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Title: Mechanism of mass transfer in the formation of hydrothermal deposits  
of sulphides

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pp 44-46. Solubility of sulphides of iron

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OL'SHANSKII Ya.I. & IVANENKO V.V. (1958)

Mechanism of mass transfer in the formation of hydrothermal deposits of sulphides.

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pp 44-46. Solubility of sulphides of iron.

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For determining the solubility of sulphides of iron, the radioactive isotope  $Fe^{59}$  was used. The solubility of two sulphides was determined: pyrite, synthesized in mixture with ground quartz glass from radioactive iron and sulphur, and sulphide, precipitated in a flask for determining solubility with reactive hydrogen sulphide in a solution of ferric chloride.

Samples of the solution, taken after mixing and settling, were boiled with the addition of hydrochloric acid up to full removal of hydrogen sulphide. Then was added nitric acid and about 0.5g of sulphate or chloride of stable iron. Further samples were boiled down and decanted in the vessel for determining activity. (see fig.10).

Some experiments were carried out with a preparation of radioactive iron, not subjected to purification. Subsequently the radioactive iron was subjected to careful purification. In this case it lost so significant a part of activity, that work with it raised difficulty, so that errors were increased in measuring activity. Most probably of all, in the original preparation was contamination of radioactive cobalt. Nevertheless, results obtained with purified and impurified preparations did not differ significantly from one another. It is possible to surmise that a small quantity of cobalt, present in the preparation, formed a solid solution in sulphide of iron, such that the relationship between iron and cobalt in the solid phase and in the solution was approximately the same.

In table 12 and figs 16, 17 and 18 are presented the basic data from the experiments on determination of the solubility of sulphides of iron.

In the same way as in the case of sulphides of silver, the solubility of precipitated sulphides of iron many times exceeds the solubility of synthesized pyrite. The solubility of precipitated sulphide decreases (fig. 16) but of crystalline (pyrite) grows with increasing length of experiment. The reduction of solubility of precipitated sulphide, evidently, involves ageing of the deposit and reduction of dispersibility. As regards growth of concentration of the solution over the pyrite, here, of course, can be shown the very slow establishment of equilibrium in the same process of solution. At the same time, one does not exclude the possibility that the increasing of the concentration in this case reflects the increasing solubility, involved with the change and the solid phase.

As seen in figs 17 and 18, the solubility of sulphides of iron - both as precipitated and as pyrite - increases with growth of pH of the solution in the same way as was observed by us and Treadwell for sulphides of silver, in the experiments of Hemley for sulphides of lead. Therefore the observed solubility of the sulphides of iron cannot be explained by the presence in solution only of the ions  $Fe^{2+}$ ,  $S^{2-}$ ,  $HS^-$ , but is chiefly involved with

the formation of other ions or non-dissociated complexes. If in the solution is found only the ions  $\text{Fe}^{2+}$ ,  $\text{S}^{2-}$  and  $\text{HS}^-$ , then the solubility must have been near to the value obtained by Verhoogen and other investigators, and decreases with increasing pH.

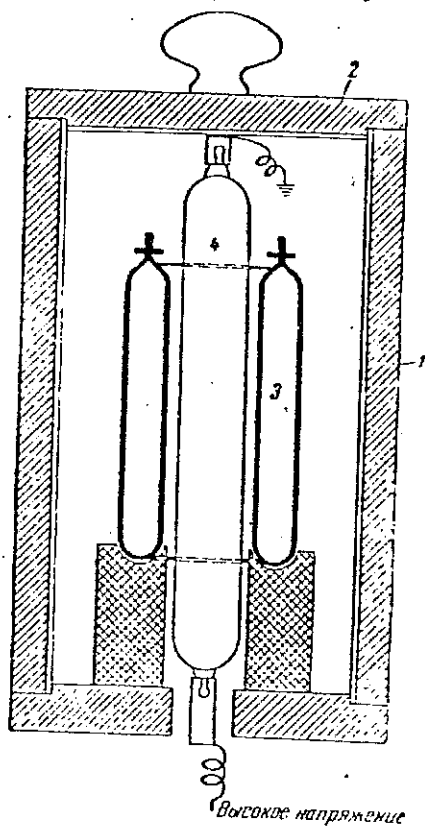
The data obtained in our experiments, unfortunately, are inadequate for that, that to try to determine with such complexes the involved observed solubility. Nevertheless the significantly greater solubility of sulphides of iron by comparison with the published data of recent years does not raise doubts.

#### Reference

Verhoogen, J. (1938) Thermodynamical calculations of the solubility of some important sulphides up to 400°C. Econ.Geol. 33, 1.

Table 12. Solubility of sulphides of iron at 25<sup>o</sup> in solutions saturated with hydrogen sulphide at 1 atm. (p.44)

