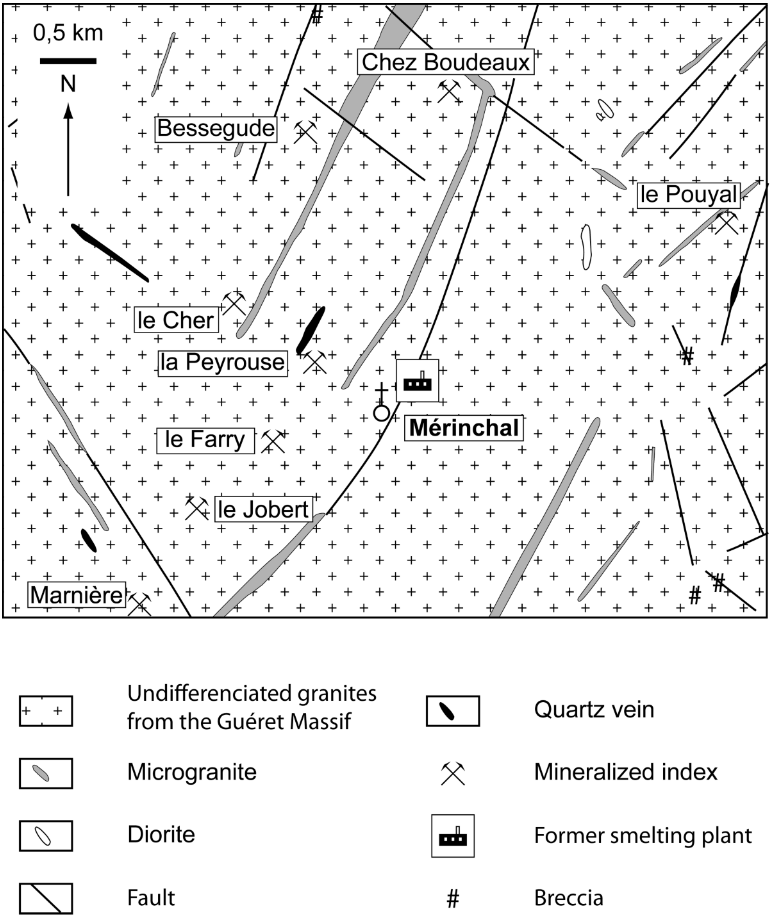

Figure 2. Geological sketch of the Mérinchal district based on a compilation of documents from Carroué (1964), Hottin et al. (1989) and Cartannaz et al. (2008).

2008). A classical metallographic study was carried out on both thin and polished sections. SEM imaging and analyses were carried out on a Hitachi S-4300SE/N SEM equipped with a Thermo Scientific Ultradry EDX detector.

Historical background

Although the first record of antimony excavations in Mérinchal dates back from 1817 (Ravinet, 1829), mining in this area began in the late nineteenth-early twentieth century (Aubignat, 1977), and finished in 1932. In limbo, the Mérinchal mine was in its time considered as "particularly rich" (de Launay, 1933), the overall antimony mining activities in the center of France were very active (Loiret, 1909). The political climate in the early twentieth century, at the dawn of the first World War, is probably at the origin of the active prospection for antimony as this metal, as alloy, is used in ammunition design (Anderson, 2012). Nowadays, the mining works are long gone, the waste dumps are difficult to find and some of them have partly been used as an aggregate source for the local roads and paths (Aubignat, 1977; Carroué, 1964). The dense vegetation does not help to recognize previously mined areas, trenches and filled wells.

Mérinchal and surrounding indexes

The main mining site was based in the vicinity of the Mérinchal village (Figure 2) and consisted of two shafts. The research shaft was 150 m deep, the exploitation shaft was 100 m deep (Aubignat, 1977). A gallery reached this shaft from the surface. The smelter was in the Mérinchal village, the remains of the chimney are now recorded in the French architectural and patrimonial database (Mérimée, database from the French ministry of culture: card n° IA00030997, http://www.culture.gouv.fr/documentation/memoire/HTML/IVR74/IA00030997/index.htm).

The overall antimony production is estimated between 500 and 900 tons of Sb metal (Carroué, 1964; Recoing, 1980c), probably mainly at the last stages of the exploitation since a 150-300 t/year yield has been mentioned (Arbos, 1932).

Several indexes in the surrounding area have been studied (Table 1) by trenches, galleries and sometimes pits, and yielded several tons of ore each.

Mineral descriptions: morphology and EDS data

The indexes of this area generally consist on small-scale quartz veins associated with a mineralization which typically consists on stibnite, pyrite, chalcopyrite, arsenopyrite (reported as being sometimes auriferous), berthierite, kermesite (Sb_2S_2O) and locally native antimony (Carroué, 1964) as well as rare malachite (Carroué, 1961). Sulfosalts have been recognized (BRGM, 1979) but not characterized. Typical antimony alteration products, the so-called “antimony ochre” (complex mixture of antimony oxides), are also present. The goal of

Table 1. Summary of indexes from the Mérinchal district.

