

# KINETICS OF GOLD AND PLATINUM SOLUBILITY IN THE ACT OF FORMING MN-COMPOUNDS

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In connection with a problem of genesis of Pt (Au)-bearing ferromanganese crusts the solubility of metallic Pt and Au in water and aqueous chloride solutions was studied experimentally at 200-400°C and 1 kb total pressure. To define the oxygen fugacity next starting mixtures were used: MnO-Mn<sub>3</sub>O<sub>4</sub> (Mn1), Mn<sub>3</sub>O<sub>4</sub>-Mn<sub>2</sub>O<sub>3</sub> (Mn2), and Mn<sub>2</sub>O<sub>3</sub>-MnO<sub>2</sub> (Mn3). The HM traditional buffer was used for comparison. Experiments were conducted in externally heated autoclaves produced of Ti and Ni alloys for temperatures less and more than 400°C, correspond-

ingly. Accuracy of T and P is equal to  $\pm 2.5^\circ\text{C}$  and  $\pm 50$  bar. As a source of Pt and Au dissolution, walls of welded Pt and Au ampoules were used. The charges include 3-5 gr of starting solution (water, 1mNaCl, or 0.1mHCl) along with 200-250 mg of buffer mix per run. Optical and X-ray diffraction analyses were used to control final buffer composition. The Pt and Au contents in quenched solutions were measured by AAS with an accuracy of  $\pm 20\%$ . Experimental results are shown in table 1.

Table 1

Platinum and gold content in quenched solutions

Solution	logmPt	$\tau$ , hrs	Buffer	logmAu	$\tau$ , hrs	Buffer
200°C						
H <sub>2</sub> O	-6.51	720	[Mn1]	-5.76	480	[Mn1]
H <sub>2</sub> O	-5.89	720	Mn3	-4.9	480	Mn3
1mNaCl	-5.68	720	[Mn1]*	-5.21	480	[Mn1]
1mNaCl	-5.01	720	Mn3	-4.47	480	Mn3
0.1HCl	-5.05	720	[Mn1]*	-4.84	480	[Mn1]
0.1HCl	-3.81	720	Mn3	-4.66	480	Mn3
300°C						
H <sub>2</sub> O	-3.86	168	[Mn1]*	-6.18	754	[Mn1]
H <sub>2</sub> O	-5.87	330	Mn2	-5.76	240	Mn2
H <sub>2</sub> O	-5.61	248	Mn3	-4.72	240	Mn3
H <sub>2</sub> O	-6.32	248	HM	-	-	-
1mNaCl	-5.55	330	[Mn1]*	-4.15	198	[Mn1]*
1mNaCl	-5.65	264	Mn2	-4.42	240	Mn2
1mNaCl	-4.15	264	Mn3	-3.3	198	Mn3
0.1mHCl	-3.85	168	[Mn1]*	-	-	-
0.1mHCl	-5.48	330	Mn2	-4.3	198	Mn2
400°C						
H <sub>2</sub> O	-5.88	188	Mn1	-6.19	238	Mn1
H <sub>2</sub> O	-5.72	188	Mn2	-5.35	238	Mn2
H <sub>2</sub> O	-4.79	168	Mn3	-4.67	240	Mn3
H <sub>2</sub> O	-5.82	168	HM	-	-	-
1mNaCl	-5.7	175	Mn1	-5.6	168	Mn1
1mNaCl	-4.95	198	Mn2	-4.81	238	Mn2
1mNaCl	-3.68	175	Mn3	-2.31	168	Mn3
1mNaCl	-5.73	175	HM	-	-	-
0.1mHCl	-5.46	175	Mn1	-4.82	144	Mn1
0.1mHCl	-5.66	175	Mn2	-4.35	238	Mn2
0.1mHCl	-2.87	166	Mn3	-	-	-
0.1mHCl	-5.39	166	HM	-	-	-

m - molality;  $\tau$  - run duration in hrs; \* - metal deposition in act of quenching;

The square parentheses mark changes of starting buffer compositions

X-ray analysis of final Mn1 phase composition has revealed that, at 200 and 300°C, MnO is oxidized to Mn<sub>3</sub>O<sub>4</sub> with spontaneous formation of new solid phases:  $\beta$ -MnOOH, Mn(OH)<sub>2</sub>, and Mn<sub>2</sub>(OH)<sub>3</sub>Cl. These intermediate hydroxides are metastable in vir-

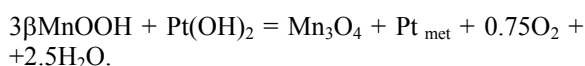
tue of their disappearance in a course of prolonged runs, which finish by crystallization of Mn<sub>3</sub>O<sub>4</sub> alone. The transformations in Pt or Au bearing systems are accompanied by increase in both Pt and Au content in coexisting solutions to about 1-2 orders of magni-

tude in term of molality. Some of the runs finished with precipitation of Pt metal globules during quenching. Such precipitation of Au was noted only in unit runs, whose final solid mixture contains about 50% of  $\text{Mn}(\text{OH})_2$ . Kinetic runs show that maxima of Pt and Au content in coexisting solutions coincide with maximal crystallization of bulk Mn-hydroxides. In the end, their spontaneous transition into  $\text{Mn}_3\text{O}_4$  is accompanied by an essential decrease in both Pt and Au content in quenched solutions. So, mentioned kinetic anomaly accompanied nonequilibrium processes in the systems.

