

Thallium, Nickel, Cobalt and Other Trace Elements in Iron Sulfides from Belgian Lead-Zinc Vein Deposits

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Fe-sulfides associated with Belgian Pb-Zn vein deposits have been analysed by DC arc spectrometry and XRF for Tl, Ni, Co, Mn, Zn, Pb, Ge, Cd, and As. They show high Tl contents (from > 30 ppm up to 6800 ppm) and Co:Ni ratios < 1. These features permit to distinguish them from Fe-sulfides of sedimentary and high temperature occurrences. The Tl distribution in a botryoidal marcasite of Vedrin (average Tl content of 0.68%) has been investigated by ion microprobe. It displays a pattern similar to colloform texture. Principal component analysis shows that the behaviour of Tl is partly controlled by a factor opposing Tl to all other elements. This is interpreted as reflecting the influence of sorption mechanisms by contrast with direct precipitation. Tl and the other elements are not considered of magmatic origin because no acidic magmatism is known during or after Variscan times. Extraction from sedimentary rocks by hydrothermal brines is favoured.

INTRODUCTION

A systematic study of the trace element geochemistry of pyrite and marcasite has been undertaken in order to characterize iron sulfides associated with Pb-Zn vein deposits, and to examine whether trace elements could help to understand the conditions of formation of the ore, and thus facilitate the detection of hidden deposits. A preliminary study by Duchesne (1964) showed the presence of relatively large amounts of thallium in marcasite from the Vedrin ore deposit (Belgium) and pointed to the similarities with Pb-Zn deposits from the Cevennes border in France. The purely syngenetic origin of these latter deposits proposed by Bernard (1961) was questioned on this basis (Duchesne,

1964), and discussed (Bernard, 1965; Duchesne, 1965). The present study corroborates these first results with the help of more powerful analytical techniques and statistical methods of interpretation.

ANALYTICAL METHODS

As a general rule, the specimens were carefully investigated under the reflected light microscope to select the homogeneous Fe-sulfide parts of the ore. The purity of the sampled parts was checked under the binocular after reduction to small fragments. When necessary hand-picking of impurities was further done and remains of calcite removed by a brief HCl 2N attack. Though greatest care was exercised in the op-

ration, the method - like any other separation method - cannot however warrant the absolute purity of the analysed aliquots of the samples. This fact was taken into consideration in the interpretation of data by means of statistical methods (see below). The use of Clerici's solution (Tl formate and malonate) as a density liquid has been prohibited to avoid contamination by Tl. The final grinding to about -150 mesh was done in agate mortars.

Three different analytical methods are used:

1. DC arc spectrography
2. X-ray fluorescence spectrometry
3. Ion microprobe analysis (SIMS)

1. DC arc spectrography is used to determine Co, Ni, Mn, Cd, Ge, Sb, Bi, Sn, Cr as well as low contents of Tl, Pb and As. The method is inspired from Hegemann and Leybold (1954). The powdered sample is mixed with 2 parts of "specpure" graphite, and loaded in the conical cavity of a graphite electrode (SCHRIBNER type - National Carbide L4024). A 3 mm diam-rod (Le Carbone-Lorraine type 207) is used as an upper electrode. A drop of Elvacite 2044 diluted in toluene is placed on the loaded electrode and dried in order to form a cake. This procedure prevents loss of material during the first seconds of arcing and regularizes burning. An optimum reproducibility ($\pm 5\%$) can thus be obtained.

A stabilized DC arc of 6.5 A and 220 V from a PHILIPS Multisource is used to burn the sample (anode) during 30 sec. All analyses are duplicated. The spectrograph is a FUESS 110 H (4 prisms) equivalent to the HILGER large spectrograph. The densitometer is mod C 1285 from FUESS. The spectra are recorded on KODAK plates (type) SA 1 in the range of 2760 Å to 3480 Å. The analytical lines (Å) are the following: Co 3044; Ni 3051; Mn 2933; Zn 3822; Cd 3261; Cu 3274; Ge 3039; Sb 3878; Bi 3068; Sn 2840; Cr 3015; Tl 2768; As 2780; Fe 3053 is used as an internal standard. Four international standard samples of pyrite: PS-1 (Schrön et al., 1975), P-1 and P-2 (Robinson and Walshe, 1977) and ASK-3 (Christie, 1975) are used for

