

Critical metals in sphalerites from Belgian MVT deposits

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Abstract. Belgium hosts a series of well documented low temperature, carbonate hosted, lead-zinc veins and lenses clearly categorized as MVT deposits. This paper revisits the distribution of trace elements in sphalerites from Belgian deposits with a special focus on Ge, Ga and In. By comparing with a database of worldwide deposits, this paper shows that Belgian sphalerites do not display a classical substitution pattern involving Cu^+ . Instead, multivariate analysis points towards similarities with the Tres Marias deposit in Mexico, although the explanation of coupled substitution with Fe^{++} does not seem to apply in the present case. From the limited set of sphalerites analysed in this paper, the following arithmetic means are obtained: $m(\text{Ge}) = 302 \text{ ppm}$, $m(\text{Ga}) = 2.2 \text{ ppm}$ and $m(\text{In}) < 0.06 \text{ ppm}$. These average values should not hide the fact that a wide variability does exist from one deposit to the other and within zoned colloform sphalerites of the same deposit.

Further and systematic work is required to better evaluate the resource and understand the mechanisms responsible for Ge incorporation into sphalerite.

Sphalerite, Germanium, Substitution

1 Critical elements in zinc deposits

Critical elements have been documented in various reports from the USGS and the European Union by combining the geological scarcity; the strategic importance in technologies and the geopolitical risks into a single index. Indium, Gallium and Germanium are among the elements that regularly show up as being critical to very critical.

It is known since their discovery that these elements are typically linked to Lead-Zinc mineralisations. Gallium was discovered by Lecoq (1875) in a mix of sphalerites from Belgium and France, whereas Indium and Germanium were discovered in Freiberg respectively by Reich and Richter (1863) and Winkler (1886).

A series of recent papers have compiled available data for sphalerites (Cook et al. 2009) 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 where previous inventories of existing deposits evaluated resources to a mere 24kt (Elsner et al. 2010).

2 Belgian MVT deposits

2.1 Geological setting

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 Muechez et al. (2005). A recent work by Coppola et al. (2008) also describes the anomalous presence of willemite at greater depth suggesting a possible hydrothermal high-silica event at some specific locations like “La Calamine”.

Belgian deposits can be categorized into vein, vein and lenses and paleokarst types. They are hosted by Carboniferous limestone and often occur at the contact between limestones and impermeable Namurian shales. Dolomitisation, dissolution features and high salinities (10%-30% wt eq NaCl) are characteristic features as are temperatures of formation in the order of 75 °C till 200 °C (Muechez et al. 2005). Recent estimations of reserves from historical drillings indicate 1,7 Mt at 11,1% Zn, 2% Pb et 30 g/t Ag (Goossens, 2014).

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).

2.2 Sphalerite samples

A preliminary analysis of critical metals with modern analytical means has been conducted using samples available from the University of Liege collections and from amateur collections. Only samples with a clear identification of the location have been considered. It should however be stressed that this sampling cannot be considered as representative of the whole district. Ten samples of colloform type sphalerites showing distinctive zonations and sometimes brecciation patterns have been kept for systematic analysis using LA-ICP-MS. Figure 1 shows a typical micrograph of one such samples. Samples come from locations known as Schmalgraf, Plombières, Moresnet and Welkenraedt.

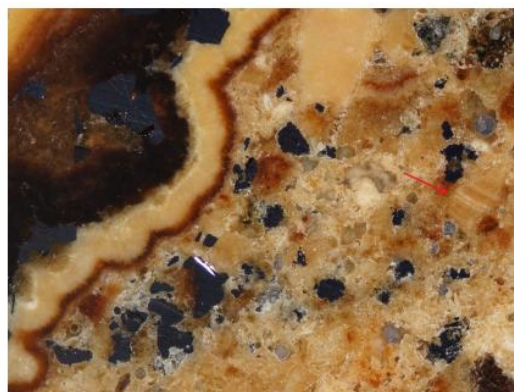


Figure 1. Crossed polars image in reflected light showing zonation patterns in sphalerite and galena inclusions. Sphalerite fragments show distinctive brecciation (red arrow, upper right quarter).

3 LA-ICP-MS analysis

The instrument used for microanalysis of critical elements in sphalerites consists of an excimer laser (GEOLAS-pro, $\lambda = 193$ nm), coupled to an Agilent 7500 mass spectro. This equipment is hosted by the Centre Géoresources at Université de Lorraine. Laser ablation was run at 5 pulses/second at a constant energy of 90mJ. A total of 200 pulses have been used to get a stable response over 40 seconds for analysis. The external standard used for calibration was the MASS-1 developed by Wilson et al. (2002). Ge is not in the certificate provided by the USGS, but is known to be $57,8 \pm 2,6$ ppm (Wilson personal comm to Belissont et al. (2014)). The data have been processed using the Iolite package in Igor Pro. 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 (Bruker Quantax) on a FEG-ESEM-XL30 Philips microscope. Due to the detection limits of EDX as compared to WDX a possible overestimation of 1 to 5 % in the results is suspected. Table 1 gives the typical detection limits of the LA-ICP-MS instrument.