Name of index	Works carried out	References
La Peyrouse (main mining site)	Pit and galleries (see description in the text)	(Aubignat, 1977; Carroué, 1961; 1964; Recoing, 1980c)
le Cher	Trenches	(Recoing, 1980d)
Chez Boudeaux	20 m deep shaft, 2 level of underground galleries	(Carroué, 1964; Recoing, 1980b)
Le Jobert	Shaft and 2 galleries from the surface	(Carroué, 1964; Recoing, 1980f)
Le Farry	Shaft	(Recoing, 1980g)
Bessegude-Le Chassaing	Shaft, trench, galleries from the surface	(Recoing, 1980d)
Le Beaudeix	Shallow pit, trench	(Recoing, 1980e)
Marnière	Trenches	(Recoing, 1980a)

this section is to present and illustrate the textural relationships between minerals. To support the attribution of complex mineral species, some EDX data are presented in Table 2.

Previously reported mineral species

Quartz. Quartz forms the gangue of all the veins in this area and forms also unmineralized veins and tectonic breccias infilling faults, the so-called "BTH" (Hypersilicified Tectonic Breccia) which are classically described within the FMC (Munoz et al., 1997; Munoz et al., 1999).

Berthierite ($FeSb_2S_4$) and Stibnite (Sb_2S_3). As those minerals are difficult to differentiate unequivocally (Stillwell, 1926), they will be presented together. Indeed, in the studied samples, the radiating needles with a strong metallic luster revealed themselves to be berthierite thanks to their EDX pattern. Thus, stibnite may not be as abundant as supposed and the massive ore may consist on an intimate association of the two minerals. Hand samples (Figure 3a,b) are generally surrounded by a crust of yellowish antimony ochre (see below); their fracture is characterized by a blue iridescent tarnish, which is common to both berthierite and stibnite (Anthony et al., 2003). Berthierite forms also small veinlets and radiating aggregates of needles on fresh fractures (Figure 4c). The only, unequivocally identified stibnite needles have been observed in thin section (Figure 3c) and confirmed by EDX microanalysis. They display a highly acicular shape. However, Carroué (1964) described massive lumps of stibnite, up to 20-30 cm in diameter.

Arsenopyrite (FeAsS). Euhedral arsenopyrite is abundant and obvious in polished section thanks to its typical rhombic and acute shape. The crystals can be up to 200 micrometers long, they occur both as single crystal within the quartz gangue or associated to galena and sphalerite (Figure 4b); locally they can include crystals of tetrahedrite (Figure 4d).

Sphalerite (ZnS). Sphalerite is quite abundant.

Table 2. Semi-quantitative composition (EDX data) of some sulfosalts from the Mérinchal district.

	Pyrargyrite		Tetrahedrite-Freibergite			Dyscrasite	
S	18.3	18.3	21.5	25.2	29.6		
Sb	23.4	23.5	26.9	23.6	20.2	24.3	24.6
Pb							
Cu			14.3	12.7	11.4		
Fe			4.9	4.7	3.5		
Ag	58.3	57.8	30.5	29.0	23.9	75.7	75.4
As				4.8	9.1		
Cd			1.8		1.5		
Zn					0.8		

