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Trace element contents and distribution maps of chalcopyrite: a micro-PIXE study

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ABSTRACT. — Micro-PIXE (Proton micro-beam Induced X-ray Emission) apparatus, with a beam scanning system, can provide information on both trace element contents and their distribution. This technique was applied to chalcopyrite samples from Italian and Slovak ore deposits. A 5 µm-diameter beam was used to obtain simultaneously trace element analysis with low detection limits and trace element distribution maps. The distribution of Zn appears to be related to sub-microscopic inclusions of sphalerite and kesterite, invisible in the corresponding SEM-BSE (Scanning Electron Microscope - Back-Scattered Electrons) and X-ray maps. In contrast, Ag and Se are homogeneously distributed, confirming the predicted tendency of these elements to replace Cu and S, respectively, in the structure of chalcopyrite.

RIASSUNTO. — La strumentazione micro-PIXE (Proton micro-beam Induced X-ray Emission) associata ad un sistema di scansione del fascio, può fornire informazioni sia sul contenuto di elementi in tracce che sulla loro distribuzione. Questa tecnica è stata applicata a campioni di calcopirite provenienti da giacimenti minerari sia italiani che slovacchi. E' stato usato un fascio del diametro di 5 µm per ottenere simultaneamente l'analisi degli elementi in tracce (con bassi limiti di rilevabilità) e le relative

mappe della distribuzione degli elementi. La distribuzione dello Zn sembra essere correlata alla presenza di inclusioni submicroscopiche di sfalerite e kesterite, che non erano state individuate nelle corrispondenti mappe effettuate al microscopio elettronico a scansione sia nella modalità a elettroni retrodiffusi che in quella a raggiX. Al contrario Ag e Se sono distribuiti omogeneamente e confermano la tendenza di questi elementi, già osservata, a sostituire Cu e S, rispettivamente, all'interno della struttura della calcopirite.

KEY WORDS: *chalcopyrite, micro-PIXE, trace elements, distribution maps, Massa Marittima, Bottino Mine, Banská Štiavnica, Montecatini, Ag and Se enrichment.*

INTRODUCTION

Study of compositional variations in trace elements plays an important role in the definition of phase boundaries at room temperature in some regions of the Cu-Fe-S ternary system (Craig and Vaughan, 1997).

Some elements are homogeneously distributed in the matrix of a sulfide host mineral and are called «invisible elements»,

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since they do not produce visible inclusions when examined by SEM (Scanning Electron Microscope) or EMPA (Electron Micro-Probe Analyser) (Cook and Chryssoulis, 1990).

Most published references on the mode of occurrence of trace elements in the structure of sulfides (mainly chalcopyrite, bornite, pyrite, galena and sphalerite) tend to be incomplete, because they cannot really clarify the limit amounts over which elements such as Zn, Ag, Sn, Cd, Se, In, Pb and Mn form inclusions of their own sulfides instead of being diffused in the host mineral (Cambel and Jarkovsky, 1974; Rose, 1967).

Due to the relatively high detection limits of micro-analytical techniques such as SEM and EMPA, very long counting times and special operating conditions are required to obtain X-ray distribution maps for elements with concentrations lower than 1000 ppm (wt). Bulk techniques with very low detection limits, like AAS (Atomic Absorption Spectroscopy) or INAA (Instrumental Neutron Activation Analysis), give representative results only if sample homogeneity is of the highest grade, which is nearly impossible to obtain in the case of sulfides.

The micro-PIXE technique, combined with a beam scanning system, yields not only multi-elemental quantitative analyses with quite low detection limits, but also corresponding element distribution maps (Campbell *et al.*, 1990).

In order to verify the reliability of the system to provide information on the mode of occurrence of some trace elements, 50 samples of chalcopyrite of the Mineralogical Museum of the University of Florence, from Italian (Montecatini Val di Cecina, Massa Marittima, Bottino Mine) and Slovak (Banska Štiavnica) ore deposits were analysed.

