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Experimental study of influence of hydrothermal solution on Sb_2S_3 solubility

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We studied the influence of solution composition on antimonite solubility in the systems Sb_2S_3–H_2O, Sb_2S_3–HCl–H_2O, Sb_2S_3–H_2S–HCl–H_2O at T=150-300°C and pressure along the line of water saturated vapor by solubility method. To clarify the effect of oxidation medium on Sb_2S_3 solubility we did preliminary runs at 200, 300 °C in the system Sb_2S_3–HNO_3–H_2O. The runs were done in autoclaves made of BT-8 alloy of 20 cm^3 in bulk. We used crystals of natural antimonite as a solid phase. They were put into titanium containers and were suspended in the upper part of the autoclave. Pressure was given by the filling coefficient on PVT data for water. Hydrogen sulfide solutions were prepared using the Kipp device. Bidistilled water saturated by hydrogen sulfide was preliminarily boiled, at cooling it was aired by argon and was made acidic by hydrochloric acid up to pH=4.2 and pH=1.35. H_2S concentration in the solution was determined before autoclave loading. The quantity of the dissolved antimonite was determined by the weight loss method. The obtained data were recalculated for antimony content in the solutions. The results of the experiments are shown in the Table and in Figs.1-3.

One should emphasize a satisfactory coincidence of the results. The main complex, determining antimonite solubility in water, is hydroxide complex $Sb(OH)_{3(aq)}$ .The system Sb_2S_3-H_2S-HCl-H_2O describes satisfactorily the processes taking place at formation of antimony deposits. We emphasized earlier in [*Dadze and Kashirtseva*, 2010] that the increase of H_2S concentration in the solutions from 0.002 to 0.1m does not practically have any effect on Sb_2S_3 solubility. Fig.2 shows the dependence of antimonite solubility on temperature in the solutions bearing HCl and H_2S with the initial pH=4.2 and pH=1.35 also in comparison with the other authors. Fig.1 shows the dependence of antimonite solubility in water on temperature as compared with the data of the other authors obtained under the same conditions.

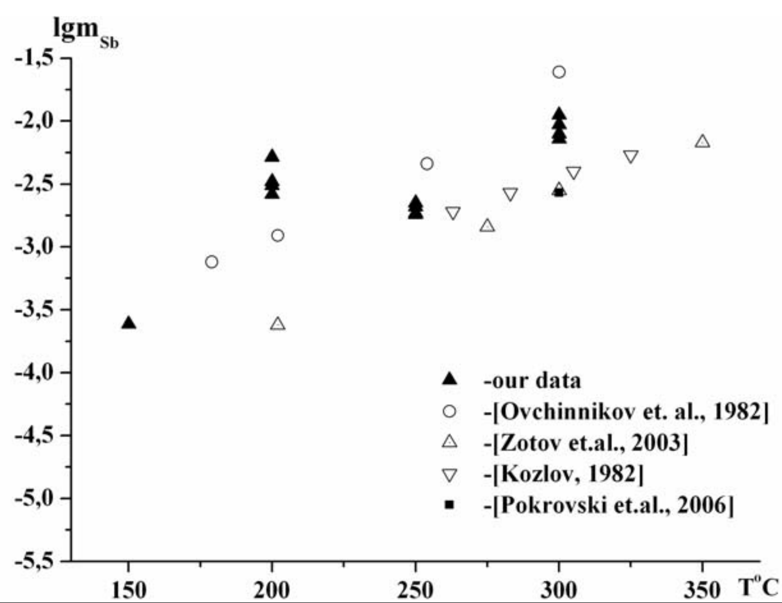

Fig.1. Dependence of antimonite solubility in water on temperature.