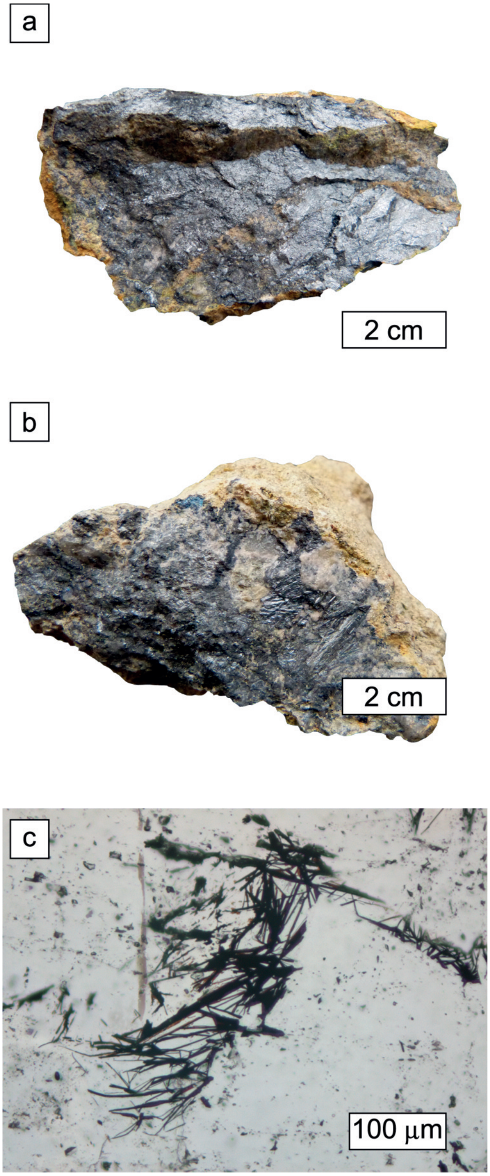

Figure 3. a) Lump of massive stibnite/berthierite from the “Chez Boudeaux” index, sample n° 64308 from the Mines Paristech mineralogical museum; b) Lump of acicular stibnite/berthierite from the “le Jobert” index, sample n° 64316. Both samples are characterized by a yellowish crust of secondary antimonochre. c) Stibnite needles seen under the microscope in transmitted light.

It is present both associated with galena and arsenopyrite (Figure 4b) as crystals up to 200 micrometers and as tiny (5-10 micrometers) inclusions in tetrahedrite-freibergite (confirmed by EDS analysis, Figure 5.2).

Chalcopyrite ($CuFeS_2$). Chalcopyrite is present as tiny micrometric and vermicular inclusions in tetrahedrite-freibergite. Moreover, some superficial deposits appear on fresh fracture, with a typical iridescent luster, and can be confidently ascribed to chalcopyrite.

Pyrite (FeS_2). Pyrite is locally abundant, associated with arsenopyrite or as single, euhedral square crystals up to 100 micrometers.

Previously unreported or less well characterized mineral species

Pyrargyrite (Ag_3SbS_3). Small, individual crystals of pyrargyrite are locally abundant. They are subeuhedral and their size ranges from 10 to 50 micrometers. They occur within the quartz gangue (Figure 4a,f). They have been confirmed by EDX analysis (Table 2).

Galena (PbS). Galena forms often overgrowths with arsenopyrite (Figure 4b), and also in polyphase grains with sphalerite. It is present as inclusions in tetrahedrite, forming both crystals up to 50 micrometers and minute vermicular blebs (Figures 4e; 5a).

Tetrahedrite ($Cu_6[Cu_4(Fe,Zn)_2]Sb_4S_{13}$) - Freibergite ($(Ag,Cu,Fe,Zn)_{12}(Sb,As)_4S_{13}$) series. Tetrahedrite refers to the most complex isotypic series of sulfosalts (Moëlo et al., 2008). Indeed, its composition is highly variable (Di Benedetto et al., 2002; Johnson et al., 1986; Peterson and Miller, 1986). It has been identified according to its optical characteristics and its complex EDS pattern (Figure 5.3). Some compositional trands are given in Table 2. In the present study, tetrahedrite occurs as subeuhedral crystals, up to

