CRITICAL METALS IN SPHALERITES FROM BELGIAN MVT DEPOSITS

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INTRODUCTION

A series of recent papers have compiled available data for sphalerites (Cook et al. 2009, Ye et al. 2011, Belissont et al. 2014) or sphalerites and zinc concentrates (Frenzel et al. 2014).This last work focussing on Ge has confirmed the potential in MVT deposits and has reevaluated Ge resources, using statistical methods, to 119 kt.

This work revisits the distribution of trace elements in sphalerites from Belgian deposits with a special focus on Ge, Ga and In.

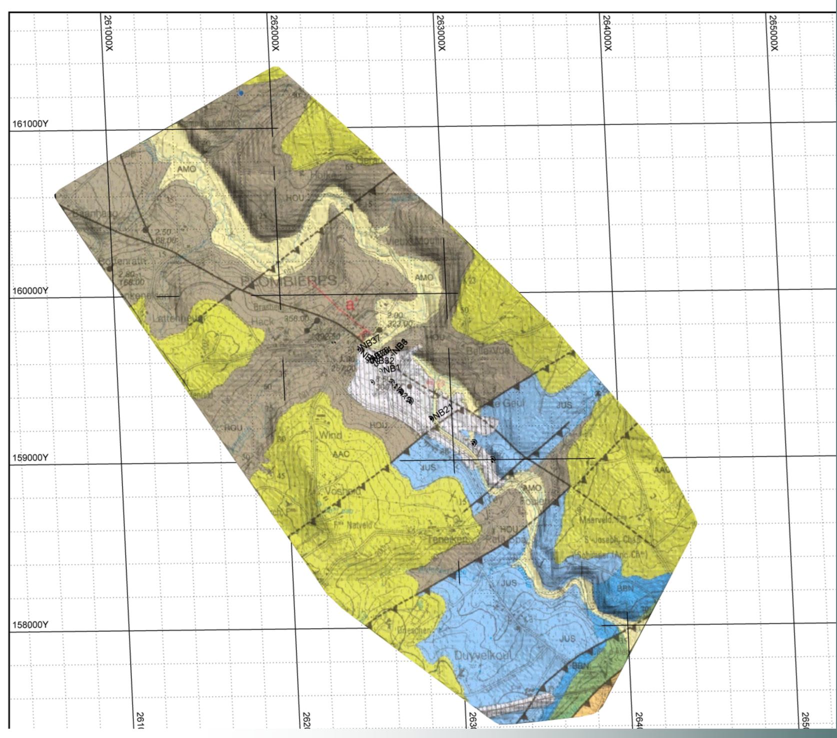

Fig. 1 Visualisation of drill holes locations and geological setting of mineralized zones in Plombières.

BELGIAN MVT DEPOSITS

Fig. 2 Engraving by Maugendre (1855) showing the Moresnet (Altenberg) zinc mine operations.

The occurrence of Pb-Zn deposits in Belgium is known since Roman times and has triggered the development of the very first industrial zinc production in 1806. The inventory and geological settings of these deposits have been documented by Dejonghe (1998) and more data relating to the structural control and temperatures of formation have been published by Muchez et al. (2005). Ongoing work concerns the geophysical exploration of the region (Evrard et al., 2015).

Belgian deposits can be categorized into vein, vein and lenses and paleokarst types. They are hosted by Carboniferous limestone.

No recent investigation of the economic potential has been conducted since the early nineties. More specifically no special attention has been drawn to trace elements in major minerals and especially sphalerite since Evrard (1945). A recent review paper by Goossens (2014) indicates the following resources : Lontzen 537 kt @ 21,9% Zn and 3,6% Pb; Bleyberg 850 kt @ 13,5% Zn and 5% Pb.

SPHALERITE SAMPLES

A preliminary analysis has been conducted on historical samples coming from Schmalgraf, Plombières, Moresnet and Welkenraedt. These samples were available from the University of Liege collections and from amateur collections. Only samples with a clear identification of the location have been considered.Clearly, this sampling cannot be considered as representative of the whole district.