calibration of Co, Ni, Mn, Zn, Cu. The four standards provide excellent working curves for Co, Ni, Mn and Zn, and a good one for Cu. Only one standard out of the four available can be used for Cd, Ag, Sb, Bi, Sn and Cr. Therefore, 45° slope working curves, passing through the standard values, in log-log coordinates, are used for these elements (Ahrens and Taylor, 1961). For Ge synthetic standards obtained by mixing Ge to a Fe₂O₃ matrix are used. Tl, Pb and As are calibrated with values measured by X-ray fluorescence. The detection limits are: 0.2 ppm Ag; 1 ppm Pb, Mn, Cu, Ge; 5 ppm Co, Ni, Sb, Bi, Sn, Cr; 10 ppm Tl; 15 ppm As, Cd.

2. X-ray fluorescence analysis is used for the determination of relatively high contents of Tl, Pb and As. A CGR alpha 2020 semi-automatic spectrometer working with a Mo-tube at 50 kV and 50 mA and a LiF100 analysing crystal is used. Analytical lines are Tl L_{β1}, As K_{β1} and Pb L_{β1}. Standard samples ASK-3 and PS-1 are used to calibrate the method for Pb and As. Synthetic samples made by mixing various amounts of Tl₂O₃ to a pyritic matrix are used for Tl. It must be noted that the Tl content of 100 ppm, given by Schrön et al. (1975) for PS-1, is highly overestimated. No Tl is detected by DC arc spectrography, which means that the Tl content is lower than 10 ppm. Inspection of the most sensitive line at 5350 Å with ICP spectrography also reveals no Tl. The limits of detection (LD), following Currie (1968), are 30 ppm Tl and Pb and 45 ppm As.

3. Secondary ion mass spectrometry (SIMS) in the ion microscope mode is used to study the distribution pattern of Tl through polished sections of about 1 cm in diameter, with a spatial resolution of 1-10 μm. Quantitative analyses with a spatial resolution of 250 μm is possible for e.g. Mn, Co, Ni, Cu and Tl. The instrument used is a Cameca IMS-300 ion microscope, and a 6 KeV Ar⁺ primary beam is used with a current density of 12 A/mm². For quantitative analyses an electrostatic sector is used to select 140-160 eV ions for Mn, Co, Ni and Cu, and 60-80 eV ions for Tl. The analysed surface is 250 μm in diameter.

For calibration of Mn, Co and Cu the four already mentioned reference samples are used in the form of pellets, as described by Dillen and Gijbels (1981). No certified standards being available for quantitative Tl analyses, a sample from Vedrin, which has been examined by SIMS and found virtually homogeneous at the 250 μm -scale (standard deviation for 14 different measuring sites of 250 μm diameter each: 11%), is used as a reference sample after determination of its Tl content by ICP-AES, in nitric acid solution, using the 5350 \AA Tl-line. The instrument is calibrated by Tl-solutions containing the same amount of

iron and acids. A concentration of 6800 ppm is found by that method for the Vedrin sample. A massive part of the specimen is used to determine a sensitivity factor for SIMS, with ^{32}S as an internal standard.

