

Korzhinskaya V.S., Zaraisky G.P. The hübnerite (MnWO₄) solubility in fluoride solutions at T = 500°C and P = 1000 bars.

Institute of Experimental Mineralogy RAS, Chernogolovka

A solubility of ore minerals in the hydrothermal fluid is an important characteristics of geochemical behavior of elements, i.e. conditions of their mobilization, transportation, and precipitation. Firstly, a solubility of a mineral determines an upper limit of saturation of ore elements in natural processes and allows estimation of the ways of their transportation at given conditions.

For tungsten-bearing ores, the data on solubility of common minerals, i.e. scheelite, ferberite, and hübnerite, are most important.

We studied a solubility of synthetic hübnerite (MnWO₄) in HF solutions (1.26-0.011 m) at T = 500°C, P = 1000 bars, and oxygen fugacity at Ni-NiO and Fe₃O₄-Fe₂O₃ buffers. The double-ampoule procedure with an

internal oxygen buffer [1] is applied. Hübnerite was synthesized hydrothermally at T = 600°C and P = 1000 bars and run duration 7-8 days. A manganese powder and WO₃ of analytical purity were used as starting compounds. A 30 %-solution of LiCl was used as a solvent.

All experiments were performed on the hydrothermal apparatus with large reaction volume and an equipment for an initiation of reactions during the experiment, which provided an accuracy ± 2.5°C and ± 10 bars with a precise control of chemical parameters [2]. The run duration was 15 days.

A mechanism of solubility and an amount of the dissolved substance were determined by the analysis of a quenched solution. Solid products were studied by x-ray and microprobe. Besides hübnerite, no additional phases were found. Solutions were analyzed with the "Specol-11" spectrometer. The Mn content was measured by KJO₃, the W content, BPR [3]. It was found that Mn concentration after the experiments was consistent with the W concentration. That means that a congruent solubility of hübnerite occurs at given oxidizing-reducing conditions.

Table 1. Conditions and results of the experiments on the hübnerite solubility (MnWO₄) in the system HF-H₂O (T=500°C, P=1 kbar).

Initial conditions			Final results			
N	Buffer	m _{HF}	mΣMn		mΣW	
			mol/kg H ₂ O	-logmMn	mol/kg H ₂ O	-logmW
1	Ni-NiO	1.26	5.82 10 ⁻⁴	3.24	5.70 10 ⁻⁴	3.24
2	Ni-NiO	1.26	9.63 10 ⁻⁴	3.02	1.16 10 ⁻³	2.94
3	Ni NiO	1	1.66 10 ⁻³	2.78	1.48 10 ⁻³	2.83
4	Ni-NiO	1	1.20 10 ⁻⁴	3.92	6.31 10 ⁻⁴	3.20
5	Ni-NiO	0.11	3.43 10 ⁻⁴	3.47	3.84 10 ⁻⁴	3.42
6	Ni-NiO	0.11	3.47 10 ⁻⁴	3.46	3.16 10 ⁻⁴	3.50
7	Ni-NiO	0.11	2.18 10 ⁻⁴	3.66	2.39 10 ⁻⁴	3.62
8	Ni-NiO	0.011	5.13 10 ⁻⁵	4.29	8.13 10 ⁻⁵	4.09
9	Ni-NiO	0.011	6.31 10 ⁻⁵	4.20	7.08 10 ⁻⁵	4.15
10	Ni-NiO	0.011	7.96 10 ⁻⁵	4.10	1.03 10 ⁻⁴	3.99
11	Fe ₃ O ₄ -Fe ₂ O ₃	1.26	3.39 10 ⁻³	2.47	1.16 10 ⁻³	2.93
12	Fe ₃ O ₄ -Fe ₂ O ₃	1.26	1.15 10 ⁻³	2.94	1.38 10 ⁻³	2.86
13	Fe ₃ O ₄ -Fe ₂ O ₃	1	1.82 10 ⁻³	2.74	1.04 10 ⁻³	2.98
14	Fe ₃ O ₄ -Fe ₂ O ₃	1	1.26 10 ⁻³	2.90	1.17 10 ⁻³	2.93
15	Fe ₃ O ₄ -Fe ₂ O ₃	0.11	1.41 10 ⁻⁴	3.85	1.15 10 ⁻⁴	3.94
16	Fe ₃ O ₄ -Fe ₂ O ₃	0.11	1.74 10 ⁻⁴	3.76	1.10 10 ⁻⁴	3.96
17	Fe ₃ O ₄ -Fe ₂ O ₃	0.011	8.10 10 ⁻⁵	4.10	4.72 10 ⁻⁵	4.32