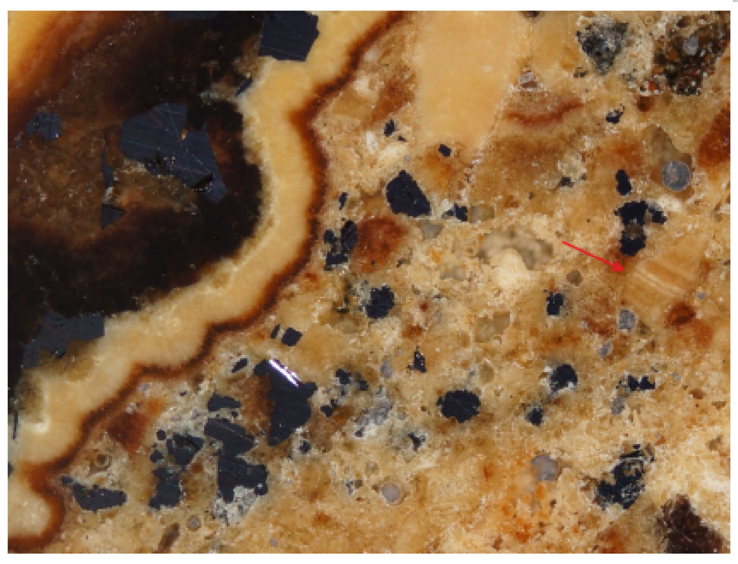

Fig. 3 Crossed polars image showing zonation patterns and distinctive brecciation in sphalerite. [Moresnet mine]

ANALYTICAL TECHNIQUE

The instrument used for microanalysis of critical elements in sphalerites consists of an excimer laser (GEOLAS-pro, λ = 193 nm), coupled to an Agilent 7500 mass spectrometer. This equipment is hosted by the Géoressources Laboratory at Université de Lorraine. The following elements have been analysed: ^{55}Mn, ^{57}Fe, ^{63}Cu, ^{71}Ga, ^{74}Ge, ^{75}As, ^{82}Se, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{206}Pb.

Internal standards of sphalerites have been used taking results from EDX analysis (Brüker Quantax). Due to the detection limits a possible overestimation of 1 to 5 % in the results is suspected.

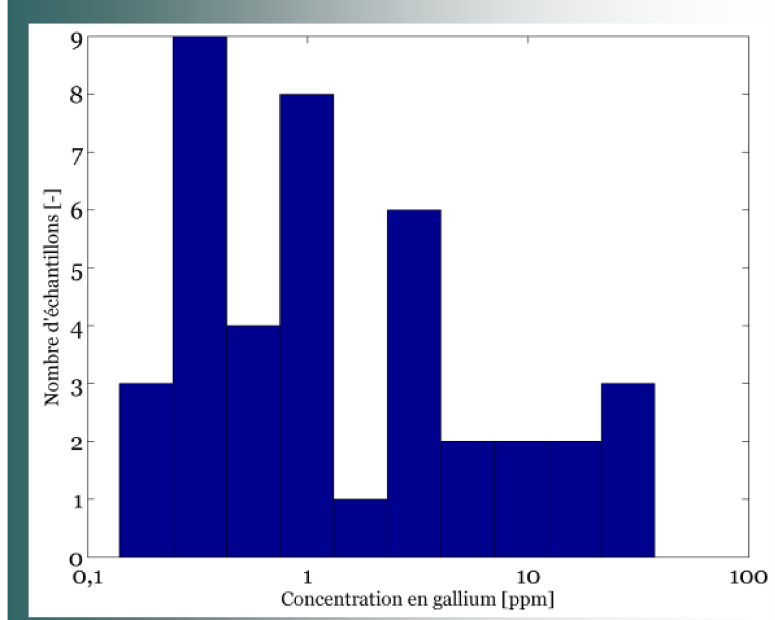

Fig. 4 Histogram of Ga in sphalerites (N=40)

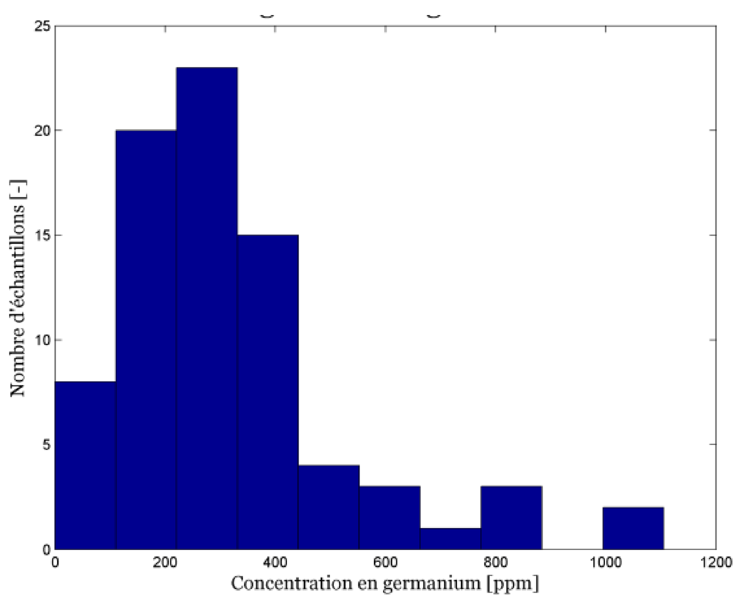

Fig. 5 Histogram of Ge in sphalerites (N=82)