No. of experiment	Solid phase	Composition of solution			No. of samples	Duration of settling, hours		Concentrations of iron in samples		pH of solution -n.				
		NaOH N.	NaCl N.	HCl N.		Total duration of mixing, hours.	Duration of settling, hours	Total duration of experiment, hours.	10 <sup>6</sup> g/l					
									10 <sup>7</sup> g-atom/l					
1	Pyrite	—	0,1	0,001	11	48	24	72	19,1	3,41	3,0	Experiments with unpurified iron		
					12	72	24	132	24,4	4,37				
					13	96	24	180	18,1	3,24				
3	Precipitated sulphide	0,007	0,1	—	31	72	15	87	798	142	5,5		Experiments with unpurified iron	
					32	72	21	93	777	139				
					33	96	24	141	757	135				
5	"	0,1	0,1	—	51	48	24	72	—	—	7,0			Experiments with purified iron
16	"	0,1	0,1	—	52	48	48	96	2610	468	7,0			
					161	36	24	60	4180	748				
18	"	0,05	0,1	—	162	36	24	60	4080	733	6,7			
					164	60	24	108	3910	702				
					181	36	24	60	2100	376				
					183	36	24	60	2170	392				
					184	60	24	108	1950	349				
19	Pyrite	0,02	0,1	—	185	60	24	108	1970	352	6,2			
					192	64	22	86	23,9	4,27				
					193	64	58	122	104	18,3				
20	"	0,007	0,1	—	202	40	38	78	13,4	2,40	5,5			
					203	40	38	78	42,5	7,62				
21	"	0,007	0,1	—	204	40	60	100	75,7	13,8	5,5			
					211	64	22	88	10,7	1,93				
					212	64	58	124	33,6	6,01				
22	Precipitated sulphide	0,007	0,1	—	221	64	22	88	453	81,1	5,5			
					222	64	22	88	500	89,5				
23	"	0,02	0,1	—	223	64	58	124	366	65,5	6,2			
					231	64	22	88	618	110				
					232	64	22	88	594	106				
					233	64	58	124	540	96,7				



high voltage

Фиг. 10. Прибор для измерения радиоактивности растворов  
 1 — свинцовый защитный кожух; 2 — крышка кожуха; 3 — кварцевый сосуд; 4 — у-счетчик.

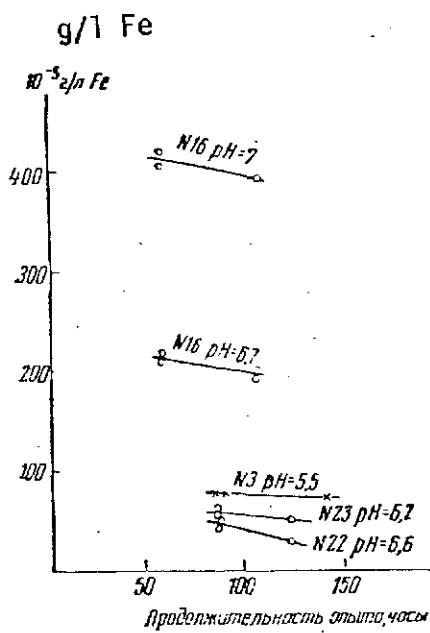
Fig. 10. Instrument for measurement of radioactivity of solutions.

1.- lead protecting case.

2 - cover of case

3 - quartz vessel

4 - y-meter.



Duration of experiment, hours

Fig. 16. Dependence of the concentration of iron in the solution over the "precipitated" sulphide on the duration of the experiments at 25°. Solutions saturated with H<sub>2</sub>S.

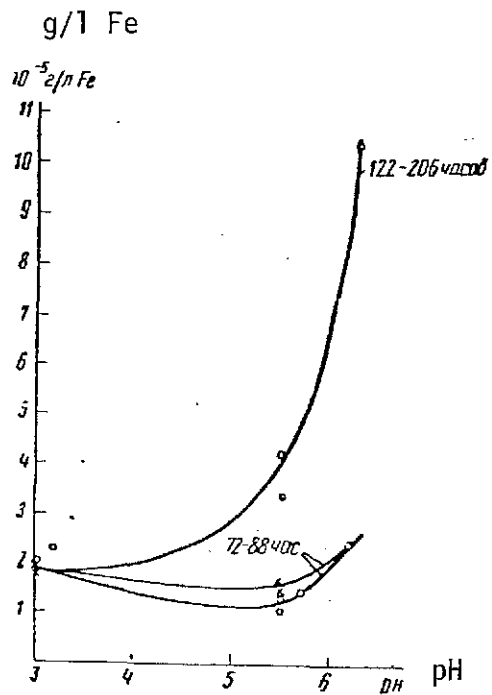
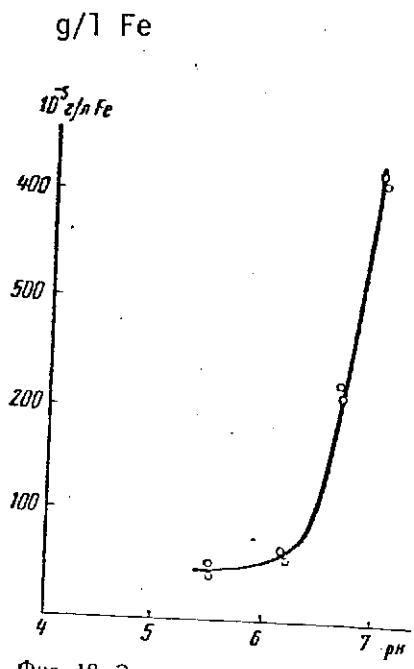


Fig. 17. Dependence of solubility of pyrite at 25° on acidity of the solutions, saturated with H<sub>2</sub>S. Duration of experiments 72-88 hours (lower curve) and 122-206 hours (upper curve).

X = experiments with unpurified iron

O = experiments with purified iron.



Фиг. 18. Зависимость растворимости «осажденного» сульфида железа при 25° от кислотности растворов, насыщенных сероводородом. Длительность опытов 88—108 час.

Fig. 18. Dependence of solubility of "precipitated" sulphide of iron at 25° on the acidity of the solution, saturated with H<sub>2</sub>S. Duration of experiments 88-108 hours.

### **Notice**

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