Ivanov I.P., Kashirtseva G.A. Thermodynamic analysis of parageneses of iron sulfides and oxides on the basis of the system Fe-S-O$_2$-H$_2$O

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Numerical study of phase relations in the "model" system Fe-S-O$_2$-H$_2$O is carried out. This system is important for ore formation and is well studied experimentally. We calculated parameters controlling parageneses of iron sulfides and oxides at elevated and high T and P. The phase relations were considered in the closed system, in the system opened for oxygen, and in the system opened for oxygen and sulfur. The calculations were carried out using the program by Yu.V. Shvarov (1999), which uses the "UNITHERM" database. In the closed system, the P-T diagram (Fig. 1) is calculated within the interval T=300-800°C and P up to 5 kbar and monovariant reactions are determined (solid lines): (1) Po + S$_{liq}$ = Py, (2) Mag + S$_{liq}$ = Py + Hem. Reaction (3) Wus = γ-Fe + Mag is firstly identified. P-T coordinates of reaction 1 are shown according to the data of the experimental study of reaction Py = Po + S$_{liq}$ (Kullerud, Yoder, 1966). According to Klark (1969), wüstite appears by reaction 3 at T = 585°C and P = 1atm. Reactions 1 and 2 significantly depend on a presence of water in the system. Presence of total porosity of 10 vol. % in "the ore body" shifts these reactions toward lower temperatures by 90-100°C. This effect is shown by dashed lines 1' and 2' (Fig. 1).
The parageneses controlling their parameters are recognized: Py+Mag+Hem; Py+Po+Mag; Po+Mag+γ-Fe; Py+Mag+S$_{liq}$;Mag+Hem+S$_{liq}$; Po+Mag+Wus; Po+Wu+γ-Fe.
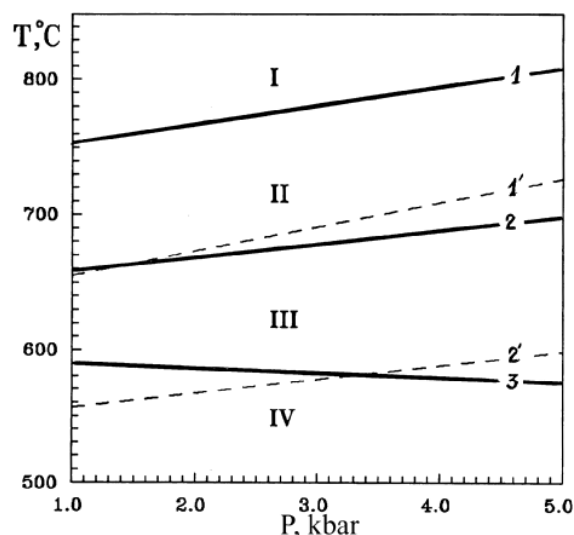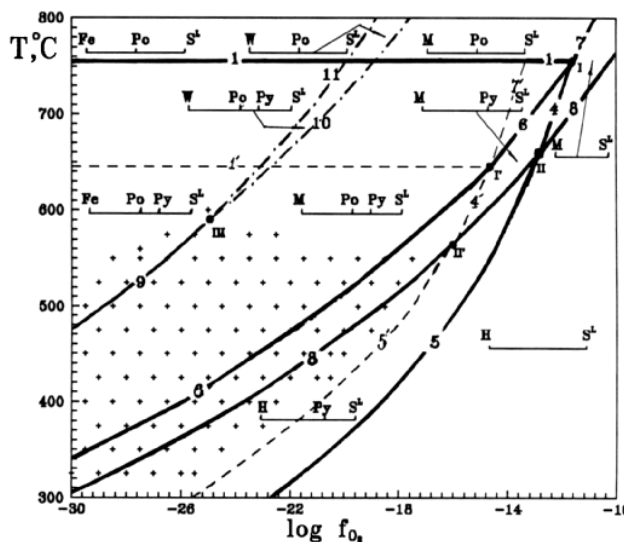
In the system opened for oxygen, the following parageneses are found: Py+Hem; Py+Mag; Py+Po; Po+γ-Fe; Po+S$_{liq}$; Mag+S$_{liq}$; Hem+S$_{liq}$. The diagram logf$_{O2}$ –T (Fig. 2) is constructed. The diagram of the "dry" multi-system includes three nonvariant points: I – Mag+Py+Po+S$_{liq}$, II - Mag+Hem+Py+S$_{liq}$, and III - γ-Fe+Wus+Mag. Within T = 300-800°C, P = 1 kbar, and –logf$_{O2}$ = 10-30, the following monovariant lines (reactions) are stable:

$$(1-x)Py = Po+(1-2x) S_l \qquad (1)$$
$$3Py + 2O_2 = Mag + 6S_l \qquad (4)$$
$$2Py + 1.5O_2 = Hem + 4S_l \qquad (5)$$
$$6Po + (2-4x)O_2 = 3Py + (1-2x)Mag \qquad (6)$$
$$3Po + (2-2x)O_2 = (1-x)Mag + 3S_l \qquad (7)$$
$$2Mag + 0,5O_2 = 3Hem \qquad (8)$$
$$3\gamma\text{-Fe} + 2O_2 = Mag. \qquad (9)$$
$$3 Wus + (0.5-2x)O_2 = (1-x)Mag \qquad (10)$$
$$(1-x)\gamma\text{-Fe} + 0.5O_2 = Wus \qquad (11)$$