ANALYTICAL METHODS

As previously mentioned, one of the most important problems in the study of trace elements in sulfides is minimizing the

interference caused by the presence of microscopically visible inclusions of other sulfides of the element analysed. As already carried out by other authors (e.g., Cambel and Jarkovsky, 1974), polished sections containing fine-grained samples with grain diameters from 0.1 to 2 μm were therefore prepared. These samples were observed under reflected-light and scanning electron microscopes, to choose inclusion-free grains for EMP and PIXE analyses.

SEM observations and EMP analyses were carried out at the CNR (Consiglio Nazionale delle Ricerche) and MEMA (Microscopia Elettronica e MicroAnalisi) laboratories of the University of Florence, on a Jeol JXA 8600 microscope, operating conditions being 20 second count time, 25 kV voltage and 50 nA sample current.

Micro-PIXE analyses were carried out at the Legnaro National Laboratories (LNL), with the Legnaro proton micro-probe (Bollini *et al.*, 1993; Boccaccio *et al.*, 1996; Cristofolini *et al.*, 1998). A proton-beam with current intensity in the range 0.1-3 nA and corresponding diameter of 0.9 to 5 μm was used.

Quantitative analyses on standard and samples were carried out with a 3-nA-ion beam and counting times of about 8 minutes. A total number of 500000 counts was reached for each trace element analysis. Beam scanning, obtained with an Oxford triplet of magnetic quadrupoles, operated on areas ranging from about 2500 μm^2 to 4 mm^2 and provided elemental distribution maps of the selected areas.

The scanning step and corresponding image pixel is 0.67 μm wide, thus giving about 7 pixels for each 5 μm -diameter point, with image resolution for a 2500 μm^2 -wide area of at least 5000 pixels. Samples were optically observed with a high-magnification TV camera and then a scanning area was selected via the acquisition-controlling computer. Beam focus was optically checked by shooting the beam on a CsI crystal. Spot dimensions and quality were then checked, recording the X-ray maps obtained by shooting the beam on copper nets

with meshes ranging from 25 to 100- μm .

A Link System Si (Li) detector was used, with a 140-eV resolution at 5.9 keV, 100- μs shaping time, 80-mm² active area and 12- μm -thick Be window, positioned at variable distances from the sample. These operating conditions detected elements starting from Na.

A 235- μm -thick Al filter was also adopted during trace element quantitative analyses, to reduce the intensity of major-element peaks and to minimize their pile-up effect. The count-rate was therefore reduced to 1 kHz, with a corresponding dead time of 28%.

Quantitative analyses were obtained processing data with GUPIX-2 software (Maxwell *et al.*, 1989) in the trace-element mode. Apart from major elements (K lines of Cu and Fe are not completely filtered), only elements heavier than Zn could therefore be analysed (K lines of elements with Z greater than about 30, L lines of elements with Z greater than about 75-80).

Filter thickness, required by GUPIX for quantitative analysis of trace element concentrations, was measured by comparing the ratios of major elements (Cu, Fe) as detected in the PIXE spectra with EMPA data on the same elements and on their ratios (Campbell *et al.*, 1987).

In order to determine minimum detection limits for some elements and to verify analytical precision and accuracy, micro-PIXE trace element analyses were also performed on the reference standard NIST 610 (Reed, 1992). The results (some of which are listed in table 1) show good agreement with certified values.

Replicate analyses on the standard were carried out at the beginning of each series of measurements, as a further check on data precision.

RESULTS AND DISCUSSION

Analytical results

The detection limits obtained vary for different elements (see table 2): whereas Zn values are quite high (due to the influence of major-element peaks), others are low and comparable with those obtained with micro-PIXE by other authors (e.g., Campbell *et al.*, 1990). Only data over the minimum detection limit (m.d.l.) are shown in table 2, with percent error in brackets. Comparisons between the number of data over the m.d.l. and the total number of analyses allowed some considerations to be made.