SAMPLING

84 samples belonging to 36 occurrences of marcasite or pyrite have been anal-

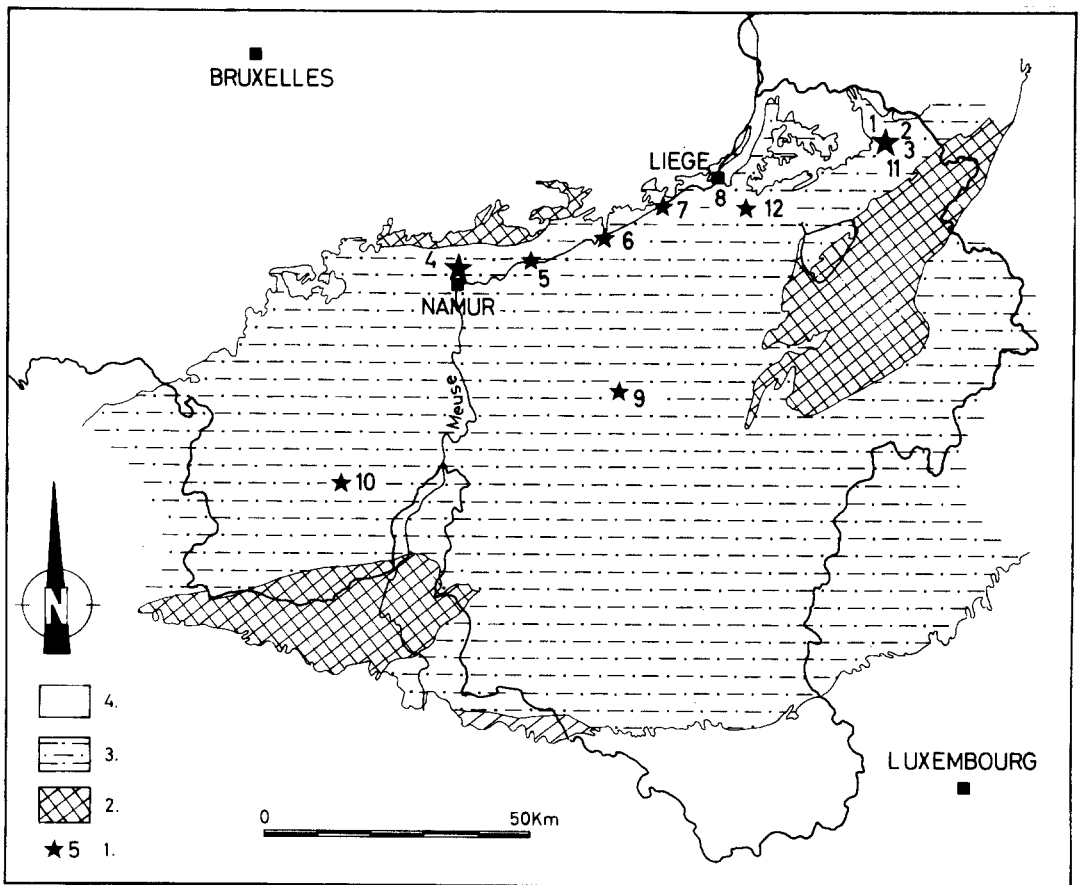


Fig. 1. Geological sketch map of South Belgium showing the provenance of the various iron sulfide samples from Pb-Zn vein deposits. 4. Post-Variscan terrains; 3. Devonian and Carboniferous terrains; 2. Cambrian and Silurian terrains; 1. Numbered stars refer to the investigated occurrences: 1, 2, 3 and 11: Poppelsberg, Stuck, Lontzen and Moresnet, respectively; 4: Vedrin; 5: Hayes-Monet; 6: Corphalie; 7: Engis; 8: Angleur; 9: Heure; 10: Villers-en-Fagnes; 12: Chaudfontaine

ysed. The main occurrences come from East Belgium (Fig. 1): Poppelsberg (11 samples) and Stuck (2 samples) are small post-Variscan Pb-Zn vein deposits cutting across Dinantian carbonate rocks and Famennian rocks of the Vesdre Massif. They were recently drilled by the Union Minière Company. Lontzen (15 samples) also belongs to the same type of mineralization and comes from the same area, but is entirely situated in siltic to pelitic rocks of Famennian age.

Another well documented site - the Vedrin Mine, near Namur - has also been investigated. It is a vein deposit in Dinantian carbonate rocks of the Namur synclinorium (Evrard, 1943). Two types of sulfides are studied. The first and most common one is the vein type (12 samples): a fibro-radiated marcasite associated with some blende and galena in a calcite gangue. The second type (5 samples) is a marcasite, filling small veins and veinlets of a brecciated dolostone, at a distance of 10-20 m from the main vein.

Other Belgian Pb-Zn occurrences have also been included: Hayes-Monet, Corphalie, Engis and Angleur (2 samples) from the Namur synclinorium; Heure and Villers-en-Fagnes in Devonian strata from the Dinant synclinorium; Moresnet and Chaudfontaine in the Vesdre Massif, the latter is a cubic pyrite associated with a baryte stratiform deposit (Dejonghe, 1979) in Devonian strata.

