



## Minor and trace element content of sulphides from the Madan polymetallic deposits, Central Rhodopes: a LA-ICP-MS study

### Елементи-примеси и елементи-следи в сулфидите от Маданските полиметални находища, Централни Родопи: LA-ICP-MS изследване

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### Introduction

Trace elements in sulphide minerals from the Madan ore district have been a subject of numerous studies with different methods. Data on minor and trace element contents were summarized recently by Bonev (2007) and are indicative for ore-forming processes in the area. However, the number of the analysed elements was restricted and the precision of the analyses was low. Nowadays, there is an extreme need for accurate knowledge of the quantity of minor elements in the sulphides, not only from mineralogical point of view, but in order of estimating their significance and influence onto the host environment during weathering processes in the active mining sites (Abraitis et al., 2004). LA-ICP-MS is a fast and efficient method for analyses of very low contents of a large number of elements. Here, we report the first data on the trace element composition of the sulphides from the largest ore district in the Rhodope Massif, Madan ore field, using the newly installed LA-ICP-MS analytical system in the Geological Institute, BAS. Studied are pyrite, sphalerite, chalcopyrite and tetrahedrite to accurately quantify Ag, As, Bi, Cd, Co, Cu, Fe, Ga, Ge, In, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, Cr, Zn, Y, Zr, Pd, Te, Ce, Ta, W, Re, Pt, Au and Hg contents. Our goal is to precisely analyse minor and trace element contents and questions we address include also the ranges of solid solution in natural samples, as well as the possible crystallochemical controls on sulphide mineralogy.

### Analytical methods and sampling

LA-ICP-MS analytical system consists of a 193 nm ArF excimer laser coupled with an ELAN DRC-e ICP quadrupole mass spectrometer. For controlled ablation, an energy density of above 10 J/cm<sup>2</sup> on the sample and a laser pulse frequency of 10 Hz were used. Analyses were performed with 50 or 75 μm beam di-

ameters. External standardization on NIST glass standard SRM-610 provides relative element concentrations, which were transformed into true values by internal standardization (a known element concentration determined by EPMA). The investigation of crystal chemistry of sulphides by EPMA and bulk ICP-AES analyses were carried out in parallel and were used for the interpretation of the obtained LA-ICP-MS data.

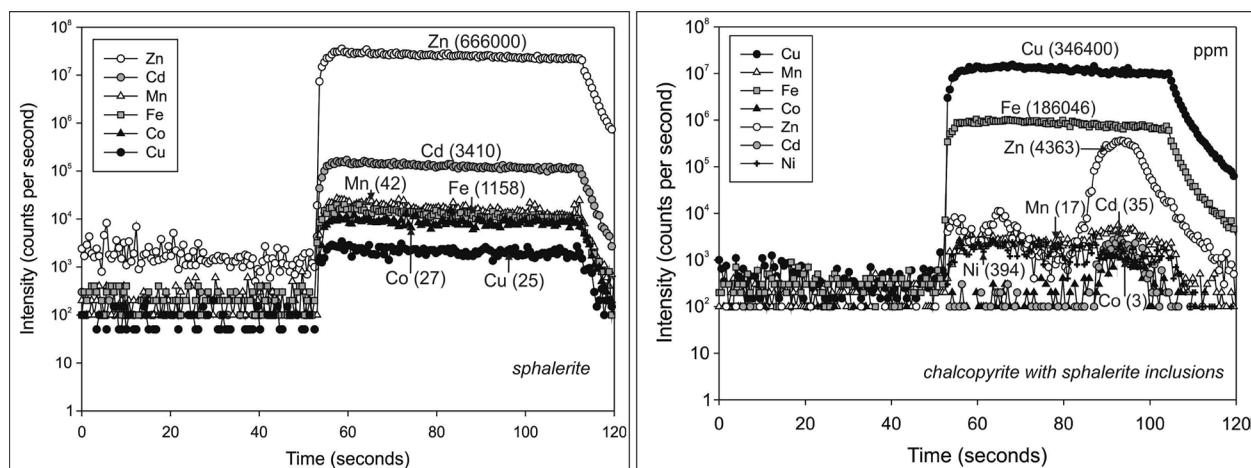
The analysed sulphide samples have been taken from vein and metasomatic ore bodies of the Ossikovo, Mogilata, Kroushev Dol, Petrovitsa, Gradishte, Gjudjurska, Erma Reka, Shoumachevski Dol and Murzian deposits. All sulphide minerals have been carefully characterized in previous studies.

