

## Plyusnina L.P., Likhoidov G.G., and Scheka J. A. Solubility of Pt and PtS in aqueous sulfide-chloride media at 300-500°C and 1 kbar

Far East Geological Institute, Vladivostok, [lplyus@hotmail.com](mailto:lplyus@hotmail.com)

Over the past decade some experimental data on platinum solubility under hydrothermal conditions have been obtained [1-4]. The experimental results provide strong evidence on differences of Pt solubility in chloride and sulfide media that may affect the Pt mobility in natural conditions. However, by now the Pt-S-Cl-H<sub>2</sub>O system was experimentally studied up to 300°C only. The aim of our study is to characterize Pt solubility at 300-500°C ( $P_{\text{tot}} = 1$  kb) in the sulfide bearing system. In runs with water, 1mNaCl and 0.1mHCl the pyrite-pyrrhotite-magnetite (PPM) buffer was used as more typical sulfides within Pt-bearing natural assemblages.

Experiments were performed in externally heated autoclaves using a furnace with accuracy about  $\pm 5^\circ\text{C}$ . Pt capsules (9•80•0.2 mm) welded after charging served as the source of Pt solubility. The charge included starting solution along with 200-250 mg of powdered PPM. The runs duration defined by special kinetic runs varied from 3 weeks (at 300°C) to one (at 500°C). Run quenching with cold water finished in 3-5 minutes. Total Pt<sup>aq</sup> from the quenched prior adapted solutions was extracted in alkylamine and then analyzed by AAS with accuracy about 20%. X-ray was used to control the solid run products.

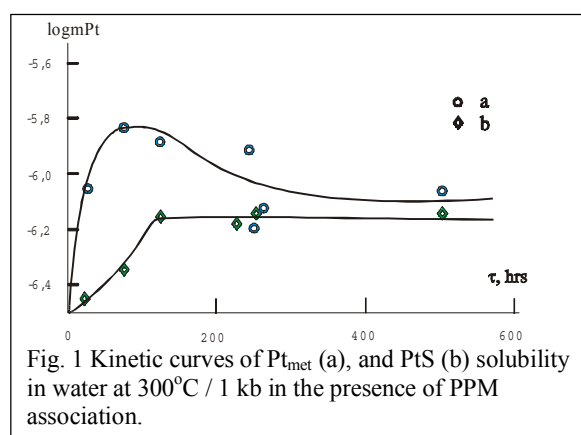


Fig. 1 Kinetic curves of Pt<sub>met</sub> (a), and PtS (b) solubility in water at 300°C / 1 kb in the presence of PPM association.

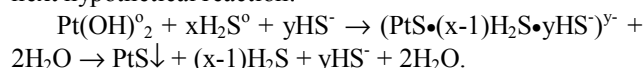
It turned out that inner walls of Pt ampoules were coated by a dark sulfide like a lampblack in the course of runs. Microprobe analysis of the coatings determined the following composition (wt.%): Pt - 85.2  $\pm$  0.5, S - 14.7  $\pm$  0.3, Fe  $\sim$  0.2 consistent with the stoichiometry of cooperite (Coop) - Pt<sub>0.95</sub>Fe<sub>0.01</sub>S<sub>1.05</sub>. It should be noted that increasing both temperature and chloride concentration accelerate Coop generation. As Pt forms the stable sulfide, PtS solubility was measured in the ampoules after its prior coating by Coop at 500°C. To measure Pt<sub>met</sub> solubility in the presence of PPM, new Pt ampoules (Coop free) were used. In this case runs were continued up to the first Coop generation, which was defined by special kinetic series. Kinetic curves of Pt and PtS dissolution are plotted on fig.1. Resulting compositions of pyrrhotite along with  $f_{\text{O}_2}$  and  $f_{\text{S}_2}$  values estimated using the published method [5]

are presented in tabl.1. The averaged ( $\Sigma\text{Pt}^{\text{aq}}$ ) data on Pt and PtS solubility are given in table 2.