Two occurrences from the Cévennes border - Soulier and St Félix de Pal-lière - previously studied by Duchesne (1964) have also been reinvestigated.

Moreover, 12 occurrences from sedimentary rocks, mainly pyrite cubes from shales, have been included for the sake of comparison (Rochelival, Bayehon, Deville, Grand-Halleux, Longfaye, Huc-corgne, Ronquière, Grufflingen, Boux-harmont, Visé, Gris-Nez - France, Ballachullish - Scotland) as well as pyrites formed at high temperature (Agrokipia-Cyprus, Calamita and Rio Marine - I. Elba, Pamour-Canada, Luzenac-France and Buranga-Ruanda).

The results of the analysis are summarized in Table 1 which gives the average and the range of variation of each trace element in each occurrence.

DISCUSSION

The results usually show a wide dispersion in the various Pb-Zn occurrences. They can however be summarized as follows:

1. The Co content is low - usually close to or below 5 ppm - in the Belgian Pb-Zn type and contrasts with the sedimentary and high temperatures occurrences, which show averages of 332 ppm and 2180 ppm respectively. The Ni content of the Pb-Zn type is higher than the Co and can be compared to the sedimentary or high temperature sulfides. Therefore, the Co:Ni ratio is < 1 in the Pb-Zn type. According to classical interpretations (see e.g. the reviews by Loftus-Hills and Solomon, 1967 and Bralía et al., 1979) this would indicate a sedimentary origin. However, the various authors usually consider that this criterion is poorly significant when used alone. The present data on sedimentary occurrences also confirm that the Co/Ni ratio has to be used with caution. Indeed, 5 out of 12 sedimentary occurrences which are studied here show Co:Ni > 1 , an inverse relation to what should be expected since they all concern typical cubic pyrites in black shales or slates. It is likely that recrystallization due to incipient metamorphism can lead to an enrichment of Co with respect to Ni, in such a way that an original Co:Ni < 1 might be modified to a Co:Ni > 1 .

It can be concluded that, in Pb-Zn deposits, the Co:Ni ratio in iron sulfides has no genetic significance since the observed relation (< 1) is not in agreement with the geological evidence. It must however be noted that the low Co content of the Pb-Zn occurrences appears to be a feature restricted to this type of deposits and is likely to have a promising genetic meaning.

2. Thallium is always present (from > 30 ppm up to 6800 ppm) in the Belgian Pb-Zn type, whatever the geological unit to which they belong (Dinant or Namur synclinoria, Vesdre Massif) or the age of the enclosing rocks (Dinantian or Devonian). It is also present in the Cévennes border (Duchesne, 1964) where Aubagne and Leleu (1981) have recently