### Results

Concentrations of trace elements in most sulphides vary over several orders of magnitude between different Madan deposits, also between the morphogenetic types of ore bodies and, in some cases, between single samples from a given deposit. Here we comment only few representative cases.

Environmentally significant metals such as Cd, Hg, and Mn do not commonly form their own sulphide minerals, and instead, occur as solid solution preferably in sphalerite (Fig. 1a). Manganese in sphalerite reaches up to a few hundreds ppm. Similar, though lower Mn concentrations are also typical for other sulphides. Sphalerite from most of the deposits incorporates significant amount of Fe and Co as well. Minor and trace element substitution is largely governed by the similarity of the size of a relatively large number of other ions to that of tetrahedrally-coordinated Zn<sup>2+</sup> (Cook et al., 2009).

Pyrite in the studied samples generally accommodates As in wide range from traces to several wt.% (averages 800 ppm). The vein pyrite contains more As, compared to the pyrite from the replacement ore



**Fig. 1.** Representative single spot LA-ICP-MS ablation spectra of selected elements

bodies. The highest As content has been established in pyrite with porous texture from Erma Reka, reaching 10 wt.%. Relatively high concentration of Co from the deposits of Kroushev Dol and Petrovitsa are found, reaching > 1500 ppm with mean values ~ 200 ppm. Some late pyrites show an intensive incorporation of Ge (averages 300 ppm) and Tl (up to 1700 ppm), correlated with the As content and zonal distribution. Cadmium is always corresponding to increased Zn, indicating presence of small sphalerite grains in pyrite.

The chalcopyrite reveals As concentration (up to 1300 ppm in Gradishte), Ni (in the range of 350–450 ppm, Ge (~ 60 ppm). The enhanced Zn and Cd contents found in chalcopyrite are due to sphalerite micro-inclusions within the host crystals (Fig. 1b). On the other hand,  $\text{Cu}^{2+}$  in sphalerite is not considered to be readily incorporated into the structure in significant quantities. Instead, the so-called “chalcopyrite disease” texture appears along crystallographic directions or twin boundaries of some samples (Cook et al., 2009).

## Discussion

Two possible types of incorporation of minor and trace elements in the studied sulphides are observed: (1) homogeneously distribution along the analyzed volume reflected in smooth ablation profiles for most of

the elements, (2) inhomogeneous distribution, due to zonation or solid inclusions. Despite instrumental considerations and the analytical accuracy (Heinrich et al., 2003; Pettke, 2008), which are beyond the scope of this study, several sources for potential uncertainties can be summarized: (i) controlled ablation of sulphides is only achieved at low laser power densities, as suggested by Woodhead et al., 2009, and that under these conditions standardization using silicate reference materials is inappropriate; (ii) crystal-structural control on minor and trace element incorporation (e.g., twinning, defects, fluid inclusions) in addition to the low melting point of sulphides and the potential presence of solid inclusions (Cook et al., 2009); (iii) the ablation volume is far more bigger than the EPMA analyzed spots, increasing the possibility of inhomogeneity of the natural samples, such as oscillatory zonation and rhythmic banding due to incorporation of minor components in sulphides, as it has been widely reported and interpreted in the literature (e.g., Fowler, L’Heureux, 1996; Baudoin, 2000; Cook et al., 2009).

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