№ exp.	Sb(aq) g/l	Sb mol/kg $H_2O \cdot 10^4$	lgm_{Sb}
	$HCl+H_2S$ $pH_{start.}=4.2$		
		150^0C	
C-163	0.0077	0.63	-4.20
C-164	0.0099	0.81	-4.09
C-161	0.0067	0.55	-4.26
C-159	0.0097	0.79	-4.10
C-218	0.0086	0.71	-4.15
C-158	0.0073	0.60	-4.22
		200^0C	
C-183	0.067	5.50	-3.26
C-47	0.101	8.30	-3.08
C-46	0.089	7.31	-3.14
C-179	0.075	6.16	-3.21
C-178	0.097	7.97	-3.10
C-117	0.073	6.00	-3.22
C-113	0.080	6.57	-3.18
		250^0C	
C-147	0.230	18.64	-2.73
C-54	0.140	11.09	-2.96
C-52	0.106	8.71	-3.06
C-143	0.108	8.87	-3.05
C-142	0.110	9.04	-3.04
C-141	0.160	13.55	-2.87
C-140	0.180	14.54	-2.84
		300^0C	
C-157	0.160	12.90	-2.89
C-156	0.140	11.50	-2.94
C-154	0.136	11.17	-2.95
C-135	0.124	10.18	-2.99
C-225	0.131	10.76	-2.97
C-223	0.176	14.46	-2.84
		H_2O	
		150^0C	
C-99	0.03	2.46	-3.61
		200^0C	
C-199	0.376	30.88	-2.51
C-200	0.400	32.85	-2.48
C-201	0.322	26.45	-2.58
C-203	0.316	25.95	-2.59
		250^0C	
C-204	0.222	18.23	-2.74
C-205	0.229	18.81	-2.73
C-207	0.275	22.59	-2.65
C-208	0.256	21.03	-2.68
		300^0C	
C-209	1.148	94.29	-2.025
C-210	1.377	113.10	-1.95
C-211	0.88	72.28	-2.14
C-213	0.963	79.10	-2.10

№ exp.	Sb(aq) g/l	Sb mol/kg $H_2O \cdot 10^4$	lgm_{Sb}
	$HCl+H_2S$ $pH_{start.}=1.35$		
		150^0C	
C-102	0.022	1.77	-3.75
C-106	0.013	1.07	-3.98
C-103	0.027	2.22	-3.65
		200^0C	
C-61	0.258	21.19	-2.67
C-60	0.179	14.17	-2.83
C-59	0.048	3.94	-3.40
C-58	0.062	5.09	-3.29
C-57	0.069	5.67	-3.25
C-56	0.097	7.97	-3.10
		250^0C	
C-68	0.249	20.45	-2.69
C-67	0.249	20.45	-2.69
C-66	0.196	16.10	-2.79
C-65	0.384	31.54	-2.50
C-64	0.376	30.88	-2.51
C-63	0.401	32.94	-2.48
		300^0C	
C-75	0.885	72.69	-2.14
C-74	1.361	110.00	-1.95
C-73	1.733	142.30	-1.85
C-72	1.620	130.00	-1.88
C-71	1.573	129.20	-1.89
C-70	1.682	138.00	-1.86
		0.05m HCl	
		200^0C	
C-55	0.145	11.91	-2.925
C-230	0.134	11.01	-2.96
C-232	0.183	15.03	-2.82
		250^0C	
C-62	0.617	50.68	-2.30
C-236	0.583	47.89	-2.36
C-237	0.394	32.36	-2.49
		300^0C	
C-69	1.929	158.44	-1.80
C-242	0.882	72.44	-2.14
C-92	1.08	88.71	-2.05
		0.05m HNO_3	
		200^0C	
C-9	2.087	170.00	-1.77
		300^0C	
C-17	2.725	220.00	-1.65