Table 1. The final compositions of pyrrhotite

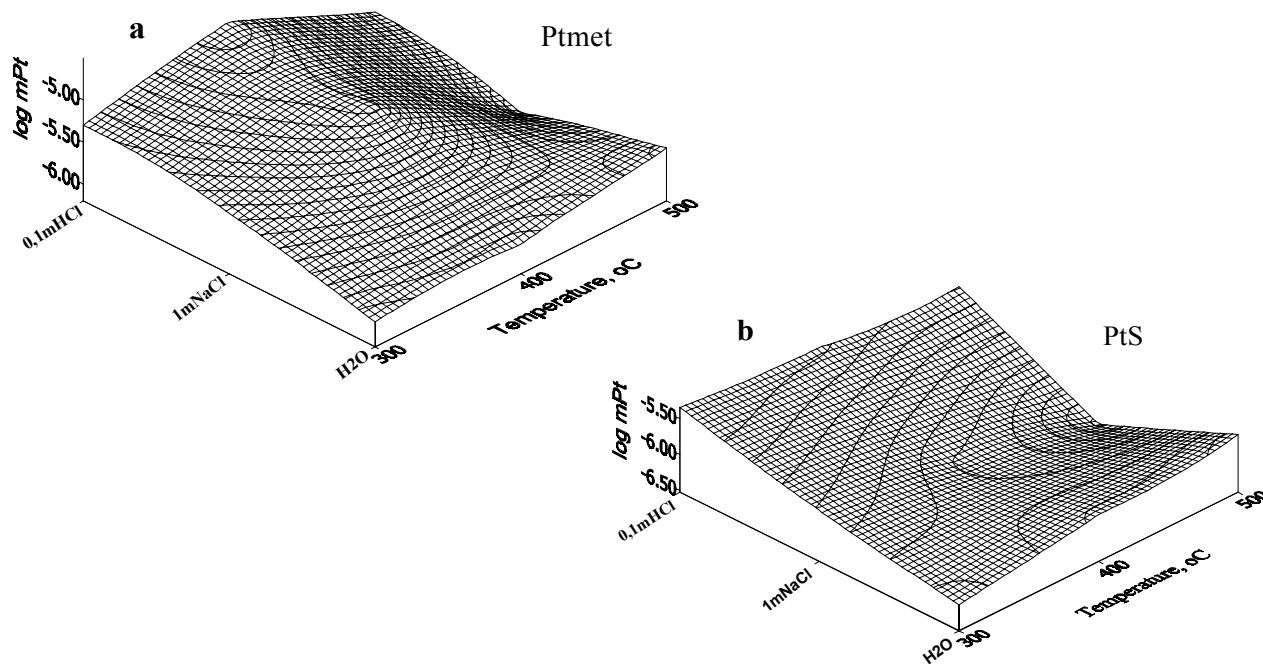
t, °C	d <sub>(102)</sub> , Å	m FeS	a FeS	log f <sub>S<sub>2</sub></sub>	log f <sub>O<sub>2</sub></sub>
300	2,065	0,94	0,53	-10,73	-32,16
400	2,060	0,94	0,50	-7,00	-26,01
500	2,056	0,93	0,48	-4,17	-20,63

The received data are summarized on the diagram (Fig.2a, b). One can see that  $\Sigma\text{Pt}^{\text{aq}}$  values are always higher at dissolution of Pt<sub>met</sub> than of PtS, however, the difference is confined by the limits of uncertainty. The proximity of  $\Sigma\text{Pt}^{\text{aq}}$  values at dissolution of both Pt<sub>met</sub> and PtS suggests similar character of their complexation under the studied conditions, although some distinctions were noted. So, at dissolution of Pt<sub>met</sub> in water, the  $\Sigma\text{Pt}^{\text{aq}}$  values grow with increasing T from 300 to 500°C, whereas in 1mNaCl or 0.1mHCl those slightly drop in the range 400-500°C (Fig. 2, a). The effect may be partly explained by a decrease in NaCl and HCl dissociation at 500°C [6]. In the runs with Coop, the values of  $\Sigma\text{Pt}^{\text{aq}}$  sequentially grow in water from 300 to 500°C, whereas in the chloride media  $\Sigma\text{Pt}^{\text{aq}}$  decrease starts from 300 and continued to 500°C (tab. 2). The reverse dependence of  $\Sigma\text{Pt}^{\text{aq}}$  on temperature is typical of hydrosulfide Pt species [2]. Thus, one can suppose that in the aqueous-chloride solutions buffered by PPM assemblage the hydrosulfide Pt species dominate, whereas at dissolution in water the hydroxide ones prevail. Noted maximum on the Pt<sub>met</sub> kinetic curve (fig.1), possibly, was caused by an initial generation of hydroxyl complexes of Pt. But in the course of PPM buffer dissolution and attainment to equilibrium of H<sub>2</sub>S<sup>0</sup> and HS<sup>-</sup> activity, the Pt hydroxides become metastable and are substituted by complex hydroxide-hydrosulfide species. The latter disproportionate with the PtS precipitation according to the next hypothetical reaction:



This step-by-step reaction mechanism explains the shape of kinetic curves of Pt and PtS solubility along with noted PtS precipitation (fig.1). The reported before formation of Coop at 85°C [7] may be a result of the similar process. This possibility is also confirmed by described precipitation of CuS at 200°C caused by similar evolution of mixed Cu complexes [8].

The reported enhanced Pt<sub>met</sub> solubility in comparison with Coop, and the disproportionation of mixed metastable Pt complexes are favorable for permanent Coop generation even from solutions under saturated with hydrosulfides and platinum. In nature similar sulfides may serve as geochemical barrier for PtS precipitation from suitable hydrothermal solutions. The mechanism of Coop crystallization in the course of Pt dissolution and stepwise evolution of mixed Pt complexes is proposed. It may cause Pt remobilization in a wide temperature range including: metamorphism [9], hydrothermal activity [10], supergenesis [11], laterization [12], and even rainwater inland drainage [13].



**Fig.2.** Total Pt<sup>aq</sup> concentration in studied media as the result of Pt<sub>met</sub> (a), or PtS (b) solubility in the presence of PPM association at 1 kbar.

**Table 2.** Total Pt concentration in quenched solutions at P<sub>tot</sub> = 1 kbar

t, °C	log mPt					
	Pt			PtS		
	300	400	500	300	400	500
H <sub>2</sub> O	-5,90±0,30 (6)	-5,85±0,17 (2)	-5,57±0,20 (2)	-6,16±0,25 (6)	-5,87±0,16 (2)	-5,72±0,30 (4)
1mNaCl	-5,48±0,27 (2)	-5,07±0,40 (3)	-6,02±0,30 (2)	-5,81±0,30 (2)	-6,12±0,40 (3)	-6,54±0,15 (3)
0,1mHCl	-5,30±0,40 (2)	-4,94±0,30 (2)	-5,69±0,30 (2)	-5,34±0,15 (3)	-5,47±0,30 (3)	-5,59±0,15 (3)

**NOTE:**

m – molality unit,  
in parentheses –  
number of runs

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