Table 1. Trace element contents (ppm) of iron sulfides

Number of samples	VENDRIN														
	POPPELSBERG STUCK			LONTZEN		MAIN VEIN		BRECCIA		OTHER BELGIAN OCCURRENCES		CEVENNES OCCURRENCES		SEDIMENTARY HIGH TEMP OCCURRENCES	
	11	2	15	12	5	12	5	9	3	12	7	3	12	7	
Tl	\bar{x} 235 range 30-1600	90 30-150	83 30-190	517 73-6800	78 54-88	229 55-650	806 460-1080	<10	<10	<10	<10				
Co	? (7) (1) range <5-90	? (1) <5-48	36 8-98	<5	<5	? (6) <5-220	<5	332 <5-1470	2180 47-6600	332 <5-1470	2180 47-6600				
Ni	\bar{x} 370 range 45-1650	300 10-600	448 42-1010	17 <5-42	10 5-17	200 <5-620	5 <5-6	374 8-2050	145 8-440	374 8-2050	145 8-440				
Co/Ni	\bar{x} <0.04-0.14	<0.1-0.5	0.05-0.15	<0.1-0.5	<0.3- ∞										
Pb	\bar{x} 3760 range 15-7500	3680 3500-3850	2590 1100-4750	4050 15-12600	4160 2720-7050	4170 25-12000	1555 325-3700	123 18-485	? (4) <1-10	123 18-485	? (4) <1-10				
Zn	\bar{x} 460 range 40-2250	? 400-15000	1123 40-9000	445 20-2200	29 20-42	925 30-5400(2)	293 95-650	108 20-610	79 10-420	108 20-610	79 10-420				
Mn	\bar{x} 23 range 1-125	7 3-11	22 3-290	245 1-1000	2 <1-3	73 1-620	113 15-310	310 <1-3400	35 <1-125	310 <1-3400	35 <1-125				
Cu	\bar{x} 163 range 4-360	150 3-310	397 115-1010	6 1-25	3 2-4	18 1-65	34 10-65	146 10-790	470 3-2200	146 10-790	470 3-2200				
Ag	\bar{x} 15 range 2-50	55 4-105	44 18-105	7 2-34	3 2-4	4 1-7	45 18-85	16 1-140	5 1-16	16 1-140	5 1-16				
Cd	\bar{x} ? (8) range <15-30	? (1) <15-1900	? (8) <15-95	? (7) <15-55	21 15-25	? (4) <15-185									
Ge	\bar{x} 23 range <1-65	? (1) <1-470	? (7) <1-95	19 <1-80	5 0	30 <1-95	<1	<1	<1	<1	<1				
As	\bar{x} 383 range <10-2450	2500 500-4500	472 50-1010	? (11) <10-40	<15	100 <10-310	2720 1300-5000	283 20-625	273 <10-850	283 20-625	273 <10-850				
Sb	\bar{x} 19 range <5-65	10-100	54 15-150	<5	<5	? (7) <5-25	310 20-660	27 <5-180	? (6) <5-10	27 <5-180	? (6) <5-10				
Bi	\bar{x} <5 range	<5	<5	<5	<5	<5	<5	<5	? (8) (50)	<5	? (8) (50)				
Cr	\bar{x} <5 range	<5	<5	<5	<5	<5	<5	<5	<5-250 (350)	<5	<5-250 (350)				

(1) average not significant: the figure into brackets gives the number of values below the detection limit
(2) with two additional values > 50000 ppm
Detailed data can be obtained from the authors

mentioned Tl-rich (0,5 to 1%) melnikovites and marcasites in Pallière.

On the other hand, Tl is absent (<10 ppm) from all sedimentary and high temperature occurrences. According to Ivanov et al. (1960), Tl is commonly found in numerous varieties of poly-metallic deposits. It is usually more enriched in sphalerite or galena than in iron sulfides, e.g. from some Caucasus deposits. Shaw (1952) and Albuquerque and Shaw (1972) also report high Tl content in marcasite from several localities (Japan, Caucasus, Central Asia, etc...). In Western Europe, since Stoiber (1940), Tl is mentioned in Pb-Zn deposits of Belgium, Westphalia, and Silesia. Except for the data of Thein (1975) on the Meggen deposit (see below), no modern analyses have been made available on sulfides and this hampers the study of the chalcophile behaviour of Tl.

In the Belgian Pb-Zn occurrences the maximum Tl content in iron sulfides is found in a radiated botryoidal marcasite from the Vedrin mine (0,68%). The distribution of Tl, as revealed under the ion microprobe, is shown on Plate 1. Tl is not incorporated as independent phases larger than 1 μm (the resolution power of the ion microprobe) and can thus be considered regularly distributed throughout the marcasite phase. At a larger scale thin alternating bands (from 1 to 50 μm) of contrasting Tl contents are disposed perpendicular to the radiating directions of the texture. The overall picture is quite similar to the so-called colloform texture and can be put together with the fact that Tl is notably enriched in colloform varieties of iron sulfides (Ivanov et al., 1960). In a second specimen from Vedrin an inclusion of a Tl and Pb bearing mineral—possibly hutchinsonite $(\text{Pb}, \text{Tl})_2(\text{Cu}, \text{Ag})\text{As}_5\text{S}_{10}$ — was also found, thus indicating that trace minerals can also control the distribution of Tl.

3. Some variations can be observed between the different Belgian deposits or even within the same deposit. The Vedrin marcasites are low in Co, Ni, As, Sb, Cu, Ag compared to the East Belgium occurrences. The Tl, Zn, Mn, Cu and Ag

contents in the Vedrin marcasite from the brecciated dolostone are lower than in the main vein occurrences; they also display less dispersed values. In Lontzen, almost all trace elements are enriched relative to the Poppelsberg-Stuck type. Since the deposits all belong to the same fault system, it is likely that this difference is due to the siltic to pelitic nature of the Famennian enclosing rocks at Lontzen as compared to the carbonate rocks at Poppelsberg and Stuck.

