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Occurrences and processes of precious metal enrichment in sulphides assessed by combining LA-ICP-MS, HR-TEM and Fe isotope LA-MC-ICP-MS analyses

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Hydrothermal ore deposits often contain economically interesting elevated concentrations of precious metals (gold and silver), frequently hosted in common sulphides like pyrite and arsenopyrite. For the prosperity of precious metal extraction, it is necessary to define type of element accommodation and their genetic relationships. Precious metals can be either structurally bonded by major element substitution [1] or more often occur as micro- to nanoscale particulates embedded in sulphide. Only in exceptional cases, native metal nuggets can be optically observed by common microscopic screening and analysed by Electron Microprobe (EMPA). High-Resolution Transmission Electron Microscopy (HR-TEM) can reveal both an atomic substitution in the crystal structure and the nanoscale exsolutions. However, sample preparation is destructive, time-consuming and spatially limited. To overcome these shortcomings, precious metal accommodation was initially screened by LA-ICP-MS and only then analysed by HR-TEM. Genetic relationships were obtained by Fe isotope compositions in pyrite using in situ LA-MC-ICP-MS.

Compared to EMPA, LA-ICP-MS technique has the advantage of much lower detection limits (< ppm level) and a high-throughput: a large number of minerals can be screened in a relatively short time. Additionally, careful study of the ablation patterns can indicate the precious metal nuggets even below the grain surface, thus enabling three-dimensional screening of mineral grains. In Au-bearing arsenopyrite from Međurečje, Serbia, the micro-region with elevated gold was first determined by LA-ICP-MS and then further analysed by HR-TEM. Different morphology of nanosized gold in arsenopyrite and its product, oxidation scorodite, was distinguished with the latter.

In-situ Fe isotope composition of precious metal carrying pyrites and arsenopyrites can gain further information about mineral deposition conditions. In pyrite from the Čoka Marin (Cu-Au-Ag-Zn-Pb) deposit, Serbia, elevated precious metal contents were determined by EMPA/LA-ICP-MS. HR-TEM revealed that only Cu is structurally bound in pyrite, while Ag and other impurities (Pb, As) formed as nanoscale particles of sulphosalts in certain pyrite zones [2]. Further on, spongy pyrite texture and strong negative δ^{56}Fe indicate rapid pyrite precipitation at the late stage together with the precious metals.

[1] Cabri, et al. (2000), *Canadian Mineralogist* 38, 1265-1281.

[2] Pačevski, et al. (2012): *Canadian Mineralogist*, 50, 1-20.