Mn (ppm)	Fe (ppm)	Cu (ppm)	Ga (ppm)	Ge (ppm)	As (ppm)	Se (ppm)
0,375	14,091	0,155	0,180	0,325	0,738	4,916
Ag (ppm)	Cd (ppm)	In (ppm)	Sn (ppm)	Sb (ppm)	Te (ppm)	Pb (ppm)
0,152	9,711	0,060	0,301	0,278	3,333	3,573

Table 1. Detection limits of the various elements using the LA-ICP-MS settings used in this study.

4 Results

4.1 Univariate analysis

Figures 2 and 3 show the histograms corresponding to all analytical results for Gallium and Germanium respectively. It is to be noted that strong variability is present between the ten individual samples but also within the same sphalerite masses due to zonation.

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 $m(\text{Ga})=2.2$ ppm but with a range going from 0.2 ppm to values above 10 ppm to even 40 ppm.

Evrard (1945) already pointed out a possible exception in Vedrin (Namur area) where Gallium averages 15 ppm whereas Germanium is relatively depleted (63 ppm). Evrard (1945) also noted that the “absence” of Ga in Belgian MVT deposits is in strong contrast with respect to the Mississippi MVT’s. This is in accordance with recent data from Viets et al. (1992). However Cook et al. (2009) reported low Ga (2.6 to 24 ppm) from Tres Marias in Mexico and other authors have similar low Ga values in China (Ye et al. 2011) and the Alps (Pimminger et al., 1985).

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

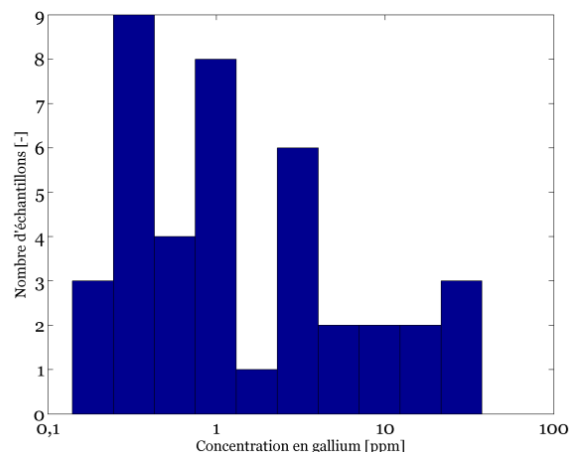


Figure 2. Frequency distribution of Ga analyses showing results above detection limit (N=40).

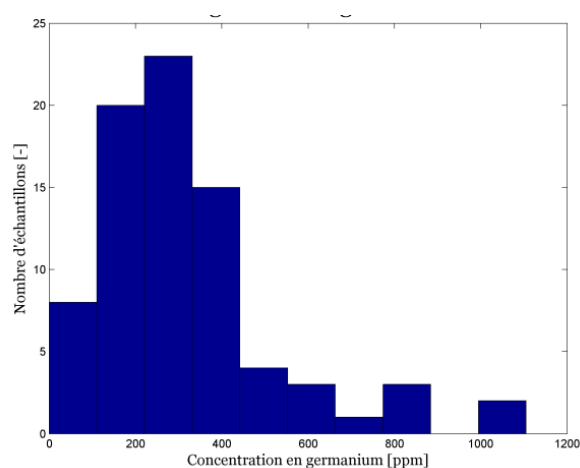
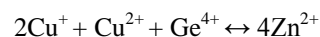


Figure 3. Frequency distribution of Ge analyses showing results above detection limit (N=82).

Indium, as expected from MVT deposits, is almost below detection limits in every sample. Cook et al. (2009) similarly reported values of 0.1 ppm to 0.2 ppm In in Tres Marias.

4.2 Multivariate analysis

Although Ge^{2+} could theoretically substitute to Zn^{2+} in sphalerite, no direct proof has been brought up to now. Instead, a coupled substitution of tri- and quadrivalent ions has been suggested by Johan (1988) based on the analysis of french sphalerites. Ge^{4+} is considered to form pairs with monovalent ions obeying the following equation:



This coupled substitution can be evidenced by plotting the sum of monovalent ions (Cu, Ag) against the sum of tri- and quadrivalent ions (Ga, In, Ge, Sn) as shown in figure 4.