4. In addition to the variations between the different occurrences, the trace elements display large intervals of variation within the different deposits. In order to investigate these variations in detail, the statistical method of principal component analysis has been applied to the Pb-Zn type. The computing has been performed by the Fortran IV program of Davis (1973) adapted for a Heathkit Z89 microcomputer with a memory of 64 K of RAM and two 5.25 inch floppy discs.

Fig. 2 summarizes the results obtained on 40 samples from Pb-Zn deposits, representing the whole population of this type except the samples from the Vedrin mine. Bi and Cr which are absent from the Pb-Zn type were not considered. The reason for discarding the Vedrin samples is that the contents in Co, Cd, As and Sb are currently below the limit of detection of the method. A large number of data below the detection limit can indeed artificially modify the true correlation between the elements.

Four factors can explain 72 % of the variance of the population. They can be interpreted as follows.

Factor 1 opposes Tl to a group of several elements which comprises elements such as Ni, Co, Zn, Cu and Ge which have an ionic radius close to that of Fe and therefore are compatible with their entering in the crystalizing iron sulfide by isomorphism. On the other hand, the opposite sign of the Tl factor loading can indicate a different controlling mechanism, possibly related to the higher value of the ionic radius ($\text{Tl}^+ = 1.40 \text{ \AA}$) (Sahl, 1974). As already mentioned, Tl is enriched in minerals presenting a collo-