Trace element contents are different in the deposits studied. Se occurs in samples from Banska Štiavnica, but is particularly high in those from Montecatini Val di Cecina (15 vs. 20 analyses gave values over the m.d.l.). Ag occurs in Banska Štiavnica and Massa Marittima; its content is higher in Bottino Mine samples (12 vs. 13 analyses over the m.d.l.). Zn is relatively high in all samples, with local concentrations in restricted areas giving values over 1800 ppm, probably due to inclusions (see below). Sn is only present in a few Banska Štiavnica samples with isolated high values. Pb occurs in most of the samples, but only few data are clearly over the m.d.l.

TABLE 1

PIXE analyses of standard NIST 610; values in p.p.m. (wt). Nominal composition of support matrix is 72% SiO₂, 12 % CaO, 14 % Na₂O, 2 % Al₂O₃

Elements	Min	Max	Median value	Error %	Certified NIST values	N° of analyses
Zn	396	440	406	10	433	10
Ag	243	279	251	9	254	10
Pb	401	452	419	7	426	10

TABLE 2

Summary of analytical data on Zn, Se, Ag, Sn and Pb contents of selected chalcopyrite samples. First column: provenance; subsequent columns: minimum, maximum and median values in p.p.m. (wt), percent error in brackets; last two columns: number of data over MDL vs total number of analyses and MDL values in p.p.m. (wt).

Provenance	Element	Min	Max	Median value	N° of data over M.D.L. / total N° of analyses	M.D.L.
Banska Štiavnica	Zn	1040 (13)	2210 (10)	1720 (11)	6 / 29	150
	Se	30 (40)	300 (10)	120 (15)	5 / 29	20
	Ag	70 (40)	630 (8)	170 (18)	15 / 29	45
	Sn	140 (45)	3260 (6)	560 (13)	5 / 29	75
	Pb	120 (25)	630 (8)	-	2 / 29	90
Montecatini Val di Cecina	Zn	310 (32)	4560 (6)	1030 (13)	14 / 20	150
	Se	50 (18)	930 (6)	300 (10)	15 / 20	20
	Ag	90 (33)	110 (30)	-	2 / 20	45
	Sn	-	-	-	0	75
	Pb	-	590 (9)	-	1 / 20	90
Massa Marittima	Zn	310 (32)	1810 (11)	920 (14)	20 / 22	150
	Se	37 (45)	174 (13)	54 (40)	5 / 22	20
	Ag	64 (45)	240 (16)	120 (28)	6 / 22	45
	Sn	-	-	-	0	75
	Pb	130 (24)	240 (20)	-	2 / 22	90
Bottino Mine	Zn	280 (33)	21800 (0.2)	1280 (12)	13 / 13	150
	Se	130 (15)	310 (7)	-	2 / 13	20
	Ag	150 (20)	1940 (6)	370 (11)	12 / 13	45
	Sn	-	-	-	0	75
	Pb	-	240 (20)	-	1 / 13	90

The dispersion of values for Ag, Se and Zn is shown, as histograms, in figg. 1 and 2.

Distribution maps

Micro-PIXE distribution maps of major elements were obtained in one or two minutes

choosing a 4-mm² scanning area and operating at low current levels (0.1 nA). These maps revealed compositionally homogeneous chalcopyrite grains suitable for further analyses. Although small areas down to 25 µm² could be selected, we investigated areas of about 2500 µm². The absence of macroscopic inclusions of other sulfides was checked in a

few minutes even on these small areas by examining the major element maps. Quantitative analyses of trace elements were then carried out on inclusion-free areas. During data acquisition, trace element distributions in these areas was also recorded. The resulting maps indicate different modes of

occurrence for some elements (see examples in figs. 3–5).

Distribution maps of Zn and Ag in sample G15362 (Bottino Mine) are shown in fig. 3. Zn(3a) is concentrated over a 100- μm^2 -wide area, indicating a small sphalerite inclusion, whereas Ag(3b) is homogeneously distributed,