RESULTS

Gallium is on the low side with half of the analyses falling below the detection limit of 0.18 ppm. The mean value corresponds to m(Ga)=2.2 ppm but with a range going from 0.2 ppm to values above 10 ppm to even 40 ppm.

depth.

Germanium on the other hand shows no results below the detection limit and corresponds to a mean m(Ge)=302 ppm with a standard-deviation σ(Ge)=216 ppm. This is significantly higher compared to the Missisipi MVT deposits (Viets, 1992) although lower than in Tres Marias (Cook et al. 2009).

Indium, as expected from MVT deposits, is almost below detection limits in every sample.

DISCUSSION

The coupled substitution $[2Cu^{+} + Cu^{2+} + Ge^{4+} \leftrightarrow 4Zn^{2+}]$ can be evidenced by plotting the sum of monovalent ions (Cu, Ag) against the sum of tri- and quadrivalent ions (Ga, In, Ge, Sn).

in Tres Marias, Cook et al. (2009) noted a strong correlation between Fe and Ge, which led them to suggest the following mechanism: $2Fe^{2+} + Ge^{4+} + \square \leftrightarrow 4Zn^{2+}$

When comparing the Eastern Belgium sphalerites to the Fe:Ge correlation observed in Tres Marias (Fig 5), a clear difference appears between both deposits calling for yet another explanation and further analytical work.

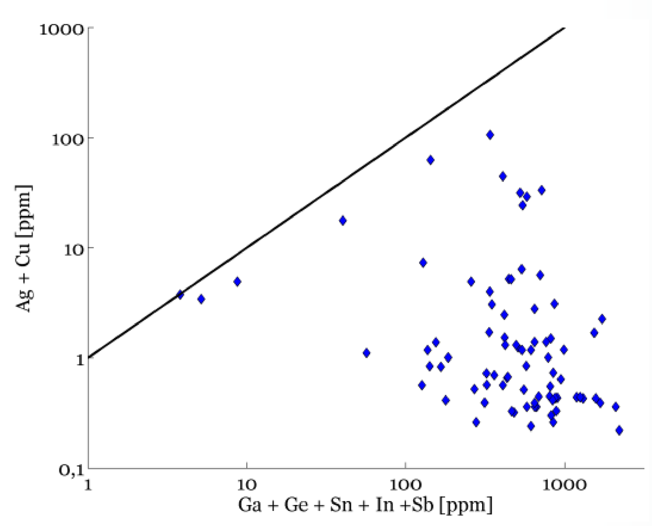

Fig. 6 A large number of analyses from Belgian MVT clearly plot below the line corresponding to coupled substitution.

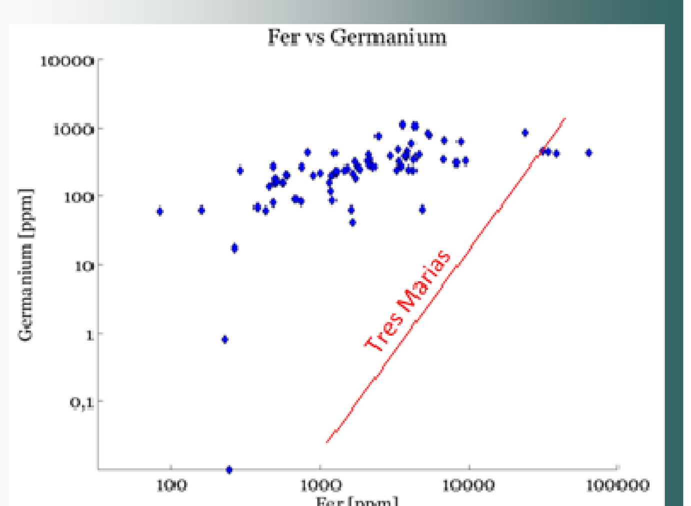

Fig. 7 Log-Log scatterplot (Fe, Ge) for Belgian MVT analyses with indication of the correlation observed at Tres Marias by Cook et al. (2009).

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