The mineral solubility increases with an increase of an initial HF concentration. Table 1 shows conditions of the experiments and results of analysis of solutions after experiments. Figure 1 shows a logarithmic dependence of a total tungsten concentration in the solution on the initial HF concentration for two buffers. Within the buffers Ni-NiO ($f_{O_2} = -22.28$) and Fe₃O₄-Fe₂O₃ ($f_{O_2} = -18.97$) in more reducing conditions, the hübnerite solubility is by 0.3-0.5 log units higher in the region of diluted solutions and is in average -3.50 logmW (for mHF = 0.011); -4.07 logmW (for mHF = 0.11). For the hematite-magnetite buffer, these values are following: -3.95 logmW (for mHF = 0.011); -4.32 logmW (for mHF = 0.11). Figure 1 shows also the calculated data on the hübnerite solubility at T = 500°C, P = 1000 bars for the Ni-NiO buffer (using the HCh program [4] and the UNITERM database) with addition of H₃WO₄ [5], HWO₃F, WO₃F, and MnF⁺ [6] species.

We have calculated a fluid composition corresponding to the experimental conditions. The following species play a major role in the hübnerite solubility in HF (0.011-1.26 m): H₃WO₄⁰, HWO₃F, WO₃F⁻, Mn⁺², MnOH⁺, HF⁰, F⁻, HF⁻. Mass fraction of other species does not exceed 1 %. Figures 2 and 3 illustrate the calculated data on distribution of predominant tungsten and manganese species in dependence on pH of the equilibrium solution.

For the buffer Ni-NiO, pH of the solution varies with an increase of HF from 5.4 (0.011 mHF) to 3.16 (1.26 mHF). The predominant tungsten specie in slightly acid solutions is H₃WO₄⁰ (89 %), while manganese specie is MnOH⁺ (up to 95 %). At mHF=0.11 a fraction of HWO₃F abruptly increases (up to 50 %), and its portion is 93 % in acid solutions. For manganese species, this transformation is more gradual, but the tendency is similar.

For the buffer Fe₃O₄-Fe₂O₃, pH of the solution varies from 5.5 to 3.3. In the slightly acid solution, a portions of H₃WO₄ and HWO₃F are similar (approximately 50 % each),

while MnOH^+ takes 95 %. As acidity grows ($\text{pH}=3.30$), HWO_3F becomes the major tungsten species, while manganese species is Mn^{+2} (up to 94 %).

The experiments showed that solubility of tungsten minerals in fluorine-bearing solutions was high enough and

10^{-3} - 10^{-4} mole per kg. of H_2O . The concentration of saturation of the fluid by tungsten depends on f_{O_2} , temperature, and complexation.

The study is supported by the Russian Foundation for Basic Research (projects no. 99-05-64106 and 00-05-98504).

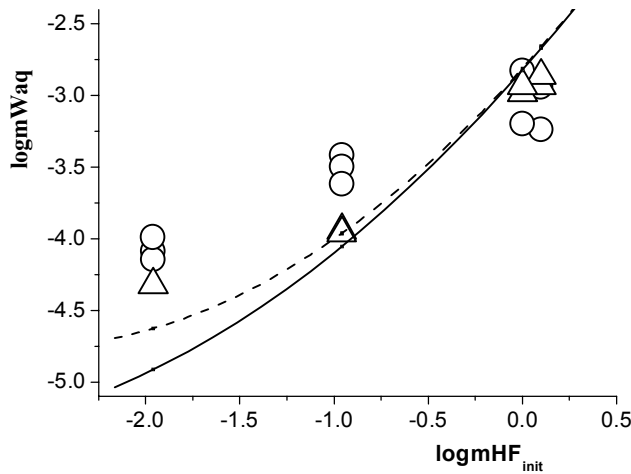


Fig. 1. Dependence of the tungsten concentration in the solution on the initial HF concentration for $T=500^\circ\text{C}$ and $P=1000$ bar (circles – Ni-NiO buffer, triangles – Fe_3O_4 - Fe_2O_3 buffer). Lines denote the calculated data (dashed line – Ni-NiO buffer, solid line – Fe_3O_4 - Fe_2O_3 buffer).