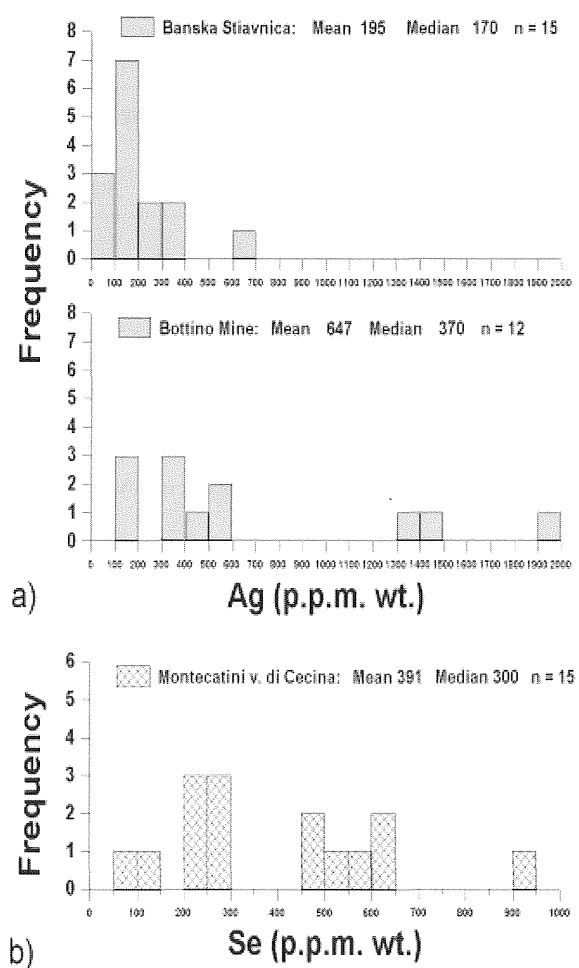


Fig. 1 – Histograms of Ag contents of chalcopyrite samples from Bottino Mine and Banská Štiavnica (a) and Se contents of samples from Montecatini Val di Cecina (b) (only data over MDL are plotted).

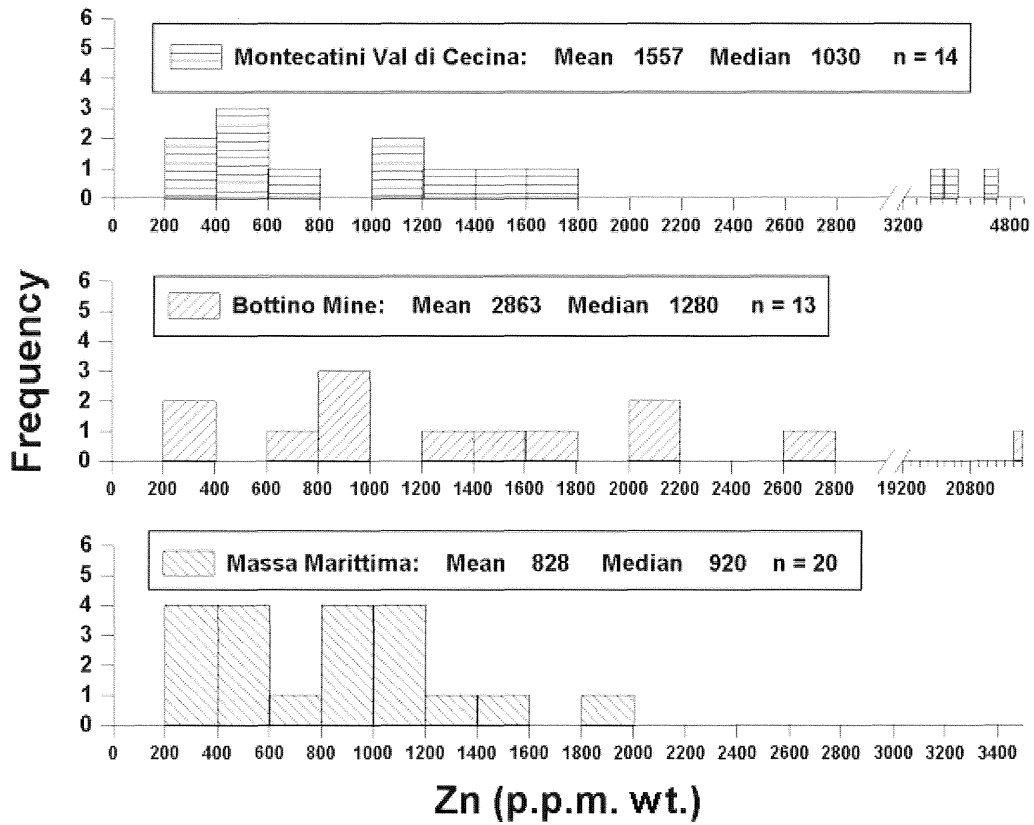


Fig. 2 – Histograms of Zn contents of chalcopyrite samples from Montecatini Val di Cecina, Bottino Mine and Massa Marittima (only data over MDL are plotted).