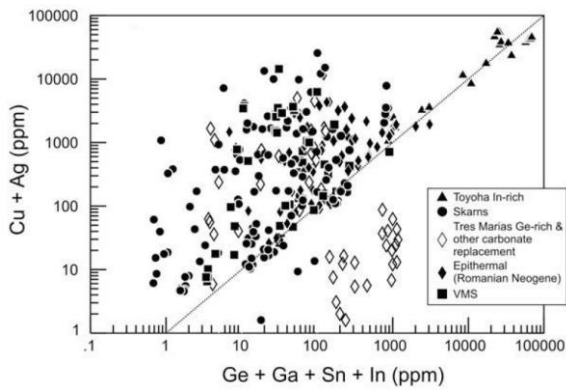


Figure 4. Evidence of coupled substitution in sphalerites from various deposits (Cook et al. 2009)

However, if some deposits show a perfect 1:1 correlation (ex. St Salvy (Belissant et al., 2014), others above the bisector suggest the presence of inclusions and one deposit (Tres Marias, Mx) exhibits an unusual behaviour. Figure 5 displays the same log-log graphic as obtained for the Eastern Belgium sphalerites clearly showing that they also claim for a different substitution mechanism.

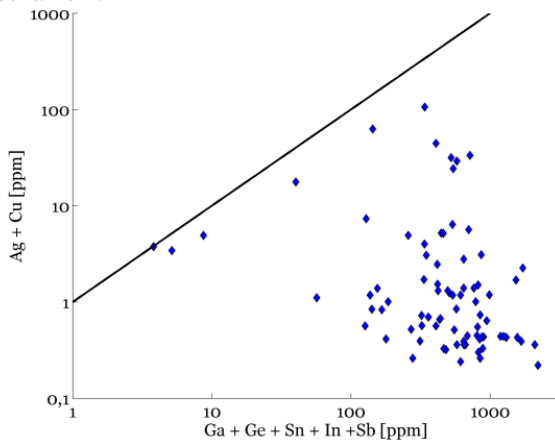


Figure 5. (Cu+Ag) vs. (Ga+Ge+Sn+In) for Eastern Belgium sphalerites.

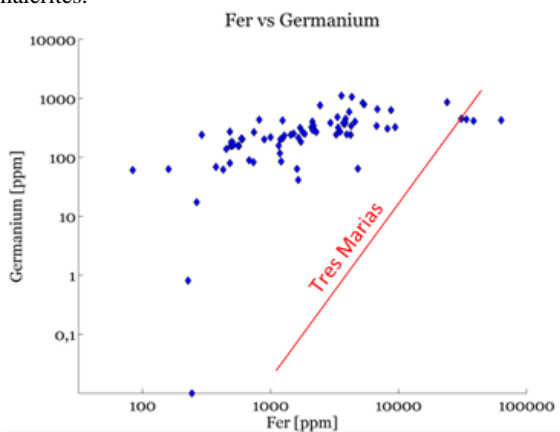
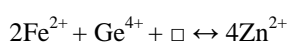


Figure 6. Scatterplot of Fe vs. Ge in Eastern Belgium sphalerites compared to the correlation demonstrated in Tres Marias by Cook et al. (2009)

Cook et al. (2009) noted in Tres Marias a strong correlation between Fe and Ge, which led them to suggest the following mechanism:



But, when comparing the Eastern Belgium sphalerites to the Fe:Ge correlation observed in Tres Marias (Fig 6), a clear difference appears between both deposits calling for yet another explanation and further analytical research.

Conclusions

Eastern Belgian sphalerites definitely show interesting Ge contents with most values well above the economic cut-off suggested by Frenzel et al. (2014) in their recent inventory of world Ge resources.

These high Ge values, together with very low In and low Ga values are consistent with observations made worldwide in MVT deposits.

A multivariate scatterplot clearly reveals that the most commonly suspected coupled substitution mechanism does not seem to hold. This draws the attention towards a strong similarity with the Tres Marias deposit in Mexico, but a closer look to the Fe:Ge correlation does not confirm the substitution suggested by Cook et al. (2009) for the Mexican deposit.

Further work is needed to better understand the crystallochemistry of Ge in Eastern Belgium sphalerites, but more importantly a systematic and more representative work has to be undertaken to improve our knowledge of Ge behaviour in both the hypogene and supergene mineralisations.

Acknowledgements

The authors would like to acknowledge the very helpful support of the Centre Géoresources in Nancy in performing the LA-ICP-MS analyses. The help and expertise of Remi Belissant was particularly appreciated. The authors would also like to thank Bernhardt Saini-Edukat for fruitful discussions.

A special thank is due to Mr Paul Simons for sharing his amateur collection with the authors to the benefit of science.

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