Tin substitution in chalcopyrite and sphalerite from hydrothermal sulfides

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Unusual tin concentrations (500-2000ppm) were measured in sulfides from the Logatchev hydrothermal field. This hydrothermal site is located on the Mid-Atlantic Ridge, at a depth of 3000 m in an ultramafic environment. The fluid temperature was measured between 300 and 350°C at the exit of the chimneys.

Tin is usually not present in marine sulfides, but detailed microprobe and SEM analyses and element mapping showed a specific distribution for this metal. High tin concentration, are mostly in sphalerite (3 to 5%wt) and chalcopyrite (1 to 2%wt) from the hot part of the chimneys. The highest concentrations, up to 6%wt, are located at the replacement front of chalcopyrite and sphalerite.

Raman spectroscopy studies exclude the presence of tin minerals, like stannite, kesterite or cassiterite, and prove that tin is substituted in the lattice of sphalerite or of chalcopyrite.

The variation of the fluid composition, the temperature and the pressure induces the evolution of the chimney and changes in its mineral composition. These changes, linked to substitution, create different types of minerals with different valence, like $Cu^{+}Fe^{3+}S^{2-}_2$ and $Cu^{2+}Fe^{2+}S^{2-}_2$ for chalcopyrite.

Fe^{2+} is oxided in Fe^{3+} at high temperature in spite of the oxygen free environment[1] and enhance the tin substitution with the reaction: $2Fe^{3+} <-> Sn^{4+}Fe^{2+}$ [2].

[1] Di Benedetto (2005), *Phys Chem Minerals* **31**, 683-690.
[2] Kase (1987), *Canadian Mineralogist* **25**, 9-13.

Interesting finds in Norilsk copper-nickel sulfide ores

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Norilsk ores contain a unique set of ore minerals among which the minerals of platinum metals have a significant place. Nowadays more than 100 PGM are described in Noril'sk ores. Along with PGM the wide range of the rare minerals, considered unusual to deposits of similar type, is discovered in these ores. During detailed research using SEM+EDD some new data about PGM paragenesis, associated ore minerals, and unexpected mineral finds are obtained.

An investigation of massive copper rich sulfide ores with chalcopyrite group minerals (talnakhite, mooihoekite, putoranite) has shown, that fine-filiform band of cooper sulfides, $Cu_2S/Cu_{2-x}S$, are often observed along PGM and sulfide mineral boundaries. The thickness of these bands generally does not exceed 0.n microns (n~ 2-5). It could be the reason for some copper "surplus" in PGM composition.

Such observation could also explain the stoichiometry deviation observed on occasion in chalcopyrite group minerals. So, some sample compositions are enriched in Cu. It causes to "strange" formula with higher Cu apfu.

Beside sulfides (i.e. Ni_{ss}) among interesting minerals discovered recently in Cu-Ni-sulfide ores it possible to mention just a few: submicro- and nano-dimentional segregations of thorium , uranium and REE minerals - thorite, uranothorianite, Th-monacite, etc. The grain size of these minerals does not exceed a fraction of a micron. They are found in pyrrhotite ores, Oktyabrsky mine. It is neccesary to note that in Taïmyr peninsula there is an uranium manifestation, named Kamenskoje. Now it is difficult to understand if there is any association of this manifestation with Cu-Fe-Ni-PGE deposits of Noril'sk region. But the finding of Pd-minerals in natural reactor Oklo, in U-bearing black shales, and some other information about "coexisting" PGE and U (Th) in nature allow one to discusse some genetic problems.