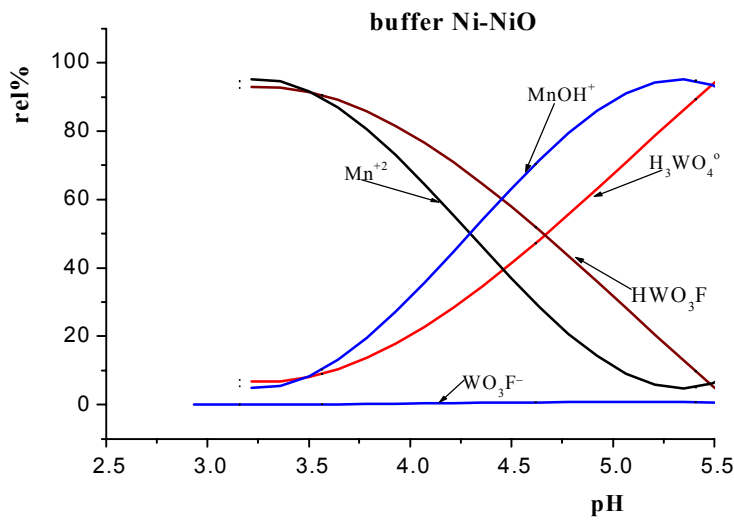
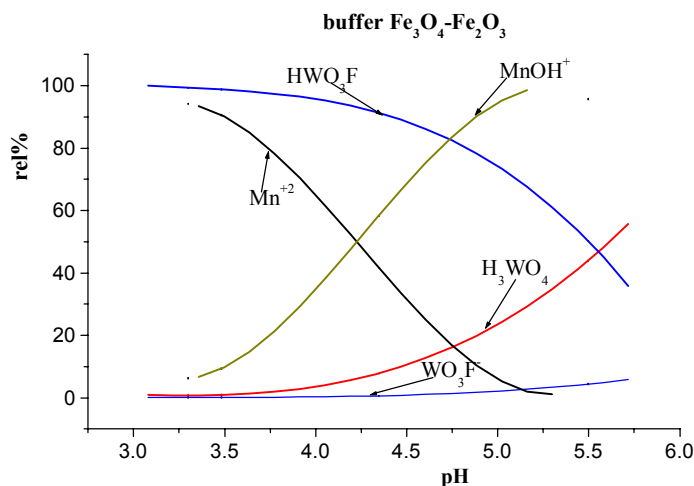


Fig. 2. Distribution of tungsten and manganese complexes in dependence on pH of the solution ($T=500^\circ\text{C}$ and $P=1000$ bar, buffer Ni-NiO).



References:

1. Korzhinskaya V.S., Zaraisky G.P. Doklady RAS, 1997, V. 353, no. 5, pp. 663-666.
2. Ivanov I.P., Chernyshova G.N., Dmitrenko L.T., Ryzhkov S.M., Korzhinskaya V.S. New hydrothermal apparatus for study of mineral equilibria and solubility.

In: Experimental problems of geology, Moscow, Nauka, 1994, pp. 706-720.

3. Andreeva I.Yu., Lebedeva L.I., Kovelina Zh.L. Zhurnal Analiticheskoi Khimii, 1992, no. 12, pp. 2202-2206.
4. Shvarov Yu.V. Geokhimiya, 1999, no. 6, pp. 646-652.
5. Redkin A.F., Cygan G. L. Experimental determination of ferberite solubility in the $\text{KCl-HCl-H}_2\text{O}$ system at

500°C and 400-1000 bar, and the Kfs-Mu-Qtz and Ni-NiO buffers (in press).

6. Smith R.M., Martell A.E. Critical stability constants: Inorganic complexes. N.Y. Plenum Press, 1976, 257 p.