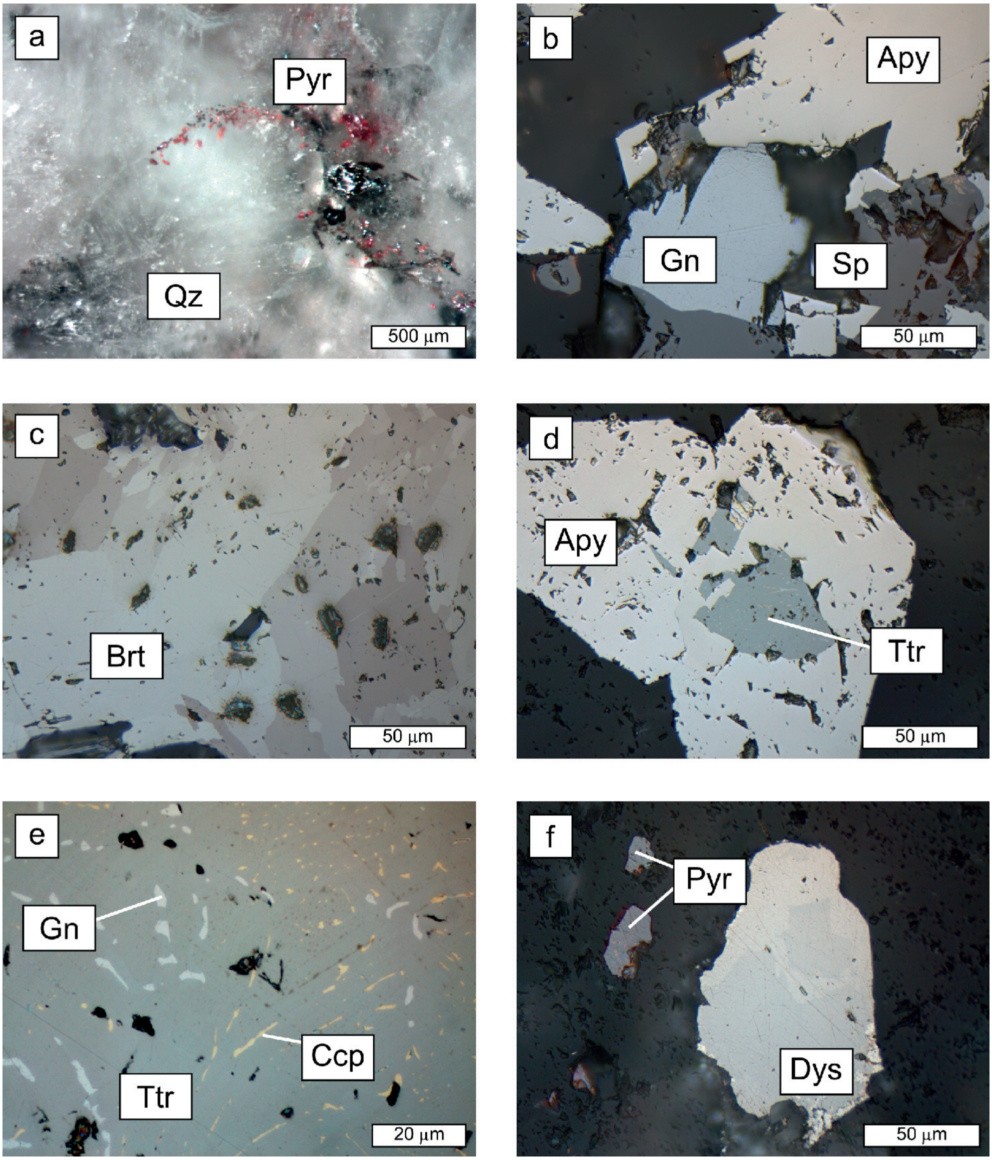

Figure 4. Photomicrograph of ore minerals from Mérinchal, taken using a metallographic microscope with reflected light under crossed polars excepted when mentioned. a) Myriad of minute pyrargyrite crystals in their quartz matrix, stereomicroscope view; b) Polyphased assemblage of arsenopyrite, galena and sphalerite, the latter showing strong brown internal reflections; c) Berthierite vein; d) Arsenopyrite containing a subeuhedral tetrahedrite crystal; e) Close-up view of a tetrahedrite crystal containing vermicular chalcopyrite and galena; f) Dyscrasite and pyrargyrite.
Apy = arsenopyrite, Ccp = chalcopyrite, Gn = galena, Sp = sphalerite, Ttr = tetrahedrite (abbreviations after Whitney and Evans, 2010), Brt = berthierite; Pyr = pyrargyrite.

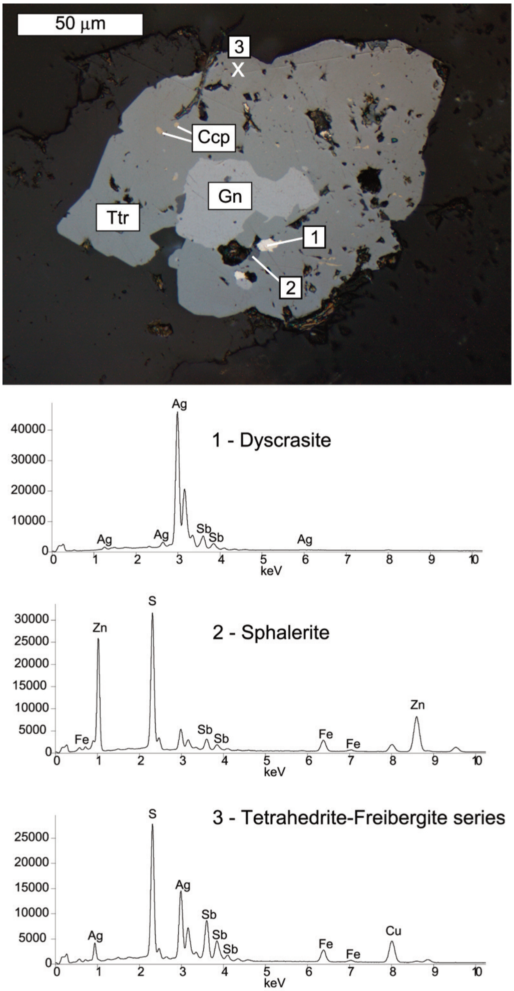

Figure 5. EDS spectra obtained on a complex tetrahedrite-freibergite crystal, containing galena, sphalerite, chalcopyrite and dyscrasite as inclusions. The sphalerite spectrum is slightly altered by a matrix effect.

