

# HYDROTHERMAL SYNTHESIS OF PLATINUM SULFIDE AND ARSENIDE

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Recently, secondary enrichment some rocks in platinum attracts considerable attention; especially it concerns Pt behavior in complex, just as in the nature, hydrothermal systems. In this context we studied solubility of  $Pt_{met}$  in chloride solutions at 300-500°C and  $P_{tot} = 1$  kb. Inner surface of ampoules used as source of Pt for solubility measurements. The ampoules were charged with mineral mix (about 200 mg) and chloride solution (2-3 ml), in accord with P-V-T relation at P-T of interest. Initially, in the presence of starting pyrite-pyrrhotite-magnetite association, spontaneous formation of cooperite (Coop)  $PtS$  was observed. It forms black in color thin coating at inner surface of Pt ampoules [1]. Total platinum content of coexisting solution ( $Pt_{aq}$ ) was measured after its quenching and particularly preparation by ISP AES at analytical center of FEGI (tab.).

**Table.** Platinum content (lgmPt) in quenched 0,1mHCl solutions at  $P_{tot} = 1$  kb

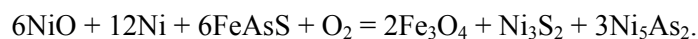
Starting association	300°C	400°C	Newly formed phases
Py-Po-Mgt	-5,81	-5,47	$PtS$
APy*-Py-Mgt- $As_{met}$	-6,28	-6,15	$PtAs_2$
APy-Ni-NiO- $As_{met}$	-6,78	-6,30	$Ni_3S_2$ , $Ni_{11}As_8$ , $Ni_5As_2$ , $Fe_3O_4$
Ni-NiO- $As_{met}$	-7,08	-7,49	$Ni_5As_2$

\* - arsenopyrite

In connection with usual presence of arsenopyrite and sperrylite (Sper) at some noble metal deposits arsenic was added to studied system. Association of arsenopyrite-pyrrhotite-magnetite-metallic. As controls arsenic activity, sulfur and oxygen fugacity, and pH of media at runs. At 300 and 400°C newly formed Sper was fixed. It forms grey in color thin coating on the ampoule walls. In this set of runs Coop does not observed. Identification of Sper was done by X-ray analyses and SEM. In spot, some arsenopyrite grains including up to 5 %wt Pt have been found among prismatic and tabular Sper grains (about 10  $\mu m$ ). This arsenopyrite differs by somewhat greater Fe/As ratio from starting one. In the case total Pt content in chilled solution becomes lower (tab.). It needs to be note that Sper contains impurities of Fe to 1.61 and sulfur to 2.14 %wt. Earlier, at study of the system Fe-Pt-Pd-As-S ingoing of 2.5% sulfur to Sper was fixed at 470-800°C [4]. Our results vindicate this data and conclusion that sulfur content of Sper does not depend on temperature.

The kinetic curves during Coop and Sper formation are characterized by the presence of extreme maxima [1]. Its peculiarities permit to explain Coop and Sper formation using theory of “activated complexes” and so called “intermediate state”. Complexity of system favors formation of intermediate metastable compounds including some ligands concurrently [5]. The compounds disproportionate with time, precipitating solid phases on the scheme:  $A + BC \rightarrow ABC \rightarrow AC + C\downarrow$ , where “C” signifies Coop or Sper. The kinetic maximum is due to decrease in a speed of metastable compounds formation and the increase of its decomposition. At rising temperature, intensity of process and outcome of Coop and Sper increase.

In the presence of Ni-NiO- $As_{met}$ -APy association, Coop or/and Sper does not appear. Newly formed  $Ni_3S_2$  (Heazlewoodite),  $Ni_5As_2$ ,  $Ni_{11}As_8$  (Maucherite), and metallic Ni coating of ampoule walls are fixed. The total Pt content of chilled solutions goes on decrease (tab). Transformations of solid phases may be presented as:



Minimal  $Pt_{aq}$  concentration in coexisting solutions is peculiar to the system without sulfur Pt-Ni- $As_{met}$ -Cl- $H_2O$  (tab). At that, along with Sper absent, nickel arsenide and Ni coating formation by the reaction  $4Ni + NiO + 2As = Ni_5As_2 + 0,5O_2$  were marked. The circumstances may be explain by the extremely low  $Pt_{aq}$  content of coexisting solutions most likely.

Thus, in complex hydrothermal systems, including As and Ni, solubility of Pt is extremely low. Hence, under the studied conditions at 300–500°C the role of Pt chloride species is negligible, and explains low  $Pt_{tot}$  concentration even in 0,1mHCl solution. Noteworthy, elevated  $Pt_{aq}$  content characterize the media coexisting with Py-Po-Mgt or APy-Po-Mgt mineral associations. Exactly, in the media newly Coop or Sper formation is fixed. Values of  $Pt_{aq}$  measured in the cases can be considered as threshold for these mineral formations at hydrothermal conditions. The runs confirmed remarkable entry of Pt to arsenopyrite.

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