Next sequence of Mn-mineral assemblages was fixed at 200°C in the 1mNaCl and 0.1mHCl solutions depending on runs duration:  $\text{MnO} \rightarrow \beta\text{MnOOH} + \text{Mn}_3\text{O}_4$  (9 days)  $\rightarrow \text{Mn}(\text{OH})_2 + \text{Mn}_3\text{O}_4 + \beta\text{MnOOH}$  (15 days)  $\rightarrow \text{Mn}_2(\text{OH})_3\text{Cl} + \beta\text{MnOOH} + \text{Mn}_3\text{O}_4$  (30 days)  $\rightarrow \text{Mn}_3\text{O}_4$  (60 days). As to the Au-bearing system, the sequence of phase transformation remains the same, but performs within more long period (fig).

With increasing T, a life expectancy of the metastable Mn-hydroxides has declined. At 300°C, the MnO converts to  $\text{Mn}_3\text{O}_4$  during 15-30 days in aqueous chloride solutions or in water, respectively. At 25°C, time for the oxidation is about 17 months [1].

Established catalysis effect of Pt on Mn(II) oxidation may be described using step-by-step reactions:  
 $\text{MnO} + \text{Pt}(\text{OH})_2^0 = \beta\text{MnOOH} + \text{Pt}_{\text{met}} + 0.5\text{H}_2\text{O} + 0.25\text{O}_2$ ,



Liberation of oxygen in course of the interaction is favorable for Mn(II) oxidation.

At 400°C, MnO is stable and the Mn1 buffer mix preserves initial phase composition forever. On the kinetic curves of the Pt and Au dissolution, any maxima are absent. Kinetic curves representing runs with the HM and Mn1 buffers, causing the same oxygen fugacity, are essentially coincided. Thus, it suggests the same mode of approachment to equilibrium.

The Mn2 and Mn3 buffers are stable at any of studied temperature. Under the stable existence of Mn-bearing oxygen buffers, the above-mentioned kinetic effect of noble metal solubility was not examined. The metastable crystallization of Mn-hydroxides is well-known in ocean floor media [2]. Thus, the kinetic effects may be used for modeling the noble metals accumulation in oceanic Mn-bearing nodules and crusts.

1. Hem J.D., Lind C.J. (1983) // *Geochim. Cosmochim. Acta*. V.47. P.2037-2046.
2. Novikov G. V.(1996) // *Proc. Russian Mineral. Soc. Pt.CXXV*: No 3. P.38-49 (in Russian).

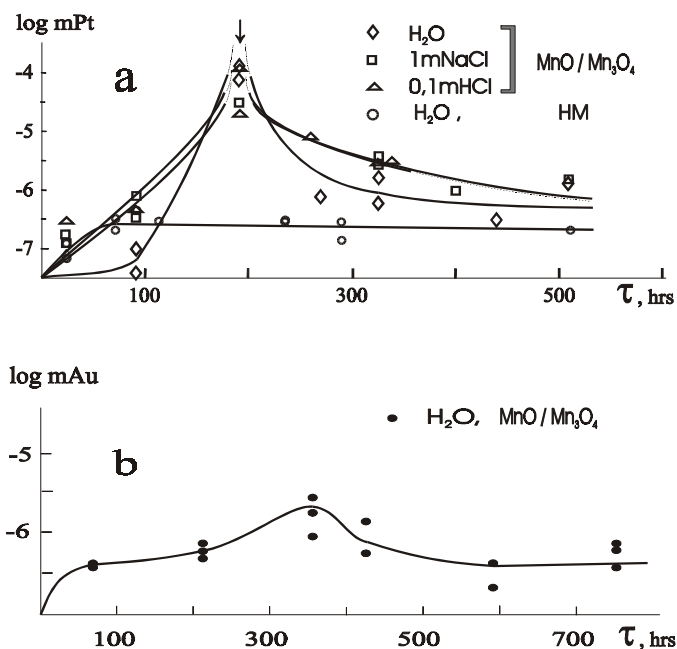


Fig. The kinetic curves of Platinum (a) and Gold (b) dissolution in different media at 300°C, and 1 kb total pressure. Arrow notes metal precipitation in the act of quenching