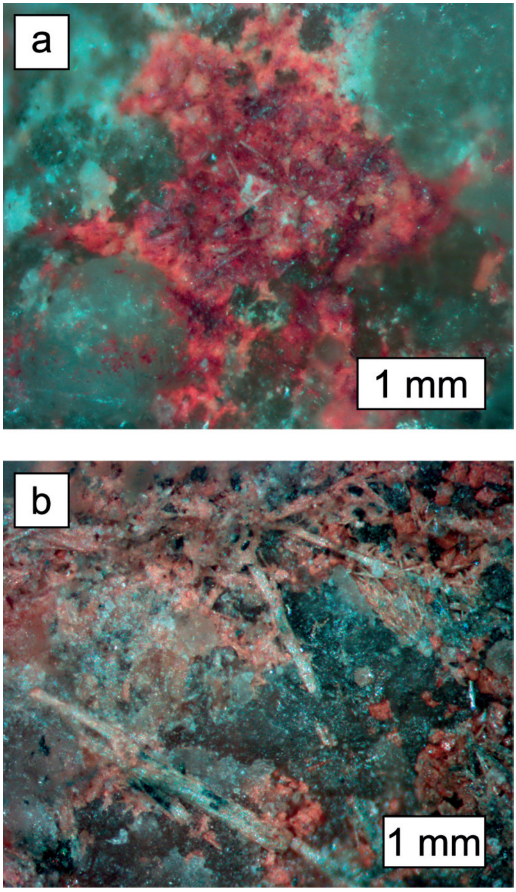

Figure 6. secondary antimony minerals seen under the stereomicroscope. a) Red needles of kermesite; b) Unidentified antimony oxides and/or hydroxides.

100 micrometers, both freely and as inclusions in arsenopyrite (Figure 4d,e). It is characterized by its overall richness in varied inclusions: blebs of galena and chalcopyrite; sphalerite and dyscrasite. From the pure textural point of view, it is worth noting that the patterns of galena and chalcopyrite inclusions resemble that of the so-called "chalcopyrite disease" (Barton and Bethke, 1987; Craig, 2001).

Dyscrasite (Ag_3Sb). Dyscrasite is not abundant; it forms anhedral crystals ranging from 5 up to 50-60 micrometers (Figure 4f). The tiniest crystals are present as inclusions in tetrahedrite, where they are associated with galena and sphalerite. They have been confirmed by EDX analysis (Figure 5.1 and Table 2).

Secondary antimony minerals. Antimony release and dispersion in the environment is controlled by supergene, secondary minerals, formed at the expense of sulfide and sulfosalts which are unstable in near-surface environment (Roper et al., 2012). However, those minerals are difficult to characterize optically. Millimetric needles of red (Figure 6a) and white (Figure 6b) minerals, even unanalyzed, can confidently be considered as kermesite and the complex sequence of antimony oxides and hydroxides, such as sénarmontite Sb_2O_3/valentinite Sb_2O_3/cervantite $Sb^{3+}Sb^{5+}O_4$, the so-called "antimony ochre" (Mason and Vitaliano, 1953; Schoeller, 1941).

Environmental implications

Antimony behavior in the environment is widely studied, especially concerning soil and water pollution (Ashley et al., 2003; Casiot et al., 2007; Filella, 2011; Filella et al., 2002). Like arsenic, it is toxic (e.g. Filella et al., 2002; Sh et al., 2012) although its bioavailability is highly dependent of pH values (Filella, 2011; Flynn et al., 2003) and thus antimony mine wastes and former smelting sites are to be described. Indeed, former mining sites and mineral processing plants, such as smelters, are sources for heavy metals and metalloids (Courtin-Nomade et al., 2012; Majzlan et al., 2007; Wilson et al., 2004). Moreover, as outlined by Filella (2011), the fate and behavior of Sb-bearing polluted soils should be studied independently as no generalization should be made. Finally, in environmental considerations, secondary Sb minerals are of paramount importance (Roper et al., 2012).

Conclusion

This paper documents a formerly mined small antimoniferous district in the French Massif Central. Based on previous studies and completed by sample investigations, it describes previously unreported minerals in this area, and particularly sulfosalts. The knowledge of such former mines and the parageneses associated is of importance nowadays in a context where new metallic resources are to be found and also in environmental studies dealing with the fate of antimony and arsenic in soils and waters.

Acknowledgements

The samples were collected during the field work for the regular mapping of France at the 1/50,000 scale ("Carte Géologique de la France") on the Aubusson (n°667) sheet, thanks to funding provided by the Bureau de Recherches Géologiques et Minières (BRGM) under the supervision of Philippe Rossi. The authors are indebted to Jean-Michel Le Cléac'h and Didier Nectoux from the mineralogical museum of Mines Paristech for providing access and allowing photography of samples from the collection. VT is indebted to Thomas Kerestedjian, Bulgarian Academy of Science, for advices concerning dyscrasite identification. The authors are grateful to A. Gianfagna for editorial handling of the manuscript and Francesco Di Benedetto for constructive reviewing of the manuscript.

