Mineral equilibria

Akimov V.V., Tauson V.L., Parkhomenko I.Yu., Men'shikov V.I., Nepomnyashchikh K.V. Effect of stoichiometric vacancies in crystals on impurity specification (with cadmium in pyrrhotite as an example)[#]

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The study of physico-chemical conditions of formation and evolution of mineral systems is generally based on a quantitative analysis of a structurally bound ("structural") impurity species inside of crystals because this form regularly reacts to changes of external parameters (T, P, μ_i) of a thermodynamic system. The majority of known geothermometers, geobarometers and geospeedometers bases on this principle. In a case of macroimpurities the structural form is usually identified with isomorphous one. For microimpurities, apparently, the situation becomes much more complicated as in this case concentrations of impurity in solid phases are comparable with or even less than concentrations of intrinsic point defects (Shottky or Frenkel defects, stoichiometric vacancies). Under certain conditions it can appear, that the competing mechanism of entry of microimpurities into structure of minerals in relation to usual isomorphism is the formation of a different type of associates of impurity atoms with intrinsic point defects. Therefore, "structural" form we may be divided to components, bound with structural defects of a particular type. Generally, adsorbed species (physically or chemically and dislocation species (such as Kottrell clouds, Suzuki segregations are also "structural" species. It is apparent that the behaviour of trace elements in particular physico-chemical conditions is determined by an opportunity of formation of certain species and their relation. Therefore, in our opinion, the methodology of study of systems characterized by strongly restricted isomorphism as well as the detection of solid state solubility of trace elements in mineral phases should be grounded on revealing of a role of structural defects in formation of a concrete species of element. The present communication is concerned with experimental and theoretical study of the effect of stoichiometric vacancies on speciation and solid state solubility of cadmium in pyrrhotite of a different stoichiometry.

Pyrrhotites were synthesized from simple substances (pure reagent grade Fe and S) in a sealed, evacuated silica-glass tubes. The experiments on FeS saturation with cadmium were also carried out with the silica-glass ampoules. Cadmium sulfide was added to the system as highly dispersed hexagonal CdS. The experiments were conducted at 700°C during 10 days and at 600°C during 20 days. Each tube contained the buffer phase(s) to maintain particular stoichiometry of pyrrhotite. The buffer was applied as metal-sulfide systems (Ag-Ag₂S, Fe-FeS, Cu-Cu₂S) or pyrrhotite of designated stoichiometry taken in 4-fold ex-

cess in relation to batch mixture $Fe_{1-x}S$ + CdS. Stoichiometry of pyrrhotite (atomic percentage of iron) was determined by a well-known procedure of Tulmin and Barton [1] using d-spacing of 102 reflection with NaCl as an internal standard. Basic analytical method of study of obtained Cd-containing pyrrhotites was the thermal atomic absorption analysis based on a principle of simultaneous registration of temperature of a sample and a signal of absorption from a spectrometer during analytical experiment. The temperature parameters of element erlease correlate with the element volatility and thermal stability of impurity species depending upon the bond strength of the element in the particular binding form. These temperature parameters are determined at a stage of calibration of a method for each binding form of an impurity using synthetic minerals. Concerning cadmium such operation was previously done [2,3].

The interval of iron vacancies concentrations from 0 (buffer Fe+FeS) up to ~3.8 at.% ("buffer" $Fe_{0.86}S$) is investigated. The kinetic experiments and approach to equilibrium from the different sites have shown, that at 700°C the equilibrium is achieved for 10 days. The results of experiments at 600 and 700°C show, that the mixing of CdS with $Fe_{1-x}S$ begins, apparently, with the formation of CdS-enriched surface film on pyrrhotite particles (sulfide-like form). This is supported with intermediate temperature of release of this form between temperatures for adsorbed species and crystalline CdS. The influence of the buffer at one and the same initial concentration of CdS is drastic. At iron vacancies concentration 1.7 at. %, set by the buffer Ag+Ag₂S, the structural species of cadmium as an isomorphous form and caused by interaction with vacancies prevails whereas at Fe-FeS buffer its content is much less as compared to sulfide-like form. On the basis of the primary experimental information the solid state solubilitiy of Cd in pyrrhotites of various stoichiometry was obtained (Table). One can see that the solid state solubility very strongly depends on pyrrhotite composition: solid state solubility increase in comparison with stoichiometric FeS almost of two orders of magnitude. The Fe vacancies concentration in troilite is conditionally accepted equal to zero.