The boundaries of stability of binary parageneses in the "dry" system are shown by solid lines, whereas the boundaries of stability of binary parageneses for the water-bearing system are shown by dashed lines. The numbers of reaction is the same. The stability field of pyrite is confined by reactions 1, 4, and 5. The stability field of pyrrhotite is confined by reactions 6 and 7. Other lines are the singular reactions in the boundary system Fe-O$_2$, where O$_2$ is a perfectly mobile component. Reactions 8 and 9 are "oxygen buffers". Reactions 10 and 11 (dashed-dotted lines) of transformations between Mag, Wus, and γ-Fe are not investigated because of inconstant composition of Wus.
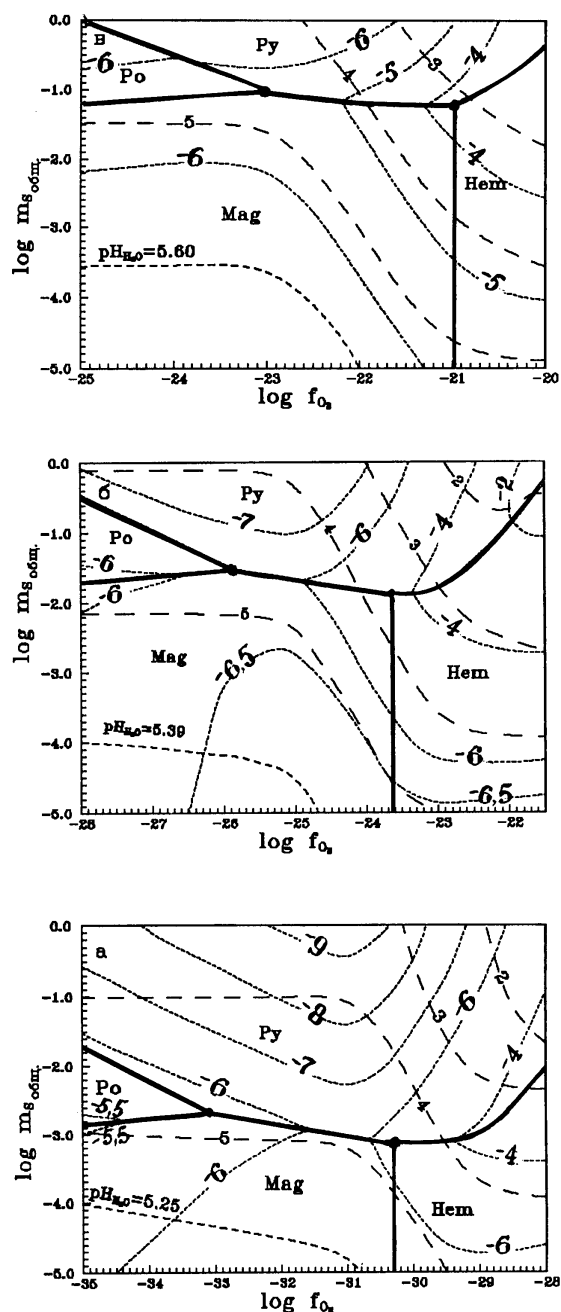

Fig. 1. P-T diagram for the system Fe-S-O$_2$-H$_2$O.
Fig. 2. logf$_{O2}$-T diagram for the system Fe-S-O$_2$-H$_2$O opened for oxygen. P = 1 kbar

as 4, 5, 7, sink by 90-100°C. The nonvariant point I "slides" along the line 6, while the point II is displaced along the line 8, being shifted to the left along the $\log f_{O_2}$-axis by 4 orders of magnitude. In the water-bearing system, the stability field of pyrite is confined by reactions 1', 4', and 5'. Crosses on the diagram (Fig. 2) show the region, where the "UNITHERM" database allows calculation of compositions of solutions in equilibrium with the binary mineral parageneses, which are shown on the diagrams "composition-paragenesis". The upper boundary of the region is 550°C.

The diagrams $\log m_{Stot}$-$\log f_{O2}$ at 300, 400, 450°C and 1 kbar (Fig. 3) are calculated for the system opened for oxygen and sulfur. The stability fields of Po, Py, Mag, Hem are determined. The isolines of pH and $\log m_{Fetot}$ are also plotted. The composition of solution and its acidity are known in any point. The stability fields of all minerals are characterized by acid solutions.

The above results are related to the problems, which allow to create the global problems of metasomatism with a numerical estimation of phase relations and composition of solutions during metasomatism related to the trans-magmatic processes.

References:

1. Kullerud G., Yoder H. Stable relations in the system Fe-S // Problems of endogenic ore deposits. Moscow, Mir, 1966, issue 3, pp. 71-131.
2. Physical constants of rocks. Hand-book. Ed.: S. Klark. Moscow, Mir, 1969.
3. Shvarov Yu.V. Algorithm of equilibrium modeling of dynamical geochemical processes // Geokhimiya, 1999, no. 6, pp. 646-652.

Fig. 3. $\log f_{O2}$- $\log m_{Stot}$ diagram for the system Fe-S-O_2-H_2O opened for oxygen and sulfur. P = 1 kabr. a) T = 300°C; a) T = 400°C; a) T = 450°C. Long-dashed lines denote the pH isolines of equilibrium solutions; average-dashed lines denote the pH isolines of pure water; small-dashed lines denote the concentration isolines of total iron in solution ($\log m_{Fetot}$).

Addition of water (10 vol. %) results in shifting toward lower temperature and lower $\log f_{O2}$ of sulfur-bearing reactions. Similar to the closed system, reaction 1, as well