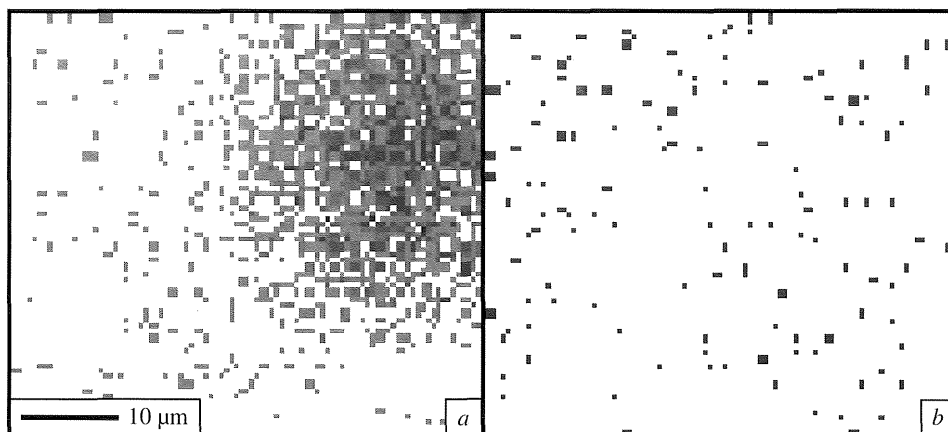


Fig. 3 – Maps of element distributions in sample G15362 (Bottino Mine); a) Zn distribution; b) Ag distribution.

as a result of Cu replacement. The presence of argentite (Ag_2S) inclusions near the surface of the micro-PIXE scanning area was excluded by means of SEM-BSE maps.

Fig. 4 shows maps of a Montecatini sample (G15403): Zn(4a) occurs mostly over a small area, and is on the whole less homogeneously distributed than Se(4b). This element clearly

replaces S, whereas Zn distribution is mostly due to a sphalerite inclusion and, to a lesser extent, to Cu replacement. The presence of selenides in sample G15403 was excluded by means of SEM maps.

The maps of fig. 5 show that Zn (5a) and, to a lesser extent, Sn (5b) are homogeneously distributed in sample G1091 (Banska Stiavnica).

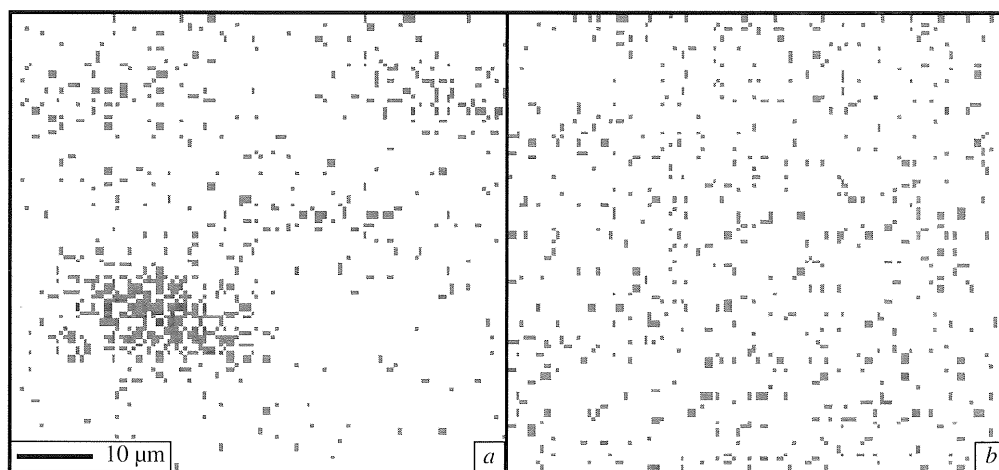


Fig. 4 – Maps of element distributions in sample G15403 (Montecatini Val di Cecina): a) Zn distribution; b) Se distribution.