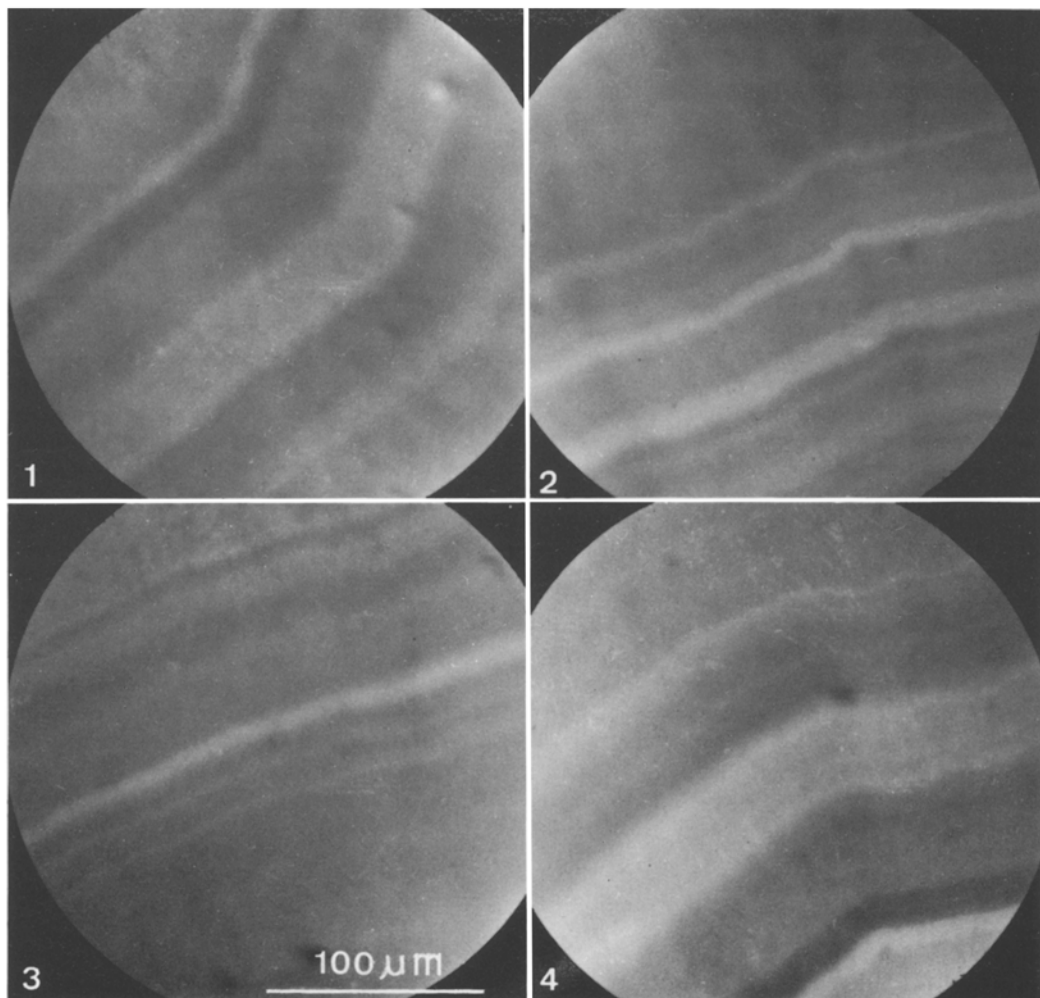


Plate 1. Tl distribution in a botryoidal marcasite from the Vedrin mine (Namur, Belgium) as revealed by secondary ion mass spectrometry (ion microprobe). Thin alternating bands (1 to 50 μm) of contrasting Tl contents - the higher the content, the darker the intensity - are perpendicular to the radiating directions (well displayed in photo 2) of the texture in a pattern similar to colloform texture

form structure, such as Schalenblende or in various "gel"-like or amorphous minerals, such as melnikovite (see Ivanov et al., 1960). Moreover, its size and chemical similarity with large alkali ions is consistent with its extraction from solutions by adsorption processes (Albuquerque and Shaw, 1972).

The similarities between the picture of the Tl distribution which is

obtained under the ion microprobe and colloform texture is striking and strongly suggests that adsorption on colloids is the mechanism which controls the behaviour of Tl. This is not in agreement with Roedder's view (1968), in which colloform texture cannot be formed by material in a colloidal state when deposited, but by direct crystallization from a fluid. We however believe that

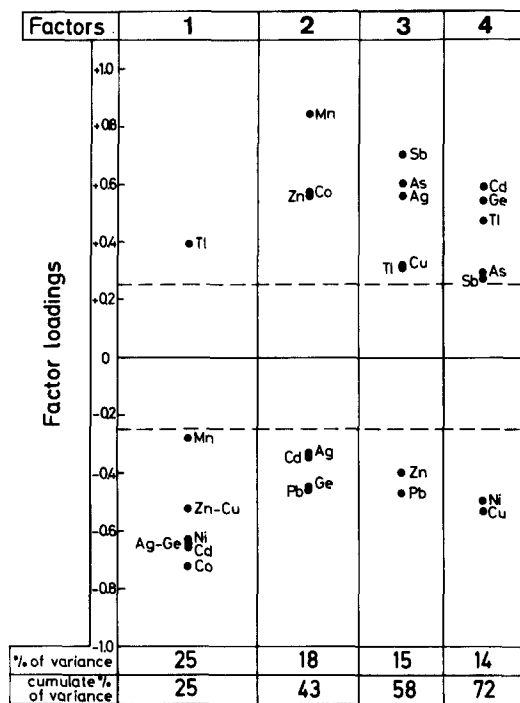


Fig. 2. Graphical representation of the principal component analysis of the trace element contents of iron sulfides from Pb-Zn vein deposits. Factor loadings less than 0.22, below the level of significance following Harman (1967), are not represented

our factor 1 is an indication that two different mechanisms play a role in the deposition of the iron sulfides and that, all things being equal, the Tl content of a sample is a measure of the relative importance of sorption effects in the process of formation of the particular sample.

Factor 3 groups together S-As-Ag and is also loaded with Cu and Tl. We interpret this as due to inclusion of trace minerals of sulfosalts, some of them containing Tl, which is known to have geochemical affinities with Sb and As (Jankovic and Le Bel, 1976).

Factor 2 is positively loaded with Mn and Zn and negatively with Pb-Ag-Cd-Ge. Factor 4 groups Tl with Cd-Ge which are opposed to Ni-Cu, and might indicate the influence of inclusions of

blende which can be rich in Tl (Evrard, 1945) and in Ge-Cd.