The theoretical analysis of the effect of vacancies on a solid state solubility of cadmium in pyrrhotites of various stoichiometry is executed within the framework of the concept of forced equilibrium [4]. According to this theory it is possible to write a condition of a chemical equilibrium in bulk of crystal which is taking place in elastically stressed solid state, as follows:

$$\frac{\partial G(\sigma_{ij}, C)}{\partial C} = \lambda, \qquad (1)$$

where $G(\sigma_{ij}, C)$ - molar Gibbs energy of pyrrhotite ($Fe_{1-x}S$); σ_{ij} - tensor of complete stress created by elastic fields of point defects - vacancies in a sublattice of iron (v), isomorphous impurity (i) and elastic dipoles (V_{Fe}+Cd); C - Cd mole fraction of local, but macroscopic region of a crystal; λ - constant dependent on activity of impurity component in a gas phase and representing constancy of chemical potential of an impurity in bulk of a crystal. In our case elastically stressed solid state corresponds to a thermodynamic state of pyrrhotite with a par-

ticular concentration of iron vacancies (x), isomorphous cadmium impurity content (C_o) and elastic dipoles concentration ($\Delta C = C - C_o$). $V_{Fe} + Cd_{oct}$ and $V_{Fe} + Cd_{tet}$ types of dipoles are considered, where Cd_{oct} and Cd_{tet} correspond to structural positions of cadmium in octahedral and tetrahedral sites in pyrrhotite structure. The troilite structure is accepted for unstrained and unstressed solid state of a crystalline matrix. Within the approximation of the linear theory of elasticity, and accepting the model of concentration expansion of an elastic medium [5] for the description of elastic fields of point defects, the expression (1) is reduced to the nonlinear equation:

$$ RT \ln\left(\frac{C}{1-C}\right) - \frac{1}{2}\left(\frac{\gamma^{-1}}{V_a}\right)^2 K \cdot V_m \left(\Delta V_a^V \cdot x + \Delta V_a^I \cdot C + \Delta V_a^{V+Cd} \cdot \Delta C\right) \Delta V_a^I = \lambda, \tag{2} $$

where R - gas constant; T - temperature; $1/V_a$ - number of atoms in a unit volume; ΔV_a - difference of atom volumes of a matrix and relevant point defect; V_m - molar volume; G and K - a shear modulus and compression modulus accordingly; $\gamma = 1 + (4G/3K)$. The solution of this equation allowed to quatify a solid state solubility of Cd in pyrrhotite with elastic interaction of impurity atoms with vacancies taken into account. The results of numerical calculations are shown in figure. When compared with experimental data, these results allows to conclude that the theory qualitatively correctly describes the dependence of a solid state solubility of cadmium in pyrrhotites on concentration of stoichiometric vacancies and temperature. However, the considerable discrepancies exist in estimations of absolute values of solid state solubilities. Apparently, it may be due to structural transformation (troilite-pyrrhotite) in region of very low vacancy concentrations. As one can deduce from Figure, the hypothetical phase FeS with ideal pyrrhotite (NiAs) structure should contain more isomorphous Cd than troilite.

Table 1. Solid state solubility of Cd in pyrrhotites of different stoichiometry

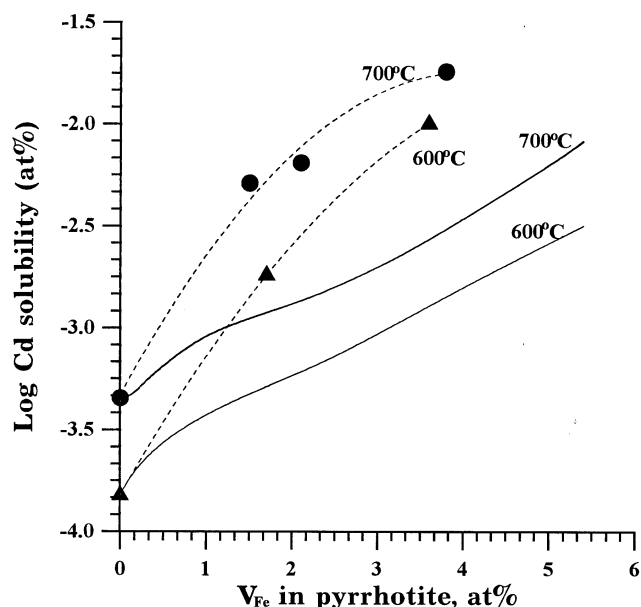| Buffer	T°C	$\lg f_{S_2}$, bar	Stoichiometry of pyrrhotite		Solid state solubility of Cd, at.%
			V_{Fe}, ат.%	x in $Fe_{1-x}S$	
$Fe_{0.86}S$	700	-1.21	3.8	0.14	$1.8 \cdot 10^{-2}$
$Fe_{0.92}S$	700	-4.02	2.1	0.08	$6.4 \cdot 10^{-3}$
$Ag_2S + Ag$	700	-5.82	1.5	0.06	$5.1 \cdot 10^{-3}$
FeS+Fe	700	-10.64	0	0	$4.5 \cdot 10^{-4}$
$Fe_{0.87}S$	600	-2.64	3.6	0.13	$1.0 \cdot 10^{-2}$
$Ag_2S + Ag$	600	-6.90	1.7	0.07	$1.8 \cdot 10^{-3}$
FeS+Fe	600	-12.49	0	0	$1.5 \cdot 10^{-4}$

Fig. Solid state solubility of Cd in pyrrhotite of various stoichiometry at 600 and 700°C. Solid lines - data of numerical simulation; dashed lines - approximation of experimental data by parabolic function

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