References

Anderson C.G. (2012) - The metallurgy of antimony. Chemie der Erde - *Geochemistry*, 72, Supplement 4, 3-8.

Anthony J.W., Bideaux R.A., Bladh K.W. and Nichols M.C. (2003) - Handbook of mineralogy. Volume 1: Elements, Sulfides, Sulfosalts. Mineralogical Society of America. 588 pp.

Arbos P. (1932) - La production de l'antimoine en France. *Annales de Géographie*, 41(233), 549-550.

Ashley P.M., Craw D., Graham B.P. and Chappell D.A. (2003) - Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. *Journal of Geochemical Exploration*, 77(1), 1-14.

Aubignat A. (1977) - Quelques notes sur les anciennes mines de Giat (P. de D.) et de Mérinchal (Creuse). *Bulletin de la Société d'Histoire Naturelle d'Auvergne*, 43, 7-13.

Barton P.B. and Bethke P.M. (1987) - Chalcopyrite disease in sphalerite: Pathology and epidemiology. *American Mineralogist*, 72(5-6), 451-467.

Bellot J.-P. 2004. Shear zone-hosted polymetallic sulfides in the South Limousin area, Massif Central France: remobilized sulfide deposits related to variscan collisional tectonics and amphibolite facies metamorphism. *Economic Geology*, 99, 819-827.

Bellot J.-P., Lerouge C., Bailly L. and Bouchot V. (2003) - The Biards Sb-Au-bearing shear-zone (Massif Central, France): an indicator of crustal scale transcurrent tectonics guiding late variscan collapse. *Economic Geology*, 98, 1427-1447.

Berquer-Gaboreau C. (1986) - Pétrologie des charbons de deux bassins limniques du Massif central Français (Blanzy-Montceau et Messeix) - Exemples d'hyperthermies locales. Ph.D, Lille. 184 pp.

Bitri A., Truffert C., Bellot J.-P., Bouchot V., Ledru P., Milési J.-P. and Roig J.-Y. (1999) - Imagerie des paléochamps hydrothermaux As-Au-Sb d'échelle crustale et des pièges associés dans la chaîne varisque: sismique réflexion verticale (GéoFrance3D: Massif central français). Comptes Rendus de l'Académie des Sciences - Series IIA - *Earth and Planetary Science*, 329(11), 771-777.

Boiron M.-C., Cathelineau M. and Trescases J.-J. (1989) - Condition of gold-bearing arsenopyrite crystallisation in the Villeranges Basin, Marche-Combrailles shear zone, France: a mineralogy and fluid inclusion study. *Economic Geology*, 84, 1340-1362.

Bouchot V., Gros Y. and Piantone P. (1994) - Dynamics of shallow late-Variscan gold mineralization: the Le Châtelet Au-arsenopyrite quartz veins, Massif Central, France. *Mineralium Deposita*, 29(6), 461-473.

Bouchot V., Ledru P., Lerouge C., Lescuyer J.-L. and Milesi J.P. (2005) - 5: Late Variscan mineralizing systems related to orogenic processes: the French Massif Central. *Ore Geology Reviews*, 27, 169-197.

Bouchot V., Milési J.P., Lescuyer J.-L. and Ledru P. (1997) - Les minéralisations aurifères de la France dans leur cadre géologique autour de 300 Ma. *Chronique de la Recherche Minière*, 528, 13-62.

BRGM (1979) - Ressources minières françaises. Tome 6. Les gisements d'antimoine (situation en 1979). 126 pp.

BRGM (2007) - L'après-mine en France. 48 pp.

Carroué J.P. (1961) - Note relative aux anciens travaux de la concession d'antimoine de Mérinchal (Creuse) et environs. BRGM, division N. Massif Central, Mission Marche-Bourbonnais. 14 pp.

Carroué J.P. (1964) - Les filons de stibine et de mispickel des Combrailles et de la partie orientale de la Marche. Description, étude géologique et métallogénique. Mémoire soutenu le 23 janvier 1964 devant la faculté de Clermont pour l'obtention du diplôme d'études supérieures de sciences naturelles. 81 pp.

Cartannaz C., Sonnet R., Émonin Y., Juillerat M., Deprez J., Thiéry V., Montaz N., Rot J. and Binetruy J.C. (2008) - Carte géol. France (1/50 000), feuille Aubusson (667). Orléans: BRGM. Notice explicative par Cartannaz C., Rolin P., Cocherie A., Henry P., and Rossy M. (2008), 106 pp.

