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### ***In-situ* trace elements by LA-ICP-MS in metamorphosed pyrites as pathfinder for hydrothermal conditions**

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Hydrothermal sulfides record the fluid composition from which they precipitated. Hence sulfide trace element signatures may be used to decipher the physico-geochemical conditions during hydrothermal events. In metamorphic terrains, the presence of trace elements in sulfide minerals may have important scientific and economic significances as they can be used to characterise the genetic type of ore deposits. However, sulfide recrystallisation during metamorphic events is a main concern when assessing the validity of primary trace element signatures, because micro-inclusions are commonly expelled. However, it is probable that trace elements occurring mainly as stoichiometric (Co, Ni and Se in pyrite), and non-stoichiometric substitutions, are unlikely to be affected by metamorphic recrystallisation. Numerous trace elements in pyrites from base and precious metal deposits hosted in the Abitibi belt, Canada, have been determined by laser ablation ICP-MS using a New Wave Nd:YAG 213 nm laser connected to a Thermo Elemental X-7 ICP-MS. Samples were ablated in a helium atmosphere using a 100 µm laser spot with laser firing frequency of 5 Hz and beam energy of 0.5 mJ. Data were collected for 60 s and monitored in the time resolved window and processed on-line using the X7 software. The PS-1 standard [1] was used as a reference material along with a custom sulfide precipitate doped with REE and trace elements. Internal standardization used <sup>33</sup>S. The time-resolved signals showed REE came from micro-inclusions of REE-bearing minerals. Elements, such as Au, Ag, Ga, Mn, Pb and Sn, had similar signal variations, also suggesting micro-inclusions. When present, Se, Ni, and Co show uniform signals, indicative of an expected homogeneous distribution within the pyrite lattice. Chalcophile metals: As, Sb, Hg, Bi, Te, which are not direct replacements for Fe or S, show surprisingly uniform ablation signals indicative of non-stoichiometric or complex stoichiometric substitutions. Ratios of elements: Se, Ni, Co, As, Sb, Hg, Bi, Te are typically comparable, within an order of magnitude, for pyrites in the same sample and characteristic of ore deposit types. Consequently, these elements are considered to be representative of primary hydrothermal signatures rather than overprinted metamorphic metal redistribution. Our ongoing study will address their metallogenic significance.

#### **Reference**

[1] Wilson et al. (2002) *JAAS* 17, 406-409.

## 3.6.65

### **Origin of the PAH – Hg association at Idrija deposit (Slovenia)**

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The fossil hydrothermal system of the Idrija world-class Hg deposit was an important natural source of pyrolytic polycyclic aromatic hydrocarbons (PAH). Hot mercuriferous fluids (~ 200°C) flushing through Upper Paleozoic to Upper Ladinian lithologies (TOC<sub>max</sub> = 1.7 wt%) precipitated Hg ore associated with highly aromatic hydrothermal petroleum. In the frame of an extensive regional inorganic and organic geochemical investigation [1, 2, 3], a combined molecular – stable isotopic approach was used to study the source and transformation of the PAH.

The concentrations of up to 7 ring PAH (e.g. phenanthrene, pyrene, chrysene, benzofluoranthene, coronene), sulfur containing heterocyclic compounds (S-PAH; e.g. dibenzothiophene, benzonapthothiophene, triphenylenothiophene) and their alkylated homologues in the ore extracts increase with the degree of mineralization (0.1-19.0 wt% Hg). Regionally, only the organic-rich Paleozoic lithologies contain small concentrations of low molecular weight aromatic hydrocarbons (e.g. biphenyls, naphthalenes). Partially reduced PAH in mineralized samples (e.g. 9,10-dihydrophenanthrene) point to hydrogen exchange between PAH and the hydrothermal fluid. The δ<sup>13</sup>C values of individual PAH and S-PAH (-28.6 to -20.9‰) increase with molecular weight and stratigraphically upwards, indicating progressive thermal and oxidative degradation with increasing residence time of the organic phase along the pathway of the hydrothermal fluid.

The molecular and isotopic data point to the following processes for the formation of PAH: i) bond cleavage in kerogen and free hydrocarbons produced free radicals and PAH precursors (e.g benzenes, biphenyls), ii) cyclization, annelation of benzene rings, and aromatization formed higher molecular weight PAH. These processes were catalyzed by sulfur, which is reflected by high S-PAH concentrations in the Hg ore.

#### **References**

- [1] Lavric J.V. and Spangenberg J.E. (2002) *GCA* 66/S1, A435.
- [2] Lavric J.V. and Spangenberg J.E. (2003) *Miner Deposita* 38, 886-899.
- [3] Lavric J.V., Spangenberg J.E., and Rezun B. (2003) *Geologija* 46/1, 129-134.