Factor 2 is difficult to interpret. It probably results from the combination of several mechanisms. Mn might come from inclusions of blende. It is however hard to understand why Mn, which could easily substitute for Fe, is mainly controlled here by its substitution with Zn and also why Cd-Ge, classically diadochic of Zn (see factor 4) appears here with factor loadings of sign different from Zn. The grouping of Pb with Ag is classical in galena and might also indicate inclusions of trace amounts of this mineral.

Though some points are still somewhat obscure, principal component analysis clearly shows that several possible mechanisms can account for the presence of Tl in the population: sorption phenomena and inclusions of sulfosalts and also possibly of blende. This is in agreement with the modes of occurrences of Tl observed under the ion microprobe and in conformity with what is known of its chalcophilic behaviour.

SOURCE OF THALLIUM: AN OPEN QUESTION

Polymetallic deposits which show the highest amount of Tl are related to acidic magmatism either volcanic or plutonic such as in the classical region of Caucasus (Ivanov et al., 1960) or in Turkey (Jankovic and Le Bel, 1976). The enrichment of Tl in the late stages of the magmatic differentiation is well in agreement with its similarity of behaviour with K.

The source of Tl in Pb-Zn deposits in carbonate environment is however a debatable question. In the Meggen deposit (Westphalia), the distribution of Tl in and around the stratiform ore body is considered to be due to the exhalative origin of the elements (Thein, 1975; Gwosdz and Krebs, 1977) and can thus be linked to a syn-sedimentary event. In Belgium however, except for some thin K-bentonites of Dinantian age (Thorez and Pirlet, 1979), volcanic rocks are not known interbedded in the Variscan sedimentary pile. In the area,

acidic plutonism is restricted to the small granitoids of La Helle and Lamersdorf (Germany) (Corin, 1965). They are situated far away from important deposits, such as the Vedrin Mine, and since they have suffered a deformation of Variscan or Caledonian age, they are certainly older than the post-Variscan tectonic event which controls the emplacement of the veins. The presence of a granitic batholith at depth under the Ardennes has been surmised by Fourmarier (in Dewez and Lespineux, 1947) to account for the distribution of the Belgian ore deposits. But no evidence in favour of such an hypothesis has ever been put forward.

Tl, if not magmatic, must find its source in sedimentary rocks from which it was scavenged by hydrothermal brines. When taking the data of Heinrichs et al. (1980) on sedimentary rocks, it is noted that the Tl content (average: 0.41 ppm; black shales: 2.5 ppm) is high relative to the Pb content (average: 16.7 ppm, black shales: 82 ppm). The Tl/Pb ratio varies between 1/50 and 1/30, values which are higher than those commonly found in sulfides from Pb-Zn deposits. Therefore it is not unlikely that any process which would extract and concentrate Pb would also be active for Tl.

CONCLUSIONS

Distribution of trace elements in various occurrences of iron sulfides indicates:

1. The iron sulfides related to Belgian Pb-Zn vein deposits, mainly in carbonate environment, belonging to different geological units (Namur Synclinorium, Dinant Synclinorium, Vesdre Massif) or situated in Devonian or Dinantian strata, form a group along with two occurrences from the Cévennes border; this group can be distinguished from iron sulfides of various origins by their Ni, Co and Tl contents. Their Co:Ni ratio (< 1) can be compared with sedimentary occurrences but is distinctly lower than in high temperature occurrences (Co:Ni > 1). Their Tl content (> 30 ppm up to 0,6%)

permits to distinguish them from all other occurrences (Tl < 10 ppm). The Co content is lower than in sedimentary occurrences.

2. The mode of occurrence of Tl in iron sulfides is either in the form of trace minerals or is dispersed in the iron sulfide phase according to a zoned and recurrent pattern, similar to a colloform texture. Several lines of evidence indicate that sorption phenomena and inclusions of sulfo-salts can account for most of the behaviour of this element in the deposition of the iron sulfides.

3. The paucity of acidic magmatism in Belgium during Devonian and Carboniferous sedimentation or in post-Variscan times makes the hypothesis of a magmatic source for the Tl difficult to accept. The hypothesis that Tl together with other elements was scavenged from sedimentary rocks by hydrothermal solutions is favoured.

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