Casiot C., Ujevic M., Munoz M., Seidel J.L. and Elbaz-Poulichet F. (2007) - Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France). *Applied Geochemistry*, 22(4), 788-798.

Copard Y., Disnard J.R., Becq-Giraudon J.-F. and Boussafir M. (2000) - Evidence and effects of fluid circulation on organic matter in intramontane coalfields (Massif Central, France). *International Journal of Coal Geology*, 44, 49-68.

Courtin-Nomade A., Rakotoarisoa O., Bril H., Grybos M., Forestier L., Foucher F. and Kunz M. (2012) - Weathering of Sb-rich mining and smelting residues: Insight in solid speciation and soil bacteria toxicity. Chemie der Erde - *Geochemistry*, 72, Supplement 4, 29-39.

Craig J.R. (2001) - Ore-mineral textures and the tales they tell. *The Canadian Mineralogist*, 39(4), 937-956.

de Launay L. (1933) - Cours de géologie appliquée professé à l'École supérieure des mines. Libr. Polytechnique ; Ch. Béranger. Paris ; Liège. 460 pp.

Di Benedetto F., Bernardini G.P., Borrini D., Emiliani C., Cipriani C., Danti C., Caneschi A., Gatteschi D., and Romanelli M. (2002) - Crystal chemistry of tetrahedrite solid-solution: EPR and magnetic investigations. *The Canadian Mineralogist*, 40(3), 837-847.

Filella M. (2011) - Antimony interactions with heterogeneous complexants in waters, sediments and soils: A review of data obtained in bulk samples. *Earth-Science Reviews*, 107(3-4), 325-341.

Filella M., Belzile N. and Chen Y.-W. (2002) - Antimony in the environment: a review focused on natural waters: I. Occurrence. *Earth-Science Reviews*, 57(1-2), 125-176.

Flynn H.C., Meharg A.A., Bowyer P.K. and Paton G.I. (2003) - Antimony bioavailability in mine soils. *Environmental Pollution*, 124(1), 93-100.

Hottin A.M., Périchaud J.J., Bois J.P. and D'Arcy D. (1989) - Notice explicative, Carte géol. France (1/50 000), feuille Saint-Gervais-d'Auvergne (668) - Orléans: Bureau de Recherches Géologiques et Minières, 66p. Carte géologique par Hottin A.M., Belin J.M., Bois J.P., Deyrieux G. and Morice E. (1989). 66 pp.

Johnson N.E., Craig J.R. and Rimstidt J.D. (1986) - Compositional trends in tetrahedrite. *The Canadian Mineralogist*, 24(2), 385-397.

Lescuyer J.-L., Milési J.P. and Bouchot V. (1993) - Les évènements métallogéniques liés à l'orogenèse varisque : nouvelles données sur les épisodes autour de 360 Ma (amas sulfurés) et 300 Ma (or) Principaux résultats scientifiques et techniques du Bureau de Recherches Géologiques et Minières, pp. 90-92, Orléans.

Loiret P. (1909) - Note sur la valeur des minerais d'antimoine. *Annales des Mines*, Mémoires, tome XVI, dixième série, 582-609.

Majzlan J., Lalinská B., Chovan M., Jurkovič L., Milovská S. and Göttlicher J. (2007) - The formation, structure, and ageing of As-rich hydrous ferric oxide at the abandoned Sb deposit Pezinok (Slovakia). *Geochimica et Cosmochimica Acta*, 71(17), 4206-4220.

Marignac C. and Cuney M. (1999) - Ore deposits of the French Massif Central : insight into the metallogenesis of the Variscan collision belt. *Mineralium Deposita*, 34, 472-504.

Mason B. and Vitaliano C.J. (1953) - The mineralogy of the antimony oxides and antimonates. *Mineralogical Magazine*, 30, 100-112.

Moëlo Y., Makovicky E., Mozgova N.N., Jambor J.L., Cook N., Pring A., Paar W., Nickel E.H., Graeser S., Karup-Moller S., Balic-Zunic T., Mumme W.G., Vurro F., Topa D., Bindi L., Bente K. and Shimizu M.(2008) - Sulfosalt systematics: a review. Report of the sulfosalt sub-committee of the IMA Commission on Ore Mineralogy. *European Journal of Mineralogy*, 20(1), 7-46.

Munoz M., Boyce A., Courjault-Rade P., Fallick A. and Tollon F. (1997) - Le filon (Zn, F) de Peyrebrune (SW Massif central, France): caractérisation géochimique des fluides au cours du Mésozoïque à la bordure orientale du bassin d'Aquitaine. Comptes Rendus de l'Académie des Sciences - Series IIA - *Earth and Planetary Science*, 324(11), 899-906.