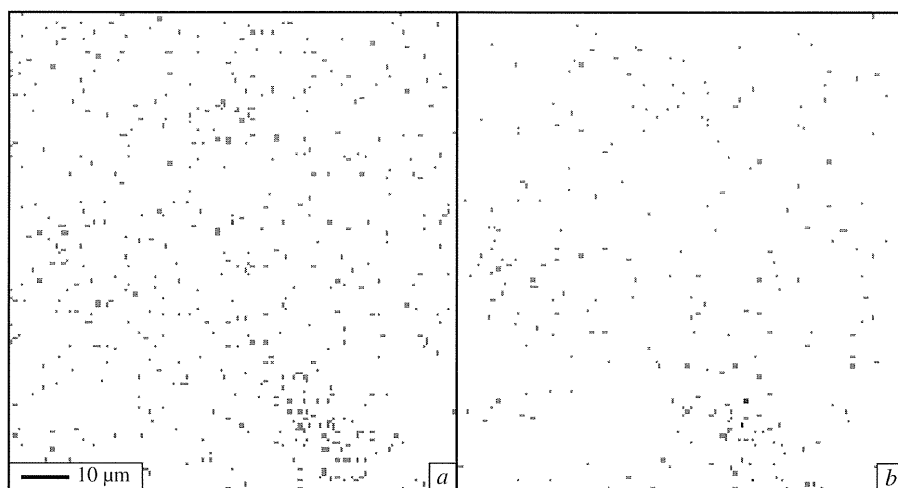


Fig. 5 – Maps of element distributions in sample G1091 (Banska Štiavnica): a) Zn distribution; b) Sn distribution.

TABLE 3

Trace element contents of chalcopyrite samples shown in Figs. 1-3; values in p.p.m. (wt), percent error in brackets.

Sample number	Elements			
	Zn	Se	Sn	Ag
G15362 (Bottino Mine)	21800 (0.2)	<20	<80	1310 (8)
G15403 (Montecatini V.C.)	1760 (11)	510 (8)	<80	<50
G1091 (Banska Štiavnica)	1990 (10)	130 (15)	560 (13)	140 (26)

In some areas of this sample, Zn and Sn distributions overlap, suggesting the presence of very small kesterite inclusions. No evident sphalerite or kesterite inclusions near the surface were noticed in these samples during the SEM map check, probably because element contents were too low to be detected by SEM (BSE or X-ray) images, even with long counting times. Analytical data for these samples (table 3) confirm this hypothesis.

CONCLUSIONS

The results of the present study suggest the importance of the proton microprobe to solve problems related to the mode of occurrence of trace elements in sulfide structures.

As regards crystal-chemical behaviour, the tendency shown by Se and Ag to substitute for S and Cu, respectively (Huston *et al.*, 1995) is confirmed, and the hypothesis of concentration-dependent behaviour for Zn (i.e. as substituting for or as inclusion-forming element) is suggested.

These results are quite interesting, also from a mineralogical point of view, because they confirm the importance of chalcopyrite as Ag carrier, as already reported by Cabri *et al.* (1984, 1985). Moreover, they confirm the

existence of Ag enrichment, also in samples from two exhausted silver mines like Bottino and Banska Štiavnica, as already found for chalcopyrite samples from other Canadian silver deposits (Harris *et al.*, 1984).

Data on Se enrichment of chalcopyrites from the Montecatini Val di Cecina ore deposit (associated with ophiolite formations) are in good agreement with those obtained on samples from present-day «black smokers» deposits on the ocean floor (Auclair *et al.*, 1987). Lastly, our results confirm Brill's (1989) hypothesis regarding the control exerted by environmental conditions on the S/Se ratio of chalcopyrite.

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