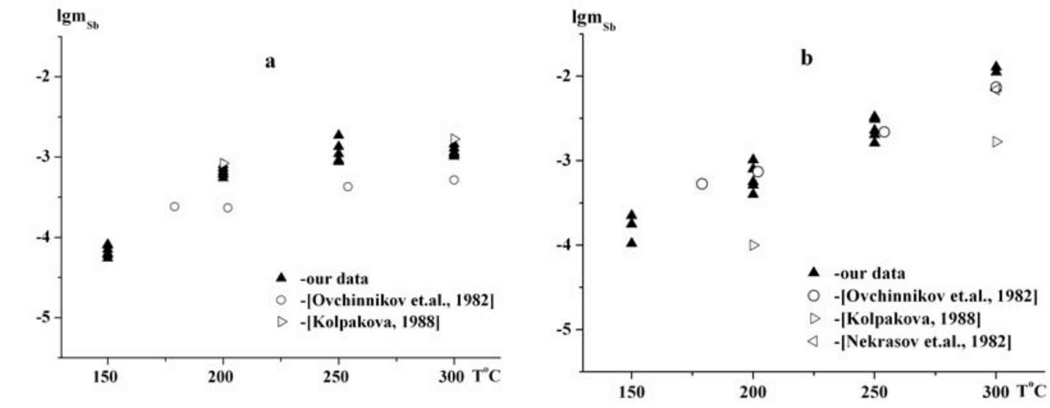

Fig. 2. Dependence of antimonite solubility on temperature in chloride-sulfide solutions.
a-pH_{start}=4.2; b- pH_{start}=1.35

We can see from Fig. 2 that in more acidic hydrothermal solutions antimonite solubility is higher than that in close neutral ones. It is probably connected with the fact that antimonite solution takes place with the formation of both hydrosulfide and chloride antimony complexes. It is necessary to notice that the data [*Ovchinnikov, et. al.*, 1982] are calculated by the equation suggested in this work.

Fig. 3 shows our experimental data (the average values are taken) on Sb_2S_3 solubility depending on temperature in the solutions different in composition.

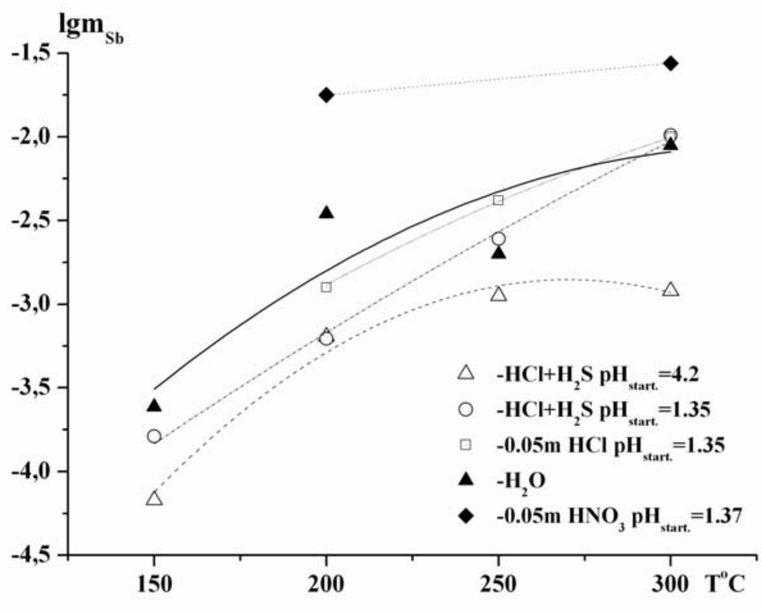

Fig. 3. Dependence of Sb_2S_3 solubility on temperature in different media.

It can be seen from the Fig. 3 that the temperature, pH and the solution redox potential have a great influence on Sb_2S_3 solubility. The largest antimony content in the solution is observed in the system Sb_2S_3-HNO_3-H_2O.

Thus, we are almost sure to say that the formation of hydroxide complexes at low contents of sulfide sulfur provides such Sb_2S_3 solubility which is enough to transfer antimony by hydrothermal solutions at elevated temperatures.

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