Munoz M., Boyce A.J., Courjault-Rade P., Fallick A.E. and Tollon F. (1999) - Continental basinal origin of ore fluids from southwestern Massif central fluorite veins (Albigeois, France): evidence from fluid inclusion and stable isotope analyses. *Applied Geochemistry*, 14(4), 447-458.

Munoz M., Courjault-Radé P. and Tollon F. (1992) - The massive stibnite veins of the French Palaeozoic basement: a metallogenic marker of Late Variscan brittle extension. *Terra Nova*, 4(2), 171-177.

Périchaud J.J. (1980) - L'Antimoine, ses minerais et ses gisements: synthèse gîtologique sur les gisements du Massif Central français. *Chronique de la Recherche Minière*, 456, 5-64.

Peterson R.C. and Miller I. (1986) - Crystal structure and cation distribution in freibergite and tetrahedrite. *Mineralogical Magazine*, 50, 717-721.

Piantone P., Wu X. and Touray J.-C. (1994) - Zoned hydrothermal alteration and genesis of the gold deposit at Le Châtelet (French Massif Central). *Economic Geology*, 89, 757-777.

Ravinet T. (1829) - Code des ponts et chaussées et des mines. Carilian-Goeury. 547 pp.

Recoing M. (1980a) - BSS - Fiche de gîte et d'indice 0667 8X 4001 - Marnière. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06914X4001/GT. [Accessed 2012/10/10].

Recoing M. (1980b) - BSS - Fiche de gîte et d'indice 0667 8X 4002 - Chez Boudaux. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06678X4002/GT. [Accessed 2012/10/10].

Recoing M. (1980c) - BSS - Fiche de gîte et d'indice 0667 8X 4003 - La Peyrouse. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06678X4003/GT. [Accessed 2012/10/10].

Recoing M. (1980d) - BSS - Fiche de gîte et d'indice 0667 8X 4004 - Le Chassaing. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06678X4004/GT. [Accessed 2012/10/10].

Recoing M. (1980e) - BSS - Fiche de gîte et d'indice 0667 8X 4005 - Le Beaudeix. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06678X4005/GT. [Accessed 2012/10/10].

Recoing M. (1980f) - BSS - Fiche de gîte et d'indice 0667 8X 4006 - Le Jobert. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06678X4006/GT. [Accessed 2012/10/10].

Recoing M. (1980g) - BSS - Fiche de gîte et d'indice 0667 8X 4007 - Le Farry. http://ficheinfoterre.brgm.fr/InfoterreFiche/ficheBss.action?id=06678X4007/GT. [Accessed 2012/10/10].

Robert P., Berquer C., Courel L., Kubler K. and Robert P. (1988) - Anomalie thermique précoce dans le bassin houiller Stéphanien de Messeix-Singles. Massif Central français. *Bulletin des sciences géologiques* (3-4), 333-349.

Roger G. (1972) - Un type de minéralisations épigénétiques familières: les filons à antimoine du Massif Central français. Hypothèse de la sécrétion latérale. *Mineralium Deposita*, 7(4), 360-382.

Roig J.Y., Faure M. and Maluski H. (2002) - Superimposed tectonic and hydrothermal events during the late-orogenic extension in the Western French Massif Central: a structural and $^{40}Ar/^{39}Ar$ study. *Terra Nova*, 14, 25-32.

Roper A.J., Williams P.A. and Filella M. (2012) - Secondary antimony minerals: Phases that control the dispersion of antimony in the supergene zone. Chemie der Erde - *Geochemistry*, 72, Supplement 4, 9-14.

Sabourdy G. and Tempier P. (1982) - Caractère composite de la partie méridionale du massif granitique de Guéret (Massif central français). *Comptes Rendus de l'Académie des Sciences*, 295, 1135-1138.

Schoeller W.R. (1941) - Observations on the alteration products of stibnite. *Mineralogical Magazine*, 26, 1941.

Sh T., Liu C.-Q. and Feng C. (2012) - Solubility, toxicity and sorption of antimony from smelter release. *Journal of Geochemical Exploration*, 118, 14-18.

Stillwell F.L. (1926) - On the Nature of Berthierite. *Mineralogical Magazine*, 21(114), 83-86.

Van Hinsberg V.J., Zinngrebe E., De Wijs H. and Vriend S.P. (2007) - Thermo-chronology of the Barlet metamorphic basement unit: evidence for a Stephanian thermal event linked to Sb mineralization in the Haut Allier, France. *Journal of the Geological Society of London*, 164, 393-404.

Whitney D.L. and Evans B.W. (2010) - Abbreviations for names of rock-forming minerals. *American Mineralogist*, 95(1), 185-187.

Wilson N.J., Craw D. and Hunter K. (2004) - Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand. *Environmental Pollution*, 129(2), 257-266.

Submitted, January 2013 - Accepted, March 2013